

Molecular Spectroscopy

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Preface

Overview of the subject

As academicians with years of experience, we feel there are two types of students: *those who learn how to learn and those who learn how to think*. Hence, we must design books in such a fashion that both categories of students benefit by them and are able to read and understand on their own without undue reliance on formal classroom instructions. Students must play an active role in the learning process and the teacher a passive one, serving only as a guide. Merely reading about experiences and observations of others is not stimulating, instead a hands-on interactive experience not only enriches a learner's knowledge base but also helps him/her grasp and remember concepts more easily.

Molecular spectroscopy plays a major role in understanding the various physical and chemical phenomena in-vivo and in-vitro. Spectroscopy/Spectrometry is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them. An application-based subject, it finds use in Astronomy, Remote-sensing, Telescopes, Microwave, NMR and MRI, Nuclear Medicine, X-Ray, Optic Fibers, Mineralogy, and Structure Determination of Biological Compounds.

The new developments and improvements in precision of spectroscopic measurements laid the basis for new applications of molecular spectroscopy in chemistry, chemical engineering, biology, biochemistry, space chemistry and other areas. In these fields, complex molecules or mixtures are accessible to molecular specific investigation under difficult experimental conditions as well as in environmental and industrial-process analysis. If students are to understand and enjoy molecular spectroscopy, they must have some of these experiences in reality.

Objective

The objective of this book is to present molecular spectroscopy in an interesting, understandable and enjoyable manner. An appreciation, rather than only a working knowledge of molecular spectroscopy, is what this book aims to impart to students. Therefore, we have laid strong emphasis on the aspects or techniques. There are clear explanations of the physical meaning of the mathematics used, thus enabling students to appreciate the importance of mathematics, the queen of all sciences, in the development of molecular spectroscopy. There is stress on practical applications throughout the book. The introduction of each new concept is followed by problems. It is our earnest hope that these examples will enable students master a concept or technique before they move on to the next. The physical concepts are amply illustrated by means of diagrams and graphs wherever possible. The text in discussion is the comprehensive and in-depth treatise encompassing all aspects of the subject and coordinated with needs of various universities. The beauty of the book is the way it starts from fundamentals of the subject as required by a beginner and goes further to detailed explanations and latest advancements in the field.

Salient Features

Briefly, the highlights of the book are given below:

- **Comprehensive in-depth explanation to all important topics:** Microwave Spectroscopy, Infrared Spectroscopy, Raman spectroscopy, Electronic Spectroscopy, Photoelectron Spectroscopy, NMR
- **Appendices on other advanced forms of spectroscopy:** Nuclear Quadrapole Spectroscopy, Electron Spin Resonance Spectroscopy, Mossbauer Spectroscopy
- **Selected multidisciplinary spectroscopy applications given at chapter end as per relevance:** will be beneficial for students of Life Sciences such as B. Pharma, B.Sc. Biotechnology, B.Tech. Biotechnology, M.Sc. Biotechnology and M.Sc. Chemistry
- **Pedagogy**
 - Over 400 Figures
 - 150 Tables to explain concepts
 - Solved Problems interspersed throughout the chapters
 - Chapter-end Review Questions

Acknowledgements

We are highly indebted to our teachers, both at undergraduate and postgraduate levels, who motivated us to join this fascinating field of chemistry. This fascination was further accentuated during our stay with teachers with whom we spent our time as research associates at different universities or institutes.

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Suggestions for the improvement of this book would be most welcome.

S K Dogra

H S Randhawa

Publisher's Note

Remember to write to us. We look forward to receiving your feedback, comments and ideas to enhance the quality of this book. You can reach us at tmh.sciencemathsfeedback@gmail.com. Please mention the title and author's name as the subject.

Greek Alphabet

Letter	Name
A α	Alpha
B β	Beta
Γ γ	Gamma
Δ δ	Delta
E ε	Epsilon
Z ζ	Zeta
H η	Eta
Θ θ	Theta
I ι	Iota
K κ	Kappa
Λ λ	Lambda
M μ	Mu
N ν	Nu
Ξ ξ	Xi
O ο	Omicron
Π π	Pi
P ρ	Rho
Σ σ	Sigma
T τ	Tau
Υ υ	Upsilon
Φ φ	Phi
X χ	Chi
Ψ ψ	Psi
Ω ω	Omega

CHAPTER 1

INTRODUCTION

A teacher should produce less heat and more light.

—Unknown

1.1 THE NATURE OF ELECTROMAGNETIC RADIATIONS

Electric and magnetic fields of radiation oscillate sinusoidally in mutually perpendicular planes at right angles to the direction of propagation of radiation as shown in Fig. 1.1. The electric (E) and magnetic (H) field components of an electromagnetic wave in the X -direction are

$$\begin{aligned} E &= E_0 \sin 2\pi \left(\frac{x}{\lambda} vt \right) \\ H &= H_0 \sin 2\pi \left(\frac{x}{\lambda} vt \right) \end{aligned} \quad (1.1)$$

Here, ν and λ represent the frequency and wavelength of the radiation; c is the velocity of light and is given by $c = \nu \lambda$.

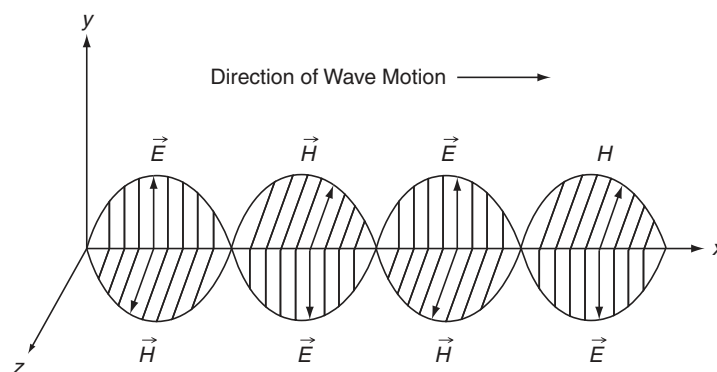


Fig. 1.1 Representation of propagation of an electromagnetic wave.

(a) Wavelength (λ) The distance between one particle in a wave and the corresponding next particle in a wave with which it is in phase is known as wavelength, i.e. the distance between two similar points on a wave is called wavelength. As we know, there is a maximum and minimum in a wave, so in practice, the distance between two minima or between two maxima is also a wavelength. The pictorial view of a wave is shown in Fig. 1.2. The distance between particles a and b or a' and b' is the wavelength. The greatest distance a wave moves up and down is called the *amplitude*, A .

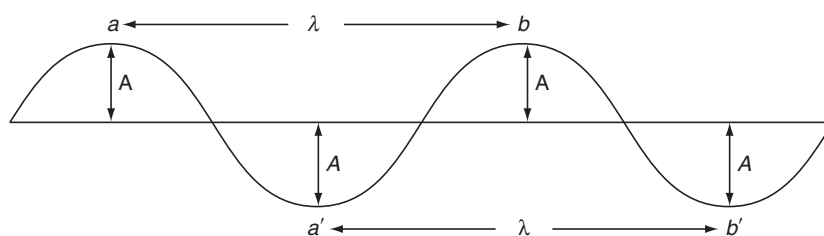


Fig. 1.2 Representation of an electromagnetic wave.

2 Molecular Spectroscopy

Units Metre (m), centimetre (cm), millimetre (mm), micrometer (μm), nanometre (nm), Angstrom ($\text{\AA}$); $1\ \mu\text{m} = 10^{-4}\text{ cm} = 10^{-3}\text{ mm}$, $1\text{ nm} = 10^{-3}\ \mu\text{m}$, $1\ \text{\AA} = 10^{-8}\text{ cm} = 0.1\text{ nm}$.

(b) Wave Number ($\bar{\nu}$) The reciprocal of wavelength is called wave number.

Units Number of waves per centimetre (cm^{-1}), Kayser (K), kilokayser (kK), $1\text{ kK} = 1000\text{ K} = 1000\text{ cm}^{-1}$.

(c) Frequency (ν) It is a measure of the number of waves passing through a given point in a unit time. It is inter linked with wave number through the following equation.

$$\nu = \frac{c}{\lambda} = c\bar{\nu} \quad (1.2)$$

Units Cycles per second (cps, C/S) or Hertz (Hz), kilocycles per second (kcps or kHz), megacycles per second (Mcps or MHz); $1\text{ MHz} = 10^3\text{ kHz} = 10^6\text{ Hz}$.

(d) Energy Energy in the form of electromagnetic radiations comes in discrete units called photons. Each photon contains an amount of energy determined by the frequency of electromagnetic radiation. The German scientist Max Planck first proposed the equation relating to frequency and energy,

$$E = h\nu = h \frac{c}{\lambda} = hc\bar{\nu} \quad (1.3)$$

where c is the velocity of light ($2.988 \times 10^{10}\text{ cm/s}$) and h is the Planck's constant with the value $6.6259 \times 10^{-27}\text{ erg s}$. According to Einstein, $h\nu = m_{\text{ph}} c^2$. Here, m_{ph} is the mass of the photon ($\sim 10^{-33}\text{ g}$). Pressure of light and bent light rays in the strong gravitational field are evidences for the mass of the photon.

Units The units and the conversion factors of energy units are given in Table 1.1, while the values of general physical constants and chemical constants are listed in Appendix 1A.

Table 1.1 Conversion factors of energy units.

Units	cm^{-1}	Ergs/molecule	Cal/mole	eV
1 cm^{-1}	1	1.9865×10^{16}	2.859	1.2398
1 erg/molecule	5.0348×10^{15}	1	1.43956×10^{16}	6.2421×10^{11}
1 cal/mole	0.34975	6.946×10^{-17}	1	4.3361×10^{-5}
1 eV	8065.8	1.6020×10^{-12}	2.306×10^4	1

1.2 MOLECULAR SPECTROSCOPY AND SPECTRAL REGIONS

The study of electromagnetic radiation with matter in all of its forms, viz., solids, liquids/solutions and gases is called spectroscopy. The radiations are characterised by their frequencies, wave numbers, wavelengths and the energy associated with the electromagnetic waves. Depending upon the energy of radiations but not the intensity (energy per unit time per unit area), which is a measure of the amount of radiations; spectroscopy has been classified into different branches, summarised in Table 1.2.

Table 1.2 Various branches of spectroscopy and the molecular phenomenon associated with them.

Branch	Phenomenon	Wavelength	Information
γ -rays	Nuclear transitions	$0.3\text{--}0.003\text{ \AA}$	Oxidation states
x-rays	Electronic transitions (inner electrons)	$100\text{--}0.3\text{ \AA}$	Core electron energies
Visible/UV	Electronic transitions (outer electrons)	$1\text{ }\mu\text{m}\text{--}300\text{ \AA}$	Electron configuration
Infrared	Molecular vibration, molecular rotation	$300\text{--}1\text{ }\mu\text{m}$	Stiffness of bonds
Microwaves, far infrared	Electron spin, molecular rotation	$30\text{--}0.3\text{ m}$	Bond lengths and bond angles
Radio waves	Nuclear magnetic resonance, nuclear quadrupole resonance	$300\text{--}3\text{ m}$	Electronic structure near the nucleus

1.3 BORN–OPPENHEIMER APPROXIMATION

The nucleus of an atom is much heavier as compared to its electrons and, therefore, the motion of the two can be considered independent of each other, e.g. the mass of the hydrogen nucleus is 1840 times than that of an electron. The total energy (E) of the system is thus the sum of energies due to electronic (E_{elec}) and nuclear (E_{nuc}) motions.

$$E = E_{\text{nuc}} + E_{\text{elec}} \quad (1.4)$$

where

$$E_{\text{nuc}} = E_{\text{trans}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{introt}} \quad (1.5)$$

Here, E_{trans} , E_{vib} , E_{rot} , and E_{introt} stand for translational, vibrational, rotational and internal rotational energies, respectively. In general, we can say that each degree of freedom can be treated independently. In the present studies, E_{trans} is omitted since it is not quantised.

1.4 SCHRÖDINGER WAVE EQUATION

This is a second-degree differential equation and is the most appropriate method of providing us the solution of one-body problems. The time-independent forms of this equation in one and three dimensions are given by the expressions (1.6) and (1.7), respectively.

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - U)\psi = 0 \quad (1.6)$$

$$\nabla^2\psi + \frac{8\pi^2m}{h^2}(E - U)\psi = 0 \quad (1.7)$$

where ψ is the wave function which describes the wave property of a particle with mass m , ∇^2 is the Laplacian operator and is expressed as follows:

$$\text{Cartesian coordinates: } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\text{Polar coordinates: } \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2};$$

where $x = r \sin \theta \cos \phi$, $y = r \sin \theta \sin \phi$, $z = r \cos \theta$; $d\tau = r^2 \sin \theta dr d\theta d\phi$.

Rearranging Eq. (1.7), we get

$$\left(\frac{-h^2}{8\pi^2m} \nabla^2 + U \right) \psi = E\psi \quad (1.8)$$

$$H\psi = E\psi \quad (1.9)$$

where $H = \frac{-h^2}{8\pi^2m} \nabla^2 + U$ is known as the *Hamiltonian operator*.

A wave function ψ is associated with a state of physical system corresponding to energy E , i.e., it represents the energy state of the system.

The energy of various types of motions, viz., electronic, vibrational, rotational, etc., can be determined with the help of Schrödinger wave equation and it is found that

$$E_{\text{elec}} > E_{\text{vib}} > E_{\text{rot}}$$

1.5 GENERAL CONDITION OF RESONANCE

Resonance phenomenon may have both useful and harmful effects. For instance, a company of soldiers was marching in step across a bridge in St Petersburg and the bridge collapsed. Investigation showed that the period of free oscillation of the bridge coincided with that of an ordinary marching step. When any atomic or molecular system is exposed to electromagnetic radiation, the absorption or emission (in emission, the sample itself serves as a source and emission is complementary to absorption) of a photon with frequency ν will occur only if the energy difference ΔE between the ground and excited states of the system matches the energy of the photon, i.e.,

$$\pm \Delta E = E_2 - E_1 = h\nu \quad (1.10)$$

This is the resonance condition, and the pictorial view of it is shown in Fig. 1.3.

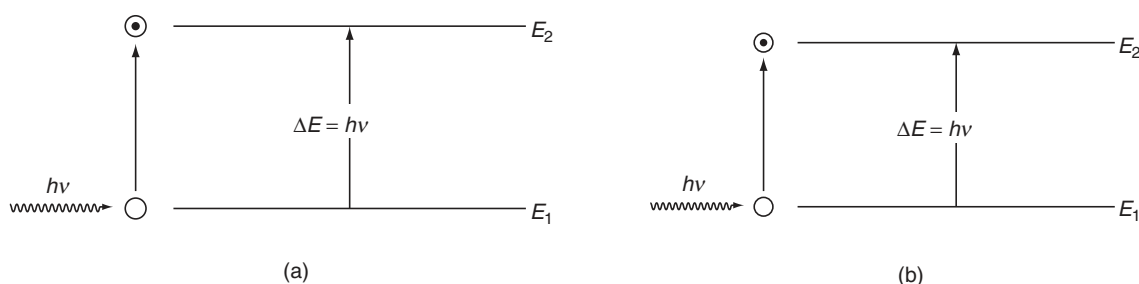


Fig. 1.3 Sketch of (a) absorption, and (b) emission phenomena under resonance conditions, O—molecule in the ground state, O—molecule in the excited state.

1.6 BOLTZMANN DISTRIBUTION LAW AND POPULATION IN ENERGY STATES

The population in any energy state is governed by the Boltzmann distribution law, i.e., at equilibrium,

$$N_x = N_0 e^{-E_x / \kappa T} \quad (1.11)$$

where N_x is the number of particles in a given state x with energy E_x . N_0 is the total number of particles in the zeroth energy level, T is the absolute temperature, κ is the Boltzmann constant: $\kappa = 1.38044 \times 10^{-16}$ erg degree $^{-1}$; $N \kappa = R$, the gas constant. The degeneracy of a state increases the population of a particular energy state.

If the number of molecules in the state with energy E_2 is N_2 , and the number in the states with energy E_1 are N_1 then the Boltzmann distribution law states that at equilibrium

$$\frac{N_1}{N_2} = \frac{e^{-E_1 / \kappa T}}{e^{-E_2 / \kappa T}} = e^{+\Delta E / \kappa T} \quad (1.12)$$

The population difference between the two states may be deduced from the population ratio expression (1.12) as follows:

$$\frac{N_1 - N_2}{N_1 + N_2} = \frac{e^{\Delta E / \kappa T} - 1}{e^{\Delta E / \kappa T} + 1}$$

Since $N_1 = N_2 = N$; $e^x = 1 + x + \frac{x^2}{2!} + \dots$ and $\frac{\Delta E}{\kappa T} \ll 1$

Therefore,
$$\Delta n = N_1 - N_2 = \frac{N \Delta E}{2 \kappa T} \quad (1.13)$$

Thus, the population difference Δn relates directly to the total population, the energy difference between the two states and inversely to the absolute temperature.

1.7 WIDTHS AND SHAPES OF SPECTRAL BANDS

Theoretically, the transition, due to absorption of photons, occurs between two exactly defined energy levels under the resonance condition, i.e. $\pm \Delta E = E_2 - E_1 = \pm h\nu$. Therefore, the absorption bands should have no width at all [Fig. 1.4(a)]. However, the observations are contrary to this hypothesis. Even with very high-resolving-power spectrometers, it is not possible to get a widthless band since there is a minimum width, called the *natural bandwidth*, inherent in any molecular or atomic transition. This width arises because energy levels of molecular systems are not precisely determined except in the ground level. According to Heisenberg's uncertainty principle, if a system exists in any energy state for a time of Δt seconds, the energy of that state will be uncertain to the extent

$$\Delta E \text{ where } \Delta E \times \Delta t \geq \frac{h}{2\pi} \approx 10^{-34} \text{ Js,}$$

where h is Planck's constant. The system will remain in the ground state for an infinite time, i.e., $t = \infty$ and $\Delta E = 0$, since the ground energy state of a system is well defined. However, the excited state has a finite lifetime. Therefore, we cannot, represent the excited level by a sharp line which represents only one value of energy, i.e., E_2 . Hence, the transition between the excited and ground levels will have an uncertainty in energy ΔE . In other words, we can say that the energy spread ΔE of the excited state manifests itself in the form of a band in the

transition between the two states. The width of the band (which actually is a contour of a bunch of lines) is called *natural bandwidth* and is defined as the width of the band at half its height [Fig. 1.4(b)].

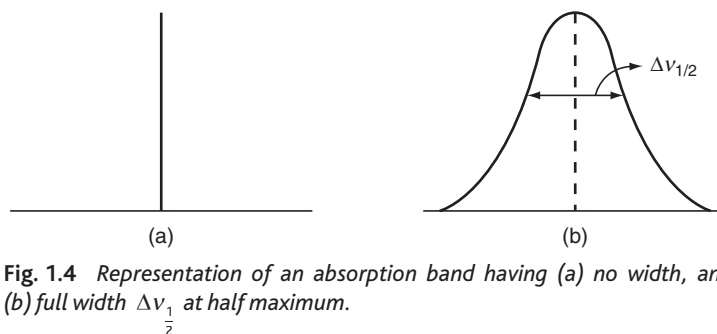


Fig. 1.4 Representation of an absorption band having (a) no width, and (b) full width $\Delta\nu_{1/2}$ at half maximum.

In general, according to the uncertainty principle, the width of a band from one excited state to another is given by

$$\Gamma = \frac{h}{2\pi} \left[\frac{1}{\tau_{ex_1}} + \frac{1}{\tau_{ex_2}} \right], \quad (1.14)$$

where τ_{ex_1} , and τ_{ex_2} are the lifetimes of the respective levels. If one of the states is well defined, i.e., $\tau_{ex_1} = \infty$, the natural width Γ_n of the excited state is given by the general expression

$$\Delta E = \Gamma_n = \frac{h}{2\pi \tau_{ex}} \quad (1.15)$$

The natural bandwidth of the absorption band or the source emission may also be expressed in terms of half-life ($t_{1/2}$) of the excited state. We know that $t_{1/2} = \tau_{ex} \ln 2$.

Therefore,
$$\Delta E = \Gamma_n = \frac{0.693}{t_{1/2}} \cdot \frac{h}{2\pi} \quad (1.16)$$

The transition times for electronic, vibrational and rotational transitions are 10^{-15} , 10^{-13} and 10^{-12} second, respectively. Therefore, the order of natural bandwidths for the respective bands will follow the order: electronic > vibrational > rotational. In general, the natural width of spectral bands is very small and is usually masked by other effects which contribute to the broadening of spectral bands. Among these, the most important are pressure or collision broadening effect and Doppler effects.

(a) Pressure Broadening Molecules of gases and liquids always collide with each other. As a result of such collisions, the energy levels of the molecules get perturbed which result in broadening of the band. The mechanism for pressure broadening may be explained as follows: The molecules/atoms emitting or absorbing radiation in gases undergo collisions. In each collision, there is a certain probability that an atom/molecule in an excited state will make a radiationless transition to the ground or lower state so that the lifetime of the excited state will be decreased. If the number of collisions/second removing atoms from the excited state is N_c then the total number of transitions out of the excited state are

$$\left(N_c + \frac{1}{\tau_{ex}} \right)$$

where τ_{ex} is the lifetime of the excited state. The total observed width of the band will then be

$$\Gamma = \Gamma_n + \Gamma_p = \frac{h}{2\pi} \left(N_c + \frac{1}{\tau_{ex}} \right) \quad (1.17)$$

where Γ_p is the contribution to bandwidth from pressure effect and is given by

$$\Gamma = \frac{1}{\pi l_0} \sqrt{\frac{8RT}{M}} \quad (1.17a)$$

Here l_0 is the mean free path, M is the molecular mass and T is the absolute temperature.

Since the number of collisions/second depends upon the pressure of the gas/liquid, this effect is called pressure broadening. In order to observe experimentally the natural line width, it is essential to reduce the pressure in the spectral source. Thus, by changing the pressure and observing the corresponding change in bandwidth, one can obtain information about the collisions occurring in a gas or a liquid. Solid-phase spectra are often sharp due to a limited number of molecular collisions. However, the splitting of spectral bands into components is evidence for molecular collisions in solids.

(b) Doppler Broadening This effect arises due to the relative motion of molecules of gases or liquids with respect to the photons. Thus, depending upon the direction of motion of the molecules, with respect to photons of frequency ν and velocity (v), the observed frequency (ν_{obs}) is shifted either towards the lower or higher frequency. The frequency shift $\Delta\nu$ is given by

$$\frac{\Delta\nu}{\nu} = \frac{\nu - \nu_{\text{obs}}}{\nu} = \pm \frac{v}{c} \quad (1.18)$$

The signs (+) and (−) indicate that the molecule is moving away from and towards the photons respectively.

Since the molecular systems under investigation have a large number of molecules moving with different velocities relative to the photons, the broadening of bands results. The contribution of Doppler effect to line broadening is given by the expression

$$\Gamma_D = \frac{2\nu_{\text{obs}}}{c} \sqrt{\frac{2RT \ln 2}{M}} = 1.665 \frac{\nu_{\text{obs}}}{c} \sqrt{\frac{2RT}{M}} \quad (1.18a)$$

$$\text{or in terms of wavelength } \Gamma_D = 1.665 \frac{1}{\lambda_{\text{obs}}} \sqrt{\frac{2RT}{M}} \quad (1.18b)$$

where the terms and symbols have their usual meanings. The Doppler broadening is least in high atomic mass atoms, so ^{198}Hg should be an ideal light source for sharp spectral lines. It is to be kept in mind that while collision broadening predominates in liquids compared to that in gases, Doppler effect often determines the natural bandwidth in gases.

From the foregoing discussion, it is evident that the net effect of all of these phenomena results in imparting a finite width to the spectral bands. There are two types of curves encountered in spectroscopy: ‘Lorentzian line shape’ and ‘Gaussian line shape’. The main difference between the two types of line shapes is that the outer wings of the Lorentzian lines are much longer and drop more slowly than those of Gaussian lines. The two types of normal spectral curves and the first and second derivatives of the respective curves have been shown in Figs 1.5(a) and (b) respectively. In practice, we obtain neither pure Lorentzian nor pure Gaussian type curves but an admixture of these curves. The Lorentzian and Gaussian curves may be fitted into the mathematical expression given by

$$I_G = \frac{p}{\sqrt{\pi}} e^{-p^2(x-a)^2} \quad (1.19)$$

$$I_L = \frac{a}{\pi} \frac{1}{a^2 + x^2} \quad (1.20)$$

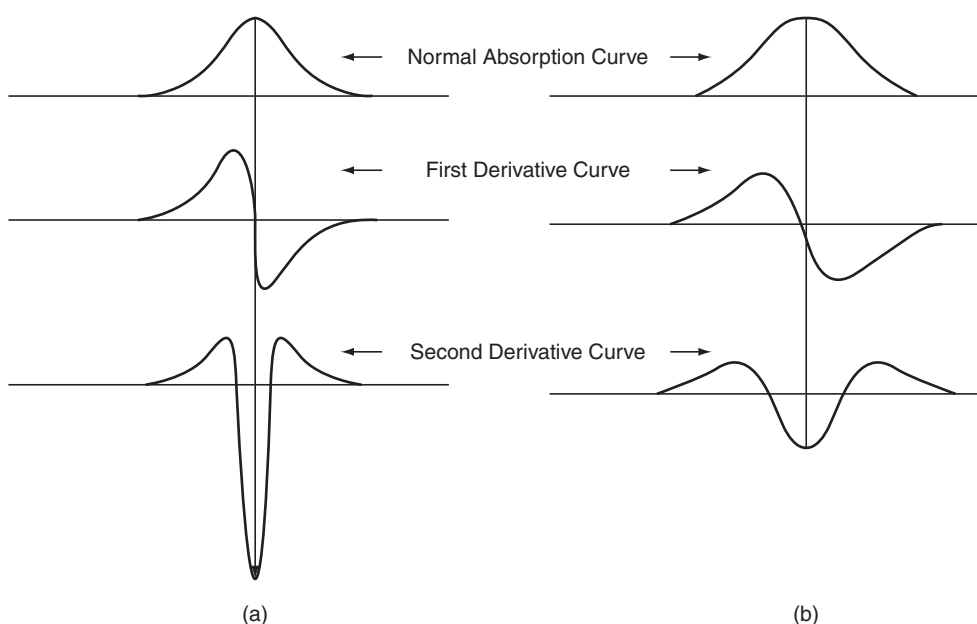


Fig. 1.5 Types of absorption line shapes: (a) Lorentzian, and (b) Gaussian.

Here, $p = \frac{1}{2b^2}$, and the constants a and b stand for standard and mean deviations respectively.

These two types of curves can be identified by the following two methods: (i) the slope of the derivative curve shown in Fig. 1.6, and (ii) the normalisation plot presented in Fig. 1.7. In this method, the baseline is divided into units of m , where m is the point on the abscissa where the curve reaches a maximum and the ordinates are normalised to unity. For broad absorption, it is preferred to record the absorption signal as the derivative curve. The latter has two advantages: (i) The point of maximum absorption is difficult to measure accurately with a broad absorption curve but is shown with great precision as the intersection- of two lines in the derivative curve. (ii) Slope is zero in the derivative curve corresponding to the maximum in the absorption curve.

The number of peaks which appear as shoulders that never pass through maximum in an absorption curve correspond to the number of maxima or minima in the derivative curve. The maxima or minima do not cross the abscissa since slope in the derivative curve corresponding to the shoulder in the absorption curve is nonzero (Fig. 1.8), and (ii) the intensity of derivative signal can be estimated more accurately as compared to the corresponding broad absorption.

Gaussian Line

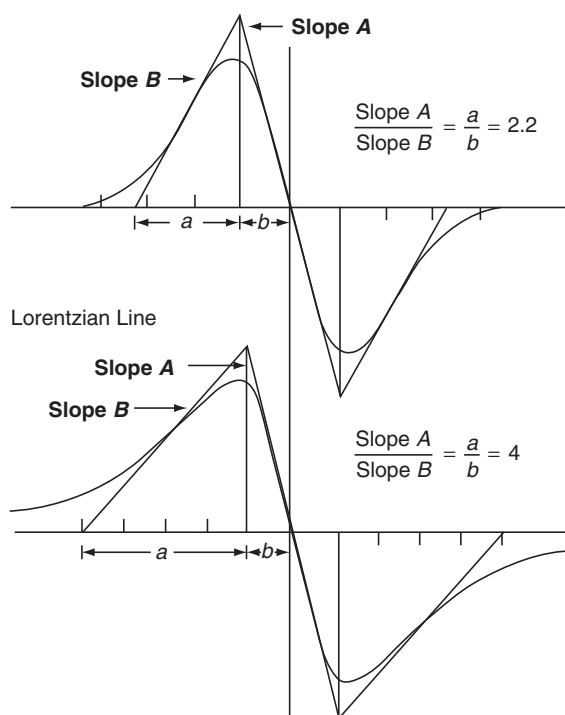


Fig. 1.6 The slope ratio method for identification of Gaussian and Lorentzian derivative curves.

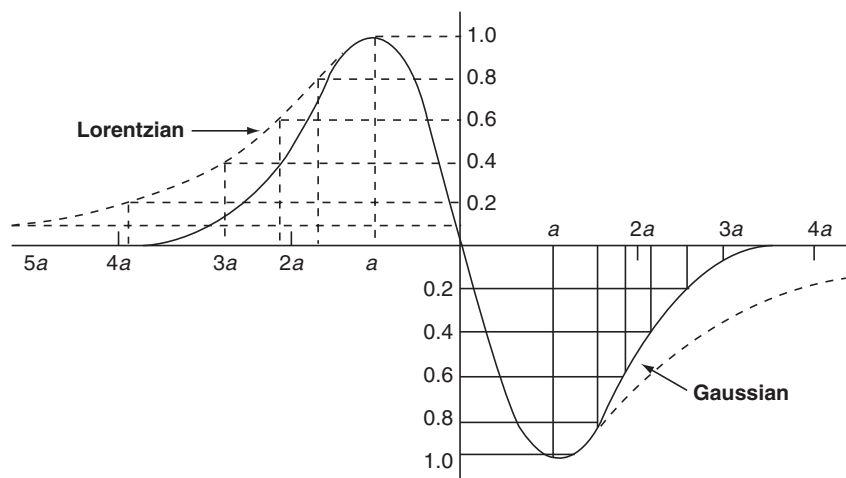


Fig. 1.7 The normalization method for identification of Lorentzian and Gaussian derivative curves.

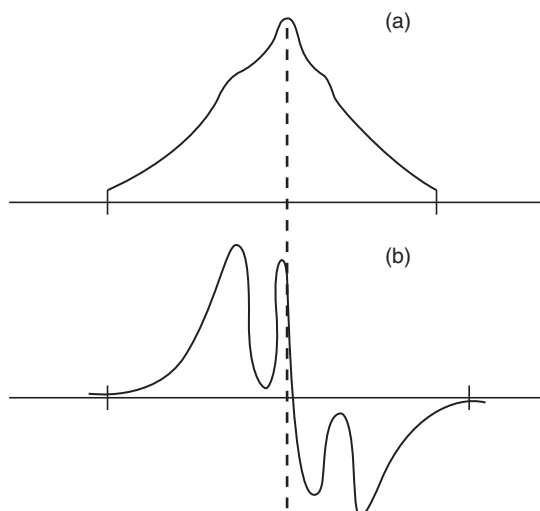


Fig. 1.8 Comparison of (a) absorption, and (b) derivative curves.

1.8 INTENSITY OF THE SPECTRAL BANDS (OR QUANTUM MECHANICAL TREATMENT OF TRANSITION BETWEEN TWO STATES)

The intensity of spectral signal depends upon the transition probability, population of the atoms or molecules in the state from which transition is occurring, and the concentration as well as the path length of the substance through which the electromagnetic radiations are passing. The transition from a lower to a higher state takes place according to certain rules, deduced quantum-mechanically and experimentally and are called selection rules.

While the transition probability for allowed or permissible transitions is nonzero, it is zero for forbidden transitions. Now let us consider that transition takes place from an initial state, with energy E_1 and population N_1 , to an excited state, with energy E_2 and population N_2 under the influence of electromagnetic radiation of frequency ν having density $\rho(\nu)$ as shown in Fig. 1.9. According to the Boltzmann distribution law (Eq. 1.11), at equilibrium, the population ratio in the two states may be expressed as

$$\frac{N_1}{N_2} = e^{h\nu_{12}/kT} \quad (1.21)$$

The number of molecules making a transition per unit time from the state 1 to 2, i.e., intensity of radiation due to induced absorption

$$= B_{12} N_1 \rho(\nu_{12}) \quad (1.22)$$

Here, B_{12} is called the *Einstein transition probability of induced absorption*, units of B_{12} are $(\text{J}^{-1}\text{m}^3 \text{s}^{-1} \text{number}^{-1})$ (number $\text{s}^{-1}) = \text{J}^{-1}\text{m}^3\text{s}^{-2} = \text{kg}^{-1}\text{m}$ and that of $\rho(\nu_{12})$ are $\text{Jm}^{-3} \text{s}$.

The number of molecules making a transition per unit time from the state 2 to 1, i.e., the intensity of radiation due to induced emission

$$= B_{21} N_2 \rho(\nu_{12}) \quad (1.23)$$

Here, B_{21} is known as the *Einstein transition probability of induced emission* which is due to the perturbation caused by the field of electromagnetic radiation. In addition, the molecules in the state 2 may emit radiation spontaneously such that $\Delta E = E_2 - E_1 = h\nu$. The spontaneous emission occurs in the absence of an external field. Thus, the number of molecules making spontaneous emission per unit time, i.e., the intensity of radiation due to, spontaneous emission is

$$= A_{21} N_2 \quad (1.24)$$

A_{21} is called the *Einstein coefficient of spontaneous emission*.

At equilibrium, the rate of absorption is equal to the rate of emission, i.e.

$$B_{12} N_1 \rho(\nu_{12}) = B_{21} N_2 \rho(\nu_{12}) + A_{21} N_2 \quad (1.25)$$

We know that $B_{12} = B_{21}$; then rearranging Eq. (1.25) we get

$$\rho(\nu) = \frac{N_2 A_{21}}{B_{21}(N_1 - N_2)} \quad (1.26)$$

Combining Eq. (1.21) and Eq. (1.26) we obtain

$$\rho(\nu) = \frac{A_{21}}{B_{21}(e^{h\nu/kT} - 1)} \quad (1.27)$$

According to Planck's law of radiation,

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{(e^{h\nu/kT} - 1)} \quad (1.28)$$

Dividing Eq. (1.28) by Eq. (1.27), we obtain

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3} \quad (1.29)$$

Thus, with the aid of Eq. (1.29) and having a knowledge of B_{21} , we can compute A_{21} and vice versa. These quantities may be determined both experimentally and theoretically. A_{21} can be determined directly from the Fermi-Dirac theory of radiation. The following relationship exists between the areas of the absorption band and the corresponding probability of absorption, B_{12} .

$$B_{12} = \frac{1}{N} \frac{c}{h\nu_{12}} \int_0^\infty A_\nu d\nu \quad (1.30)$$

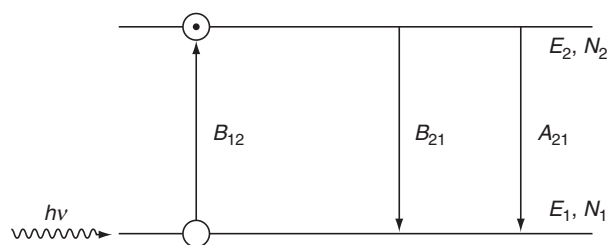


Fig. 1.9 Transition between two states of a molecule.

Thus, the probability of quantum transition may be determined from the area of the absorption band, i.e.

$$\int_0^{\infty} A_{\nu} d\nu$$

which is determined from the dependence of the absorption coefficient, A_{ν} of the appropriate band on the frequency, ν . The area of the absorption curve may be measured most accurately by the paperweight method.

If N_2^0 is the number of molecules in the excited state at $t = 0$ and N_2^t is the number at any time t then

$$\frac{-dN_2^t}{dt} = A_{21}N_2^t$$

or

$$N_2^t = N_2^0 e^{-A_{21}t} \quad (1.31)$$

After a certain time

$$\tau = \frac{1}{A_{21}}, N_2^t = \frac{N_2^0}{e} \quad (1.32)$$

For allowed transitions, $\tau \approx 10^{-8}$ s; while for some excited states, τ is of the order of 10^{-3} s, and are called *metastable states*.

The spontaneous emission is always in all the 4π , solid angles, and thus its contribution in the direction of induced emission will be very small and is, therefore, neglected. Mathematically, when the solid angle (dw) in the direction of observation is very small, then $dw/4\pi$ will be very small, i.e., when $dw \rightarrow 0$, $dw/4\pi \rightarrow 0$.

Since only the induced emission is coherent with the incident beam of radiation, the net absorption intensity is given by

$$\begin{aligned} I_a &= N_1 \rho B_{12} - N_2 \rho B_{21} \\ &= \rho B_{21} (N_1 - N_2) = \rho B_{21} \Delta n \end{aligned} \quad (1.33)$$

That is, the intensity of radiation depends upon the population difference between the states with energies E_1 and E_2 , provided ρ is constant and transition between these states is permissible according to the selection rule, i.e., transition probability $B_{21} = B_{12} \neq 0$.

Since by Eq. (1.13),

$$\Delta n = \frac{N \Delta E}{2kT}$$

consequently, Eq. (1.33) reduces to,

$$I_a = \rho B_{21} \frac{N \Delta E}{2kT} \quad (1.34)$$

i.e., the net intensity of the absorption line depends on the total population in the ground state, the energy difference between the two states, absolute temperature and population difference between the two states at equilibrium, provided ρ is kept constant.

Now, if transition is occurring as per selection rules from two initial states with different populations to some other state then the intensity of the transition from initial state with greater population will be higher as compared to the state with a smaller population.

The net intensity of absorption is related to the concentration C of the sample and the path length l by the Beer–Lambert law represented by

$$T = \frac{I_t}{I_0} = e^{-\epsilon Cl} \quad (1.35)$$

$$A = \ln \frac{I_0}{I_t} = \epsilon Cl \quad (1.36)$$

where I_t is the intensity of the transmitted radiation, I_0 is the intensity of incident radiation, A is the absorbance, C is the concentration of the absorbing species, l is path length, and ϵ is the molar extinction or molar absorbance or molar decadic extinction coefficient which is different for different transitions. ϵ depends upon transition probability—the larger the value of ϵ , the larger will be the transition probability. This law is strictly valid for radiation of a single wavelength, i.e. for monochromatic radiation. Lambert's law ignores the concentrations. A common student version of the Beer–Lambert law is

“The taller the glass the thicker the brew, the less light that gets through.”

The terms and symbols for use in the Beer–Lambert law are given in Table 1.3. It should be noted that Beer's law does not hold good in all cases. The deviations from Beer's law are accounted for by the different degrees of association, solvation and dissociation of molecules in solutions of different concentrations. Therefore, in

Table 1.3 Terms and symbols used in Beer–Lambert law.

Current Symbol	Definition	Current Name	Obsolete Symbol	Obsolete Name
T	$\frac{I_t}{I_0}$	Transmittance	–	Transmission
A	$\ln \frac{I_0}{I_t}$	Absorbance	D, E	Optical density, Extinction
a	$\frac{A}{bC}$	Absorptivity	k	Extinction coefficient, Absorbancy index
E	$\frac{AM}{bC}$	Molar absorptivity	a_M	Molar (molecular) coefficient, Molar absorbancy index
b	–	Path length	l, d	–

M is the molecular mass of absorbing species, C is the concentration in g/litre^{-1} , l is the path length in cm. $E_{1\text{cm}}^{1\%} = A/bC'$ where C' is in per cent by weight and $b = 1$ cm. Note that when the Beer–Lambert law is written in terms of natural logarithm instead of the base ten logarithm, the molar extension coefficient (ϵ) is called the Napierian absorption coefficient (ϵ_e), and the absorption (A) is called the Napierian absorption (A_e). $\epsilon_e = 2.3026\epsilon$.

measuring absorption spectra in solutions of different concentrations, it is necessary to check whether conformity of Beer's law is observed, e.g. the double increase of concentration must be equivalent to the doubled thickness of the absorbing layer at the same concentration.

Problem 1.1: (a) Prove that photometric accuracy is the maximum at 37 per cent transmittance and remains within tolerable limit over a range of transmittances about 15 to 65 per cent (absorbances of 0.8 to 0.2). (b) Plot a hypothetical curve between per cent transmittance and $\log C$. Does this graph give any indication of the relative precision at various levels of absorbance?

Solution (a) Even for a system which obeys Beer's law, the concentration range over which photometric analyses are useful is limited at both high and low values. Therefore, at both high (little radiant energy is transmitted) and low (large amount of radiant energy is transmitted) concentrations of absorbing material, the uncertainty in the measurement of A or T exceeds the permissible experimental limits. For the greatest accuracy in the measurement of absorbance A , the increment ΔA , which corresponds to the intensity change ΔI_t , must be as small a fraction as possible of the actual absorbance A , i.e. the quantity $\Delta A/A$ should be minimum. This is proved as follows:

According to Beer's law,

$$I_t = e^{-A} I_0$$

$$A = \log \frac{I_0}{I_t} = \log I_0 - \log I_t \quad (1.37)$$

Differentiating with respect to I_t

$$dA = -(\log e) \frac{1}{I_t} dI_t \quad [I_0 \text{ is constant}]$$

Dividing both sides by A and substituting the value of $\log e (= 0.4343)$, we obtain,

$$\frac{dA}{A} = \frac{0.4343}{A} \frac{1}{I_t} dI_t$$

Since

$$I_t = e^{-A} I_0$$

Therefore,

$$\frac{dA}{A} = -\frac{0.4343}{A} \frac{1}{I_0 10^{-A}} \cdot dI_t$$

Replacing differentials by finite increments

$$\frac{\Delta A}{A} = -\frac{0.4343 \Delta I_t}{I_0} \left(\frac{1}{A \times 10^{-A}} \right)$$

Differentiating with respect to A (ΔI_t is constant)

$$\frac{d(\Delta A/A)}{dA} = -\frac{0.4343}{I_0} \left(\frac{10^A \ln 10}{A} - \frac{10^A}{A^2} \right)$$

For $\frac{\Delta A}{A}$ to be minimum, $\frac{d(\Delta A/A)}{dA} = 0$
This means

$$\frac{10^A \ln 10}{A} = \frac{10^A}{A^2}$$

from which

$$A = \frac{1}{\ln 10} = 0.4343$$

This means that the optimum value for the abundance is 0.4343 which corresponds to transmittance $T = 36.8$ per cent. The relative error in an analysis resulting from 1 percent error in the photometric measurements for varying transmittance and absorbance is shown in Fig. 1.10, which reveals that although the error is least at 37 per cent T , it will not be much greater over a range of transmittances about 15 to 65 per cent (absorbances 0.8 to 0.2).

(b) The conventional method of plotting a calibration graph for spectrophotometric analyses is either the exponential curve or the straight line. The latter has the advantage of showing the region over which Beer's law is obeyed, but it fails to give any indication of the relative precision at various levels of absorbance. However, a plot between per cent transmittance and $\log C$ shown in Fig. 1.11 gives some additional features. If a sufficient range of concentrations are covered, an S-shaped curve called *Ringbom curve* always results. If the system does not deviate from Beer's law, the point of inflection occurs at 37 percent transmittance, otherwise, the inflection is at some other value but the general shape of the curve is the same. The curve generally has a considerable region which is nearly straight. From the straight-line portion, the optimum range of concentrations can be selected for the particular spectrophotometric analyses. The precision of analyses can be estimated from the slope of the curve. The steeper the curve, the more sensitive the test is.

It can be proved by a differentiation procedure that if the absolute photometric error is 1 percent, the percent relative error in the analysis is given by $230/m_s$, where m_s is the slope taken as the transmittance change (read from the vertical axis) in percent corresponding to a tenfold change in concentration.

The commercial spectrometers record the percentage of light transmitted by the absorbing species and is given by the expression

$$\text{Per cent transmittance} = 100 \frac{I_t}{I_0} \quad (1.38)$$

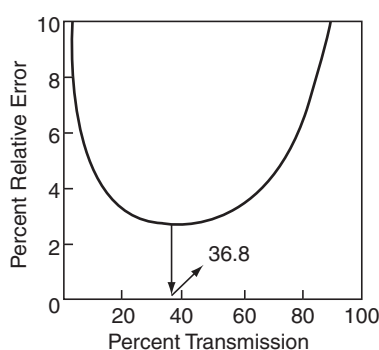


Fig. 1.10 Relative error as a function of transmittance.

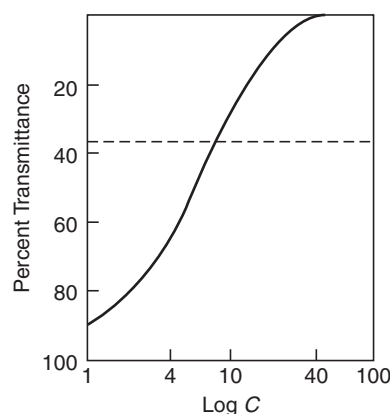


Fig. 1.11 Percent transmittance as a function of logarithm of concentration.

1.9 SPECTRUM AND BASIC ELEMENTS OF A SINGLE-BEAM AND DOUBLE-BEAM ABSORPTION SPECTROMETER

We know that when a beam of radiation falls on a sample, it may induce, depending upon its energy, electronic, vibrational or rotational transitions between the ground and excited states of the sample under resonance condition, i.e., $\pm \Delta E = h\nu$. The radiation falling on the sample may undergo absorption, transmission, scattering and reflection. If I_0 is the intensity of the incident radiation, then

$$I_0 = I_a + I_t + I_s + I_r \quad (1.39)$$

where I_a , I_p , I_s and I_r are the intensities of the respective phenomena. At the glass–air interface, I_r is very small (0.2–0.5%) and hence can be neglected. Thus, Eq. (1.39) may be written as

$$I_0 = I_a + I_t + I_s \quad (1.40)$$

The intensity of the absorbed radiation is measured as a function of energy with the help of an instrument called *absorption spectrometer*. The curve between absorbance versus wavelength is termed the *absorption spectrum*. In general, we can say that the spectrum, which is a characteristic of any electromagnetic radiation, is a graph on which the intensity is plotted in the vertical direction and the energy or wave number in the horizontal direction. The hypothetical spectrum for a single transition is shown in Fig. 1.12.

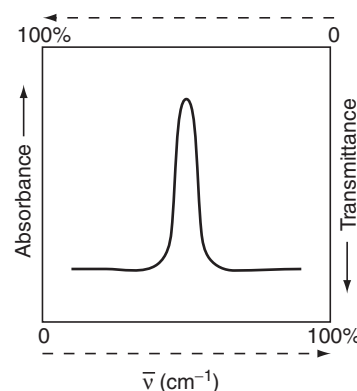


Fig. 1.12 Hypothetical spectrum corresponding to a single transition.

The width of a beam of monochromatic radiation is controlled with the aid of a slit element of the spectrometer. This beam is made to fall on a sample where it gets partially absorbed and causes transitions in the sample. The transmitted part of radiation is then detected by the detector and analysed in an analyser. In a double-beam spectrometer, the monochromatic beam is split into two components, namely, sample and reference beam, by an additional element known as splitter, and are passed through the sample and the reference. The transmitted radiation from the sample and the reference is then detected and analysed separately. In practice, in a double-beam spectrometer, the intensity of transmitted radiation I_0 through reference, but not the intensity of radiation I from the source, is taken as the intensity of incident radiation. On the other hand, in a single-beam spectrometer, since no reference is involved, I automatically takes the status of I_0 . The advantage of a double-beam over a single beam spectrometer is that the spectral signals due to reference and source get automatically eliminated. The fundamental elements of single-beam and double-beam absorption spectrometers are shown in Figs 1.13 (a) and (b) respectively.

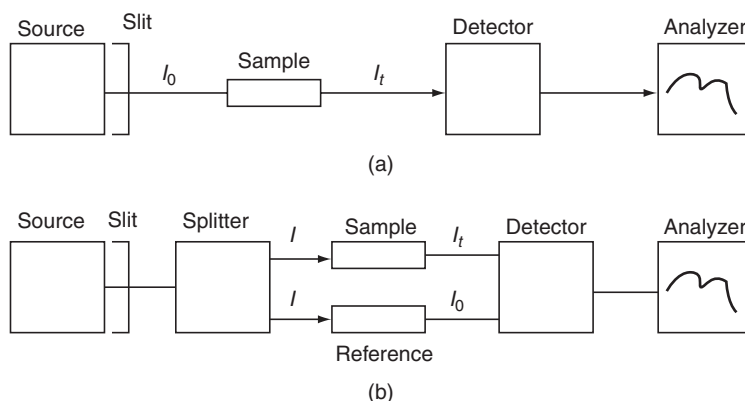


Fig. 1.13 Arrangement to observe absorption spectrum with (a) single, and (b) double-beam spectrometer.

Emission spectrum, which is only recorded in special studies, is generally ignored due to the following reasons. Firstly, since every sample to be studied has to be made an emission source for all the samples, emission studies are not simple and economical. Secondly, during emission itself (especially in the case of γ - and x -rays) there could be radiation damage that may change the structure of the sample.

1.10 SIGNAL-TO-NOISE RATIO

In modern spectrometers, the signal produced by a detector is amplified by electronic amplifiers. Resulting random fluctuations due to electronic signals, called noise, appear in the spectrum. Therefore, the real peak in the spectra will easily be detected if its intensity is large in comparison to noise. The sensitivity of detection of the actual peak is maximum when signal-to-noise ratio is of the order of 3–4.

1.11 RESOLVING POWER OF A SPECTROMETER AND ITS RELATION TO SLIT WIDTH

The efficiency of a spectrometer in separating the bands in a spectra is called its resolving power. According to Lord Rayleigh's criterion, two wavelengths differing by $\Delta\lambda$ are said to be resolved when the central maximum of one coincides with the first minimum of the other. Resolving power is then defined as

$$R_p = \frac{\lambda}{\Delta\lambda} = \frac{\bar{\nu}}{\Delta\bar{\nu}} \quad (1.41)$$

where λ or $\bar{\nu}$ is the average of two wavelengths or wave numbers, and $\Delta\lambda$ or $\Delta\bar{\nu}$ is the smallest difference between two wavelengths or wave numbers that can be measured on a spectrometer (Fig. 1.14).

As such, the quantity $\lambda/\Delta\lambda$ is called the theoretical resolving power. We know that molecular absorption does not take place at a single wavelength only but occurs over a range of wavelengths that depends upon the width of the entry slits. This parameter, which reduces the theoretical resolving power and width of slits, is called the *finite* or *mechanical slit width*, while the small region of energy isolated by the exit slits is called the *spectral slit width*. The distribution of energy as a function of wavelength emitted from the exit slit is known as *slit function*. Thus, resolution of an instrument depends upon the spectral slit width and is proportional to the mechanical slit width. Hence, narrower slits result in better resolution. Further, the energy received by the detector is proportional to the square of the mechanical slit width. Thus, narrowing of this width to improve resolution has a negative effect on the efficiency of the instrument, i.e. narrow slit width allows less energy from the beam to reach the detector, and as a result, the strength of a signal will decrease. At a certain value of the slit width, the signal-to-noise ratio becomes less than 3–4. Thus, it is fixed at such a value where signal-to-noise ratio is maintained.

Since large slit widths broaden the band, so in any quantitative work the slit width should be less than the width of the band under consideration. In high-resolution spectroscopy, which requires narrowing the slit, the pen output response is slower since the detector is hard worked as less energy is received by it. Hence, fast scanning under these conditions leads to a considerably erroneous spectrum. Deviations from Lambert–Beer's law are observed when the ratio of slit width to bandwidth is greater than an order of 0.4. The deviations are the greatest both at the largest slit widths and where the extinction coefficients have approached a maximum. When slit width is equal to half the value of the bandwidth, the difference between the true and observed maximum extinction coefficient is found to be of the order of 20 per cent.

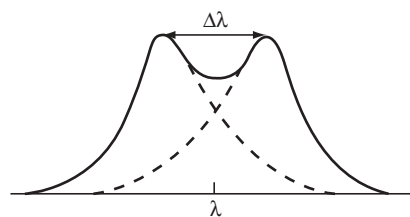


Fig. 1.14 Sketch showing the resolving power of a spectrometer.

1.12 LIMIT OF SENSITIVITY OF THE SPECTROSCOPIC METHOD OF IDENTIFICATION OF SUBSTANCES

The limit of sensitivity of the spectroscopic method of identification of substances is defined as

$$\delta = \frac{I_0 - I_t}{I_0} = \frac{I_a}{I_0} \quad (1.42)$$

For diatomic molecules, it is approximated by

$$\delta = \frac{1}{40} \frac{\lambda_0^3}{\pi c} \cdot A_{21} R_p \ln \quad (1.43)$$

where λ_0 is the wavelength of absorbed radiation. A_{21} is the probability of transition (emission), R_p is the resolving power of the instrument, l is the path length, n is the number of gas molecules in cm^{-3} , i.e. the gas concentration.

Let $\delta = 0.05$, i.e., absorption is 5 percent, $\lambda_0 = 400$ nm (boundary between ultraviolet and visible regions of radiation), $A = 10^8 \text{ s}^{-1}$ and $l = 1$ cm and $R_p = 10^4$ (the theoretical resolving power of an average spectral device), $n = 10^{13} \text{ molecules cm}^{-3}$ or $p = 10^{-4} \text{ mmHg}$ (at 300 K). At high temperatures and also in the case of polyatomic molecules, which have large number of rotational and vibrational degrees of freedom, only a fraction of n molecules absorb the radiation of wavelength λ_0 . In such cases, the limit of sensitivity rarely exceeds corresponding to partial pressures of the order of 10^{-1} – 10^{-3} mmHg . Further, since A is small in the infrared region, the sensitivity in the IR region is very small as compared to the electronic absorption spectrum of the molecules. Due to this very reason, the infrared absorption spectral method is used for the identification of substances in condensed states, i.e. the liquid and solid states. The limit of sensitivity of the spectral method of identification based on emission is higher as compared to that of absorption.

1.13 FOURIER TRANSFORM (FT) AND COMPUTER AVERAGE TRANSIENT (CAT)

The method of Fourier transform spectroscopy is nearly about one hundred and fifty years old and Michelson and Rubens already applied it in principle. Some historical papers are: H Fizeau, Ann. Chim. Phys. (3) 66, 429 (1862), A A Michelson, Phil. Mag. (5) 31, 256 (1891) and (5) 34, 280, (1892), H Rubens and R W Wood, Phil. Mag. 21,

249 (1911). In the last five decades or so, the technique though initially applied by chemists, for optical investigations, especially in the far-infrared region has now made inroads in other fields of spectroscopy also.

The spectroscopic data, say intensity is invariably collected in the time domain, i.e. the data are collected as a function of time and stored. In other words, the Free Induction Decay (FID) signal is stored. Since the spectroscopists are interested in the frequency domain, the time domain is converted to the frequency domain by the mathematical tool known as Fourier Transform (FT). FT relates the time domain data $f(t)$ with the frequency domain data $f(w)$ by the expression

$$f(w) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(t) e^{+iwt} dt \quad (1.44)$$

This is called continuous transform since the limits of integration extend from $-\infty$ to $+\infty$. When the integral limits extend over a finite time, the discrete FT is defined as

$$f(w) = \frac{1}{\sqrt{2\pi}} \sum_{-t}^{+t} f(t) e^{+iwt} dt \quad (1.45)$$

The inverse FT is expressed as

$$f(t) = \frac{1}{\sqrt{2\pi}} \sum_{-w}^{+w} f(w) e^{-iwt} dw \quad (1.46)$$

A strong pulse (each pulse is actually a packet of radiation) is applied to the sample and the resultant spectral response pattern is stored in a small computer. The spectrum, i.e., position and width of the frequency package can be extracted from this information by taking the inverse FT with the help of a large digital computer. FT is equally applicable to emission and absorption spectroscopy and FT spectra can successfully be recorded in the NMR, ESR, UV and IR regions. The FT Raman spectrum can also be recorded.

FT of a time-domain decaying exponential and sinusoidal or cosinusoidal oscillation is a Lorentzian line as shown in the Figs 1.15(a) and (b) respectively. In the latter case, the line shifts from the central zero frequency. This shift is equal to the frequency of the oscillation of the sinusoidal or cosinusoidal. Shown in Fig. 1.16 is the FT of time-domain signal of summed sine waves into frequency-domain spectrum.

The beat frequency is independent while the rate of decay of the overall time-domain signal is dependent on the width of original spectral peak. The larger the width, the larger the decay, provided the spectral peak is at the same central frequency. However, two spectral lines having the same width but at different central frequencies in the frequency domain will have different beat frequencies in the time domain. The beat frequency in the time domain signal increases with the increase in the frequency of line of the spectral peak.

The advantage of FT spectroscopy over conventional spectroscopy is its speed. This is due to the fact that the whole FT spectrum is recorded instantaneously and simultaneously while in the latter case, each point in the spectrum is to be recorded as a function of frequency. So, slit-width adjustment and focusing are no problems in the FT spectrum. The computing and plotting time is of the order of 10 seconds which is much shorter compared to 10–15 minutes required by the conventional method to obtain similar resolutions. The other advantage is that resolving power stays constant over the entire spectrum.

A time-averaging computer or Computer Average Transient (CAT) is used as an accessory with commercial spectrometers in order to enhance the weak signal. The use of CAT in conjunction with FT is useful for obtaining better signal-to-noise (S/N) ratio. The narrow region of the frequency-domain spectrum in which the signal is expected is

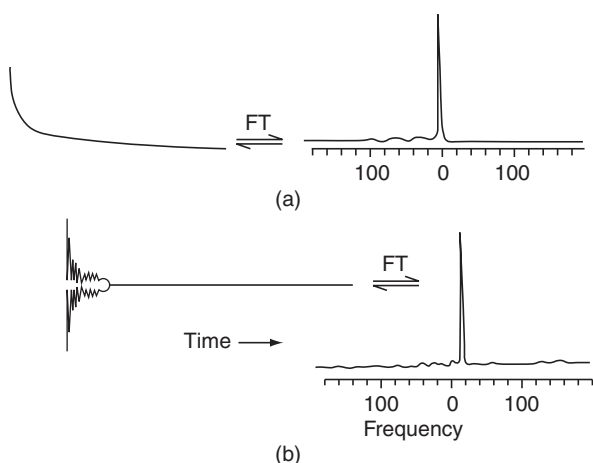


Fig. 1.15 FT of time domain signal of (a) a decaying exponential, and (b) sinusoidal or cosinusoidal oscillation.

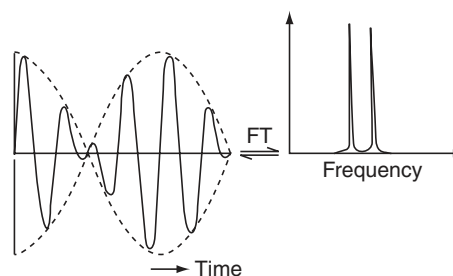


Fig. 1.16 FT of time-domain signal of summed sine waves.

scanned several times. The information obtained in each scan is fed to a small computer and the total information is automatically stored in the main computer. After n summed scans, the signal will be n times enhanced in the store, whereas the noise will accumulate less rapidly due to its random nature. It can easily be shown that n scans will enhance the noise level in the store by $\sqrt{n}$. Hence, the net gain in S/N is $n/\sqrt{n} = \sqrt{n}$. In other words, we can say that an increase in the intensity of the signal is proportional to the square root of the number of scans.

In brief, we can say that in comparing conventional spectroscopy methods and explaining their principles, we are concerned mainly with the problem of how to separate electromagnetic radiation into its spectral elements and to determine the wavelength and frequency as a function of their intensity simultaneously. The problem of separation into spectral elements becomes trivial if a tunable source emitting monochromatic radiation, i.e. laser is used. While with the techniques of optical FTS, the electromagnetic radiation is not separated into spectral elements, rather a two-beam interferometer is used and the interference properties of the electromagnetic radiation as a function of the path difference between the waves are studied; the results of the study, (i.e. the plot between intensity of the constructive interference of waves and path difference (s) called interferogram) are then converted mathematically to the spectrum (i.e. I versus $\bar{\nu}$) on a computer. This conversion is a Fourier transform, which is why the technique is called Fourier transform spectroscopy. This method employs mathematics, computers and electronic data, perhaps new tools, and is hard to digest especially for organic spectroscopists!

1.14 LASER

Laser stands for ‘light amplification by stimulated emission of radiation’. Sometimes, lasers are also called ‘optical masers’. The word *maser* stands for ‘microwave amplification by stimulated emission of radiation’. However, light is not the correct word to be used, because lasers also produce beams in the infrared, ultraviolet, γ -ray and x-ray regions of the spectrum. The use of lasers in science and technology is due to their three important properties: (i) laser radiation is extremely energetic, (ii) laser beams are highly monochromatic and possess an extremely narrow line width, and (iii) laser radiation is highly directional.

In 1964, C H Townes of the Columbia University (USA) shared the Nobel prize with the Soviet physicists A M Prokhorov and N G Basov, of the Lebedev Physical Institute of the USSR Academy of Sciences, in the field of quantum electronics and specifically in the invention of the maser and the laser. The maser was invented prior to the laser.

1.14.1 What is Stimulated Emission?

Consider a box with perfectly reflecting walls containing atoms of a gas and photons. Due to heat energy, the atoms collide with each other and with the walls of the box, continuously interchanging energy which puts some atoms in a higher energy level above the ground level. Einstein in 1919 postulated that in this ‘radiation field’, a photon may interact with an atom and give rise to the following three distinct phenomena, namely (i) absorption, (ii) spontaneous emission, and (iii) stimulated emission of photons.

If a photon strikes an excited atom which has a photon absorbed in it, it would stimulate the atom to emit its absorbed photon, provided the energy of the absorbed photon is equal to that of the impinging photon. This process of emission of radiation is called stimulated emission of radiation.

The essential requirement to get more stimulated emission is to have a larger population of excited atoms (not less than five or so) in the system, so that a photon may have more encounters with the excited atoms, rather than with those in the ground state. It is also essential that the atoms should stay in the excited state long enough, so that interactions between photons and excited atoms may take place before the excited atom spontaneously emits the absorbed photon. The process of maintaining maximum atoms in the excited state is called population inversion and is achieved by (a) electrical pumping, (b) optical pumping, and (c) chemical pumping.

(a) Electrical Pumping It consists of exciting the gaseous atoms by electron impact and is achieved by passing an electric discharge through the system.

(b) Optical Pumping It is also possible to produce a larger population in the excited state by an absorption mechanism in which atoms in the ground state absorb photons of energy corresponding to the energy difference between the ground state and the excited state of the atom. This is called optical pumping.

(c) Chemical Pumping It is based on breaking of chemical bonds. The lasers which are made to work by chemical reactions are called *chemical lasers*. The chemical reactions useful for laser activity are exothermic reactions.

Now, when the photon strikes an excited atom which has a photon absorbed in it, it would stimulate the atom to emit its absorbed energy, provided the energy of the absorbed photon is equal to that of the impinging photon. The photons thus stripped may be in phase and constitute a monochromatic beam of radiation with very large amplitude. The emission of monochromatic radiation by two photons (say '1' with amplitude A_1 and '2' with amplitude A_2 ; $A_2 > A_1$) in and out of phase is shown in Fig. 1.17. The monochromatic radiation may be continuous or it may be in the form of a pulse. The direction of the laser beam is defined by optical resonant cavity which in its simplest version is a pair of spherical mirrors (totally reflecting and output mirrors) set on an optic axis. The active material is placed in between these mirrors. Solid active materials are often in the shape of a cylinder whose axis is aligned with the axis of the optic resonator, the length of the cylinder being about ten times its diameters.

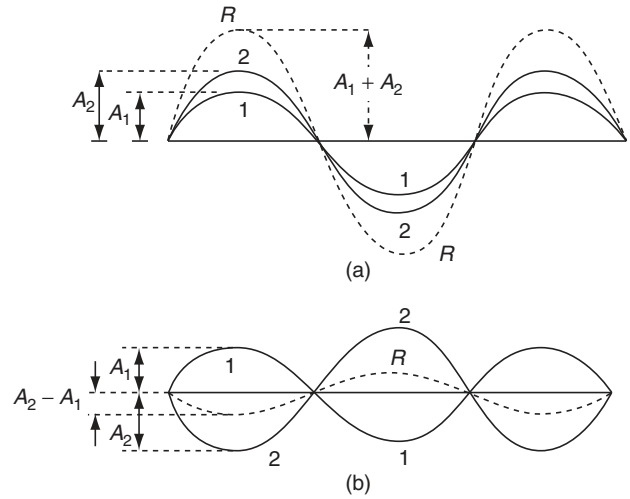


Fig. 1.17 Superimposition of two waves: (a) in phase, and (b) out of phase.

The dimensionless quality factor Q of the resonant cavity is expressed as

$$Q = 2 \pi \nu \tau \quad (1.47)$$

Here, the parameter $1/\tau$ defines the rate of decay of the field energy in the passive resonant cavity. The smaller the losses in the resonator, the smaller $1/\tau$ and consequently, the higher the resonator's Q . The quality factor Q is used to show the ability of the cavity to store energy and is related to the loss factor α having the dimension of reverse length by the expression.

$$\frac{1}{Q} = \frac{\lambda \alpha}{2\pi} \quad (1.48)$$

If the causes of loss are many, say, absorption and radiation through the side surface, we may associate with each type of loss its own α -factor, α_i , and its own Q -factor, Q_i so that

$$\frac{1}{Q_i} = \frac{\lambda \alpha_i}{2\pi} \quad (1.49)$$

If these losses are independent of each other then

$$\alpha = \sum \alpha_i \text{ and } \frac{1}{Q} = \sum \frac{1}{Q_i} \quad (1.50)$$

The loss factor due to radiant losses, α_{rad} has the form

$$\alpha_{\text{rad}} = \ln \frac{(1/r)}{2L} \quad (1.51)$$

where L is the resonator length and r is the reflectivity (reflection factor) of the output mirror (the ratio of the light flux reflected by the mirror to the incident flux).

Diffraction losses increase as the mirror diameter ' a ' decreases and the wavelength and resonator length increase. In order that a resonator be low in diffraction losses at wavelength λ , it should be so long that

$$\frac{a^2}{4\lambda L} \gg 1 \quad (1.52)$$

The dimensionless parameter on the left-hand side is called the Fresnel number

$$N_F = \frac{a^2}{4\lambda L} \quad (1.53)$$

This number is not the only criterion used in estimating diffraction losses. Other features of resonator geometry should also be taken into account. These are determined by resonator length and mirror radii of curvature as laser resonators normally use spherical rather than flat mirrors. So, two resonators of the same Fresnel number may incur different diffraction losses due to different geometry.

Assume for generality that the mirrors have different apertures (a_1 and a_2) and different radii of curvature [$r_c(1)$ and $r_c(2)$]. Such a resonator is defined by three principal parameters:

$$\begin{aligned} N_F &= a_1 a_2 / 4\lambda L \\ G_1 &= (a_1/a_2) [1 - L/r_c(1)] \\ G_2 &= (a_2/a_1) [1 - L/r_c(2)] \end{aligned} \quad (1.54)$$

Two resonators will have equal diffraction losses, if they are identical in these parameters. Such resonators are called equivalent resonators.

The relationship for the line width of the laser at half maximum power in terms of the 'angular frequency' is given below:

$$\Delta = \frac{c^2(1-r)^2}{L^2} \cdot \frac{1}{P} \cdot \frac{N_2}{N_2 - N_1} h\omega_0 \quad (1.55)$$

where c is the velocity of light.

From the above equation, one can easily see that for a laser radiation of angular frequency ω_0 :

(a) line width is inversely proportional to the square of the length of the resonant tube, i.e.

$$\Delta \propto \frac{1}{L^2}$$

(b) line width is also proportional to the reflectivity r , and larger values of r will give narrower line width;

(c) line width is inversely proportional to the power output, i.e.

$$\Delta \propto \frac{1}{P}$$

(d) line width is also proportional to the number of atoms in the excited state.

If we substitute $r = 0.98$, $L = 100$ cm, $N_2/(N_2 - N_1) = 2$, $P = 100$ mW ($1 \text{ W} = 1 \text{ Js}^{-1}$) and the value of ω_0 for 6328 Å line of the He-Ne laser, we end up with a value of Δ which is far less than a wave number. Experimental value of Δ , however, is found to be of the order of 0.05 cm^{-1} .

1.14.2 Wavelength Range and Power Output of Lasers

The wavelength range for coherent radiation emission of gas lasers extends from about 2358 Å to 120.08 μm. Table 1.4 gives the wavelengths of commercial lasers.

The present power output limits of the commercial gas lasers are He-Ne = approx. 125 mW; Ar = 10 W; Kr = 5 W; Xe = 1 W; CO₂ ~1000 W. Commercially available ruby and neodymium solid-state lasers provide pulses ranging from fractions of a joule to 12 kJ. The lifetime of a pulse varies from a microsecond to a nanosecond.

The CO₂ laser produces a beam that can be focused on an area of 0.001 cm² with an intensity of 1000 kW/cm² in a continuous operation and one million kW/cm² in pulsed operation with the pulse time equal to one nanosecond. The N₂ in CO₂ laser does not produce any emission but it transfers energy from the electron to the CO₂ molecules and lifts it to an upper laser level as shown in Fig. 1.18. A molecule of CO₂ gas has a lifetime in the upper laser level (2) equal to about 0.001 second. The molecule has a good chance of encountering a photon of suitable energy that will force it down to a lower level (1). He in CO₂ laser helps in dissipating the thermal energy.

Table 1.4 Wavelengths of some commercial lasers.

Gas lasers	
Gas	Å
Ar	4880
Ar	5145
Kr	5208
Xe	5413
He-Ne	5940
Kr	6271
He-Ne	6328
Kr	6871
CO ₂	33910
CO ₂	10600
Solid-state lasers	
Solid	—
Ruby	3472
Ruby	6943
Neodymium	10600 (10 ¹² W)
	Pulse = 0.1 nanosecond

Note: 1 W = 1 Js⁻¹

The lasing range covered by various dyes runs from 0.3 to 1.3 μm . Rhodamine 6G is a practically important lasing dye of the xanthene group.

The wavelength of photodissociation laser, i.e. iodine laser ($\text{CF}_3\text{I}/\text{C}_3\text{F}_7\text{I} + h\nu (= 0.3 \mu\text{m}) \rightarrow \text{I}^* + \text{CF}_3/\text{C}_3\text{F}_7$) is 1.315 μm . It is to be noted that after lasing, the iodine molecules join up with the molecular residue, i.e. $\text{C}_3\text{F}_7 + \text{I} \rightarrow \text{C}_3\text{F}_7\text{I}$. The mechanism of lasing action of iodine laser is shown in Fig. 1.19.

Excimer or excited state dimer lasers are rare gas dimer (Ar_2^* , Kr_2^* , Xe_2^*), a rare-gas oxide (ArO^* , KrO^* , XeO^*) or a rare-gas atom in combination with a halide atom (ArF^* , KrF^* , XeCl^* , ArCl^*). The lasing for ArCl^* is at $\lambda = 175 \text{ nm}$ while for Ar_2^* is at $\lambda = 126 \text{ nm}$.

The available pulse plasma lasers are Mg–Ca, and Sr–He. The Sr–He system lases in the violet portion of the spectrum at $\lambda = 0.416$ and $0.431 \mu\text{m}$.

The examples of semiconductor lasers pumped by electron beams are GaAs, CdS, CdSe, etc., CdS lases at $\lambda = 0.49 \mu\text{m}$; GaAs doped with tellurium (for degenerate p region) and zinc (for degenerate n region) called injection laser (p – n junction) oscillates in the wavelength range from 0.82 – $0.9 \mu\text{m}$ in the infrared. Bidirectional semiconductor lasers, have also been designed, i.e., a single experimental light source at two widely different wavelengths depending on the direction of electrical current flowing through it. The direction is changed by switching between negative and positive voltages applied across the device.

A ruby pulse laser lases at $\lambda = 6943 \text{ \AA}$. The rubies used in lasers are synthetic gemstones. They are made by fusing aluminium and chromium oxide to produce large crystals. The amount of chromium in a synthetic ruby is about 0.05 per cent. The laser action depends upon the amount of chromium present. The ruby crystal is about 0.64 cm in diameter and 3.80–5.10 cm in length. The mechanism of a ruby laser is shown in Fig. 1.20.

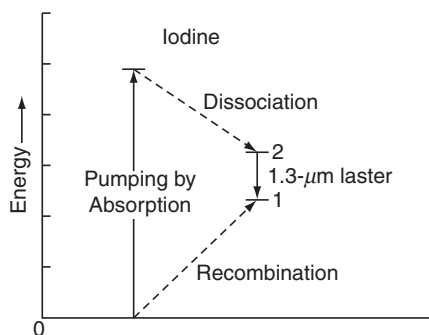


Fig. 1.19 Sketch showing the mechanism of iodine laser.

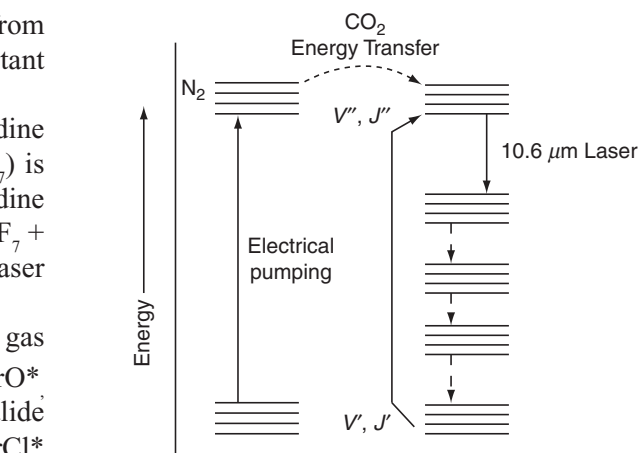


Fig. 1.18 Sketch showing the mechanism of carbon dioxide laser.

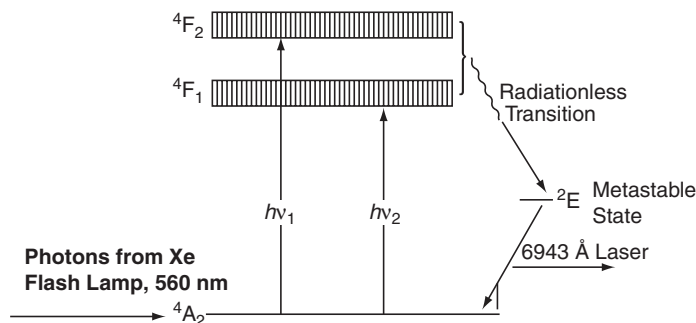


Fig. 1.20 Sketch showing the mechanism of a ruby laser.

Chromium ions are particularly responsive to light having a wavelength of $5600 \text{ \AA}$. A flash from a Xe lamp (rich in yellow-green region) excites chromium ions from their ground state $^4A_2$ to the excited states $^4F_2$ and $^4F_1$. By radiationless transition, these states decay to the metastable state, ^2E , and cause the crystal to heat up. The ions remain in the metastable state for several milliseconds from where they begin to emit photons spontaneously as they fall to the ground state $^4A_2$ giving an emission line at $6943 \text{ \AA}$. While the chromium ions are trying to get back to ground level, the flash lamp keeps on radiating more chromium ions and reproduces a population inversion. The photons at $\lambda = 6943 \text{ \AA}$ now start interacting with the excited ions in the inversion state ^2E and produce the lasing action. Laser output is of shorter duration varying from about 1–2 ms.

The continuous wave neodymium doped with yttrium aluminum garnet (Nd:YAG) laser emits at $\lambda = 1.0615$ and $1.0642 \mu\text{m}$ in the infrared. YAG is doped with chromium ions in addition to Nd^{3+} lases at $\lambda = 0.43$ and $0.59 \mu\text{m}$.

In glass lasers, the active material is glass doped by ions of rare-earth elements, specifically by neodymium. The Nd glass pulse laser emits at $\lambda = 1.06 \mu\text{m}$.

Free-electron lasers which can be tuned even in the infrared and ultraviolet regions have also been produced.

Stimulated spin-flip transitions result in coherent, tunable Raman scattering and a source of laser-type radiation in the far infrared. Tuning is achieved by a change of the magnetic field. Such a type of laser is called Spin-Flip Raman Laser (SFRL) or Magneto Raman Laser (MRL).

Lasers with extremely sharp colours can now be constructed and with the frequency-comb technique, precise readings can be made of light of all colours. It is now possible to measure frequencies with an accuracy of up to fifteen digits.

1.15 PLANE-POLARISED RADIATION AND DICHROISM

When unpolarised radiation is passed through specifically cut crystals of tourmaline or quartz (called polarisers), the radiation splits up into two linearly or plane-polarised components. One component has displacements or vibrations, i.e. electric vector parallel to the plane of the paper, and is termed as *parallel component* (π -component), while the other has electric vector perpendicular to the plane of the paper and is called *perpendicular component* (σ -component). The intensity of these two components

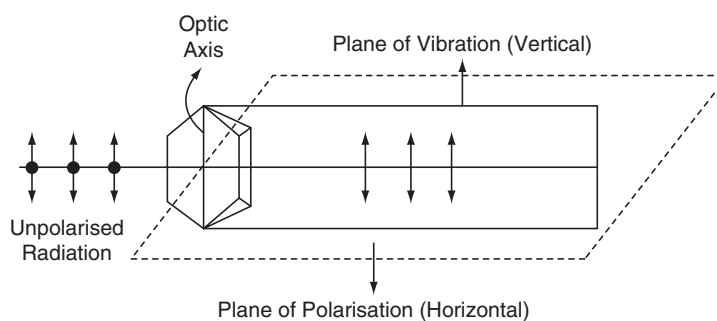


Fig. 1.21 Polarisation of radiation; $\uparrow$ —electric vector parallel in the plane of the paper; and $\bullet$ —electric vector perpendicular to the plane of the paper.

is the same while the wavelength and refractive indices are different. This process of production of linearly polarised radiation components, i.e. σ and the π , from unpolarised radiation, is called *dichroism*. When the optic axis of the polariser is parallel to the electric vector in the plane of the paper of unpolarised light ($\uparrow$) then only the π -component passes through the polariser while the σ -component ($\bullet$) gets eliminated. The vibration of the π -component occurs in a vertical plane called the *plane of vibration*, while the horizontal plane is termed as the *plane of polarisation*. The production of such a plane-polarised radiation is shown in Fig. 1.21.

Let us now examine the behaviour of plane polarised radiation in different natured media under different conditions. The electric field vector E of linearly polarised radiation can be imagined to have right- (E_R) and left- (E_L) hand components. In an isotropic medium such as water or glass, the right- and left-hand components will be equal and in phase, i.e. they have the same speed of rotation and amplitude. In other words, we can say that the indices of refraction and absorptivities of the medium corresponding to these two components are equal, i.e., $n_L = n_R$ and $a_L = a_R$. Consequently, the direction of plane polarised radiation in such media remains fixed.

However, when polarised radiation is passed through an anisotropic medium such as quartz or sugar solution, the radiation will be resolved into two components with same amplitude and a phase difference of $\pi/2$. The indices of refraction of the medium corresponding to two components will be different, i.e. $n_L \neq n_R$, while the absorptivities will be equal, i.e. $a_L = a_R$. Radiation having this property is said to be circularly polarised. In case the amplitudes and hence absorptivities as well as the indices of refraction of the medium are not equal, i.e. $n_L \neq n_R$ and $a_L \neq a_R$, the radiation with such a property is said to be elliptically polarised. The quantity $(n_L - n_R)$ is called *birefringence*, and $(a_L - a_R)$, the circular dichroism of the medium. By right- and left-handed rotation, we mean that the plane of polarisation rotates in the clockwise and anticlockwise directions respectively with respect to an observer looking towards the incoming beam of the radiation.

Further, any medium that exhibits circular birefringence may also exhibit circular dichroism. This phenomenon of combination of these two effects in the region in which the optically absorption bands are observed is termed the *Cotton effect*. When a beam of plane polarised radiation is passed through an optically inactive substance which is placed in a magnetic field, the emerging radiation will be rotated through a certain angle provided the direction of magnetic field and the incident beam are parallel to each other. This phenomenon is known as *Faraday effect* or Magneto-Optical Rotatory Dispersion (MORD). In addition to this, there is also Magneto-Circular Dichroism (MCD). On the other hand, when an optically isotropic medium is placed in an external electric field E , the medium becomes doubly refracting, i.e. the indices of refraction parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) to the direction of the field are not equal ($n_{\parallel} \neq n_{\perp}$) and the phenomenon is known as *Kerr electric-optic effect* or simply, *Kerr effect*.

1.16 LIQUID CRYSTALS

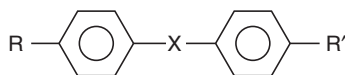
The term 'liquid crystals' was first coined by Lehmann in 1890. Liquid crystals behave like ordinary isotropic liquids and exhibit isotropic properties similar to those of solid crystals. In other words, we can say that though these compounds have a crystalline arrangement of molecules, yet they flow like a liquid. Due to their intermediary nature, they are also called *mesophases* or *mesomorphic phases*.

About 3 per cent of all organic compounds will form the liquid crystalline phase when heated above their melting points, and will appear as turbid, more or less viscous liquids. Such liquid crystals are called *thermotropic*. At higher temperature, the transition to other mesophases may occur in some cases, while others exhibit only one mesophase. The turbidity suddenly disappears and a clear liquid is formed at some higher temperature, which is characteristic of the system. The phase transition is reversible and of the first-order type, with a latent heat of $100 \text{ cal mole}^{-1}$. Mesophases are also formed in some suitable solvents and are called *lyotropic*, e.g., long-chain fatty acids in aqueous solutions. They play an important role in biological systems.

1.16.1 Classification of Liquid Crystals

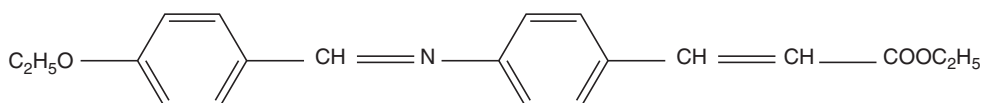
Depending on the arrangement of the molecules in the mesophases, liquid crystals have been classified as (a) nematic (thread), (b) smectic (soap), and (c) cholesteric.

(a) Nematic Liquid Crystals They exhibit one-dimensional arrangement in which the long molecular axes lie approximately parallel to each other. The molecules move, almost unhindered, as in a normal liquid. The degree of orientation in their arrangement is described by an order parameter with values lying between zero (liquid) and one (crystal). The simple structure of compounds forming nematic liquid crystals is



where R and R' are the short chains or small groups. $-X-$, $-N=N-$, $-N=NO-$, $-CH=CH-$, $-C\equiv C-$, $-CH=N(O)-$, $-CH=N-$, $O-CO-$, *p*-azoxyanisole (PAA) is the best nematic liquid crystal. Its nematic range is 118–136°C. The nematic range of MBBA (i.e. 4-methoxy-4'-n-butyl-benzylideneaniline nematogen) is 21–48°C while that of EBBA (i.e. 4-ethoxy-4'-n-butylbenzylideneaniline) is 37–80°C. The nematic range of MBBA can be extended by mixing it with EBBA.

(b) Smectic Liquid Crystals They display two-dimensional structure in which the molecules are arranged in layers. The centres of gravity of the elongated molecules are arranged in equidistant planes and their arrangement may be random or regular. Depending on the orientation of these molecules in their layers, they are designated as A, B, C,... The long axes of the molecules are parallel to the preferred direction which may be normal to the planes in smectic A or tilted by a certain angle in smectic C. Molecular ordering of seven types have been observed in smectic liquid crystals on the basis of x-ray diffraction studies. The various smectic types can be distinguished by their textures in a polarising microscope. *p*-(*p'*-ethoxybenzylideneamino)-ethyl cinnamate is a typical compound forming smectic phases. The structure of the compound is



Phase Transition

Phase Transition:



(c) Cholesteric Liquid Crystals Like nematogens, they also display a one-dimensional arrangement in which the long molecular axes lie approximately parallel to each other. However, in this case, the orientation alters in a regular manner from location to location—e.g. many cholesterol esters form this type of liquid crystals (cholesterol itself exhibits no mesophase). A necessary condition for the formation of cholesteric mesophase is that the molecules are chiral. The pictorial view of different mesophases is shown in Fig. 1.22.

1.16.2 Liquid Crystalline States in Living Nature

This state is a precondition for life itself. Biological membranes are the most important liquid crystalline states in living nature. They consist of phospholipid bilayers in which the 'hydrophobic' fatty acid chains are oriented inwards and the 'hydrophilic' head groups outwards. The bilayers act as molecular barriers segregating various

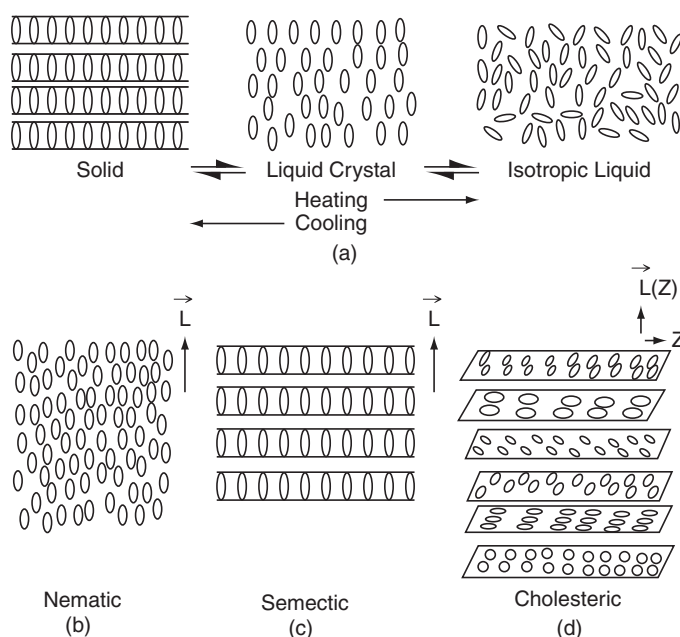


Fig. 1.22 (a) Molecular arrangement in the various condensed states of long-chain molecules, (b) nematic orientation without periodicity, (c) smectic orientation and arrangement in equispaced planes, but no periodicity within planes, and (d) cholesteric-twisted orientation with periodicity $\vec{L}$ —preferred direction/structural symmetry axis—optic axis.

organelles (areas) of the cell from each other. The specific vital transport of materials through the bilayers is regulated by proteins embedded in the phospholipid membrane. It is assumed that important biological processes such as photosynthesis, the respiratory chain and sensory stimulation occurring in the membranes are due to specific interactions between the phospholipids and proteins. Thus, the function of biological membranes at the molecular level can be understood provided we have a thorough knowledge of liquid crystalline properties.

1.16.3 Liquid Crystals as Anisotropic Solvents

The mesomorphic guest molecules may be incorporated into liquid crystals up to fairly high concentration without destruction of the distant order prevailing in the liquid crystalline matrix. The liquid crystalline solutions can be oriented by electric, magnetic, or mechanical forces, i.e. bulk samples of highly oriented solute molecules can be easily prepared. The molecular properties of the guest are not altered appreciably by the weak intermolecular forces. This forms the basis for the applicability of liquid crystals as anisotropic solvents for spectroscopic investigations of the anisotropic molecular properties. Organic thermotropic nematogens are most widely applicable solvents. Some typical liquid-crystal solvents are recorded in Table 1.5.

Table 1.5 Typical liquid-crystal solvents.

Compound	Structure	Mesomorphic Range(°C)	Applications
N-(<i>p</i> -methoxybenzylidene)- <i>p</i> -butylaniline (MBBA)	$\text{CH}_3\text{O} - \text{C}_6\text{H}_5 - \text{CH} = \text{N} - \text{C}_6\text{H}_5 - \text{C}_4\text{H}_9$	nem 20-42:	NMR, ESR, IR
<i>p</i> -azoxyanisole	$\text{CH}_3\text{O} - \text{C}_6\text{H}_4 - \text{N}(\text{O}) = \text{N} - \text{C}_6\text{H}_4 - \text{OCH}_3$	nem: 117-135	ESR
Equimolar mixture of N-(<i>p</i> -methoxy nitrosobenzene)- <i>p</i> -butylaniline	$\text{CH}_3\text{O} - \text{C}_6\text{H}_4 - \text{N}(\text{O}) = \text{N} - \text{C}_6\text{H}_4 - \text{C}_4\text{H}_9$		NMR
N-(<i>p</i> -butylnitroso benzene)- <i>p</i> -methoxy aniline	$\text{CH}_3\text{O} - \text{C}_6\text{H}_4 - \text{N} = (\text{O})\text{N} - \text{C}_6\text{H}_4 - \text{C}_4\text{H}_9$	nem: -5-75	NMR, ESR
N-(<i>p</i> -ethoxy nitroso benzene)- <i>p</i> -butylaniline	$\text{C}_2\text{H}_5\text{O} - \text{C}_6\text{H}_4 - \text{N}(\text{O}) = \text{N} - \text{C}_6\text{H}_4 - \text{C}_4\text{H}_9$ and		
N-(<i>p</i> -butyl nitroso benzene)- <i>p</i> -methoxy aniline	$\text{C}_2\text{H}_5\text{O} - \text{C}_6\text{H}_4 - \text{N} = (\text{O})\text{N} - \text{C}_6\text{H}_4 - \text{C}_4\text{H}_9$		
Butyl- <i>p</i> -(<i>p</i> -ethoxyphenoxy carbonyl) phenyl carbonate	$\text{C}_4\text{H}_9\text{O} - \text{COO} - \text{C}_6\text{H}_4 - \text{COO} - \text{C}_6\text{H}_4 - \text{OC}_2\text{H}_5$	nem: 56-87	NMR, ESR, UV, IR
4,4'-di-hexyloxyazoxy benzene	$\text{C}_6\text{H}_{13}\text{O} - \text{C}_6\text{H}_4 - \text{N}(\text{O}) = \text{N} - \text{C}_6\text{H}_4 - \text{OC}_6\text{H}_{13}$	nem: 81-127 } sm: 72-81 }	NMR
4,4'-di-heptyloxyazoxy benzene	$\text{C}_7\text{H}_{15}\text{O} - \text{C}_6\text{H}_4 - \text{N}(\text{O}) = \text{N} - \text{C}_6\text{H}_4 - \text{OC}_7\text{H}_{15}$	nem: 92-123 } sm: 74-92 }	
Terephthal-bis-(4- <i>n</i> -butyl)-aniline (TBBA)	$\text{C}_4\text{H}_9 - \text{C}_6\text{H}_4 - \text{N} = (\text{H})\text{C} - \text{C}_6\text{H}_4 - \text{C}(\text{H}) = \text{N} - \text{C}_6\text{H}_4 - \text{C}_4\text{H}_9$	sm A: 199.6-172.5 sm B: 172.5-144.1 sm C: 144.1-113.0 }	NMR
4-methoxybenzylidene-4-amino- α -methyl cinnamic acid- <i>n</i> -propylester	$\text{CH}_3\text{O} - \text{C}_6\text{H}_4 - \text{CH} = \text{N} - \text{C}_6\text{H}_4 - \text{CH} = \text{C}(\text{CH}_3) - \text{COOC}_3\text{H}_7$		NMR

1.17 FITTING OF A STRAIGHT LINE AND PRINCIPLE OF LEAST SQUARES

Let us consider the fitting of a straight line

$$y = c' + mx \quad (1.56)$$

to a set of n points (x_i, y_i) ; $i = 1, 2, 3, \dots, n$. The problem is to determine the intercept c' and slope m so that the line (1.56) is the line of best fit.

The term 'best fit' is interpreted in accordance with the Legendre's of least squares. The principle consists in minimising the sum of the squares of the deviations of the actual values from its estimated values as given by the line of best fit. According to principle of least squares, we have to determine c' and m so that

$$E = \sum_{i=1}^n (y_i - c' - mx_i)^2 \text{ is minimum} \quad (1.57)$$

Differentiating Eq. (1.57) with respect to c' and m and applying the condition of maxima and minima, we get

$$\begin{aligned}\left(\frac{\partial E}{\partial c'}\right)_m &= 0 = -2 \sum_{i=1}^n (y_i - c' - mx_i) \\ \left(\frac{\partial E}{\partial m}\right)_{c'} &= 0 = -2 \sum_{i=1}^n x_i (y_i - c' - mx_i)\end{aligned}\quad (1.58)$$

Consequently,

$$\begin{aligned}\sum_{i=1}^n y_i &= nc' + m \sum_{i=1}^n x_i \\ \sum_{i=1}^n x_i y_i &= c' \sum_{i=1}^n x_i + m \sum_{i=1}^n x_i^2\end{aligned}\quad (1.59)$$

Equations (1.58) and (1.59) are known as the *normal equations* for estimating c' and m .

All the quantities, $\sum_{i=1}^n x_i$, $\sum_{i=1}^n x_i^2$, $\sum_{i=1}^n y_i$ and $\sum_{i=1}^n x_i y_i$ can be obtained from the given set of points (x_i, y_i) ;

$i = 1, 2, 3, \dots, n$ and the Eq. (1.59) can be solved for c' and m . With the values of c' and m so obtained, Eq. (1.56) is the line of best fit to a given set of points (x_i, y_i) ; $i = 1, 2, 3, \dots, n$.

Problem 1.2: By the method of least-square fit, find the slope and the intercept of the line $y = c' + mx$ from the following data:

x :	1	2	3	4	6	8
y :	2.4	3	3.6	4	5	6

Solution The line is $y = c' + mx$.

x	y	x^2	xy
1	2.4	1	2.4
2	3.0	4	6.0
3	3.6	9	10.8
4	4.0	16	16.0
6	5.0	36	30.0
8	6.0	64	48.0
$\sum_{i=1}^6 24$	24	130	113.2

Using normal Eq. (1.59), we get $6c' + 24m = 24$; $24c' + 130m = 113.2$. Solving these equations for c' and m , we obtain, intercept $c' = 1.976$ and slope $m = 0.50$.

PROBLEMS

- Using the data in Table 1.2, compute the energy-, frequency- and wave number range for the various regions of electromagnetic radiation.
- In what units is the molar decadic coefficient measured?
(a) cm^{-1} (b) moles/cm^2 (c) cm^2/mole (d) moles (e) It is a dimensionless quantity. **[Ans: (c)]**
- Which of the equations listed below gives the correct relation between the transmittance T , the optical density D , the concentration C , the molar extinction coefficient ϵ and the layer thickness l ?
(a) $T = -\log \frac{1}{D}$ (b) $T = -\log D$ (c) $\log \frac{1}{T} = \epsilon Cl$ (d) $\log T = \epsilon Cl$
(e) $T = -\epsilon Cl$ (f) $\epsilon = D/Cl$ (g) $-\log T = \epsilon Cl$ (h) $T \times 10^0 = 1$
(i) $D = \log T$ **[Ans: (b), (c), (g)]**
- Which of the equations listed below reflect correctly the relations that exist between the variables if the Beer-Lambert law is obeyed?
(a) At $l = \text{const}$ if $C_1 < C_2 < C_3$ then $D_1/\epsilon_1 > D_2/\epsilon_2 > D_3/\epsilon_3$

- (b) If
- $C_1 < C_2 < C_3$
- then

$$\epsilon_1 l_1 / D_1 > \epsilon_2 l_2 / D_2 < \epsilon_3 l_3 / D_3$$

- (c) At
- $l = \text{const}$
- ,
- $\epsilon = \text{const}$
- and
- $D_0 = \text{const}$
- , if
- $C_1 > C_2 > C_3$
- then

$$l'_t < l''_t < l'''_t$$

- (d) At
- $l = \text{const}$
- ,
- $\epsilon = \text{const}$
- and
- $l_0 = \text{const}$
- , if
- $C_1 > C_2 > C_3$
- then

$$l'_t > l''_t > l'''_t$$

- (e) At
- $\epsilon = \text{const}$
- and
- $D = \text{const}$

$$\frac{C_1}{l_1} = \frac{C_2}{l_2} = \frac{C_3}{l_3}$$

- (f) If
- $C_1 < C_2 < C_3$
- then

$$\epsilon_1 l_1 / D_1 > \epsilon_2 l_2 / D_2 > \epsilon_3 l_3 / D_3$$

- (g) At
- $l = \text{const}$
- if
- $C_1 < C_2 < C_3$
- then

$$D_1 / \epsilon_1 < D_2 / \epsilon_2 < D_3 / \epsilon_3 \quad [\text{Ans: (c), (f), (g)}]$$

5. The absorbance of some unknown solution having a concentration C_x is A_x . What will be the value of absorbance in terms of A_x if the (a) path length is reduced by one half, and (b) path length is doubled? [Ans: (a) $2A_x$ (b) $0.5A_x$]

6. A sample of a solution having concentration C_x obeys Beer-Lambert's law. The solution shows 80 per cent transmittance when measured in a cell 10 cm in length: (a) Calculate the per cent transmittance for a solution half and twice the concentration in the same cell. (b) What will be the length of the cell to give the same transmittance (80%) for solution of twice the original concentration? (c) Compute the per cent transmittance of the original solution when contained in cells of 1, 2 and 5 cm in length.

7. Sharp-line spectra are observed in gases while in case of solids and liquids, they are broad and diffused. Explain.

- **Hint:** In gases the atoms or molecules are at a distant apart, so a single quantum transition independent of other transitions can take place.

8. Light absorption may be registered as graphs in the form of various quantities, (a) I_t/I_0 (b) $100 \cdot I_t/I_0$ (c) $(I_0 - I_t)/I_0$ and $100(I_0 - I_t)/I_0$ (d) $D = A = \ln I_0/I_t$ (e) $A = 100 \ln I_0/I_t$ (f) $\epsilon = A/C \cdot l$, which of the quantities listed above are plotted as a function of frequency (in cm^{-1}) or less often, the wavelengths in microns (μ) in infrared spectroscopy? [Ans: (b), (e)]

9. What frequency range corresponds to the interval of light wavelengths from 0.1 to 10 μm ?

$$[\text{Ans: } 3 \times 10^{13} - 3 \times 10^{15} \text{ Hz}]$$

10. What is the photon energy for a light wavelength of 0.6 μm ? [Ans: 2 eV]

11. The quality factor of an optical resonator is $Q = 2 \times 10^7$ at 0.6 μm wavelength. Compute the loss coefficient for this Q . [Ans: 0.5 m^{-1}]

12. Compute the peak power of a pulse, given that the laser operates at a pulse repetition rate of $f = 1 \text{ MHz}$ yielding pulses of $\tau = 20 \text{ ns}$ duration with an average power of train being $P = 10 \text{ W}$.

- **Hint:** The peak power in this case is P/τ .

$$[\text{Ans: } 500 \text{ W}]$$

13. Suppose we have doubled all the linear dimensions of the resonator, (i.e., cavity length and mirror curvature radii and apertures). Will the new resonator be equivalent to the original one? [Ans: No, $N_F = 2$]

14. When a source emitting radiation of frequency ν moves with velocity ν towards or away from the observer, the observer detects the radiation if frequency ν_{obs} given by

$$\nu_{\text{obs}} = \nu \left[\frac{1 \pm \frac{\nu}{c}}{1 \mp \frac{\nu}{c}} \right]^{1/2}$$

where the plus and minus signs have their usual meanings. Calculate the frequency of the radiation source detected by the observer if the source with a 500 cm^{-1} frequency is moving with a 300 m/s velocity away from or towards the observer. [Ans: 499.99 cm^{-1} , 500 cm^{-1}]

15. (a) What is the width of a transition from a state with a lifespan of 10.0 ps? (b) A laser line occurs at 500 nm whereas the observer detects it at 500.1 nm. In what direction and with what speed is the laser moving relative to the observer? (c) An observer is moving towards the red traffic light (660 nm). At what speed would it appear green (520 nm)? (d) Calculate the Doppler broadening for $H\alpha$ (6562.79 Å) and $H\beta$ (4861.33 Å) lines of helium at 300 K.

[Ans: (a) 0.53 cm^{-1} (b) Away from the observer with a speed of $6 \times 10^4 \text{ m/s}$ (c) $6.36 \times 10^7 \text{ m/s}$ (d) 0.0576 Å ; 0.0426 Å]

16. The energies of different coloured photons of visible light are given below.

Colour	Energy $\times 10^{-19} (\text{J})$
Violet	4.7
Blue	4.2
Green	3.7
Yellow	3.4
Orange	3.2
Red	2.8

What would be the wavelengths of the respective colours? [Ans: 420, 470, 530, 580, 620 and 700 nm]

17. (a) A Nd^{3+} : YAG laser ($\lambda_{\text{YAG}} = 1064.1 \text{ nm}$) produces pulses at a repetition rate of 1 kHz. If each pulse is 150 ps in duration and has a radiant energy of $1.25 \times 10^{-6} \text{ kJ}$, calculate P the radiant power of each laser pulse and $\langle P \rangle$, the average radiant power of the laser, the radiant energy of the laser photon and the number of photons in a single pulse.

- **Hint:** Radiant power $P = \text{Radiant energy per unit time}$.

Average radiant power $P = \text{Total power emitted per second} = (\text{Energy/pulse}) \times [\text{Number of pulses per second}]$

Number of photons in the laser pulse

$$= \frac{\text{Radiant energy per pulse}}{\text{Radiant energy of } 1064.1 \text{ nm photon}}$$

- (b) Calculate the number of photons in a 2.00 mJ light pulse at 1.06 μm , 537 nm and 266 nm.

[Ans: (a) $8.3 \times 10^6 \text{ W}$, $1.867 \times 10^{-19} \text{ kJ}$, 6.70×10^{15} (b) 107×10^{14} , 54×10^{14} and 268×10^{13} photons]

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18. A CO₂ laser operating at 9600 nm uses an electric power of 5 kW. This laser produces 100 ns pulses at a repetition rate of 10 Hz and has an efficiency of 27%. Calculate the number of photons in each pulse.

• **Hint:** Radiant power of pulse = 5 kW

[Ans: 652 × 10¹⁹ photons per pulse]

19. A titanium sapphire laser ($\lambda = 780$ nm) produces pulses at a repetition rate of 100 MHz. If each pulse is of 25 fs duration and the average radiant power of the laser is

1.4 W, calculate the radiant power of each laser pulse. How many photons are produced by this laser in one second? [Ans: 560 kW, 549 × 10¹⁶ photons]

20. The ratio of areas under the peaks in the ultraviolet, visible and infrared regions in the electromagnetic spectrum of the sun as measured in the upper atmosphere is 1:4.44:5.66. What might be the per cent composition of solar radiation emanating from the surface of the sun at 6000 K? [Ans: 9, 40, 51 per cent]

APPENDIX 1 A: GENERAL PHYSICAL AND CHEMICAL CONSTANTS AND THEIR VALUES

Avogadro's constant	$N_A = 0.60229 \times 10^{24} \text{ mole}^{-1}$
Velocity of light	$c = 2.997925 \times 10^8 \text{ m s}^{-1}$
Electron mass	$m = 0.91083 \times 10^{-30} \text{ kg}$
Electron charge	$e = 0.106206 \times 10^{-18} \text{ C}$
Faraday	$F = N_A e = 96,490 \text{ C mole}^{-1}$
Dalton	$D = 1.66033 \times 10^{-27} \text{ kg}$
Planck's constant	$h = 0.66252 \times 10^{-33} \text{ J s}$ $= 3.9901 \times 10^{13} \text{ amu } \text{\AA}^2 \text{ s}^{-1}$
Quantum of angular momentum	$\hbar = h/2\pi = 0.105443 \times 10^{-33} \text{ J s}$
Proton mass	$m_p = 1.67239 \times 10^{-27} \text{ kg}$
Neutron mass	$m_n = 1.67470 \times 10^{-27} \text{ kg}$
Boltzmann constant	$\kappa = 1.3805 \times 10^{-23} \text{ J K}^{-1}$ $= 8.3142 \times 10^{23} \text{ amu } \text{\AA}^2 \text{ s}^{-2} \text{ K}^{-1}$
Gas constant per mole	$R = N_A \kappa = 8.3146 \text{ J mole}^{-1} \text{ K}^{-1}$
Gas constant	$R = 0.08206 \text{ litre atm deg}^{-1} \text{ mole}^{-1}$ $= 22.415 \text{ litre}$
Standard molar volume of gas at 273K and 1.013 × 10 ⁵	$t^0 \text{ C} = T \text{ K} - 273.15$
Centigrade temperature	$1 \text{ atm} = 101.325 \text{ kN m}^{-2}$
Atmospheric pressure	$0.1602 \times 10^{-28} \text{ C m (4.8029 D)}$
Electric dipole moment	$1 \text{ D} = 10^{-18} \text{ esu cm}$
Electron-volt	$1 \text{ eV} = 96,4905 \text{ kJ mole}^{-1}$

$$\text{gcm}^2 = 6.0226 \times 10^{39} \text{ amu } \text{\AA}^2$$

$$\text{kg m}^2 = 6.0226 \times 10^{46} \text{ amu } \text{\AA}^2$$

$$1 \text{ amu} = 1.6604 \times 10^{-27} \text{ kg}$$

$$1.6604 \text{ J} = 10^{47} \text{ amu } \text{\AA}^2 \text{ s}^{-2}$$

Dimensions of charge

$$[Q] = [\text{Length}]^{3/2} [\text{Mass}]^{1/2} [\text{Time}]^{-1}$$

$$Q^2 = \text{L}^3 \text{M}^1 \text{T}^{-2} = \text{cm}^3 \text{g s}^{-2}$$

$$\text{Thus } e^2 r^2 = \text{cm}^3 \text{g s}^{-2} \text{cm}^2 = \text{g cm}^5 \text{s}^{-2}$$

CHAPTER 2

MICROWAVE
SPECTROSCOPY

To find out from theoreticians what methods they use, stick closely to one principle, do not listen to their words, fix attention on their deeds.

—Einstein

2.1 INTRODUCTION

Rotation of molecules manifests itself in the heat capacity of gases and in the structure of the rotational spectra. The discrete nature of the spectra reveals that the molecular motion is quantised. Classical mechanics fails to explain the fine structure of the spectra. However, the solution of the Schrödinger wave equation for the rotational motion of the molecule suggests that the rotational motion is quantised.

The rotational spectra of all molecules except the lightest of the diatomics fall in the microwave region, i.e. $0.2\text{--}200\text{ cm}^{-1}$, while those of light diatomics such as HCl occurs in the far infrared region, i.e. $< 400\text{ cm}^{-1}$. Furthermore, depending upon the spectroscopic nature of the molecules, the rotational spectrum may also be deduced from the infrared, electronic and Raman spectra of the molecules. The rotational spectra in the far infrared and microwave regions are recorded on a spectrometer, the working of which is described here.

2.2 MICROWAVE SPECTROMETER

The block diagram of a spectrometer for recording pure rotational spectra in the microwave ($0.2\text{--}200\text{ cm}^{-1}$) and far infrared ($< 400\text{ cm}^{-1}$) regions is shown in Fig. 2.1. The monochromatic beam of microwave radiation ($22\text{--}60\text{ GHz}$) generated in the Klystron tube are passed through the wave guide metallic pipe ($\sim 10\text{ m}$ long), fitted with mica windows at the end, containing a gaseous sample. The modified radiation, i.e. the transmitted radiation detected by the crystal diode detector (which is capable to provide a 100 kHz output), is amplified. The amplified signals are analysed with the help of an analyser. The frequency of the Klystron tube is adjusted electrically by the power-supply unit which in turn is synchronised with the analysing system. Harmonic generators are employed to provide higher frequencies, i.e. 250 GHz . The microwave spectrometer is generally fitted with a square wave Stark modulator (100 kHz modulation). The function of the Stark modulator is to study the effect of electric field on the rotational spectra of molecules. When the spectrum is to be recorded in the far infrared region, the source employed is a 'Nernst glower' which is electrically heated rare earth oxides.

The microwave spectra are not recorded in the solid and liquid phases. In liquids, the time period of molecular collision ($10^{-12} - 10^{-13}\text{ s}$) is very small as compared to the time for complete molecular rotation ($\sim 10^{-10}\text{ s}$). There is also no free rotation in solids. In the light of this, the rotational motion in liquids and solids is not quantised and hence their rotational spectra cannot be studied by this technique. On the other hand, in gases at very low pressure ($\sim 10^{-4}\text{ mmHg}$), a number of free rotations result before any molecular collision occurs. Therefore, the rotational spectra of gases are recorded by this technique.

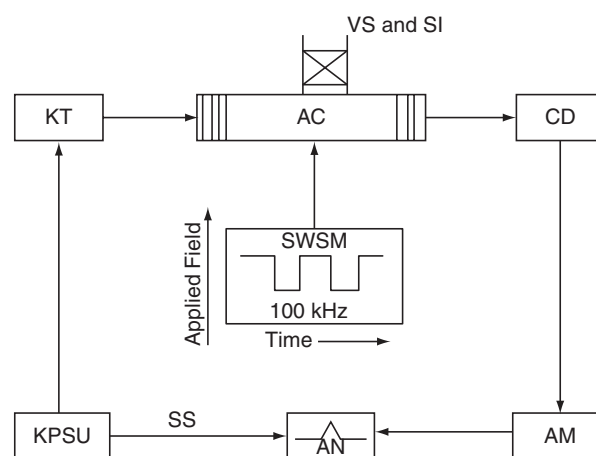


Fig. 2.1 Basic elements of a microwave spectrometer: KPSU—Klystron power supply unit, KT—Klystron tube, VS and SI—vacuum system and sample inlet, CD—crystal detector, SWSM—square wave stark modulator, SS—synchronising signal, AC—absorption cell, AM—amplifier, AN—analyser.

2.3 MOMENTS OF INERTIA OF MOLECULES

The moments of inertia of a molecule rotating about the principal axis passing through its centre of mass will be

$$I_x = \sum_i m_i r_{ix}^2, I_y = \sum_i m_i r_{iy}^2, I_z = \sum_i m_i r_{iz}^2 \quad (2.1)$$

where m_i stands for the masses of atomic nuclei and r_{ix} , r_{iy} and r_{iz} are the equilibrium distances from the atomic nuclei to the axis of rotation.

Assume that the origin of coordinates is the molecule's centre of mass, whose ordinates will be determined from the expression

$$\sum_i m_i r_{ix} = 0, \sum_i m_i r_{iy} = 0, \sum_i m_i r_{iz} = 0 \quad (2.2)$$

Thus, in general we can write

$$I = \sum_i m_i r_i^2 \quad (2.3)$$

$$\sum_i m_i r_i = 0 \quad (2.4)$$

Problem 2.1: Determine the moment of inertia of a diatomic molecule about an axis passing through its centre of mass and normal to the molecular axis if the equilibrium bond distance is r Å.

Solution Knowing the atomic masses of the nuclei in the diatomic molecule, we can determine the moment of inertia of the molecule from Eq. (2.3). The geometrical configuration of a diatomic molecule is presented in Fig. 2.2.

Let m_1 and m_2 be the masses of the nuclei of the diatomic molecule and r_1 and r_2 be the distances of the respective nuclei from the centre of mass C_m of the molecule such that the bond length is

$$r = r_1 + r_2 \quad (2.5)$$

By Eq. (2.4), i.e. taking moments about C_m , we get

$$m_1 r_1 = m_2 r_2 \quad (2.6)$$

From Eqs (2.5) and (2.6)

$$r_1 = \frac{m_2 r}{m_1 + m_2}; r_2 = \frac{m_1 r}{m_1 + m_2} \quad (2.7)$$

From Eq. (2.3), the general expression for the moment of inertia of a diatomic molecule is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (2.8)$$

In diatomics, the moment of inertia about the molecular axis is zero since all the masses concentrate on this axis, i.e. for this particular rotation in diatomics; since $r = 0$, hence $I = 0$. Substituting the values of r_1 and r_2 from Eq. (2.7) into Eq. (2.8), we get

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu_m r^2 \quad (2.9)$$

where

$$\mu_m = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_1 m_2}{M_m} \quad (2.10)$$

Here, μ_m is called the *reduced mass of the molecule*, and M_m is the molecular mass of the diatomic molecule. For example, let us now calculate the moment of inertia of $^{35}\text{Cl}^{37}\text{Cl}$ if the equilibrium bond distance is 1.99 Å. We know that $m_1 = 35$ amu, $m_2 = 37$ amu, and $r = 1.99$ Å.

From Eq. (2.9), we obtain

$$\begin{aligned} I &= \frac{35 \text{ (amu)} \times 37 \text{ (amu)}}{(35 + 37) \text{ amu}} \times (1.99)^2 (\text{Å})^2 \\ &= 71.22 \text{ amu Å}^2 = 71.22 \text{ au} \end{aligned}$$

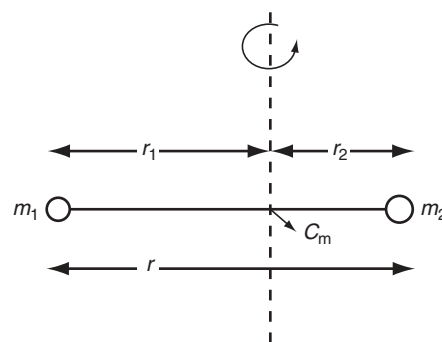


Fig. 2.2 Geometrical configuration of a diatomic molecule.

Problem 2.2: Derive the general expression for the moment of inertia of (a) linear triatomic molecules of the type XYZ, and (b) symmetric triatomic linear molecules of the type XY_2 .

Solution (a) The linear triatomic molecules such as ICN, COSe, HCN, OCS, etc., are of XYZ type. By taking HCN as an example, we have to proceed as follows. The geometrical configuration of HCN is shown in Fig. 2.3.

Here, m_H , m_C , m_N are the masses of hydrogen, carbon and nitrogen atoms respectively; r_{CH} and r_{CN} are the bond distances of CH and CN bonds respectively and r is the distance of the carbon atom from the centre of mass of the molecule.

Using Eq. (2.4), i.e. taking moments about C_m , we obtain

$$m_H(r_{CH} + r) + m_C r - m_N(r_{CN} - r) = 0 \quad (2.11)$$

Rearranging Eq. (2.11), we get

$$r = \frac{(m_N r_{CN} - m_H r_{CH})}{m_H + m_C + m_N} = \frac{(m_N r_{CN} - m_H r_{CH})}{M_m} \quad (2.12)$$

where $M_m = m_H + m_C + m_N$ is the molecular mass of HCN.

Further by Eq. (2.3), i.e. $I = \sum_{i=1}^3 m_i r_i^2$, we get

$$\begin{aligned} I &= m_H(r_{CH} + r)^2 + m_C r^2 + m_N(r_{CN} - r)^2 \\ &= M_m r^2 + 2r(m_H r_{CH} - m_N r_{CN}) + (m_H r_{CH}^2 + m_N r_{CN}^2) \end{aligned} \quad (2.13)$$

Substituting the value of r from Eq. (2.12) into Eq. (2.13), we obtain

$$I = m_H r_{CH}^2 + m_N r_{CN}^2 - \frac{(m_H r_{CH} - m_N r_{CN})^2}{M_m} \quad (2.14)$$

Thus employing Eq. (2.14), we can determine the moment of inertia of any molecule of type XYZ, e.g. let us determine the moment of inertia of OCS. For OCS, the expression (2.14) may be written as

$$I_{OCS} = m_O r_{CO}^2 + m_S r_{CS}^2 - \frac{(m_O r_{CO} - m_S r_{CS})^2}{M_m}$$

where

$$M_m = m_O + m_C + m_S = 16 + 12 + 32 = 60 \text{ amu.}$$

We know,

$$r_{CO} = 1.163 \text{ \AA} \text{ and } r_{CS} = 1.558 \text{ \AA}.$$

Therefore,

$$I_{OCS} = 16 \times (1.163)^2 + 32 \times (1.558)^2 - \frac{(16 \times 1.163 - 32 \times 1.558)^2}{60} = 83.04 \text{ amu \AA}^2$$

(b) CO_2 and CS_2 belong to XY_2 type of molecules. The geometrical configuration of XY_2 systems is given in Fig. 2.4. Thus, the general expression for the moment of inertia of XY_2 systems is

$$I = mr^2 + mr^2 = 2mr^2 = \sum_{i=1}^2 m r_i^2$$

Problem 2.3: Describe the general method to determine the product of moments of inertia of bent triatomic molecules such as H_2S , H_2O , SO_2 , etc., and apply the method to SO_2 if SO bond distance is $1.432 \text{ \AA}$ and OSO bond angle is $119^\circ 21'$.

Solution Assume that the origin of coordinates is the molecule's centre of mass; then from Eq. (2.2),

$$\sum_i m_i r_{ix} = 0, \sum_i m_i r_{iy} = 0, \sum_i m_i r_{iz} = 0$$

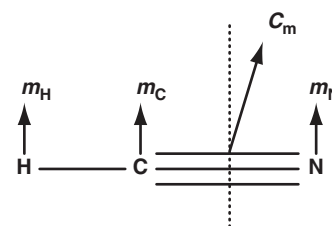


Fig. 2.3 Geometrical configuration of HCN.

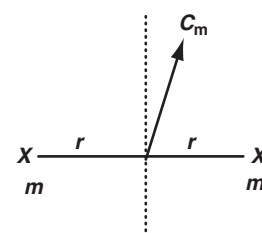


Fig. 2.4 Geometrical configuration for XY_2 systems.

The moments of inertia will be determined from the expression (2.1), i.e.

$$I_x = \sum_i m_i r_{ix}^2, I_y = \sum_i m_i r_{iy}^2, I_z = \sum_i m_i r_{iz}^2$$

The product of the principal moments of inertia of the molecule can be calculated using the third-order secular equation,

$$I_A I_B I_C = \begin{vmatrix} +I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & +I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & +I_{zz} \end{vmatrix}$$

$$= I_{xx}(I_{yy}I_{zz} - I_{yz}I_{yz}) - I_{xy}(I_{xy}I_{zz} + I_{yz}I_{xz}) - I_{xz}(I_{xy}I_{yz} + I_{yy}I_{xz}) \quad (2.15)$$

where

$$I_{xx} = \sum m_i (y_i^2 + z_i^2) - \frac{1}{M_m} \left(\sum m_i y_i \right)^2 - \frac{1}{M_m} \left(\sum m_i z_i \right)^2$$

$$I_{yy} = \sum m_i (x_i^2 + z_i^2) - \frac{1}{M_m} \left(\sum m_i x_i \right)^2 - \frac{1}{M_m} \left(\sum m_i z_i \right)^2$$

$$I_{zz} = \sum m_i (x_i^2 + y_i^2) - \frac{1}{M_m} \left(\sum m_i x_i \right)^2 - \frac{1}{M_m} \left(\sum m_i y_i \right)^2$$

$$I_{xy} = \sum m_i x_i y_i - \frac{1}{M_m} \left(\sum m_i x_i \right) \left(\sum m_i y_i \right)$$

$$I_{xz} = \sum m_i x_i z_i - \frac{1}{M_m} \left(\sum m_i x_i \right) \left(\sum m_i z_i \right)$$

$$I_{yz} = \sum m_i y_i z_i - \frac{1}{M_m} \left(\sum m_i y_i \right) \left(\sum m_i z_i \right)$$

Now, let us apply this method to determine the product of moments of inertia I_A, I_B, I_C of the sulphur dioxide molecule. The equilibrium internuclear distance $r_{S-O} = 1.432 \text{ \AA}$ and the equilibrium bond angle is equal to 119.34° . The equilibrium geometrical configuration of SO_2 is shown in Fig. 2.5.

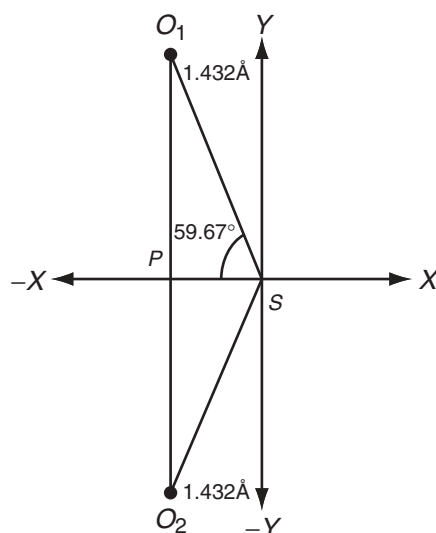


Fig. 2.5 Equilibrium geometrical parameters of molecule of SO_2 for determining the product of moment of inertia.

From right-angle triangle O_1PS

$$x = r \cos \theta = 1.432 \cos 59.67^\circ = 0.723$$

$$y = r \sin \theta = 1.432 \sin 59.67^\circ = 1.236$$

$$m_{\text{O}} = 16 \text{ amu}; m_{\text{S}} = 32 \text{ amu}$$

The data generated are recorded in tabular form as under.

Atomic masses and coordinates of the atoms.

Atom	m, amu	$x, \text{\AA}$	$y, \text{\AA}$	$z, \text{\AA}$
S	32	0	0	0
O ₁	16	-0.723	1.236	0
O ₂	16	-0.723	-1.236	0
	$M_m = \sum_{i=1}^3 m_i = 64 \text{ amu}$			

Terms involved in the secular equation.

Atom	O_1	O_2	$\sum_{i=1}^3$
x_i^2	0.523	0.523	
y_i^2	1.528	1.528	
$x_i y_i$	-0.894	0.894	
$m_i x_i$	-11.568	-11.568	-23.136
$m_i y_i$	19.776	-19.776	0
$m_i x_i y_i$	-14.298	14.298	0
$m_i (x_i^2 + y_i^2)$	32.804	32.804	65.608
$m_i (x_i^2 + z_i^2)$	8.363	8.363	16.726
$m_i (y_i^2 + z_i^2)$	24.443	24.443	48.886

Now from Eq. (2.15),

$$I_{xx} = \sum m_i (y_i^2 + z_i^2) - \frac{1}{M_m} \left(\sum m_i y_i \right)^2 - \frac{1}{M_m} \left(\sum m_i z_i \right)^2 = 48.886 \text{ au}$$

$$\begin{aligned} I_{yy} &= \sum m_i (x_i^2 + z_i^2) - \frac{1}{M_m} \left(\sum m_i x_i \right)^2 - \frac{1}{M_m} \left(\sum m_i z_i \right)^2 \\ &= 16.726 - \frac{(-23.136)^2}{64} = 16.726 - 8.363 = 8.363 \text{ au} \end{aligned}$$

$$\begin{aligned} I_{zz} &= \sum m_i (x_i^2 + y_i^2) - \frac{1}{M_m} \left(\sum m_i x_i \right)^2 - \frac{1}{M_m} \left(\sum m_i y_i \right)^2 \\ &= 65.608 - \frac{(-23.136)^2}{64} = 65.608 - 8.363 = 57.245 \text{ au} \end{aligned}$$

$$I_{xy} = I_{xz} = I_{yz} = 0$$

$$I_A I_B I_C = 48.886 \times 8.363 \times 57.245 \text{ (au)}^3 = 23.403 \times 10^3 \text{ (au)}^3$$

Problem 2.4: Apply the secular Eq. (2.15) to determine the moments of inertia of molecules of the XY_3AB type. Find also the reduced moment of inertia.

Solution CH_3OH , CH_3SH , etc., belong to XY_3AB type molecules. Taking CH_3OH as an example, let us apply Eq. (2.15) to work out the moments of inertia from the bond distances and bond angles of methyl alcohol. The structural parameters of methyl alcohol are:

$$\angle\text{COH} = 110^\circ, \angle\text{HCH} = 109^\circ 28', r(\text{O—H}) = 0.96 \text{ \AA},$$

$$r(\text{C—O}) = 1.43 \text{ \AA} \text{ and } r(\text{C—H}) = 1.11 \text{ \AA}.$$

Let the carbon atom be the origin of coordinates. The X -axis is in the direction of the C—O bond. The equilibrium bond distances, bond angles and two projections in the XZ and YZ planes are presented in Fig. 2.6.

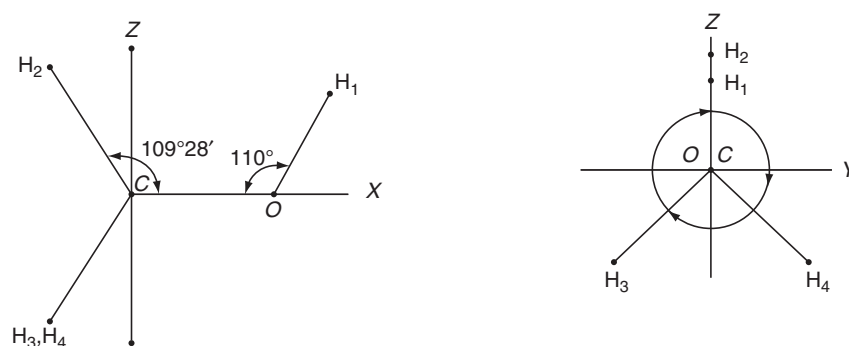


Fig. 2.6 Projections and geometrical configurations of the CH_3OH molecule.

The data required for Eq. (2.15) are generated and recorded in tabular form as follows:

Atom	m, amu	$x, \text{\AA}$	$y, \text{\AA}$	$z, \text{\AA}$
C	12	0	0	0
O	16	1.43	0	0
H ₁	1	$1.43 + 0.96 \cos 70^\circ = 1.76$	0	$0.96 \sin 70^\circ = 0.90$
H ₂	1	$1.11 \cos 109^\circ 28' = -0.37$	0	$1.11 \sin 70^\circ 32' = 1.05$
H ₃	1	-0.37	$1.11 \cos 240^\circ = -0.96$	$1.11 \sin 240^\circ = -0.56$
H ₄	1	-0.37	0.96	-0.56

$M_m = \sum_{i=1}^6 m_i = 32$

Atom	C	O	H ₁	H ₂	H ₃	H ₄	$\sum_{i=1}^6$
x^2	0	2.045	3.098	0.137	0.137	0.137	
y^2	0	0	0	0	0.922	0.922	
z^2	0	0	0.810	1.013	0.314	0.314	
xy	0	0	0	0	-0.355	-0.355	
xz	0	0	1.584	-0.389	0.207	0.207	
yz	0	0	0	0	-0.538	-0.538	
mx	0	22.880	1.760	-0.370	-0.370	-0.370	23.530
my	0	0	0	0	-0.960	0.960	0
mz	0	0	0.900	1.050	-0.560	-0.560	0.830
mx_y	0	0	0	0	0.355	-0.355	0

Atom	C	O	H ₁	H ₂	H ₃	H ₄	$\sum_{i=1}^6$
mxz	0	0	1.584	-0.389	0.207	0.207	1.609
myz	0	0	0	0	0.538	-0.538	0
m (x ² + y ²)	0	32.704	3.097	0.136	1.057	1.057	38.051
m (x ² + z ²)	0	32.704	3.907	1.238	0.449	0.449	38.747
m (y ² + z ²)	0	0	0.810	1.102	1.234	1.234	4.380

Solution of the secular Eq. (2.15) gives the following moments of inertia.

$$I_{xx} = 4.38 - \frac{0 + 0.688}{32} = 4.38 - 0.021 = 4.359 \text{ au}$$

$$I_{yy} = 38.747 - \frac{553.660 + 0.688}{32} = 38.747 - 17.323 = 21.424 \text{ au}$$

$$I_{zz} = 38.051 - \frac{553.660 + 0}{32} = 38.051 - 17.301 = 20.750 \text{ au}$$

$$I_{xy} = 0 - \frac{0}{32} = 0 \text{ au}$$

$$I_{xz} = 1.609 - \frac{23.53 \times 0.83}{32} = 1.609 - 0.610 = 0.999 \text{ au}$$

$$I_{yz} = 0 - \frac{0}{32} = 0 \text{ au}$$

Thus, the product of the principal moments of inertia is

$$I_A I_B I_C = I_{xx} (I_{yy} I_{zz} - I_{yz} I_{yz}) - I_{xy} (I_{xy} I_{zz} + I_{yz} I_{xz}) - I_{xz} (I_{xy} I_{yz} + I_{yz} I_{xz})$$

$$\begin{aligned} I_A I_B I_C &= 4.359 (21.424 \times 20.750 - 0 \times 0) - 0.999 (0 \times 0 + 21.424 \times 0.999) \\ &= 1937.784 - 21.381 = 1916.403 \text{ (au)}^3 \end{aligned}$$

The group CH₃ rotates relative to the OH group. The rotation of these groups is free since C—O is a sigma bond. Hence the rotational energy exceeds that of the potential barrier. The reduced moment of inertia,

$$I_{\text{red}} = \frac{I_{\text{CH}_3} \times I_{\text{OH}}}{I_{\text{CH}_3} + I_{\text{CO}}}$$

$$I_{\text{CH}_3} = 3m_{\text{H}}(r_{\text{C-H}} \sin 70^\circ 32')^2 = 3(1.11 \times 0.943)^2 = 3.286 \text{ au.}$$

$$I_{\text{OH}} = 1 \times m_{\text{H}}(r_{\text{O-H}} \sin 70^\circ)^2 = 1(0.96 \times 0.94)^2 = 0.814 \text{ au.}$$

Hence,

$$I_{\text{red}} = \frac{3.286 \times 0.814}{3.286 + 0.814} = \frac{2.674}{4.1} = 0.652 \text{ au}$$

The symmetry number of CH₃OH is equal to the product of symmetry numbers of CH₃ and OH groups, i.e. $3 \times 1 = 3$

The principal moments of inertia of some important typical molecular systems can be determined directly from the following simple expressions:

(i) For symmetric triangular molecules of the type of XY₂, i.e. H₂O, H₂S, etc., the expression for the moments of inertia are

$$I_x = \frac{m}{2} r_1^2$$

$$I_y = \frac{2mm'}{2m+m'} \left[r_2^2 - \left(\frac{r_1}{2} \right)^2 \right] \quad (2.16)$$

$$I_z = I_x + I_y$$

where r_1 is the distance between identical atoms, r_2 is the distance between different atoms, m is the mass of each of the identical atoms and m' is the mass of the third atom. The validity of the relation $I_z = I_x + I_y$ will be discussed else where in this chapter.

(ii) In case of symmetric tetrahedral molecules such as CH_4 , CCl_4 , etc., the moments of inertia are expressed as

$$I_x = I_y = \frac{m}{2} r_1^2 \text{ and } I_z = m r_1^2 \quad (2.17)$$

where m is the mass of each of the end atoms and r_1 is the distance between these end atoms. The distance between the end atom and the central one, i.e. between the vertex and centre of the tetrahedron, is

$$r_2 = \sqrt{\frac{3}{8}} r_1 \quad (2.18)$$

For CH_3D ,

$$I_B(\text{CH}_3\text{D}) = \left[\frac{5}{3} m_H + m_D - \frac{(m_D - m_H)^2}{m_C + 3m_H + m_D} \right] r^2(\text{CH}) \quad (2.19)$$

(iii) For planar XY_3 type molecules, e.g. BF_3 ,

$$I_B = \frac{I_A}{2} = \frac{3}{2} m_y r_{xy}^2 \quad (2.20)$$

and for nonplanar XY_3 type molecules, e.g. NH_3 , ND_3 ,

$$r_{\text{HH}} = \sqrt{3(r_{\text{NH}}^2 - h_p^2)} \quad (2.21)$$

$$\cos \alpha = \left[1 - \frac{3(r^2 - h_p^2)}{2r^2} \right] \quad (2.22)$$

Here, $\alpha = \text{HNH}$

$$I_A = 3m_y r_{xy}^2 \sin^2 \beta$$

$$I_B = \frac{3m_y r_{xy}^2}{2 \left(1 + \frac{3m_y}{m_x} \right)} \left[2 - \left(1 - \frac{3m_y}{m_x} \right) \sin^2 \beta \right] \quad (2.23)$$

Height of pyramid $h_p = r \cos \beta$ (2.24)

where β is the angle of X-Y with the threefold axis.

(iv) For linear X_2Y_2 type molecules, e.g. C_2H_2 , C_2HD , the expression for moments of inertia is deduced as follows: The geometrical configurations of C_2H_2 and C_2HD are given in Fig. 2.7. In C_2HD the centre of mass C_m is shifted towards D.

Equation (2.3) yields

$$I = \sum_{i=1}^4 m_i r_i^2 = 2m_C y^2 + 2m_H x^2 \text{ for } \text{C}_2\text{H}_2 \quad (2.25)$$

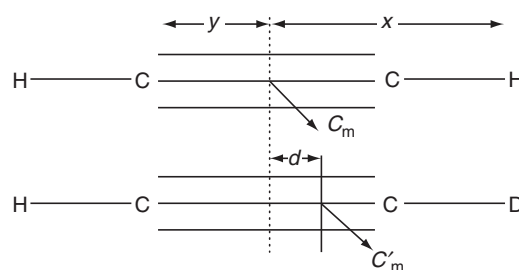


Fig. 2.7 Geometrical configurations of C_2H_2 and C_2HD .

For C_2HD , from Eq. (2.4) we write,

$$\sum_{i=1}^4 m_i r_i = m_H(x+d) + m_C(y+d) - m_D(x-d) - m_C(y-d) = 0 \quad (2.26)$$

Rearranging Eq. (2.26) we obtain

$$d = \frac{(m_D - m_H)x}{M_m^*} \quad (2.27)$$

where $M_m^* = 2m_C + m_D + m_H$

Thus, the moment of inertia of C_2HD about its centre of mass is

$$I^* = 2m_C y^2 + (m_H + m_D)x^2 - M_m^* d^2 \quad (2.28)$$

From I and I^* we can obtain x and y , i.e.

$$\begin{aligned} x &= \frac{1}{2}r_{CC} + r_{CH} = \sqrt{\frac{M_m^*(I^* - I)}{M_m(m_D - m_H)}} \\ y &= \frac{1}{2}r_{CC} = \sqrt{\frac{I - 2m_H x^2}{2m_C}} \end{aligned} \quad (2.29)$$

Problem 2.5: Determine the principal moments of inertia of methane if its bond length is $1.09 \text{ \AA}$.

Solution From Eq. (2.18), we get

$$r_1 = \sqrt{\frac{8}{3}} \quad r_2 = \sqrt{\frac{8}{3}} \times 1.09 = 1.779 \text{ \AA}$$

Thus, from Eq. (2.17)

$$I_x = I_y = \frac{1}{2}(1.779)^2 = 1.582 \text{ au}$$

and

$$I_z = (1.779)^2 \times 1 = 3.164 \text{ au}$$

2.4 DIATOMIC MOLECULE AS A RIGID ROTATOR

The mass of a nucleon is approximately 1840 times than that of an electron. The diameter of the lightest nuclei is of the order of 10^{-13} cm while the bond lengths are of the order of 10^{-8} cm . The total mass is concentrated in the two nuclear regions. In the light of these facts, we can assume that the diatomic molecule behaves as a rigid dumb-bell, i.e. when the molecule rotates, the bond distance remains unaltered. Let us now study the rotational motion of the rigid diatomic molecule about an axis passing through its centre of mass C_m and perpendicular to the molecular axis as shown in Fig. 2.8.

Here, m_1 and m_2 are the masses of the nuclei of the diatomic molecule, r is the bond length, r_1 and r_2 are the distances of the nuclei from C_m such that $r = r_1 + r_2$. Proceeding as in Problem (2.1), we obtain

$$I = \mu_m r^2 \quad (\text{Eq. 2.9})$$

Thus, we are able to reduce a two-body problem to a one-body problem. According to classical mechanics, the energy of rotation is expressed as

$$E_{\text{rot}} = 2\pi I \omega^2 = \frac{P^2}{2I} \quad (2.30)$$

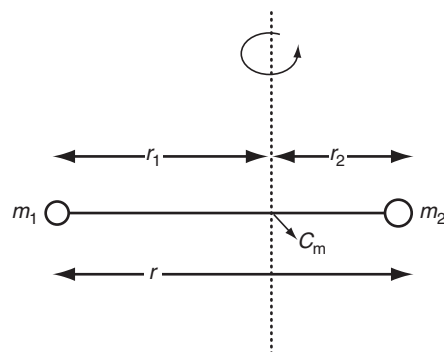


Fig. 2.8 Rigid dumb-bell model of a diatomic molecule.

where ω is the frequency of rotation in Hz and P is the angular momentum about an axis through the centre of mass and normal to symmetry axis. According to this expression, all energies are possible with a frequency of rotation ω , i.e. the rotational spectra should be continuous. But this is contrary to the experimental observations. Actually, the rotational spectra of diatomic molecules have a fine structure. In order to explain the fine structure of the rotational spectra, let us describe the rotational motion of a diatomic molecule of mass μ_m by Schrödinger wave equation in the polar coordinates, i.e.

$$\nabla^2 \psi + \frac{8\pi^2 \mu_m}{h^2} E_{\text{rot}} = 0 \quad (\text{For solution see Appendix A 2.1A}) \quad (2.31)$$

where ∇^2 is the Laplacian operator in polar coordinates. The solution of Eq. (2.31) leads to the expression

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \quad (2.32)$$

or the rotational term value,

$$F_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1), \text{ in cm}^{-1}$$

where E_J is the energy of the allowed energy levels and J represents the total angular momentum of the molecule, i.e. $P = \sqrt{J(J+1)} \cdot \frac{h}{2\pi}$. It is called the *rotational quantum number* and can take up any integral value including zero, i.e. $J = 0, \pm 1, \pm 2, \pm 3, \dots$. Equation (2.32) holds good if the molecular motion is considered due to the motion of the nuclei only. Equation (2.32) may also be expressed as

$$E_J = BhcJ(J+1) \quad (2.33)$$

Here, B is called the *rotational constant* and is defined as

$$B = \frac{h}{8\pi^2 Ic} = \frac{16.8575}{I} \text{ cm}^{-1} \quad (2.34)$$

The quantum mechanical derivation based on Schrödinger wave equation of energy levels of a restricted rotator is dealt with in Appendix 2.2A.

2.4.1 Spacing Between Two Adjacent Allowed Energy Levels

The energies of the two successive levels may be expressed as

$$E_J = BhcJ(J+1) \quad (\text{Eq. 2.33})$$

$$E_{J+1} = Bhc(J+1)(J+2) \quad (2.35)$$

Subtracting Eq. (2.33) from Eq. (2.35), we obtain

$$\Delta d_J = \frac{\Delta E_{\text{rot}}}{hc} = \frac{E_{J+1} - E_J}{hc} = 2B(J+1) \text{ cm}^{-1} \quad (2.36)$$

From Eq. (2.36), we get

J	Spacing, Δd_J
0	$2B$
1	$4B$
2	$6B$
3	$8B$
...	

Thus, the spacing between the two successive levels grows with the growth of J and the difference between the adjacent spacings is $2B$. The behaviour of Δd_J with J is shown in Fig. 2.9.

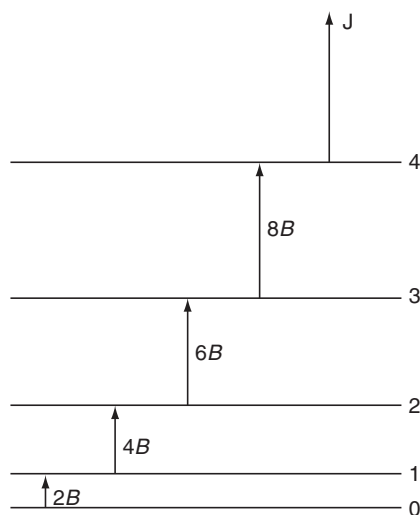


Fig. 2.9 A sketch showing the influence of quantum number on the permissible energy levels and the separation between the adjacent levels of a rigid rotator.

2.4.2 Selection Rules and Transition Between Permissible Energy Levels

The discrete nature of the spectrum suggests that not all transitions are permissible among all the energy levels. The transition between any two adjacent levels occurs in accordance with some specific rules known as selection rules. Let M be the permanent dipole moment of the molecule and M_x , M_y and M_z are its components in the direction of three axes such that $M^2 = M_x^2 + M_y^2 + M_z^2$. The selection rules have been deduced quantum mechanically from the solution of the integral

$$M_i = \int \Psi_i^* \hat{M}_i \Psi_j d\tau \quad (2.37)$$

where M_i is the transition dipole moment during the transition between the states j and i , $\hat{M}_i$ is the transition dipole moment operator and is related to the permanent dipole moment M . Ψ_i and Ψ_j are the wave functions of energy states i and j respectively and are orthogonal to each other, and $d\tau$ is the volume element. The transition dipole moment arises due to the interaction of the oscillating electric field of radiation (periodically reversing) with the dipole moment of the molecule. It is discussed in Chapter 3 on infrared spectroscopy. The components of M_i along three axes are

$$M_i(x) = \int \Psi_i \hat{M}_i(x) \Psi_j d\tau \quad (2.38)$$

$$M_i(y) = \int \Psi_i \hat{M}_i(y) \Psi_j d\tau \quad (2.39)$$

$$M_i(z) = \int \Psi_i \hat{M}_i(z) \Psi_j d\tau \quad (2.40)$$

The transition dipole moment operator in the three directions is

$$\hat{M}_i(x) = ex, \quad \hat{M}_i(y) = ey, \quad \hat{M}_i(z) = e \quad (2.41)$$

where e is the electronic charge and x, y, z are the Cartesian coordinates:

From Eqs (2.38) to (2.41), we obtain

$$M_i(x) = e \int \Psi_i x \Psi_j d\tau \quad (2.42)$$

$$M_i(y) = e \int \Psi_i y \Psi_j d\tau \quad (2.43)$$

$$M_i(z) = e \int \Psi_i z \Psi_j d\tau \quad (2.44)$$

In polar coordinates, we may write

$$\left. \begin{aligned} M_x &= M \sin \theta \cos \phi \\ M_y &= M \sin \theta \sin \phi \\ M_z &= M \cos \theta \end{aligned} \right\} \quad (2.45)$$

The transition dipole moment can now be expressed as

$$\begin{aligned} M_t(x) &= \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} \psi_i \hat{M}_t(x) \sin\theta \cos\varphi \psi_j d\tau \\ M_t(y) &= \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} \psi_i \hat{M}_t(y) \sin\theta \sin\varphi \psi_j d\tau \\ M_t(z) &= \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} \psi_i \hat{M}_t(z) \cos\theta \psi_j d\tau \end{aligned} \quad (2.46)$$

where $d\tau = \sin\theta d\theta d\varphi$.

The wave functions for the two states may also be expressed as

$$\begin{aligned} \psi_i &= \psi_{j''}, M_{j''} \\ \psi_j &= \psi_{j'}, M_{j'} \end{aligned} \quad (2.47)$$

where double prime stands for upper level while single prime corresponds to lower level, and M_j is the component of J along the direction of an external electric or magnetic field. Thus, in the absence of any external field, the selection rules are as follows:

(a) $M \neq 0$, i.e. Molecules having Permanent Dipole Moment will be Microwave Active.

In other words, we can say that molecules whose electrical centre do not coincide with their centre of mass, will be microwave active, e.g. CO, $^{16}\text{O}^{18}\text{O}$, $^{35}\text{Cl}^{37}\text{Cl}$, HD, etc. Thus, symmetric molecules such as H_2 , O_2 , Cl_2 , N_2 , etc., with $M = 0$ will be microwave inactive.

(b) $M_t \neq 0$

Only those transitions are allowed for which at least one of the components of M_t , namely $M_t(x)$, $M_t(y)$ or $M_t(z)$ is nonzero, i.e. the permanent dipole moment should change during the transition between the two states. In non-symmetric diatomics, we know that the electric centre of the molecule does not coincide with the centre of mass, so that when the state of the molecule changes, i.e. J changes, its dipole moment changes.

(c) The Pauli–Fermi Principle Should be Followed, i.e. the Transitions for which $\Delta J = \pm 1$, $\Delta M_j = 0$, are Permissible.

Let J' and J'' be the rotational quantum numbers of two states. With the aid of Eq. (2.33), the energy difference between the two states may be expressed as

$$\bar{\nu}_{\text{rot}} = \frac{E_{J''} - E_{J'}}{hc} = \frac{\Delta E_{\text{rot}}}{hc} = B(J'' - J')(J'' + J' + 1) \quad (2.48)$$

According to the Pauli–Fermi principle, i.e. $J'' - J' = \pm 1$, we obtain

$$\bar{\nu}_{\text{rot}} = 2BJ'' \quad (2.49)$$

where $J'' = 1, 2, 3, \dots$

or

$$\bar{\nu}_{\text{rot}} = 2B(J' + 1) \quad (2.50)$$

where $J' = 0, 1, 2, 3, \dots$

Thus, according to Eq. (2.49) or (2.50), the rotational transitions $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3, \dots$ will be positioned at $2B$, $4B$, $6B, \dots \text{ cm}^{-1}$, respectively. Interestingly, the spacing between the adjacent lines in the spectrum and the difference between the successive spacings of the energy levels are the same, i.e. $2B$. Since B is very small, i.e. in case of HCl, $B = 10 \text{ cm}^{-1}$, the energy difference between any two adjacent rotational energy levels will also be very small. Therefore, even at ambient temperatures, the higher rotational levels are also populated. Consequently, the rotational spectra of diatomic molecules consist of a number of equally spaced lines as shown in Fig. 2.10.

Knowing $2B$ from the spectrum, the moment of inertia and hence, bond length of the diatomic molecule can be determined with the aid of Eq. (2.34). The experimental data on the rotational spectra of diatomics reveal that the lines are not equally spaced as expected on a theoretical basis. The difference between the observed and theoretical value of $2B$ is significant. This discrepancy may be because of the assumption that the diatomic molecule behaves as a rigid rotator. In reality, when the molecule rotates, due to centrifugal force, the bond length is slightly stretched

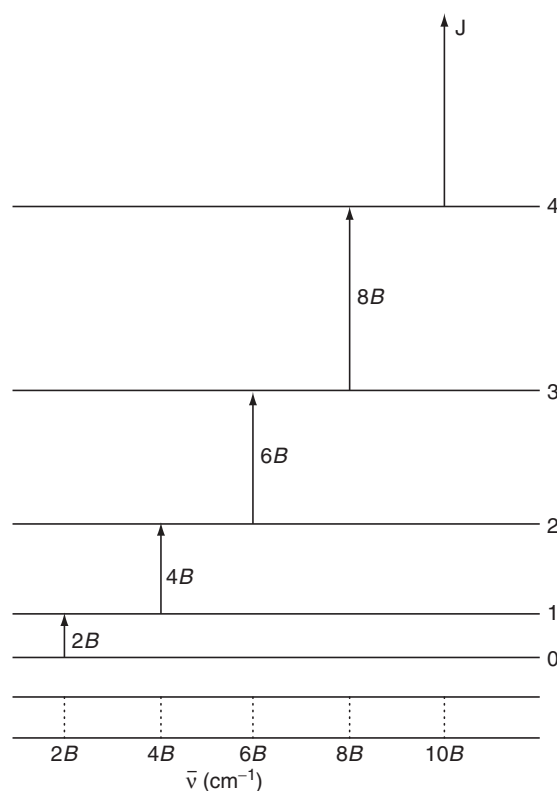


Fig. 2.10 Allowed rotational energy levels and the spectrum of a rigid diatomic molecule.

and the equilibrium distance is dependent on J . In the light of this, a 'correction' corresponding to this effect should be introduced in the rotational energy expression of the diatomic molecule, i.e. in Eqs. (2.32) and (2.33).

Problem 2.6: The lines in the far IR spectrum of HCl are positioned at the following wave numbers:

Line No.	1	2	3	4	5	6	7
$\bar{\nu}_{\text{rot}}, \text{cm}^{-1}$	85.384	106.730	128.076	149.422	170.768	192.114	213.466

Find the average value of moment of inertia and bond length of HCl.

Solution The average value of difference between the wave numbers of successive lines, $2B = 21.346 \text{ cm}^{-1}$. Thus $B = 10.673 \text{ cm}^{-1}$.

Using Eq. (2.34) we obtain

$$\begin{aligned}
 I &= \frac{3.9890 \times 10^{13} (\text{amu } \text{\AA}^2 \text{ s}^{-1})}{8 \times 3.14 \times 3.14 \times 3 \times 10^{10} (\text{cm sec}^{-1}) \times 10.673 (\text{cm}^{-1})} \\
 &= \frac{16.8575}{10.673} \text{amu } \text{\AA}^2 = 1.57945 \text{ au}
 \end{aligned}$$

Thus, from Eqs (2.9) and (2.10)

$$\begin{aligned}
 \mu_m &= \frac{35 \times 1}{35 + 1} = \frac{35}{36} \text{ amu} \\
 r &= \sqrt{\frac{1.57945 \text{ amu } \text{\AA}^2}{(35/36) \text{ amu}}} = 1.274 \text{ \AA}
 \end{aligned}$$

Problem 2.7: The average value of spacing between the adjacent lines in the rotational spectrum of the diatomic molecule CX is 3.84235 cm^{-1} . The equilibrium distance is $1.131 \text{ \AA}$. Find the atomic mass of X.

Solution Given $2B = 3.84235 \text{ cm}^{-1}$. Thus, $B = 1.921175 \text{ cm}^{-1}$.

$$r = 1.131 \text{ Å}$$

From Eqs (2.34) and (2.9) we get

$$I = \frac{16.8575}{1.921175} = 8.7745 \text{ au}, \quad \mu_m = \sqrt{\frac{8.7745}{(1.131)^2}} = 6.859 \text{ amu}$$

Let the mass of atom X in CX is m_x . Then applying Eq. (2.10), we obtain

$$6.859 = \frac{12m_x}{12 + m_x} \text{ or } m_x = 16 \text{ amu}$$

Hence the CX molecule is actually CO.

Problem 2.8: Calculate the wave numbers of the lines in the rotational spectrum of CO for the $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$ transitions if the equilibrium bond distance of CO is 1.131 Å .

Solution From the preceding problem,

$$I = 6.859 \times (1.131)^2 = 8.7737 \text{ au}$$

From Eq. (2.34),

$$B = \frac{16.8575}{8.7745} = 1.9213 \text{ cm}^{-1}$$

Hence,

$$\begin{aligned} \bar{\nu}_{\text{rot}}(0 \rightarrow 1) &= 2B = 3.8426 \text{ cm}^{-1} \\ \bar{\nu}_{\text{rot}}(1 \rightarrow 2) &= 4B = 7.6852 \text{ cm}^{-1} \\ \bar{\nu}_{\text{rot}}(2 \rightarrow 3) &= 6B = 11.5278 \text{ cm}^{-1} \end{aligned}$$

Problem 2.9: The average value of spacing between the adjacent rotational lines in the spectrum of NaCl is 0.432 cm^{-1} . Show that ion pairs are present in the vapours of NaCl.

Solution Given $2B = 0.432 \text{ cm}^{-1}$. Therefore, $B = 0.216 \text{ cm}^{-1}$.

From Eq. (2.10) we obtain the reduced mass of NaCl, i.e.

$$\mu_m = \frac{23 \times 35.5}{23 + 35.5} = \frac{23 \times 35.5}{58.5} \text{ amu}$$

Now using Eq. (2.34),

$$r = \sqrt{\frac{16.8575}{B\mu_m}} = \sqrt{\frac{16.8575 \times 58.5}{0.216 \times 23 \times 35.5}} = 2.364 \text{ Å}$$

The calculated value of bond distance, i.e. 2.364 Å , agrees well with the bond distance of NaCl determined by x-ray diffraction technique. From this, it is inferred that in the vapours of NaCl, ions pairs are also present in addition to the Na^+ and Cl^- ions.

Problem 2.10: Determine the rotational energy of CO on the quantum levels $J = 1$ and 2 if the equilibrium nuclear distance of CO is 1.131 Å .

Solution From Eqs (2.10) and (2.9), we obtain

$$\mu_m = \frac{16 \times 12}{16 + 12} = \frac{192}{28} = 6.857 \text{ amu}$$

From problem 2.8,

Therefore, $I = 6.859 \times (1.131)^2 = 8.7737 \text{ au}$.

With the aid of Eq. (2.32), we can determine the energy of the rotational levels for $J = 1$ and 2 .

$$\begin{aligned}
 E_1 &= \frac{(3.9890 \times 10^{13} \text{ amu } \text{\AA}^2 \text{ s}^{-1})}{8 \times 3.14 \times (8.7737 \text{ amu } \text{\AA}^2)} \times 1(1+1) \\
 &= 45.986 \times 10^{23} \text{ amu } \text{\AA}^2 \text{ s}^{-2} \\
 &= 45.986 \times 10^{23} \times 1.6604 \times 10^{-47} \text{ J} \\
 &= 0.763 \times 10^{-22} \text{ J} \\
 E_2 &= 22.993 \times 10^{23} \times 2(2+1) \\
 &= 137.958 \times 10^{23} \text{ amu } \text{\AA}^2 \text{ s}^{-2} \\
 &= 137.958 \times 10^{23} \times 1.6604 \times 10^{-47} \text{ J} \\
 &= 0.229 \times 10^{-21} \text{ J}
 \end{aligned}$$

Problem 2.11: Predict and sketch the general behaviour of isotopic substitution on the position of the rotation line as well as on the spacing between the adjacent lines in the rotational spectra of molecules.

Solution A slight change in bond length on isotopic substitution occurs because of the zero point energy which depends upon the mass of the atoms. However, for all practical purposes, the bond length in the different isotopic species of the same molecule is assumed to be the same. From Eq. (2.34), we write

$$B = \frac{h}{8\pi^2 I c} \quad (\text{Eq. 2.34})$$

$$B^* = \frac{h}{8\pi^2 I^* c} \quad (\text{Eq. 2.34}^*)$$

where * stands for heavy molecule.

Dividing Eq. (2.34) by Eq. (2.34)*, we obtain

$$\frac{B}{B^*} = \frac{I^*}{I} = \frac{\mu_m^*}{\mu_m} \quad (2.51)$$

Since B varies inversely with the moment of inertia of the molecule, the effect of isotopic substitution results not only in shifting the rotational lines but also in decreasing the separation between the adjacent lines in the spectra of the diatomic molecules and is shown in Fig. 2.11.

With the aid of Eq. (2.51), we can also determine the atomic mass of the isotope of the molecule.

Problem 2.12: Determine the difference between the wave numbers corresponding to $1 \rightarrow 2$, transition in the rotational spectra of $^{12}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$. The equilibrium bond length in both the cases is $1.131 \text{ \AA}$.

Solution From Eq. (2.9) we obtain

$$\begin{aligned}
 I(^{12}\text{C}^{16}\text{O}) &= \frac{12 \times 16}{12 + 16} \times (1.131)^2 = 8.7713 \text{ au} \\
 I(^{12}\text{C}^{18}\text{O}) &= \frac{12 \times 18}{12 + 18} \times (1.131)^2 = 9.2099 \text{ au}
 \end{aligned}$$

Thus, from Eq. (2.34) we get

$$\begin{aligned}
 B(^{12}\text{C}^{16}\text{O}) &= \frac{16.8575}{8.7713} = 1.9218 \text{ cm}^{-1} \\
 B(^{12}\text{C}^{18}\text{O}) &= \frac{16.8575}{9.2099} = 1.8303 \text{ cm}^{-1}
 \end{aligned}$$

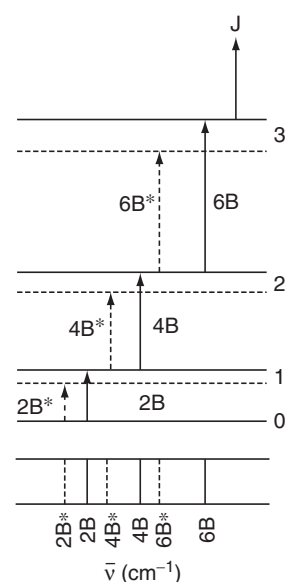


Fig. 2.11 A sketch showing the effect of isotopic substitution on the energy levels and the spectrum of the rigid diatomic molecule.

Hence, for the transition 1→2

$$\bar{\nu}_{\text{rot}}(^{12}\text{C}^{16}\text{O}) = 4B = 7.6872 \text{ cm}^{-1}$$

$$\bar{\nu}_{\text{rot}}(^{12}\text{C}^{18}\text{O}) = 4B = 7.3212 \text{ cm}^{-1}$$

Thus, the isotopic substitution shifts the wave number of the spectral line corresponding to 1 → 2 transition to the lower side and the magnitude of shift is 0.3660 cm⁻¹.

Problem 2.13: The average value of difference between the wave numbers of adjacent lines in the rotational spectra of ¹²C¹⁶O and ¹²CX* are 3.8436 and 3.6606 cm⁻¹ respectively. Determine the atomic mass of an isotope of the atom X, i.e. X*.

Solution We know that isotopic substitution does not affect the bond length. Let atomic mass of the atom X* be m*. Given B = 1.9218 cm⁻¹ and B* = 1.8303 cm⁻¹.

Now employing Eq. (2.51), we get

$$\frac{1.8303}{1.9218} = \frac{12 + m^*}{12 m^*} \times \frac{12 \times 16}{16 + 12} = \frac{16 \times 12(m^* + 12)}{28 \times 12 m^*} = \frac{4(m^* + 12)}{7 m^*}$$

$$m^* = \frac{12 \times 4 \times 1.9218}{(7 \times 1.8303 - 4 \times 1.9218)} = \frac{48 \times 1.9218}{5.1249} = 17.999 \text{ amu}$$

Thus, the atomic mass of the isotope of atom X, i.e. X* is 18 amu. The molecular formula of isotopically substituted molecule will be ¹²C¹⁸O.

2.5 DIATOMIC MOLECULE AS A NONRIGID ROTATOR

As we have already discussed, during the rotation of the molecule, the bond distance does not remain fixed. Thus, taking into consideration the role of centrifugal force in the rotational motion of the molecule, the allowed energy of the rotational level, as deduced from the solution of the Schrödinger wave equation, is expressed as

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2 + \dots$$

$$= hcBJ(J+1) - hcDJ^2(J+1)^2 + \dots$$
(2.52)

where D is the centrifugal distortion constant and is defined as

$$D = \frac{4B^3}{\omega^2}$$
(2.53)

Here, $D \ll B$ and D is $10^{-4} B$, ω is the vibrational frequency of the harmonic oscillator and is expressed as

$$\omega(\text{cm}^{-1}) = 1303.16 \sqrt{\frac{k(\text{millidynes}/\text{\AA})}{\mu_m(\text{amu})}}$$
(2.54)

where k is the force constant and is defined as the restoring force to bring the molecule back to its original position.

An approximate value for k of the diatomic molecule can also be obtained from the expression

$$k = a N_{bo} \left[\frac{X_1 X_2}{r} \right]^{3/4} b$$
(2.54a)

in which N_{bo} is the bond order (number of bonds between the two atoms), X_1 and X_2 are the electronegativities of the atoms, r is the internuclear distance, a and b are constants with values 1.67 and 0.30 respectively.

The restoring force

$$F = -k(r - r_e) = -k\Delta r$$
(2.55)

where $\Delta r = r - r_e$ is the displacement from the equilibrium position. The Potential Energy (PE) of a harmonic oscillator is expressed as

$$U(r) = \frac{1}{2} k (r - r_e)^2$$
(2.56)

The PE curve of a harmonic oscillator will be a parabola as shown in Fig. 2.12.

The harmonic assumption is valid only in the lowest vibrational state of the molecule and will be discussed in detail in Chapter 3 on infrared vibrational spectroscopy. However, if the molecule is not in the lowest vibrational state then the correction due to molecular vibration which changes the moment of inertia of the molecule must be applied.

The correction for the rotational constant B_v in the V th vibrational level is

$$B_v = B_e - \alpha_e \left(V + \frac{1}{2} \right) + \gamma_e \left(V + \frac{1}{2} \right)^2 \quad (2.57)$$

where B_e is the rotational constant for the theoretical equilibrium state of no vibration, α_e and γ_e are the rotational-vibrational coupling constants. α_e and γ_e are very small and

$$\alpha_e = \frac{B_e}{100} \quad (2.58)$$

Consequently, the value of B , D , and r will be different in different vibrational states. B_0 , D_0 and r_0 thus correspond to the ground vibrational state, i.e. $V=0$ while B_e , D_e and r_e stand for equilibrium state. B_e , D_e and r_e can only be determined theoretically but not experimentally. In the light of the above facts, the energy of the allowed levels of a nonrigid rotator in the higher vibrational states should be expressed as

$$E_J = hcBJ(J+1) - hcDJ^2(J+1)^2 - \alpha_e \left(V + \frac{1}{2} \right) \quad (2.59)$$

The higher terms being smaller are ignored. Quantum mechanical derivation of this equation is given in Appendix 3.3A of infrared spectroscopy.

2.5.1 Spacing Between Two Adjacent Allowed Energy States

The spacing between two successive energy levels, Δd_J , may be deduced from Eq. (2.52) as follows.

$$E_J = hcBJ(J+1) - hcDJ^2(J+1)^2 \quad (\text{Eq. 2.52})$$

$$E_{J+1} = hcB(J+1)(J+2) - hcD(J+1)^2(J+2)^2 \quad (2.60)$$

Proceeding as in the case of a rigid rotator, we get from Eqs (2.52) and (2.60)

$$\Delta d_J = \frac{E_{J+1} - E_J}{hc} = \frac{\Delta E_{\text{rot}}}{hc} = 2B(J+1) - 4D(J+1)^3 \quad (2.61)$$

From Eq. (2.61), we obtain the spacing between the two adjacent levels and is recorded in tabular form as under.

J	Spacing, Δd_J
0	$2(B - 2D)$
1	$4(B - 8D)$
2	$6(B - 18D)$
...	

The results indicate that the spacing between the adjacent energy levels in comparison to rigid rotator model of the diatomic molecule (where $D=0$) is small. However, as expected, the spacing grows with the quantum number J . The spacing between the adjacent levels, i.e. $2(B - 2D)$, $4(B - 8D)$, $6(B - 18D)$,..., as well as the gap between the adjacent spacings, i.e. $2(B - 14D)$, $2(B - 38D)$, $2(B - 74D)$,..., are not uniform as in the case of a rigid rotator model of the diatomic molecule. The non-uniform behaviour may be due to centrifugal distortion which increases as the rotational quantum number increases.

2.5.2 Transition Between Two Adjacent Energy Levels

The selection rules for a nonrigid rotator model are the same as for the rigid rotator model of the diatomic molecule, i.e. $M \neq 0$, $M_l \neq 0$, and $\Delta J = \pm 1$. Let J'' and J' be the rotational quantum numbers for the upper and lower energy levels respectively. From Eq. (2.52), the energy expressions for the two states may be written as

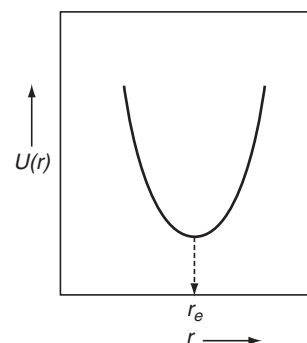


Fig. 2.12 The change in potential energy with internuclear bond distance of a diatomic oscillator.

$$E_{J''} = hcBJ'' - hcDJ''^2(J'' + 1)^2 \quad (2.62)$$

$$E_{J'} = hcBJ' - hcDJ'^2(J' + 1) \quad (2.63)$$

From Eqs (2.62) and (2.63), we obtain

$$\begin{aligned} \bar{\nu}_{\text{rot}} &= \frac{E_{J''} - E_{J'}}{hc} = \frac{\Delta E_{\text{rot}}}{hc} \\ &= B[(J'' - J')^2 + (J'' - J')] - D[(J'' + 1) - J'(J' + 1)][J''(J'' + 1) + J'(J' + 1)] \\ &= (J'' - J')(J'' + J' + 1)[B - D\{J''(J'' + 1) + J'(J' + 1)\}] \end{aligned} \quad (2.64)$$

Applying the selection rule, $\Delta J = J'' - J' = +1$, Eq. (2.64) reduces to

$$\bar{\nu}_{\text{rot}} = 2BJ'' - 4DJ''^3 \quad (2.65)$$

$$\frac{\bar{\nu}_{\text{rot}}}{J''} = 2B - 4DJ''^2 \quad (2.66)$$

where $J'' = 1, 2, 3, \dots$

In terms of lower level, we may write

$$\frac{\bar{\nu}_{\text{rot}}}{(J' + 1)} = 2B - 4D(J' + 1)^2 \quad (2.67)$$

where $J' = 0, 1, 2, 3, \dots$

The plot between $\frac{\bar{\nu}_{\text{rot}}}{J''} / \frac{\bar{\nu}_{\text{rot}}}{(J' + 1)}$ and $J''^2/(J' + 1)^2$ will be a straight line with slope $= -4D$ and intercept $= 2B$. From slope and intercept, one can determine D and B and hence the bond length of the diatomic molecule.

The energies of the different transitions as worked out from Eq. (2.65) or (2.67) have been recorded in the tabular form as under:

J	Transition	$\bar{\nu}_{\text{rot}}, \text{cm}^{-1}$
0	0 → 1	$2B - 4D$
1	1 → 2	$4B - 32D$
2	2 → 3	$6B - 108D$
3	3 → 4	$8B - 256D$

Thus, according to nonrigid rotator model of the diatomic molecule, just like rotational energy levels, there is also a decrease in the separation between the spectral lines as compared to the rigid model. The energy-level scheme and the lines in the spectrum of rigid and nonrigid diatomic molecules are presented in Fig. 2.13.

Problem 2.14: The following lines have been identified in the high-resolution rotational spectrum of CO.

Line No.	1	2	3	4	5
J	0	1	2	3	4
$\bar{\nu}_{\text{rot}}, \text{cm}^{-1}$	3.845	7.690	11.534	15.379	19.222

Determine analytically and graphically the values of r_0 and D_0 for the molecule if the vibrational frequency of CO is at 2300 cm^{-1} . Analyse the data by the method of least-square fit also.

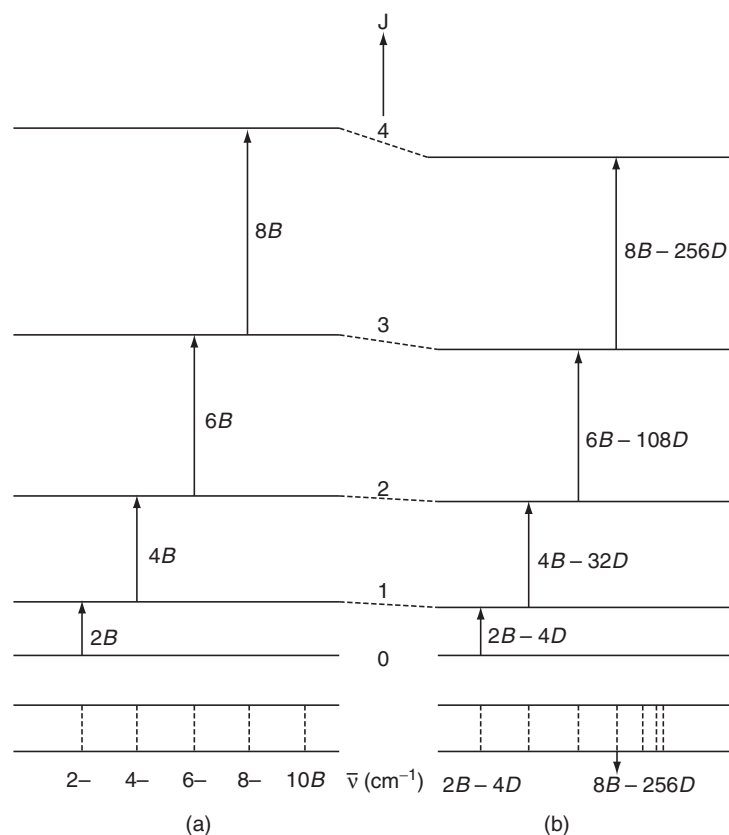


Fig. 2.13 The change in rotational energy levels and spectrum of a diatomic molecule in passing from (a) a rigid to (b) a nonrigid rotator.

Solution Assuming the molecule to be in the ground vibrational state, the value of the B_0 can be determined from the average value of the difference of wave numbers between the adjacent lines. The average value of $2B_0 = 3.844 \text{ cm}^{-1}$. Hence $B_0 = 1.922 \text{ cm}^{-1}$.

From Eq. (2.10), we obtain

$$\mu_m = \frac{12 \times 16}{12 + 16} = \frac{192}{28} \text{ amu}$$

Substituting B_0 and μ_m into Eq. (2.34), we get

$$r_0 = \sqrt{\frac{16.8575}{\mu_m B}} \quad [\text{Since } I = \mu_m r^2]$$

$$= \sqrt{\frac{16.8575 \times 28}{192 \times 1.922}} = 1.131 \text{ \AA}$$

From Eq. (2.53),

$$D_0 = \frac{4 \times (1.922)^3}{(2300)^2} = 5.97 \times 10^{-6} \text{ cm}^{-1}$$

Graphically, the values of B_0 and D_0 can be obtained with the aid of Eq. (2.67), i.e.

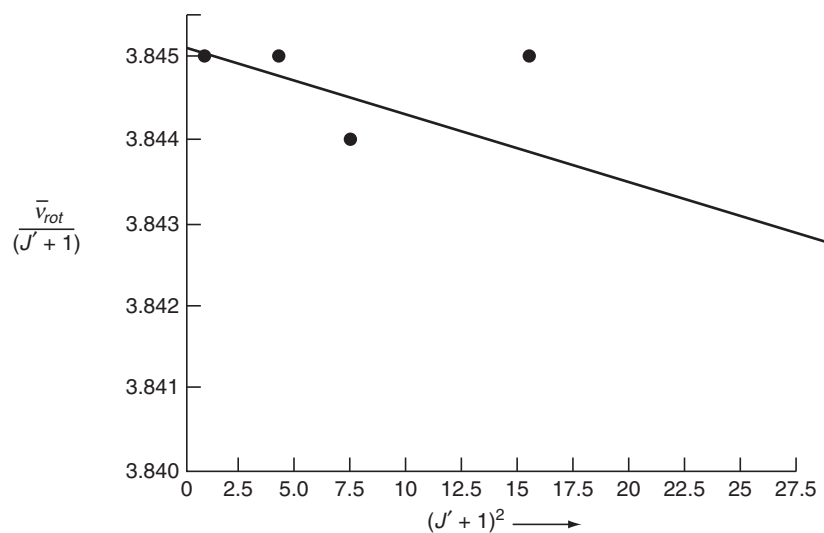
$$\frac{\bar{\nu}_{\text{rot}}}{(J' + 1)} = 2B - 4D(J' + 1)^2$$

where $J' = 0, 1, 2, 3, \dots$

The data to be employed in the plot between $\frac{\bar{\nu}_{\text{rot}}}{(J' + 1)}$ and $(J' + 1)^2$ are generated and recorded in the tabular form as follows:

The plot is shown in Fig. 2.14.

J'	$(J' + 1)$	$(J' + 1)^2$	$\frac{\bar{\nu}_{rot}}{(J' + 1)}, \text{cm}^{-1}$
0	1	1	3.845
1	2	4	3.845
2	3	9	3.844
3	4	16	3.845
4	5	25	3.843

Fig. 2.14 Plot of $\bar{\nu}_{rot}/(J' + 1)$ against $(J' + 1)^2$.

From the graph,

$$B_0 = \frac{\text{Intercept}}{2} = \frac{3.8452}{2} = 1.9226 \text{ cm}^{-1} \text{ and}$$

$$D_0 = \frac{\text{Slope}}{4} = \frac{8.8 \times 10^{-5}}{4} = 2.2 \times 10^{-5} \text{ cm}^{-1}$$

Therefore,

$$r_0 = \sqrt{\frac{16.8575 \times 28}{1.922 \times 192}} = 1.1307 \text{ \AA}$$

Since the points on the graph are scattered, the results of graphical method can be improved upon by the method of least-square fit rather than manual fitting. The method of least-square fit has already been discussed in detail in Chapter 1. The data needed for the method are generated and reported in the tabular form as under:

J'	$(J' + 1)$	$(J' + 1)^2$ (x)	$\bar{\nu}_{rot}/(J' + 1), \text{cm}^{-1}$ (y)	$(J' + 1)^4$ (x ²)	$(J' + 1)^2 \frac{\bar{\nu}_{rot}}{(J' + 1)}, \text{cm}^{-1}$ (xy)
0	1	1	3.845	1	3.845
1	2	4	3.845	16	15.380
2	3	9	3.844	81	34.596
3	4	16	3.845	256	61.520
4	5	25	3.843	625	96.075
		$\sum_{i=1}^5 = 55$	19.222	979	211.4160

Using normal equations from Chapter 1, we get

$$10B_0 - 220D_0 = 19.222$$

$$110B_0 - 3916D_0 = 211.416$$

Solving for B_0 and D_0 , we get

$$B_0 = 1.922 \text{ and } D_0 = 1.73 \times 10^{-5} \text{ cm}^{-1}$$

Thus,

$$r_0 = \sqrt{\frac{16.8575 \times 28}{192 \times 1.922}} = 1.131 \text{ \AA}$$

2.6 HYPERFINE STRUCTURE

The rotating molecule has a magnetic field associated with it and is normal to the axis of the molecule. The magnetic moments of the rotating nuclei perturb slightly the rotational energy levels which, in turn, result in splitting of the rotational lines in the spectrum. This splitting is due to the interaction between the rotational motion of the molecule and the motion of the electrons. In the light of this, the rotational quantum number, J , consists of two numbers—one characterising the motion of the nuclei and the other, the motion of the electrons. J for the three Hund's cases framed from the vector model of diatomic molecule may be expressed as

$$\left. \begin{array}{l} \text{(i) } J = J_{\text{nuc}} + \Omega \\ \text{(ii) } J = J_{\text{nuc}} + \Lambda + S = K + S \\ \text{(iii) } J = J_{\text{nuc}} + \Omega \end{array} \right\} \quad (2.68)$$

The squares of the vectors J and K are equal to $\left(\frac{h}{2\pi}\right)^2 J(J+1)$ and $\left(\frac{h}{2\pi}\right)^2 K(K+1)$, respectively, whereas the squares of Ω and Λ , which are projections of vectors $L + S$ and L of the molecule, are equal to $\left(\frac{h}{2\pi}\right)^2 \Omega^2$ and $\left(\frac{h}{2\pi}\right)^2 \Lambda^2$ respectively.

Accordingly, the energy of the rotational levels is expressed as

$$\left. \begin{array}{l} \text{(i) } E_J = Bhc[J(J+1) - \Omega^2] \\ \text{(ii) } E_J = Bhc[K(K+1) - \Lambda^2] \\ \text{(iii) } E_J = Bhc[J(J+1) - \Omega^2] \end{array} \right\} \quad (2.69)$$

where $\Omega = \Lambda \pm \Sigma$. A comparison of this expression with $J = L + S$ indicates that Ω , Λ and Σ are respectively related to the numbers J , L and S where J , L and S are the total, orbital and spin angular momenta respectively. Ω , Λ and $\pm \Sigma$ are the projections of total, orbital and spin angular moments respectively on the molecular axis. The quantum numbers Λ and Σ characterise the orbital and spin motion of the electrons respectively. For every value of S , there are $2S + 1$ values of Σ , given by

$$\Sigma = \Lambda + S, \Lambda + S - 1, \dots, \Lambda - S \quad (2.70)$$

where $\Lambda = 0, 1, 2, 3, \dots$

The corresponding electronic molecular terms are designated as

$\Sigma, \Pi, \Phi, \dots$

The quantum numbers for the various molecular electronic terms are as follows:

For Σ terms $^1\Sigma(S=0, \Lambda=0)$, $^2\Sigma(S=1, \Lambda=0)$, $^2\Sigma(S=1/2, \Lambda=0)$, $^3\Sigma(S=1, \Lambda=0)$;

2.6.1 Designation of Molecular Orbital Corresponding to the Value of Λ

For one electron—Total: $\lambda = 0$ (σ); $\Lambda = 0$ (Σ); $\lambda = 1$ (π); $\Lambda = 1$ (Π); $\lambda = 2$ (δ); $\Lambda = 2$ (Δ). This is similar to the designation of atomic orbitals (s, p, d, f, ..., for $l = 0, 1, 2, 3, \dots$) and total angular momentum (S, P, D, F... for $L = 0, 1, 2, 3, \dots$)

Various Symbols in the Notation $^{2S+1}\Sigma_u^-$:

- (i) Σ corresponds to electronic state for which the orbital or electronic angular momentum Λ is zero.
- (ii) 2 represents, the multiplicity of the state, i.e. $2S + 1 = 2$, $\therefore S = 1/2$
- (iii) Negative sign indicates that electronic wave function of a molecule changes sign on reflection through a symmetry plane.
- (iv) When the electronic wave function of a molecule changes sign on reflection through centre of symmetry, it is termed as ungerade (u).

For Π terms: $^2\Pi(S = 1/2, \Lambda = 1)$, $^1\Pi(S = 0, \Lambda = 1)$, $^3\Pi(S = 1, \Lambda = 1)$;

For Δ terms: $^2\Delta(S = 1/2, \Lambda = 2)$, $^1\Delta(S = 0, \Lambda = 2)$.

The complete molecular electronic terms can be worked out from the formula

$$^{2S+1}\Lambda_{\Omega} \quad (2.71)$$

e.g. for $\Lambda = 1, S = \frac{3}{2}$, the complete term may be worked out with the aid of Eqs (2.70) and (2.71) as follows:

$$\Omega = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, \frac{-1}{2} \text{ and } 2S+1 = 2 \times \frac{3}{2} + 1 = 4.$$

Thus, the term $^4\Pi : ^4\Pi_{5/2}, ^4\Pi_{3/2}, ^4\Pi_{1/2}$ and $^4\Pi_{-1/2}$.

Similarly, we can show that the components of $^4\Delta$ state are $^4\Delta_{7/2}, ^4\Delta_{5/2}, ^4\Delta_{3/2}, ^4\Delta_{1/2}$.

The selection rules for the transition between the energy levels expressed by the expression (2.68) are

$$\Delta\Lambda = 0, \pm 1 \quad (2.72)$$

$$\Delta\Omega = 0, \pm 1 \quad (2.73)$$

$$\Delta\Sigma = 0 \quad (2.74)$$

$$\Delta S = 0 \quad (2.75)$$

According to Rule (2.72), $\Sigma \leftrightarrow \Sigma$, $\Pi \leftrightarrow \Pi$, $\Delta \leftrightarrow \Delta$, $\Sigma \leftrightarrow \Pi$, $\Pi \leftrightarrow \Delta$ combinations are allowed while $\Sigma \leftrightarrow \Delta$ and $\Pi \leftrightarrow \Phi$ combinations are not allowed.

By Rule (2.73), $0 \leftrightarrow 0$, $1 \leftrightarrow 1$, $2 \leftrightarrow 2$, $0 \leftrightarrow 1$, $1 \leftrightarrow 2$ combinations are permissible while $0 \leftrightarrow 2$, $1 \leftrightarrow 3$ are forbidden.

Rule (2.74) is helpful in understanding the peculiar behaviour of fine structure of molecular spectra (Hund's case ii). By Rule (2.75), intercombinations, i.e. combinations between terms of different multiplicities, are not allowed.

Further, according to the important rule associated with the kind of symmetry of molecular terms, positive terms (+) combine with negative (−) and even terms (g) combine only with odd terms (u), e.g. we may have the rule $\Delta S = 0$, $g \leftrightarrow u$ and the like. Here g stands for gerade and u for ungerade.

Equation (2.69) is valid under the following conditions:

For $E_J \geq 0$, $J \geq \Omega$, and $K \geq \Lambda$ must be satisfied. Thus, $J = 0$ (in the case of integral J) and $K = 0$ are possible only if $\Omega = 0$ and in turn $\Lambda = 0$. When $\Omega > 0$, $\Lambda > 0$, the minimum values of J and K are determined by the values of Ω and Λ .

Now coming to the fine structure which results due to the interaction of molecular rotation and the motion of the electrons, it is found that the magnitude of splitting increases with increase in quantum number J (or K). This increase is due to a build up of the intramolecular magnetic field with rotation of the molecule. The number of sublevels into which a particular rotational level splits is given by $2S + 1$.

The rotational level in the case of level $^1\Sigma$ shows no splitting since in this case $\Lambda = 0$ and $S = 0$.

For the level $^2\Sigma$, the rotational level splits into two components since $S = 1/2$ while into three components in case of level $^3\Sigma$ since $S = 1$. Further when $\Lambda > 0$, the rotational level splits up into two sublevels and the splitting is independent of the multiplicities of the Π terms, i.e. $^1\Pi$, $^2\Pi$ and $^3\Pi$. However, the splitting in this case is due

to the interaction between J_{nuc} and Λ but not between J_{nuc} and S . The levels corresponding to $\Lambda > 0$ are doubly degenerate since the same energy corresponds to the values of $+\Lambda$ and $-\Lambda$. For this reason, when there is intra-molecular magnetic field due to the molecular rotation, each such level splits into two components (+ and -) as shown in Fig. 2.15. This type of splitting is termed as Λ type doubling.

In case of Π -, Δ -, and Φ -levels, there is strong interaction between S and Λ for small values of J . The splitting in this case is independent of rotation. However, as J grows, the (S, J_{nuc}) type interaction becomes stronger, consequently splitted components become closer.

The properties of symmetry of the rotational terms as deduced from the wave function $\Psi = \pm \Psi_{\text{elec}} \pm \Psi_{\text{rot}}$ that characterises the rotational term belonging to corresponding electronic level of the molecule, have been recorded as

Ψ_{elec}	J	Ψ_{rot}	Ψ_{elec}	J	Ψ_{rot}
+	Even	+	-	Even	-
	Odd	-		Odd	+

Thus, in the case of Σ terms, the corresponding rotational terms will alternately be positive and negative as shown in Fig. 2.15 (a). In case of Π -, Δ -, Φ -, etc., terms, one of the components of Λ -type doubling of each rotational level will be (+) and the other (-) and is shown in Fig. 2.15 (b).

In case of molecules having same nuclei, the symmetry properties are also summarised in the tabular form as follows and are shown for Σ^+ - states in Fig. 2.16 (a) and (b).

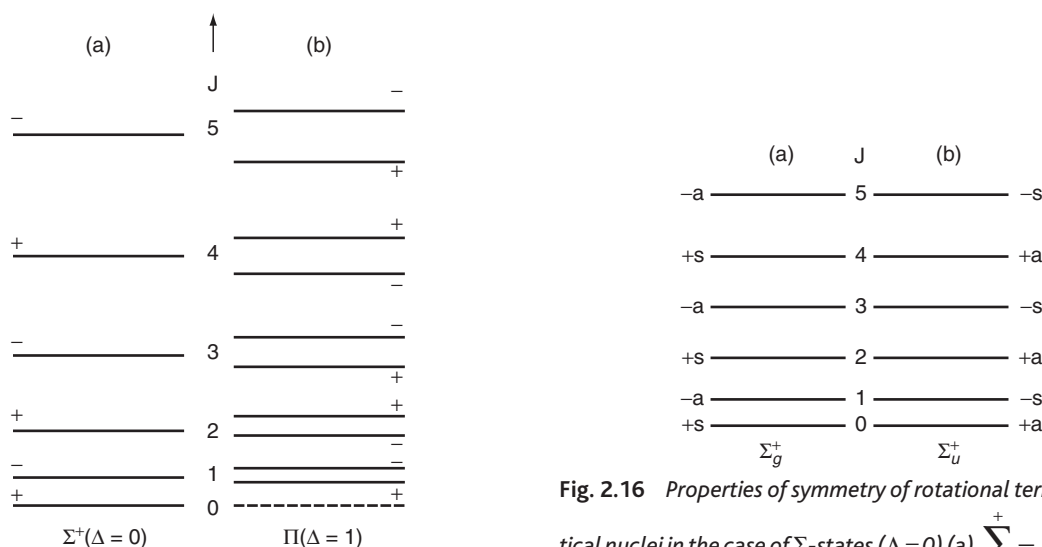


Fig. 2.15 Positive and negative rotational terms in case of (a) Σ^+ , and (b) Π electronic terms.

Fig. 2.16 Properties of symmetry of rotational terms of the identical nuclei in the case of Σ -states ($\Lambda=0$) (a) Σ_g^+ - term is positive and symmetric, and (b) Σ_u^+ - term is negative and symmetric.

Ψ_{elec}	J	Ψ_{rot}	Ψ_{elec}	J	Ψ_{rot}
Even (g)	Even	+s	Odd (u)	Even	+a
	Odd	-a		Odd	-s

The components of Λ -type doubling Π -, Δ -, Φ -, etc, terms have different symmetries (s and a). The selection rules for J are as follows:

- For $\Lambda \neq 0$, $\Delta J = 0, \pm 1$ and for $\Lambda = 0$, $\Delta J = \pm 1$.
- The selection rules for combining positive and negative rotational terms are $+\leftrightarrow -$ and $-\leftrightarrow +$. This rule does not contradict the rule $\Delta J = \pm 1$ ($\Lambda = 0$).
- For Raman spectrum, the rule for the transition between positive and negative rotational terms are $+\leftrightarrow +$ and $-\leftrightarrow -$ and is in agreement with the rule $\Delta J = 0, \pm 2$ for Raman scattering of radiation (Chapter 4).

In case of molecules with identical nuclei, only symmetric-symmetric and antisymmetric-antisymmetric combinations of terms are possible: $s \leftrightarrow s$ and $a \leftrightarrow a$. Hence according to this rule, molecules such as H_2 , N_2 , O_2 cannot exhibit rotational spectrum since only the transitions $+s \leftrightarrow -a$ are permissible.

2.7 ROTATIONAL SPECTRA OF POLYATOMIC MOLECULES

Based on the moments of inertia of molecules in the three principal axes, the molecules have been classified as follows:

(a) Linear Polyatomic Molecules of the type XY_2 and XYZ , etc., have two rotational degrees of freedom about axes perpendicular to that of the molecule. In such molecules, $I_x = I_y$, $I_z = 0$, e.g. CO_2 , CS_2 , OCS , HCN , SCSe , etc. On the other hand, nonlinear molecules have three rotational degrees of freedom.

(b) Spherical Top Molecules of this type have several axes of symmetry of the order $n \geq 3$. The moments of inertia of these type of molecules about all axes passing through the centre of mass are exactly equal, i.e. $I_x = I_y = I_z$, e.g. CH_4 , CCl_4 , SF_6 , P_4 , etc.

(c) Asymmetric Top Molecules of this type lack axes of symmetry of the order $n \geq 3$. In such cases, $I_x \neq I_y \neq I_z$, e.g. H_2O , CH_2Cl_2 , etc.

(d) Symmetric Top In these type of molecules, two of the three moments of inertia are equal to each other, i.e. $I_x = I_y \neq I_z$ or $I_x \neq I_y = I_z$. Such molecules have further been subdivided into two classes:

(i) *Oblate top*: $I_x > I_y = I_z$, e.g. BCl_3 , NH_3 , C_6H_6 , etc.

(ii) *Prolate top*: $I_x < I_y = I_z$, e.g. CH_3Cl , CH_3F , etc.

I_x , I_y and I_z are also denoted by I_A , I_B and I_C , respectively.

2.7.1 Moments-of-inertia Defect

As will be discussed in Chapter 3, each vibrational level, say V , is associated with rotational levels. The effective moments of inertia $I_A^{(V)}$, $I_B^{(V)}$ and $I_C^{(V)}$ are obtained from the respective effective rotational constants $A_{(V)}$, $B_{(V)}$, $C_{(V)}$. The average values of rotational constants, A , B , and C but not average values of I_A , I_B and I_C matter in the rotational energy states of the vibrating molecule. At equilibrium, the relation

$$I_C^{(e)} = I_A^{(e)} + I_B^{(e)}$$

holds good and to a fair degree of approximation, and

$$I_C^{(0)} = I_A^{(0)} + I_B^{(0)} \quad (2.76)$$

also holds good.

But this relation does not, in general, hold good for effective moments of inertia because in this case

$$\frac{h}{8^2 \pi A C} = \frac{1}{(1/I_A)_{\text{average}}}, \quad \frac{h}{8\pi^2 B C} = \frac{1}{(1/I_B)_{\text{average}}} \quad \text{and} \quad \frac{h}{8\pi^2 C C} = \frac{1}{(1/I_C)_{\text{average}}}$$

$$\text{since } I_{\text{average}} \neq \frac{1}{(1/I)_{\text{average}}} \quad (2.77)$$

Consequently, the following relation results in

$$\Delta = I_C^{(V)} - I_A^{(V)} - I_B^{(V)} \quad (2.78)$$

where Δ is termed as moments-of-inertia defect. This defect is prevalent in nonlinear triatomic molecules such as H_2S , H_2O , etc. This defect was first of all observed in H_2O and exists even for the lowest vibrational state. The moments-of-inertia defect enhances as V increases, e.g. in case of cyanogen isocyanate, the values of I_A , I_B , and I_C are 6.7966633, 187.24865 and 194.54080 $\text{amu } \text{\AA}^2$ respectively in the ground state, while they are 6.1053922, 186.88268 and 194.39776 $\text{amu } \text{\AA}^2$ for the first excited state. The inertial defects in the ground and first excited vibrational states are 0.49548 and 1.40969 $\text{amu } \text{\AA}^2$ respectively.

For nearly symmetrical top molecules, the B value obtained from ($\parallel$) bands is $\bar{B} = \frac{1}{2}(B + C)$. For plane molecules such as N_3H , C_2H_4 , the relation $I_C = I_A + I_B$ holds good for the equilibrium moments of inertia and also for ground-state moments of inertia under very good approximations. Thus if A is known, B and C can be determined separately from $\bar{B}$. The following relations are easily found.

$$B = -(A - \bar{B}) + \sqrt{A^2 + \bar{B}^2} \quad (2.79)$$

$$C = (A + \bar{B}) - \sqrt{A^2 + \bar{B}^2} \quad (2.80)$$

For nonplanar molecules, B and C cannot be obtained from $\bar{B}$.

2.7.2 Rotational Spectra of Linear Polyatomic Molecules

The expression for the rotational energy and hence the spectrum of linear polyatomics is similar to diatomic molecules. Further, the ground states of all linear polyatomic molecules are Σ states. For $\Lambda \neq 0$, the rotational energy of these types of molecules is expressed by Eqs (2.68) (i) and (ii). Further, if the linear polyatomic molecules have a nuclei with quadrupole moment, i.e. HCN, the rotational levels will split up into sublevels as a result of interaction between rotational motion and nuclear spin of the quadrupole nuclei of the molecule. The perturbation of energy levels results in the splitting of rotational lines in the spectrum. The energy of a perturbed level is given by

$$E_{J, F_J} = BJ(J+1) + eQq \left[\frac{\frac{3}{4}C(C+1) - I(I+1)J(J+1)}{2I(2I+1)2J(2J+1)} \right] \quad (2.81)$$

This equation is valid for $J \geq I$ and I and $J \neq 0$. Here, $C = F_J(F_J+1) - I(I+1) - J(J+1)$ and $F_J = J+I, J+I-1, 0, \dots, |J-I|$.

The resultant angular momentum, $\frac{h}{2\pi} \sqrt{F_J(F_J+1)}$ is quantised in gas phase only while in solids the nuclear spin angular momentum is quantised with respect to the electric field. The splitting of energy levels is governed by the $(2I+1)$ rule if $J > I$ and $(2J+1)$ if $I > J$. Thus, except for $J=0$, higher levels will split up into three components as shown in Fig. 2.17.

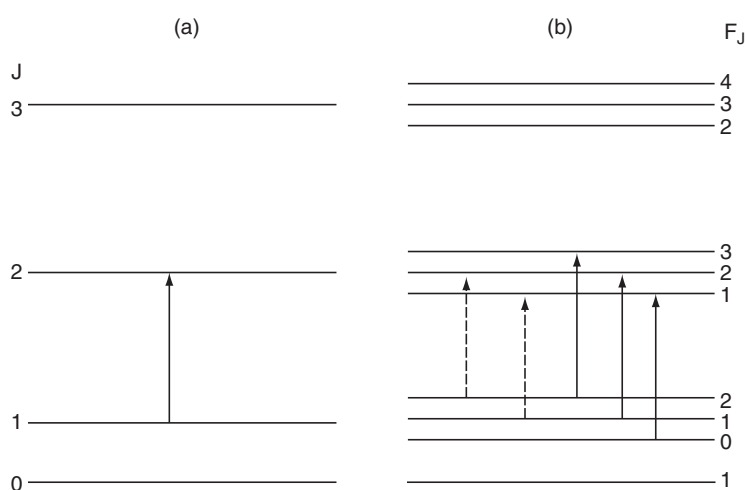


Fig. 2.17 Splitting of allowed rotational energy levels by nuclear quadrupole coupling field: (a) the energy levels are without quadrupole field, and (b) the energy levels with quadrupole field, $I=1$. The dark arrows are for $\Delta F_J = +1$ while the broken arrows are for $\Delta F_J = 0$.

In other words, we can say that for $J \neq 0$, the splitting of energy levels is independent of the rotational motion of the molecule, i.e. J . The transition between the energy levels occurs according to the selection rule

$$\Delta J = \pm 1, \Delta F_J = 0, \pm 1 \quad (2.82)$$

From Eq. (2.81), it is evident that we can determine the nuclear quadrupole coupling constant eQq from microwave spectroscopy.

Let us now work out the quadrupole splitting for the $J=1 \rightarrow 2$ transition. The allowed transitions between the sublevels according to rule $\Delta J = \pm 1$ and $\Delta F_J = 0, \pm 1$ are also presented in Fig. 2.17. Applying Eq. (2.81) for two sets of quantum numbers say (J, F_J) , and $(J+1, F_{J'})$, we get

$$\bar{\nu}_{\text{rot}} = \frac{\Delta E_{\text{rot}}}{hc} = \frac{E_{J+1, F_{J''}} - E_{J, F_{J'}}}{hc} = 4B + eqQ(X_{J+1, F_{J''}} - X_{J, F_{J'}}) \quad (2.83)$$

Here X is the coefficient of Q of Eq. (2.81).

The coefficients of eqQ for $J = 1 \rightarrow 2$ transition as determined from Eq. (2.83) are recorded in the tabular form as follows:

State	Coefficients of eqQ
$J = 1, I = 1$	$F = 2$ +1/72
	$F = 1$ -5/72
	$F = 0$ +5/36
$J = 2, I = 1$	$F = 3$ +1/40
	$F = 2$ -7/80
	$F = 1$ +7/80

From Eq. (2.83), we write, for $J = 1 \rightarrow 2, I = 1$

$$\left. \begin{aligned} \bar{\nu}_{\text{rot}}(F = 2 \rightarrow 2) &= 4B - 0.101 eqQ \\ \bar{\nu}_{\text{rot}}(F = 1 \rightarrow 1) &= 4B + 0.156 eqQ \\ \bar{\nu}_{\text{rot}}(F = 2 \rightarrow 3) &= 4B + 0.011 eqQ \\ \bar{\nu}_{\text{rot}}(F = 1 \rightarrow 2) &= 4B - 0.018 eqQ \\ \bar{\nu}_{\text{rot}}(F = 0 \rightarrow 1) &= 4B - 0.150 eqQ \end{aligned} \right\} \quad (2.84)$$

Thus, from Eq. (2.84), magnitude as well as the sign of eqQ can be determined.

Problem 2.15: (a) The moment of inertia of CO_2 as determined from its rotational Raman spectrum is 43.217 au. Determine the bond length of CO_2 .

(b) The average value of separation between the adjacent rotational lines as deduced from the ultraviolet emission spectrum of ionised carbon dioxide CO_2^+ in the ground state is 0.7612 cm^{-1} . Determine the bond distance of (CO_2^+) if the ground state is 0.7612 cm^{-1} . Determine the bond distance of CO_2^+ in the ground state.

Solution (a) The geometrical configuration of CO_2 is $\text{O} = \text{C} = \text{O}$. From Eq. (2.3), we write

$$I = \sum_{i=1}^2 m_i r_i^2 = m_{\text{O}} r_{\text{CO}}^2 + m_{\text{O}} r_{\text{CO}}^2 = 2m_{\text{O}} r_{\text{CO}}^2 = 2 \times 16 r_{\text{CO}}^2 = 32 r_{\text{CO}}^2$$

Since $I = 43.217 \text{ au}$

$$r_{\text{CO}} = \sqrt{\frac{43.217}{32}} = 1.1621 \text{ \AA}$$

(b) Since $2B_0 = 0.7612 \text{ cm}^{-1}$. Therefore, $B_0 = 0.3806 \text{ cm}^{-1}$. With the aid of Eq. (2.34), we obtain

$$I = \frac{16.8575}{0.3806} = 44.292 \text{ au}$$

From Eq. (2.9), we get

$$r = \sqrt{\frac{44.292}{32}} = 1.1765 \text{ \AA}$$

Problem 2.16: Determine the moment of inertia of $^{13}\text{CS}_2$ if the bond length of $^{12}\text{CS}_2$ is $1.2151 \text{ \AA}$.

Solution We know that isotopic substitution does not affect the bond length of molecule. The geometrical configuration of $^{13}\text{CS}_2$ is



Given $r_{cs} = 1.2151 \text{ \AA}$, from Eq. (2.3), we obtain

$$I = \sum_{i=1}^2 m_i r_i^2 = m_s r_{cs}^2 + m_s r_{cs}^2 = 2 \times 32 \times (1.2151)^2 = 94.49 \text{ au}$$

The moments of inertia of $^{12}\text{CS}_2$ and $^{13}\text{CS}_2$ are the same since in this case isotopic substitution does not alter the centre of mass of the molecule.

2.7.3 Structural Parameters of Linear Triatomics of the Type XYZ

As we already know that the rotational constant varies inversely with moment of inertia, consequently the spacing between adjacent lines in the rotational spectra will decrease on isotopic substitution. Isotopic substitution also does not affect the bond lengths of molecules. Therefore, in order to determine the bond lengths of XYZ type molecules, the moments of inertia of some isotopes of XYZ should also be known, e.g. if we want to determine the bond distances of HCN, the moments of inertia of its isotopes, viz. DCN or HCN¹⁵, should also be known. This method is illustrated by taking the example of OCS in the next problem.

Problem 2.17: (a) The microwave absorption spectrum of OCS shows the following absorption lines:

Line No.	1	2	3	4
$\bar{\nu}_{rot} \text{ cm}^{-1}$	0.81143	1.21714	1.26686	2.02886

Determine the bond lengths of OCS if the moment of inertia of ^{18}OCS as determined from its microwave absorption spectrum is 88.659 au.

(b) Determine the bond lengths of C_2H_2 if the rotational constants for C_2H_2 and C_2HD as determined from the rotational Raman spectra are 1.1838 and 0.9967 cm^{-1} respectively.

Solution (a) Since OCS is a linear molecule, there are only two rotational degrees of freedom. Hence $I_x = I_y$ and $I_z = 0$, The average of difference between the wave numbers of adjacent lines in the spectrum is

$$2B = 0.40581 \text{ cm}^{-1}, \text{ Hence } B = 0.2029 \text{ cm}^{-1}$$

Using Eq. (2.34) we get

$$I(\text{OCS}) = \frac{16.8575}{0.2029} = 83.121 \text{ au}$$

$$I^*(^{18}\text{OCS}) = 88.65 \text{ au.}$$

The bond lengths of OCS can now be determined with the aid of Eq. (2.14). For OCS and ^{18}OCS , we may write

$$I(\text{OCS}) = m_o r_{co}^2 + m_s r_{cs}^2 - \frac{(m_o r_{co} - m_s r_{cs})^2}{M_m} \quad (2.85)$$

$$I^*(\text{OCS}) = m_o^* r_{co}^2 + m_s r_{cs}^2 - \frac{(m_o^* r_{co} - m_s r_{cs})^2}{M_m + 2} \quad (2.86)$$

Subtracting Eq. (2.85) from Eq. (2.86), we obtain

$$\Delta I = I^* - I = r_{co}^2 (m_o^* - m_o) + \frac{(m_o r_{co} + m_s r_{cs})^2}{M_m} - \frac{(m_o^* r_{co} + m_s r_{cs})^2}{M_m + 2} \quad (2.87)$$

Combine Eqs (2.87) and (2.85) in order to eliminate the term $r_{co} r_{cs}$. The resultant equation will then be in terms of r_{co}^2 and r_{cs}^2 . Substitute the value of r_{cs}^2 in terms of r_{co}^2 into Eq. (2.85) to get r_{co} . Once r_{co} is obtained, r_{cs} can easily be determined. $r_{co} = 1.163 \text{ \AA}$ and $r_{cs} = 1.558 \text{ \AA}$.

(b) From Eq. (2.34), we get

$$I = \frac{16.8575}{1.1838} = 14.240 \text{ au}$$

$$I^* = \frac{16.8575}{0.9967} = 16.913 \text{ au}$$

$$M_m^* = 2 \times 12 + 2 + 1 = 27 \text{ amu}$$

$$M_m = 24 + 1 + 1 = 26 \text{ amu}$$

With the aid of Eq. (2.29), we obtain,

$$x = \frac{1}{2}r_{\text{CC}} + r_{\text{CH}} = \sqrt{\frac{27(16.913 - 14.240)}{26(2-1)}} = 1.666 \text{ \AA}$$

$$y = \frac{1}{2}r_{\text{CC}} = \sqrt{\frac{14.240 - 2 \times 1 \times (0.601)^2}{2 \times 12}} = 0.601 \text{ \AA}$$

Therefore, $r_{\text{CC}} = 1.202 \text{ \AA}$ and $r_{\text{CH}} = 1.065 \text{ \AA}$.

Problem 2.18: The spectroscopically measured values of moments of inertia of the molecules HCN and DCN are 11.403 and 13.947 au respectively. Determine the bond lengths of HCN.

Solution We know that bond length is independent of isotopic substitution. Thus proceeding as in Problem 2.17 (a), it is found that $r_{\text{CH}} = 1.058 \text{ \AA}$ and $r_{\text{CN}} = 1.157 \text{ \AA}$.

Problem 2.19: The wave numbers in the far infrared rotational spectrum of HCN are given below:

J	0	1	2	3	20	22
$\nu_{\text{rot}}, \text{cm}^{-1}$	2.96	5.92	8.87	11.83	61.98	67.85

Determine the values of B and D by the method of least-squares fit.

Solution B and D can be determined with the aid of Eq. (2.67), i.e.

$$\frac{\bar{\nu}_{\text{rot}}}{(J' + 1)} = 2B - 4D(J' + 1)^2, \text{ where } J' = 0, 1, 2, 3, \dots$$

J	$J' + 1$	$(J' + 1)^2$	$\frac{\bar{\nu}_{\text{rot}}}{(J' + 1)} \text{ cm}^{-1}$	$(J' + 1)^4$	$(J' + 1)^2 \times \frac{\bar{\nu}_{\text{rot}}}{(J' + 1)}, \text{ cm}^{-1}$
0	1	1	2.960	1	2.960
1	2	4	2.960	16	11.840
2	3	9	2.956	81	26.604
3	4	16	2.957	256	47.312
20	21	441	2.951	194481	1301.391
22	23	529	2.950	279841	1560.550
	$\sum_{i=1}^6$	1000	17.734	474676	2950.657

The data required for the method of least-squares fit is recorded in the tabular form as above:
Using normal Eq. (1.58) we get

$$12B_0 - 4000 D_0 = 17.734$$

$$2000B_0 - 1898704 D_0 = 2950.657$$

Solving for B_0 and D_0 , we obtain

$$B_0 = 1.479 \text{ cm}^{-1} \text{ and } D_0 = 4.06 \times 10^{-6} \text{ cm}^{-1}$$

2.7.4 Rotational Spectra of Spherical-Top Molecules

The rotational energy levels of nonlinear polyatomic molecules in terms of angular momenta and moments of inertia are expressed as

$$E_J = \frac{P_x^2}{2I_x} + \frac{P_y^2}{2I_y} + \frac{P_z^2}{2I_z} \quad (2.88)$$

where P_x , P_y , and P_z are the angular momenta about the three principal axes. According to quantum mechanics the angular momentum, is quantised, i.e.

$$P = \frac{h}{2\pi} P_J = \frac{h}{2\pi} \sqrt{J(J+1)} \quad (2.89)$$

where P_J is a quantum number and can take up values $-J$ to $+J$ including 0. Thus, P_J can have $(2J+1)$ values. In case of spherical tops, $I_x = I_y = I_z$, consequently Eq. (2.88) reduces to,

$$E_J = \frac{1}{2I} (P_x^2 + P_y^2 + P_z^2) = \frac{P^2}{2I} \quad (2.90)$$

where $P^2 = (P_x^2 + P_y^2 + P_z^2)$.

Combining Eqs (2.89) and (2.90), we obtain

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) = BhcJ(J+1) \quad (2.91)$$

Thus, the energy of the rotational level of rigid spherical tops is the same as for diatomics. For a nonrigid spherical top, we have to add the term $-BhcDJ^2(J+1)^2$ to Eq. (2.91). Consequently, just like diatomics, the rotational spectrum of polyatomic spherical tops should consist of equally spaced lines with spacing between the adjacent lines in the spectrum of the order of $2B$. Further, since these types of molecules have three degrees of freedom, a third quantum number, K , characterising the angular momentum about one of the symmetry axes rotating together with the molecule needs to be introduced such that

$$P_K = \left[\frac{h}{2\pi} \right] K \quad (2.92)$$

Here $K = J, J-1, J-2, \dots, 0, \dots, -J$ and can have $(2J+1)$ values. The degeneracy of the energy level in such molecules is then given by

$$g_J = (2J+1) \cdot (2J+1) = (2J+1)^2 \quad (2.93)$$

The population of molecules among the energy states is then given by

$$N_J = (2J+1)^2 N_0 e^{\frac{-h^2 J(J+1)}{8\pi^2 I} / \pi T} \quad (2.94)$$

$$\frac{N_J}{N_A} = \frac{(2J+1)}{\sigma Z_{\text{rot}}} e^{\frac{-h^2 J(J+1)}{8\pi^2 I} / \pi T}$$

It is to be remembered that the spherical top molecules are microwave inactive since their dipole moment is zero, i.e. $M = 0$

2.7.5 Rotational Spectra of Symmetric-Top Molecules

We know that symmetric top molecules are of two types, i.e. prolate symmetric top and oblate symmetric-top. In case of prolate symmetric-top molecules, $I_x < I_y = I_z$. Therefore, for such molecules, Eq. (2.88) transforms to

$$\begin{aligned}
 E_J &= \frac{P_x^2}{2I_x} + \frac{1}{2I_y} (P_y^2 + P_z^2) \\
 &= \frac{P_x^2}{2} \left(\frac{1}{I_x} - \frac{1}{I_y} \right) + \frac{1}{2I_y} (P_x^2 + P_y^2 + P_z^2) \\
 &= \frac{P_x^2}{2} \left(\frac{1}{I_x} - \frac{1}{I_y} \right) + \frac{P^2}{2I_y}
 \end{aligned} \quad (2.95)$$

Just like spherical top molecules, symmetric tops have also three degrees of freedom. Consequently, in addition to the quantum number J , the quantum number K , characterising the motion of the molecule about the symmetry axis passing through the centre of mass of the molecule is introduced such that

$$P_K = \left(\frac{h}{2\pi} \right) K \quad (\text{Eq. 2.92})$$

Relation between J and K in case of symmetric tops is presented in Fig. 2.18. From Eqs (2.95), (2.92) and (2.89), we obtain the energy of the rotational levels of the prolate symmetric-top molecules, i.e.

$$E_{J,K} = \left(\frac{h^2}{8\pi^2 I_x} - \frac{h^2}{8\pi^2 I_y} \right) K^2 + \frac{h^2}{8\pi^2 I_y} J(J+1) \quad (2.96)$$

$$E_{J,K} = (A - B)hcK^2 + BhcJ(J+1) \quad (2.97)$$

$$\text{where } A = \frac{h}{8\pi^2 I_x c}; B = \frac{h}{8\pi^2 I_y c} \quad (2.98)$$

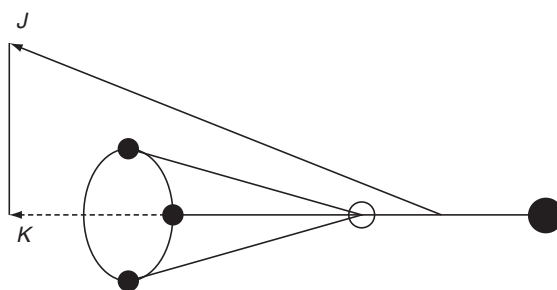


Fig. 2.18 Relation between J and K for a symmetric-top molecule.

Proceeding as above, we can work out the energy of the rotational levels of oblate symmetric top molecules. The quantized energy states for such molecules are given by

$$E_{J,K} = BhcJ(J+1) + (C - B)K^2 \quad (2.99)$$

where

$$C = \frac{h}{8\pi^2 I_z c} \quad (2.100)$$

The effect of axial rotation on the moment of inertia of symmetric top molecules XY_3Z is presented in Fig. 2.19.

Since in Eqs. (2.97) and (2.99), the K^2 term is involved, the clockwise and anticlockwise rotations about the symmetry axis do not affect the results. The degeneracy of each level will be equal to $2(2J+1)$ except for the zeroth level where $K=0$ and the degeneracy is $(2J+1)$ folds. Since K^2 terms are involved, for $K>0$, each line will split up into $(J+1)$ components, i.e. same energy corresponds to their levels $+K$ and $-K$ and will be doubly degenerate.

2.7.6 Transition Between Two Adjacent Energy States (Prolate/Oblate Tops as Rigid Rotators)

Let J' , K' and J'' , K'' be the quantum numbers for the lower and upper levels respectively. From Eq (2.97), we may write for the two levels,

$$E_{J',K'} = BhcJ' (J' + 1) + hc(A - B) K'^2 \quad (2.101)$$

$$E_{J'',K''} = BhcJ'' (J'' + 1) + hc(A - B) K''^2 \quad (2.102)$$

Combining Eqs (2.101) and (2.102), we obtain

$$\bar{\nu}_{\text{rot}} = \frac{\Delta E_{\text{rot}}}{hc} = \frac{E_{J'',K''} - E_{J',K'}}{hc} \quad (2.103)$$

$$= B(J'' - J')(J'' + J' + 1) + (A - B)(K'' - K')(K'' + K')$$

Applying selection rules, i.e. $\Delta J = \pm 1$, $\Delta K = 0$, we obtain

$$\bar{\nu}_{\text{rot}} = 2B(J' + 1) \quad (2.104)$$

where $J' = 0, 1, 2, 3$.

The selection rule of ΔK arises because there is no dipole moment about the symmetry axis (rotation about symmetry axis is denoted by K), hence radiation cannot interact with the rotations about this axis. Consequently, it is expressed as $\Delta K = 0$.

From Eq. (2.104), it is clear that the rotational spectrum of prolate or oblate top molecules is similar to linear, di- and polyatomic molecules and is independent of K , i.e. the axial rotation does not affect the dipole moment normal to the axis which is always zero.

2.7.7 Nonrigid Rotator Model of Prolate/Oblate Symmetric-Top Molecules

Let us now work out the microwave spectrum of symmetric top molecules taking into consideration the effect of centrifugal force. The energy of the rotational levels as deduced quantum mechanically is expressed as

$$E_{J,K} = Bhc J(J+1) + (A-B)hc K^2 - D_J hc J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4 \quad (2.105)$$

where D_J , D_{JK} and D_K are the centrifugal distortion constants arising due to different types of motions.

Now for two energy states, we write

$$E_{J',K'} = Bhc J'(J' + 1) + (A - B)hc K'^2 - D_J hc J'^2(J' + 1)^2 - D_{JK} J'(J' + 1)K'^2 \quad (2.106)$$

$$E_{J'',K''} = Bhc J''(J'' + 1) + (A - B)hc K''^2 - D_J hc J''^2(J'' + 1)^2 - D_{JK} J''(J'' + 1)K''^2 \quad (2.107)$$

Combining Eqs. (2.106) and (2.107), we obtain

$$\bar{\nu}_{\text{rot}} = \frac{\Delta E_{\text{rot}}}{hc} = \frac{E_{J'',K''} - E_{J',K'}}{hc}$$

$$= B(J'' - J')(J'' + J' + 1) + (A - B)(K''^2 - K'^2) - D_J [J''(J'' + 1) - J'(J' + 1)][J''(J'' + 1) + J'(J' + 1)]$$

$$- D_{JK} [(J''K'' - J'K')(J''K'' + J'K') + (J''K''^2 - J'K'^2)] \quad (2.108)$$

$$= (J'' - J')(J'' + J' + 1)[B - D_J]\{J''(J'' + 1) + J'(J' + 1)\}$$

$$+ (A - B)(K''^2 - K'^2) - D_{JK} [(J''K'' - J'K')(J''K'' + J'K') + (J''K''^2 - J'K'^2)]$$

Applying selection rules, i.e. $\Delta J = J'' - J' = +1$, $\Delta K = K'' - K' = 0$, we get

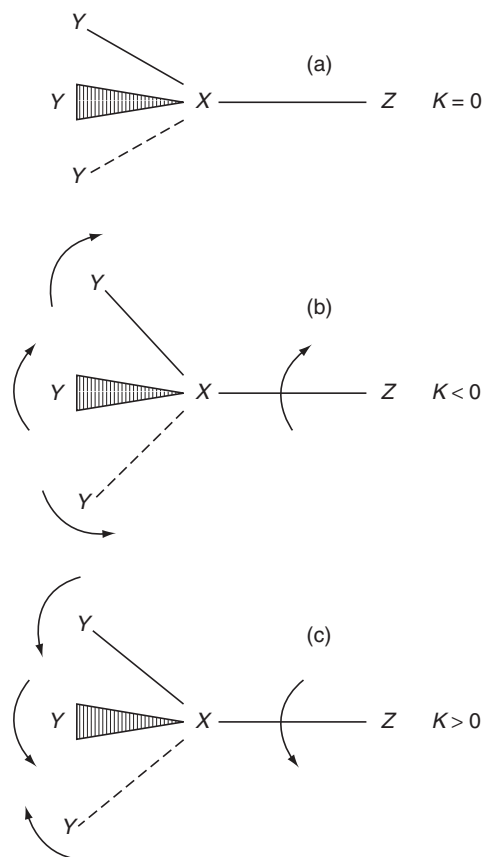


Fig. 2.19 The effect of axial rotation on the moment of inertia of a symmetric top molecule: (a) there is no axial rotation ($K=0$), (b) there is clockwise ($K>0$), and (c) anticlockwise axial rotation ($K>0$).

$$\bar{\nu}_{\text{rot}} = 2BJ'' - 4D_J J'' - 2D_{JK} J'' K'' \text{ cm}^{-1} \quad (2.109)$$

or

$$\bar{\nu}_{\text{rot}} = 2B(J'+1) - 4D_J (J'+1)^3 - 2D_{JK} (J'+1)K'^2, \text{ cm}^{-1} \quad (2.110)$$

Equations (2.109) or (2.110) reveal that rotational spectrum now depends upon K although the axial rotation does not change the dipole moment perpendicular to the axis. The axial rotation actually increases the YXY angle as well as the $X-Y$ bond length as shown in Figs 2.19 (b) and (c). Consequently, the moment of inertia changes and hence spectrum becomes dependent on K . The allowed energy levels of prolate symmetric top molecules have been shown in Fig. 2.20. Some of the lines in the rotational spectrum as worked out from Eq. (2.110) are recorded in the tabular form as follows and are sketched in Fig. 2.21.

State	No. of Lines ($J'+1$)	Wave Number, $\bar{\nu}_{JK}, \text{cm}^{-1}$
$J' = 0, K' = 0$	1	$\bar{\nu}_{0,0} = 2B - 4D_J$
$J' = 1, K' = 0$	2	$\bar{\nu}_{1,0} = 4B - 32D_J$
$K' = \pm 1$		$\bar{\nu}_{1,\pm 1} = 4B - 32D_J - 4D_{JK}$
$J' = 2, K' = 0$	3	$\bar{\nu}_{2,0} = 6B - 108D_J$
$K' = \pm 1$		$\bar{\nu}_{2,\pm 1} = 6B - 108D_J - 6D_{JK}$
$K' = \pm 2$		$\bar{\nu}_{2,\pm 2} = 6B - 108D_J - 24D_{JK}$
$J' = 3, K' = 0$	4	$\bar{\nu}_{3,0} = 8B - 256D_J$
$K' = \pm 1$		$\bar{\nu}_{3,\pm 1} = 8B - 256D_J - 8D_{JK}$
$K' = \pm 2$		$\bar{\nu}_{3,\pm 2} = 8B - 256D_J - 32D_{JK}$
$K' = \pm 3$		$\bar{\nu}_{3,\pm 3} = 8B - 256D_J - 72D_{JK}$

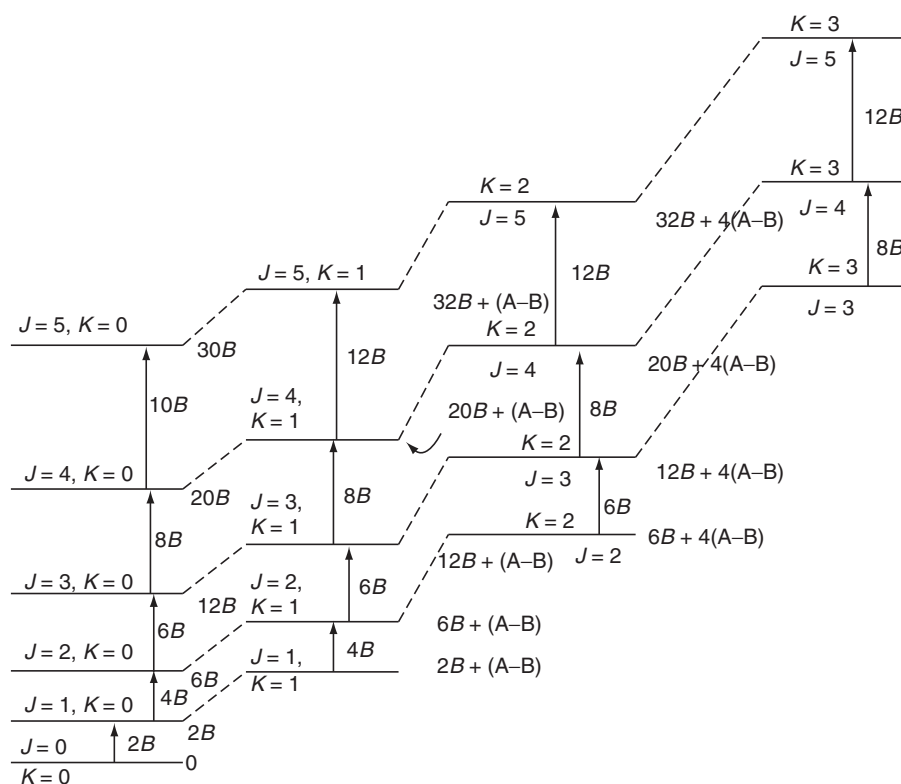


Fig. 2.20 Rotational energy levels of prolate symmetric-top molecules.

It is to be noted that Eq. (2.104) permits determination of only one rotational constant. Hence the complete geometry of a symmetric-top molecule cannot be determined by using this single value of B obtained from the rotational spectra. In such a case, isotopic substitution is used in structure determination. The centrifugal distortion leads to a slight separation of the components of J .

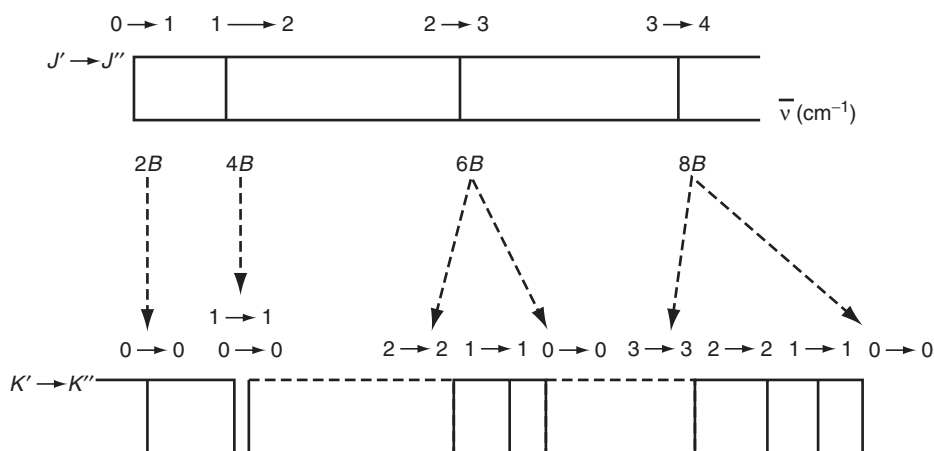


Fig. 2.21 Splitting of rotational lines for symmetric-top molecules of the type CH_3F .

Problem 2.20: The $\bar{\nu}_{10}$, $\bar{\nu}_{20}$, and $\bar{\nu}_{30}$ lines in the microwave spectrum of CH_3F have been observed at 3.40475, 5.10701 and 6.80912 cm^{-1} respectively. Determine the moment of inertia of CH_3F .

Solution The average difference of wave numbers between the adjacent lines is

$$2B = 0.702185 \text{ cm}^{-1}; \therefore B = 0.351092 \text{ cm}^{-1}$$

From Eq. (2.34), we get

$$I = \frac{16.8575}{0.351092} = 48.01 \text{ au}$$

Problem 2.21: The wave numbers (cm^{-1}) in the microwave spectrum of CH_3F are given below:

$\bar{\nu}_{10}$	$\bar{\nu}_{11}$	$\bar{\nu}_{30}$
3.40475	3.40470	6.80912

Determine the values of B, DJ and DJK.

Solution From Eq. (2.111), we write

$$3.40475 = 4B - 32D_J$$

$$3.40470 = 4B - 32D_J - 4D_{JK}$$

$$6.80912 = 8B - 256D_J$$

Solving for B, D_J and D_{JK} , we get

$$B = 0.851 \text{ cm}^{-1}$$

$$D_J = 1.979 \times 10^{-6}$$

$$D_{JK} = 1.25 \times 10^{-5} \text{ cm}^{-1}$$

2.7.8 Rotational Spectra of Asymmetric-top Molecules

The three moments of inertia are different in such molecules. Consequently, the rotational spectrum of asymmetric tops is complicated and hence difficult to analyse. Just like linear and symmetric-top molecules, there is no general expression for the energy of the levels. The energy expressions are very complicated and are manipulated from the energy expressions of oblate and prolate symmetric top molecules. The theoretical spectrum is then computed from the approximated expression for the energy levels of asymmetric tops from the assumed values of structural

parameters. The structural parameters are varied by the iterative method till the theoretical spectrum matches with the observed spectrum of the system under investigation.

Problem 2.22: Determine the equilibrium bond distances and bond angle of water if $I_{xx} = 1.1443$, $I_{yy} = 0.6083$, $I_{zz} = 1.7526$ au.

Solution The geometrical configuration of the water molecule is shown in Fig. 2.22.

Knowing the Cartesian coordinates $(-x_1, y_1)$, $(-x_2, -y_2)$, we can determine the bond distances and bond angle from the expressions

$$r_{OH} = \sqrt{x_1^2 + y_1^2} \quad (2.112)$$

and
$$\tan \theta = \frac{y_1}{x_1} \quad (2.113)$$

Using Eq. (2.15), we proceed as under.

$$I_{xx} = \sum_{i=1}^3 m_i (y_i^2 + z_i^2) - \frac{1}{M_m} \left(\sum_{i=1}^3 m_i y_i \right)^2 - \frac{1}{M_m} \left(\sum_{i=1}^3 m_i z_i \right)^2$$

Here, z_i and the second term are zero.

Therefore,
$$I_{xx} = 2my^2$$

or
$$y^2 = \frac{I_{xx}}{2m} = \frac{1.1443}{2} = 0.5721$$

Consequently, $y = 0.7564$.

Further,
$$I_{zz} = \sum m_i (x_i^2 + y_i^2) - \frac{1}{M_m} \left(\sum_{i=1}^3 m_i x_i \right)^2 - \frac{1}{M_m} \left(\sum_{i=1}^3 m_i y_i \right)^2$$

Here, the third term is zero.

Thus,
$$I_{zz} = 2m(x^2 + y^2) - \frac{4m^2 x^2}{M_m} = x^2 \left(2m - \frac{4m^2}{M_m} \right) + 2my^2$$

Rearranging

$$x^2 = \frac{(I_{zz} - 2my^2)}{\left(2m - \frac{4m^2}{M_m} \right)} = \frac{(1.7526 - 2 \times 0.5721)}{\left(2 - \frac{4}{18} \right)} = \frac{9}{16} (1.7526 - 2 \times 0.5721)$$

$$= 0.3422$$

$$\therefore x = \sqrt{0.3422} = 0.5850$$

From Eqs. (2.112) and (2.113), we get

$$r_{OH} = \sqrt{0.3422 + 0.5721} = 0.956 \text{ \AA}$$

$$\tan \theta = \frac{0.7564}{0.5850} = 1.2929$$

$$\text{Hence } \theta = 52.28^\circ$$

Thus, the bond angle of water is 104.56° .

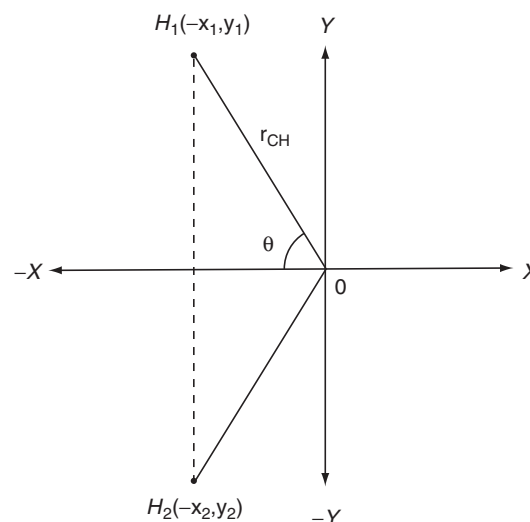


Fig. 2.22 Geometrical configuration of the water molecule.

2.8 THERMAL DISTRIBUTION OF POPULATION AMONG THE ROTATIONAL LEVELS

The Boltzmann distribution law for the population of every possible rotational energy level may be written as

$$N_J = N_0 e^{-E_J / \kappa T} \quad (2.114)$$

Some of the energy levels are degenerate, i.e., several levels have the same energy. Degeneracy can be lifted by the Stark effect. Consequently,

$$N_J = \frac{N_0}{g_0} g_J e^{-E_J / \kappa T} \quad (2.115)$$

where g_0 is the degree of degeneracy of the zeroth energy level and g_J of the J th energy level.

If degeneracy of all the energy levels for one mole of substance is taken into account then

$$N_A = \frac{N_0}{g_0} \sum_J g_J e^{-E_J / \kappa T} \quad (2.116)$$

where $\sum_J N = N_A$, i.e. the sum of molecules occupying all energy levels for one mole of the substance equals the Avogadro's constant, N_A .

$$N_A = \frac{N_0}{g_0} Z_{\text{rot}} \quad (2.117)$$

$$Z_{\text{rot}} = \frac{\sum_J g_J e^{-E_J / \kappa T}}{\sigma} \quad (2.118)$$

Here, σ is the symmetry number.

The physical significance and determination of Z_{rot} , the rotational partition function will be discussed later on in this chapter.

From Eqs (2.115) and (2.116),

$$\frac{N_J}{N_A} = \frac{1}{\sigma} \frac{g_J e^{-E_J / \kappa T}}{Z_{\text{rot}}} \quad (2.119)$$

For linear molecules $g_J = 2J + 1$, and the energy of the rotational levels of linear molecules is expressed by Eq. (2.33), i.e.

$$E_J = B h c J(J + 1)$$

Combination of Eqs. (2.33) and (2.119) yields

$$\frac{N_J}{N_A} = \frac{1}{\sigma} \frac{(2J + 1)}{Z_{\text{rot}}} e^{-B h c J(J + 1) / \kappa T} \quad (2.120)$$

The effect of correction due to centrifugal distortion on the statistical mechanics of the rotator is negligibly small and hence not taken into account.

Equation (2.120) shows that the population of different levels decreases exponentially as J grows. Further, more degeneracy of a given state increases the population of that particular state.

Differentiating Eq. (2.120) with respect to J at constant temperature and applying the condition of maxima, i.e.

$$\left(\frac{dN_J}{dJ} \right)_T = 0$$

we obtain
$$J_{\text{max}} = \left(\frac{\kappa T}{2 B h c} \right)^{\frac{1}{2}} - \frac{1}{2} \quad (2.121)$$

Thus, the value of J at which population is maximum increases (i) with temperature, and (ii) as the molecule gets heavier. J_{max} can also be determined graphically. At a particular temperature, for different values of J , N_J / N_A is calculated

and then from the plot of J against N_J/N_A , $J_{\max}$ can be determined. The behaviour of J with N_J/N_A is presented in Fig. 2.23.

The maximum in the curve arises due to the degeneracy factor, i.e. $(2J + 1)$ otherwise the shape of the curve is governed solely by the exponential term. Figure 2.23 indicates that the population and hence intensities of rotational lines at given temperature for low, and high values of J will be low and is maximum near the value of $J = J_{\max}$. To summarise, we conclude that the intensities of rotational lines are not only proportional to the square of the transition dipole moment M_r , but are also dependent on the degeneracy of the state, moment of inertia of the molecule and the temperature. The rotational lines in the spectrum of ortho-hydrogen are three times intense than lines of para-hydrogen. This is because of the difference in statistical weights of the symmetric and antisymmetric rotational states. The ratio of line intensities in some of the systems exhibiting ortho-para modifications are given in the tabular form as under.

From the comparison of the absorption intensities of two lines corresponding to the same transition of different isotopic species of the same molecule, we can determine the natural abundance of isotopes.

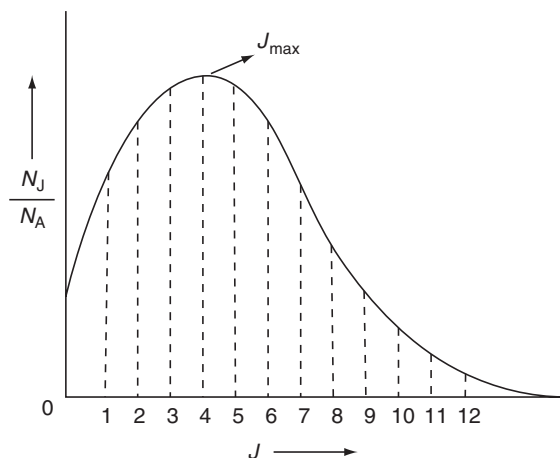


Fig. 2.23 Hypothetical sketch showing the thermal distribution of the rotational levels at TK . The curve represents the function $N_J/N_A = (2J + 1) e^{-BhcJ(J+1)/kT}$ as a function of rotational quantum number J . The broken line ordinates give the relative populations of the corresponding rotational levels.

Molecule	Intensity Ratio
	Q:P
H ₂	3:1
D ₂	2:1
⁷ Li ₂	1.67:1
³¹ P ₂	3:1
³⁵ Cl ₂	1:4:1
¹²⁷ I ₂	1.4:1
¹⁴ N ₂	2:1
He ₂ , ¹² C ₂ , ¹⁶ O ₂ , ³² S ₂ , ⁸⁰ Se ₂	∞

Problem 2.23: (a) Determine which is the most intense line in the microwave spectrum of CO at (i) 27°C, and (ii) 500°C. The bond length of CO is $r_e = 1.131 \text{ Å}$. (b) Determine the fraction of CO molecules on the rotational quantum level $J = 5$ relative to zeroth vibrational level at 500 K. $Z_{\text{rot}} = 179.9$.

Solution (a) Knowing the value of moment of inertia of CO from its bond distance and atomic masses of its atoms, we can determine the value of $J_{\max}$ at different temperatures from Eq. (2.121). We know

$$\kappa = 1.38 \times 10^{-23} \text{ JK}^{-1} = \frac{1.38 \times 10^{-23} \times 10^{47}}{1.6604} \text{ amu Å}^2 \text{ s}^{-2} \text{ K}^{-1} = 8.31 \times 10^{23} \text{ amu Å}^2 \text{ s}^{-2} \text{ K}^{-1}$$

$$h = 3.9890 \times 10^{13} \text{ amu Å}^2 \text{ s}^{-1}$$

From Eqs (2.9) and (2.10), we get

$$I = \frac{12 \times 16}{12 + 16} \times (1.131)^2 = 8.7737 \text{ amu Å}^2$$

From Eq. (2.34)

$$B = \frac{16.8575}{8.7737} = 1.921 \text{ cm}^{-1}$$

Substituting the values of B , h , κ , c and T in Eq. (2.121), we obtain

$$J_{\max}(300 \text{ K}) = -\frac{1}{2} + \left[\frac{8.31 \times 10^{+23} (\text{amu } \text{\AA}^2 \text{ s}^{-2} \text{ K}^{-1}) \times 300(\text{K})}{2 \times 1.921(\text{cm}^{-1}) \times 3 \times 10^{10} (\text{cm s}^{-1}) \times 3.9890 \times 10^{13} (\text{amu } \text{\AA}^2 \text{ s}^{-1})} \right]^{\frac{1}{2}}$$

$$= (54.16)^{1/2} - 0.5 = 7$$

$$J_{\max}(773 \text{ K}) = \left[54.16 \times \frac{773}{300} \right]^{\frac{1}{2}} - 0.5 = 11$$

Thus, the rotational lines corresponding to the transition $= 6 \rightarrow 7$ at 27°C and $J = 10 \rightarrow 11$ at 500°C will be more intense as compared to the other lines in the respective spectrum.

(b) The value of $J_{\max}$ at any temperature can also be determined graphically as follows. In order to determine $J_{\max}$ by this method, the factor $e^{-Bhc/\kappa T}$ needs to be defined. Given $B = 1.9319 \text{ cm}^{-1}$

$$\frac{-Bhc}{\kappa T} = \frac{-1.9319(\text{cm}^{-1}) \times 6.626 \times 10^{-34} (\text{Js}) \times 3 \times 10^{10} (\text{cm/s})}{1.380 \times 10^{-23} (\text{JK}^{-1}) \times 300 \text{ K}}$$

$$\text{or } e^{\frac{-Bhc}{\kappa T}} = e^{-0.0092759}$$

J	$(2J+1)$	$J(J+1)$	$e^{-0.0092759J(J+1)} = \phi$	$(2J+1) \phi$
0	1	0	1	1
1	3	2	0.981	2.944
2	5	6	0.945	5.675
3	7	12	0.894	6.262
4	9	20	0.830	7.476
5	11	30	0.757	8.327
6	13	42	0.677	8.805
7	15	56	0.594	8.922
8	17	72	0.512	8.717
9	19	90	0.433	8.245
10	21	110	0.360	7.569
11	23	132	0.293	6.760
12	25	156	0.235	5.881
13	27	182	0.184	4.990
14	29	210	0.142	4.134
15	31	240	0.107	3.346
16	33	272	0.080	2.647
17	35	306	0.058	2.048
18	37	342	0.041	1.550
19	39	380	0.029	1.148
20	41	420	0.020	0.833
21	43	462	0.013	0.591
22	45	506	0.009	0.411
23	47	552	0.005	0.280
24	49	600	0.003	0.187
25	51	650	0.002	0.122

Using Eq. (2.94), the data required for the plot of N_J/N_A against J is generated and recorded as under: The curve of $N_J Z_{\text{rot}}/N_A$ as a function of J is shown in Fig. 2.24. From the graph, the value of J_{max} comes out to be 7 and is in agreement with the value of J determined from Eq. (2.121).

(b) Using Eq. (2.120) we obtain

$$\begin{aligned}\frac{N_5}{N_A} &= \frac{(2 \times 5 + 1)}{179.9} e^{-\frac{1.9218 \times 5(5+1) \times 3 \times 10^{10} \times 6.6252 \times 10^{-34}}{1.3805 \times 10^{-23} \times 500}} \\ &= \frac{11}{179.9} e^{-0.166} = 0.0518\end{aligned}$$

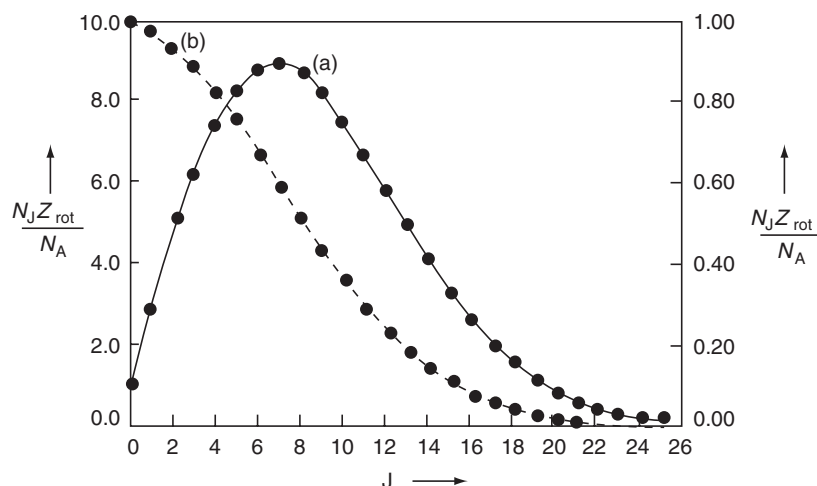


Fig. 2.24 The plot between $(N_J/N_A) \times Z_{\text{rot}}$ and rotational quantum number J , at 300 K (a) with degeneracy, and (b) without degeneracy.

Problem 2.24: Determine the natural abundance of H^{35}Cl and H^{37}Cl in HCl if the relative intensity of the two lines for the same transition in the infrared rotational spectrum of HCl is 3:1.

Solution We know that intensity is proportional to the relative abundance of isotopic species of the same molecule and for the same transition.

$$\text{Thus, natural abundance of } \text{H}^{35}\text{Cl} = \frac{I}{I + I^*} \times 100 = \frac{3}{3+1} \times 100 = 75\%$$

where I^* is the intensity due to H^{37}Cl .

Therefore, natural abundance of $\text{H}^{37}\text{Cl} = 100 - 75 = 25\%$.

Problem 2.25: Determine the relative intensity of the two rotational lines corresponding to the same transition in case of CO if the natural abundance of $^{13}\text{C}^{16}\text{O}$ in CO is 0.8%.

Solution The natural abundance of $^{13}\text{C}^{16}\text{O} = 0.8\%$.

Hence the natural abundance of $^{12}\text{C}^{16}\text{O} = 100 - 0.8 = 99.2\%$.

We know that natural abundance of $^{12}\text{C}^{16}\text{O}$

$$= \frac{I}{I + I^*} \times 100 \quad (2.122)$$

where I^* is the intensity due to $^{13}\text{C}^{16}\text{O}$.

Therefore, natural abundance of $^{13}\text{C}^{16}\text{O}$

$$= \frac{I^*}{I + I^*} \times 100 \quad (2.123)$$

Comparing Eqs (2.122) and (2.123), we get

$$\frac{I}{I^*} = \frac{99.2}{0.8} = 124:1$$

i.e. for the same transition, the rotational line of $^{12}\text{C}^{16}\text{O}$ is 124 times intense than that of $^{13}\text{C}^{16}\text{O}$.

2.9 STARK EFFECT IN RELATION TO DIPOLE MOMENT DETERMINATION FROM ROTATIONAL SPECTRUM

The splitting and shifting (with respect to unperturbed line) of spectral lines under the influence of an external electric field E is known as *Stark effect*. Thus, when a molecule is simultaneously subjected to microwave radiation and an electric field, the splitting of rotational lines occurs. The electric splitting and displacement of spectral lines is due to the interaction of dipole moment of the molecule with the external electric field. The electric field splits the levels specified by J into $(J + 1)$ levels specified by quantum number, M_J , M_J actually is the component of J in the direction of external field, i.e. electric or magnetic and determines which of the possible $(2J + 1)$ orientations, the molecule can take up. The nine possible Stark rotational orientations of molecule for $J = 4$ are shown in Fig. 2.25. M_J can take up any integral value including zero, i.e. $M_J = 0, 1, 2, 3, \dots$, i.e. $J, J - 1, \dots, -J, \dots$. The magnitude of splitting depends not only on J but also on M_J^2 . Thus depending upon $|M_J|$, some levels are moved upward and others downward by the field.

The energy of perturbed rotational levels as deduced from the solution of Schrodinger wave equation is expressed as

$$E_{J,K,M_J} = E_J + \alpha_{J,K,M_J} E + \frac{1}{2} \beta_{J,K,M_J} E^2 + \dots \quad (2.124)$$

where E_J is the energy of the rotator in the absence of field E ; α_{J,K,M_J} and β_{J,K,M_J} are the first- and second-order Stark effects, respectively. When dipole moment M has a component in the direction of J , we have the first-order Stark effect and second-order Stark effect when it is perpendicular to the direction of J as shown in Fig. 2.26.

The Stark frequency of transition is determined from the solution of the integrals,

$$\Delta E_{J'} = \int \psi_{J'} M E \cos \theta \psi_J d\tau \quad (2.125)$$

$$\Delta E_{J''} = \int \psi_{J''} M E \cos \theta \psi_{J''} d\tau \quad (2.126)$$

It is found that the Stark shift

$$\Delta \bar{\nu}_{\text{rot}} \propto (ME)^2 \quad (2.127)$$

for linear molecules

and

$$\Delta \bar{\nu}_{\text{rot}} \propto (ME) \quad (2.128)$$

for symmetric top molecules.

Thus, from the slope of the straight-line plot between $\Delta \bar{\nu}_{\text{rot}}$ and E^2/E as the case may be, the value of dipole moment M can be determined. For linear molecules, $M = \sqrt{\text{slope}}$ while for symmetric-top molecules, $M = \text{slope}$.

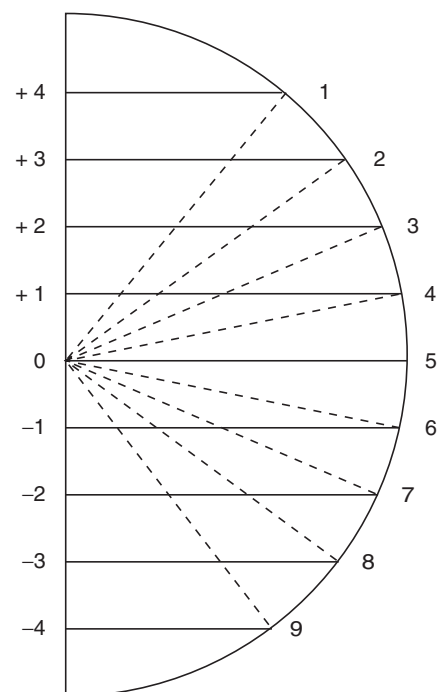


Fig. 2.25 The nine degenerate rotational orientations of a molecule with $J = 4$ downward by the field.

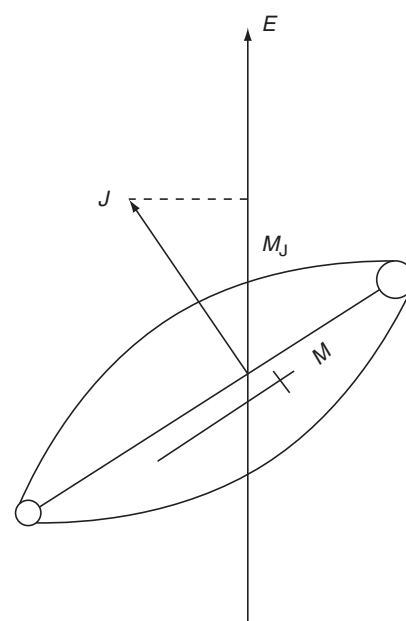


Fig. 2.26 A diatomic molecule under the influence of an external electric field.

2.9.1 Stark Transition Between Adjacent Levels in Symmetric-Top Molecules

Depending upon convenience, the first- or second-order Stark effect may be exploited to determine M of symmetric-top molecules. For symmetric-top molecules, the energy correction due to first-order Stark effect is given by,

$$\alpha_{J,K,M_J} = \frac{-M K M_J}{J(J+1)} \quad (2.129)$$

Thus, for symmetric-top molecules, Eq. (2.124) becomes

$$E_{J,K,M_J} = BhcJ(J+1) - \frac{M K M_J}{J(J+1)} hcE \quad (2.130)$$

The selection rule is $\Delta M_J = 0$ when an electric field is applied in the direction of the incident radiation while $\Delta M_J = \pm 1$ when the direction is perpendicular to the incident radiation.

Let us now consider the transition between two adjacent levels characterised by $(J, K', M_{J'})$ and $(J+1, K'', M_{J''})$. From Eq. (2.130) we write

$$E_{J,K',M_{J'}} = BhcJ(J+1) - \frac{M K' M_{J'}}{J(J+1)} hcE \quad (2.131)$$

$$E_{J+1,K'',M_{J''}} = Bhc(J+1)(J+2) - \frac{M K'' M_{J''}}{(J+1)(J+2)} hcE \quad (2.132)$$

From Eqs (2.131) and (2.132), we get

$$\begin{aligned} \bar{\nu}_{\text{rot}} &= \frac{\Delta E_{\text{rot}}}{hc} = \frac{E_{J+1,K'',M_{J''}} - E_{J,K',M_{J'}}}{hc} \\ &= 2B(J+1) - M \left[\frac{K'' M_{J''}}{(J+1)(J+2)} - \frac{K' M_{J'}}{J(J+1)} \right] E \end{aligned} \quad (2.133)$$

Applying selection rules, $\Delta K = 0$, $\Delta M_J = 0$ we get $K' = K'' = K$; $M_{J''} = M_{J'} = M_J$ (say).

Consequently, Eq. (2.133) becomes

$$\bar{\nu}_{\text{rot}} = 2B(J+1) + \frac{2M K M_J E}{J(J+1)(J+2)} \quad (2.134)$$

The first-order Stark rotational lines for the $J=1 \rightarrow 2$ transition as worked out from Eq. (2.134) are recorded in the tabular form as follows. We know that for $J=1$, $K=0, 1$ and $M_J=0, \pm 1$.

State	No. of Lines	Wave Number $\bar{\nu}_{J,K,M_J}, \text{cm}^{-1}$
$J=1, K=0, M_J = -1$		$\bar{\nu}_{1,0,-1} = 4B + 0$
$= 0$	3	$\bar{\nu}_{1,0,0} = 4B + 0$
$= +1$		$\bar{\nu}_{1,0,+1} = 4B + 0$
$J=1, K=1, M_J = -1$		$\bar{\nu}_{1,1,-1} = 4B - \frac{ME}{3}$
$= 0$	3	$\bar{\nu}_{1,1,0} = 4B + 0$
$= +1$		$\bar{\nu}_{1,1,+1} = 4B + \frac{ME}{3}$

Thus, the Stark lines for $J=1 \rightarrow 2$ transition appear symmetrically on both sides of the original line, i.e. the line in the absence of external electric field. The Stark shift of symmetric tops for $J=1 \rightarrow 2$ transition is $\frac{ME}{3}$. For $M=1$ Debye unit (10^{-18} esu), $E=1$ esu ($300 \text{ volts cm}^{-1}$); $\frac{ME}{3}$ comes out to be of the order 0.0016 cm^{-1} and is easily observable.

2.9.2 Stark Transition Between Adjacent Levels in Linear Molecules

In case of linear molecules, there is no component of dipole moment M in the direction of J , consequently the energy of the rotational levels may be expressed as

$$E_{J,M_J} = Bhc J(J+1) + \frac{1}{2} hc \beta_{J,M_J} E^2 \quad (2.135)$$

The values of β are defined by

$$\beta_{0,0} = \frac{-2M^2}{B} \text{ cm}^{-1} \text{ for } J=0 \quad (2.136)$$

$$\beta_{J,M_J} = \frac{-2M^2}{B} \cdot \frac{3M_J^2 - J(J+1)}{J(J+1)(2J-1)(2J+3)} \quad (2.137)$$

Let (J', M_J') and (J'', M_J'') be the quantum numbers for ground and excited states respectively. With the aid of Eq. (2.135) and selection rule, $\Delta J = 1$, we arrive at the result

$$\bar{\nu}_{\text{rot}} = \frac{\Delta E_{\text{rot}}}{hc} = \frac{E_{J'',M_J''} - E_{J',M_J'}}{hc} \quad (2.138)$$

$$= B(J'' - J')(J'' + J' + 1) + \frac{1}{2} [\beta_{J'',M_J''} - \beta_{J',M_J'}] E^2$$

Since $\Delta J = +1$

$$\bar{\nu}_{\text{rot}} = 2B(J' + 1) + \frac{1}{2} [\beta_{J'',M_J''} - \beta_{J',M_J'}] E^2 \quad (2.139)$$

The factor $[\beta_{J'',M_J''} - \beta_{J',M_J'}]$ can be deduced from Eqs. (2.136) and (2.137). The Stark shifts for some typical transitions have been worked out with the aid of Eq. (2.139).

(a) Stark Shift for $J = 1 \rightarrow 2$ transition

For the transitions, $J = 1 \rightarrow 2$ and $J = 0 \rightarrow 1$, the Stark splitting is shown in Fig. 2.27.

From Eq. (2.139), we write

For $J = 1 \rightarrow 2$, $M_J = 0 \rightarrow 0$, $\Delta M_J = 0$, we get

$$\beta_{20} - \beta_{10} = \frac{-32M^2}{105B}$$

For $J = 1 \rightarrow 2$, $M_J = 1 \rightarrow 1$, $\Delta M_J = 0$, we get

$$\beta_{21} - \beta_{11} = \frac{26M^2}{105B}$$

Thus, for $J = 1 \rightarrow 2$ transition, from Eq. (2.139) we get

$$\bar{\nu}_{\text{rot}}(M_J = 0 \rightarrow 0) = 4B - \frac{16M^2 E^2}{105B} \quad (2.140)$$

$$\bar{\nu}_{\text{rot}}(M_J = 1 \rightarrow 1) = 4B + \frac{13M^2 E^2}{105B}$$

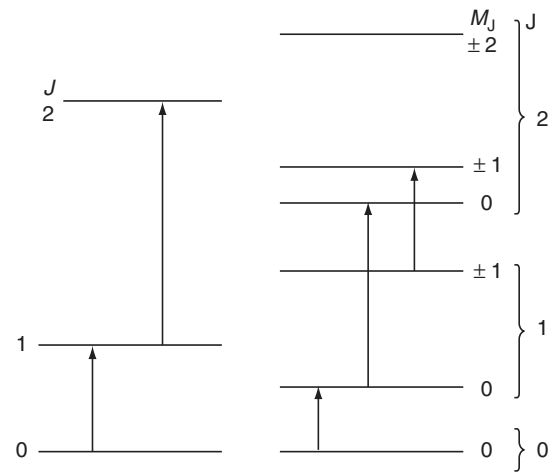


Fig. 2.27 Stark splitting for $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$ transitions.

From Eq. (2.140), it is evident that for $J = 1 \rightarrow 2$ transition in case of linear molecules, the two Stark lines are not exactly symmetrical on both sides of the original line. The Stark shifts are $-16M^2 E^2 / 105B$ and $13M^2 E^2 / 105B$.

(b) Stark Shift for $J = 0 \rightarrow 1$ Transition

For $J = 0 \rightarrow 1$ transition, Eq. (2.139) is written as

$$\bar{\nu}_{\text{rot}} = 2B(J' + 1) + \frac{1}{2} (\beta_{10} - \beta_{00}) E^2 \quad (2.141)$$

From Eqs (2.139) and (2.136), we obtain

$$\beta_{10} - \beta_{00} = \frac{16M^2}{15B} \quad (2.142)$$

Thus, Eq. (2.141) becomes

$$\bar{\nu}_{\text{rot}} = 2B + \frac{8M^2 E^2}{15B} \quad (2.143)$$

Hence, the Stark shift in case of $J = 0 \rightarrow 1$ transition is $8M^2 E^2/15B$.

To conclude, we can say that unlike symmetric-top molecules, the Stark shifts in linear molecules not only depend on M and E but also on B and hence I_B .

The observed splitting for $J = 1 \rightarrow 2$ transition in case of OCS is shown in Fig. 2.28 while the plot between $\Delta \bar{\nu}_{\text{rot}}$ and E^2 is presented in Fig. 2.29.

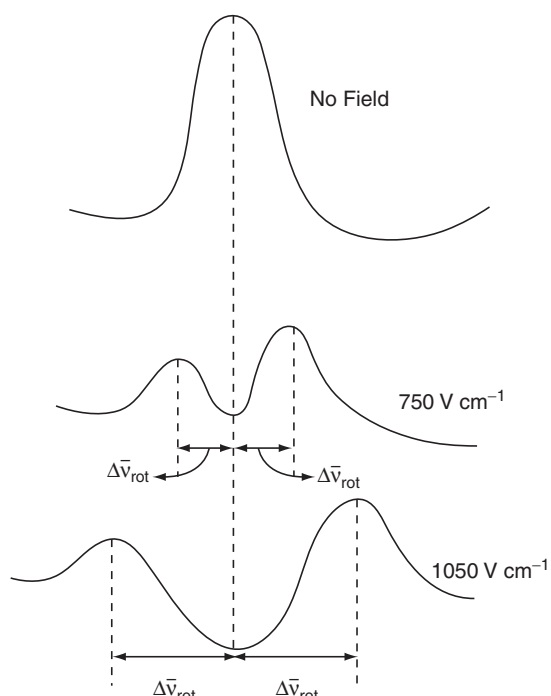


Fig. 2.28 Stark splitting of the $J = 1 \rightarrow 2$ lines of OCS.

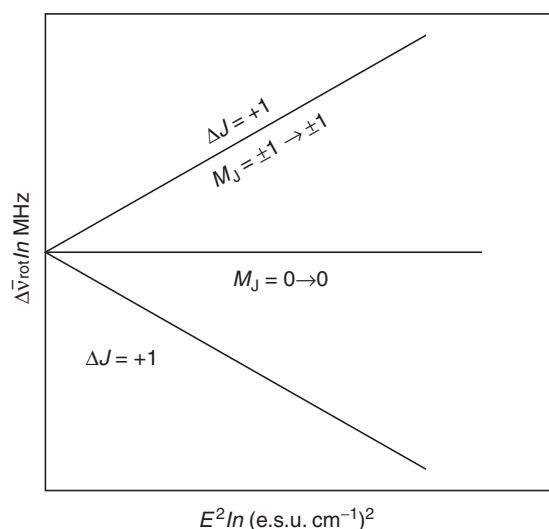


Fig. 2.29 A curve between $\Delta \bar{\nu}_{\text{rot}}$ and E^2 for the $J = 1 \rightarrow 2$ transition of the linear OCS.

The second-order Stark energy correlation for linear molecules under a weak field is expressed as

$$\beta_{J,F_J} = -\frac{M^2}{B} \frac{[3M_J^2 - F_J(F_J + 1)][3C(C - 1) - 4F_J(F_J + 1)J(J + 1)]}{2J(J + 1)(2J - 1)(2J + 3)2F_J(F_J + 1)(2F_J - 1)(2F_J + 3)} \quad (2.144)$$

Here, $C = F_J(F_J + 1) - J(J + 1) - I(I + 1)$ and

$$F_J = J + I, J + I - 1, \dots, 0, \dots, (J - I)$$

When F_J is an integer, $M_J = F_J + 1$;

$$M_J = F_J, F_J - 1, F_J - 2, \dots, 0$$

When F_J is an integral multiple of $1/2$,

$$M_J = F_J + \frac{1}{2}; M_J = F_J, F_J - 1, F_J - 2, \dots, \frac{1}{2}$$

The selection rules are $\Delta J = \pm 1, \Delta F = 0, \pm 1$.

Therefore, for $J = 0$, $\beta_{0,F_J} = \frac{-M^2}{6B} \text{ cm}^{-1}$, which does not depend on F_J nor M_J .

The additional effect due to polarisability of the molecules, i.e. the polarisabilities along the molecular axis ($\alpha_{\parallel}$) and in a direction perpendicular to the molecular axis ($\alpha_{\perp}$) is not considered. The coefficients of the main term M^2/B for $J = 1$ states are recorded in the tabular form as follows.

Spectrum	I	F_J	$ M_J $	β_{J,F_J}
HCN	1	0	0	0
			0	-0.050
		1	1	+0.025
			0	+0.050
		2	1	+0.025
			2	-0.050
HBr	3/2	1/2	1/2	0
or HCl		3/2	1/2	-0.04
			3/2	+0.04
			1/2	+0.04
		5/2	3/2	+0.01
			5/2	-0.05
CO	0	1	0	-0.20
			1	+0.10
HF	1/2	1/2	1/2	0
			1/2	-0.10
		3/2	3/2	+0.10

In case of HI, $I = 5/2$, the spin of H is neglected. In case of DF, DC1, etc., the spin of D is also neglected.

The coefficients for $J = 2$ state can also be obtained from Eq. (2.144). After applying the selection rules, the position of the Stark lines and hence Stark shift for $J = 1 \rightarrow 2$ transition relative to the original line can be obtained.

Further, we know that the degeneracy of any rotational level is given by $(2J + 1)$ and the energy of each degenerate level is the same. Thus, in the absence of an external field, the transitions between the states will have the same energy and the observed rotational spectrum will be simple. Since the degeneracy gets lifted under the influence of an external electric field, the Stark rotational spectrum will have multiple structures for all the possible transitions between the Stark rotational levels. Thus, with the aid of Stark effect, we can assign a particular value of J to an observed spectral line.

2.10 INVERSION IN AMMONIA AND ITS ANALOGUES

The phenomenon of inter-transformation of an atom X in pyramidal molecules XY_3 , namely NH_3 , ND_3 , PH_3 , AsCl_3 , AsH_3 , etc., from one side of Y_3 plane to the other side of the plane gives rise to an inverted configuration with respect to the original configuration and is termed as inversion or mirror reflection. The inversion of XY_3 type molecules is presented in Fig. 2.30.

These two configurations necessarily have the same energy. The inverted configuration cannot be obtained with

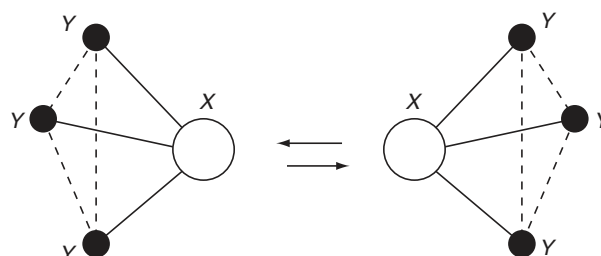


Fig. 2.30 The inversion of a pyramidal molecule XY_3 .

the rotation of the molecule. Basically, inversion is a vibrational problem and is associated with the vibrations of the atom X relative to Y_3 .

The potential energy of a pyramidal molecule as a function of distance of atom X from the Y_3 plane is shown in Fig. 2.31.

The two minima, separated by a potential hill (which actually represents the hindrance to inversion), correspond to the two configurations. The vibrational levels associated with the vibrational motion of the atom X relative to Y_3 is also presented in Fig. 2.31. The splitting of levels into two sublevels is due to the resonance interaction between the two identical configurations and is known as *inversion doubling*. The magnitude of splitting grows with the growth of the vibrational quantum number. The fundamental vibrational bands of NH_3 appear as doublets, i.e. ($3325.9, 3337.5 \text{ cm}^{-1}$) and ($931.58, 968.08 \text{ cm}^{-1}$) in its gaseous infrared spectrum. It is to be noted that the interaction involves energy difference in the microwave region.

According to classical mechanics, the inversion is not possible since necessary activation energy is not available to cross over the inversion barrier. In reality, the quantum mechanical particle, i.e. the atom X here, leaks or tunnels through the classically forbidden region (potential hill) from one classically allowed region, i.e. potential minimum to the other allowed region, i.e. the second minimum. The time taken by the atom X to tunnel through the barrier depends upon its height and shape. Consequently, the inversion is possible due to the finite height of the potential barrier. The average time of inversion is inversely proportional to the energy difference of the two sublevels for a given V and is given by,

$$t_i = \frac{1}{2\pi\Delta E_i} = \frac{5.307 \times 10^{-11}}{\Delta E_i} \quad (2.145)$$

where ΔE_i is in cm^{-1} .

The phenomenon of inversion has been thoroughly studied theoretically as well as experimentally in case of ammonia. The inversion doubling splits the rotational lines of NH_3 into doublets as shown in Fig. 2.31. The doublet splitting of the lines is twice the separation of the inversion doublet levels. The height of NH_3 pyramid is one half of the separation between the two maxima. PH_3 , AsH_3 , AsCl_3 , AsD_3 , BiCl_3 , etc., do not show inversion doubling since the inversion frequencies in these systems are slower because of the increasing height of potential barrier and increasing of the mass of the atom concerned. Further, pyramidal-type molecules do not exhibit optical isomerism while tetrahedral types exhibit optical isomerism. In these systems, if the substituents are bulky, the time of inversion by the mechanism of tunnelling may be of the order of 10^9 years. This led to infer why bacteria consume only one of the two forms, i.e. right or left of a certain carbon compound. The asymmetric molecules in bacteria have not undergone inversion since the particular genus came into being.

Problem 2.26: Determine the time of inversion and barrier to inversion in case of NH_3 if the separation of inversion doublet for the ground state is 0.66 cm^{-1} . [The splitting of the upper levels, i.e. $\Delta E_i = 1$ ($V_1 = 1$), 35.7 ($V_2 = 1$), 312.5 ($V_2 = 2$) cm^{-1}]

Solution The time of inversion can be determined from Eq. (2.145), i.e.

$$t_i = \frac{5.307 \times 10^{-11}}{0.66} = 8.04 \times 10^{-11} \text{ s.}$$

Thus, the time of inversion in case of ammonia is of the order of 10^{-11} s. However, the time decreases as the vibrational quantum number increases. The average time of inversion is of the order of 2.5×10^{-11} s. In case of PH_3 this time is 1.1×10^{-7} s. The time of inversion may be in hours or even in years also. The barrier to inversion may be determined from the expression,

$$k = Ze^{-E_a/RT} \quad (2.146)$$

where Z is the frequency factor; $R = 1.985 \text{ cal mole}^{-1} \text{ K}^{-1}$; and $T = 298 \text{ K}$.

Substituting the values of k , R and T into Eq. (2.146), we obtain

$$\begin{aligned} E_a &= 1.985 \times 298 \ln Z - 1.985 \times 298 \ln (8.04 \times 10^{-11})^{-1} \\ &= 591.53 \ln Z - 13749.527 \end{aligned}$$

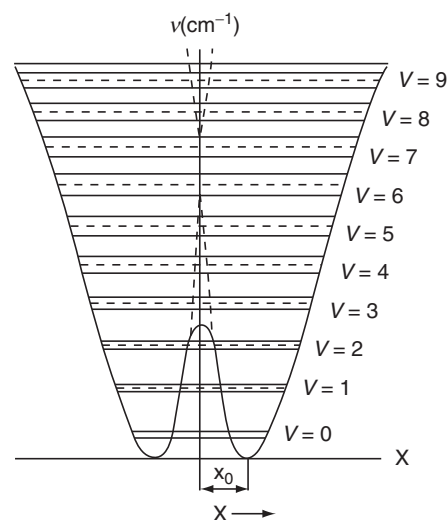


Fig. 2.31 Potential energy of pyramidal molecules XY_3 as a function of distance of the X atom from the Y_3 plane.

Assuming Z to be of the order 10^{14} , we get

$$E_a = 5.319 \times 10^3 \text{ cal mole}^{-1} = 5.319 \text{ kcal mole}^{-1}$$

The actual value of E_a is of the order of 6 kcal mole^{-1} . The estimated value of Z for ammonia is 3.161×10^{14} . It gives $E_a = 6 \text{ kcal mole}^{-1}$.

Problem 2.27: The average values of rotational constants **as** deduced from the pure rotational spectra of NH_3 and ND_3 are 9.945 cm^{-1} and 5.138 cm^{-1} respectively. Determine the geometrical parameters of NH_3 .

Solution In order to determine the bond distance of NH_3 , we write from Eq. (2.23)

$$I = \frac{3m_H r_{NH}^2}{2 \left[1 + \frac{3m_H}{m_N} \right]} \left[2 - \left(1 - \frac{3m_H}{m_N} \right) \sin^2 \beta \right] \quad (2.147)$$

$$I^* = \frac{3m_D r_{NH}^2}{2 \left[1 + \frac{3m_D}{m_N} \right]} \left[2 - \left(1 - \frac{3m_D}{m_N} \right) \sin^2 \beta \right] \quad (2.148)$$

Dividing Eq. (2.147) by Eq. (2.148), we obtain

$$\frac{I}{I^*} = \frac{m_H \left[1 + \frac{3m_D}{m_N} \right] \left[2 - \left(1 - \frac{3m_H}{m_N} \right) \sin^2 \beta \right]}{m_D \left[1 + \frac{3m_H}{m_N} \right] \left[2 - \left(1 - \frac{3m_D}{m_N} \right) \sin^2 \beta \right]} \quad (2.149)$$

We know that $B = 9.945 \text{ cm}^{-1}$ and $B^* = 5.138 \text{ cm}^{-1}$;

From Eq. (2.34), we get

$$\frac{I}{I^*} = \frac{B^*}{B} = \frac{5.138}{9.945} = 0.5166, \quad I = 1.695 \text{ au}, \quad I^* = 3.280 \text{ au} \quad (2.150)$$

Substituting the values of $\frac{I}{I^*}$ from Eq. (2.150), m_N , m_D and m_H into Eq. (2.149) and solving the resulting equation, we obtain

$$\sin \beta = 0.927$$

Therefore,

$$\beta = 67.971^\circ.$$

Substituting the values of I , and the masses of the respective atoms into Eq. (2.147), we get

$$r_{NH}^2 = 1.036 \text{ \AA}^2$$

Hence,

$$r_{NH} = 1.018 \text{ \AA}$$

From Eq. (2.24), the height of the pyramid is $h_p = 1.018 \times \cos 67.971^\circ = 0.381 \text{ \AA}$.

From Eq. (2.21), we get

$$r_{HH} = \sqrt{3(1.018 \times 1.018 - 0.381 \times 0.381)} = 1.634 \text{ \AA}$$

From Eq. (2.22), we obtain

$$\begin{aligned} \cos \alpha &= 1 - \frac{3(1.018 \times 1.018 - 0.381 \times 0.381)}{2 \times 1.018 \times 1.018} \\ &= 1 - 1.289 = -0.289 \end{aligned}$$

Hence, $\alpha = 106.79^\circ$.

2.11 BARRIER TO INTERNAL ROTATION

The rotation of one part of the molecule relative to another part of the molecule about a single or double bond is termed as internal rotation, e.g. two groups, viz. CH_3 and OH of methanol rotate about the C—O bond, two chemically equivalent CH_3/CH_2 groups of $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ rotate about the C—C/C=C bond. Absolute free internal rotation is possible only when the hindrance, i.e. potential-energy barrier to internal rotation, is zero which of course is not possible theoretically and experimentally in real molecular systems. Therefore, for internal rotation to occur, some energy is required to overcome the potential-energy hill. When the potential-energy barrier is $\leq \kappa T$ (2 kcal), the internal rotation is said to be free internal rotation, e.g. CH_3NO_2 (C—N), CH_3OH (C—O), C_2H_6 (C—C), $\text{CH}_3\text{—CCl}_3$ (C—C), $(\text{CH}_3)_2\text{S}$ (C—S), $(\text{CH}_3)_2\text{SiH}_2$, CH_3SiH_3 (C—Si), CH_3COOH (C—C), N_2H_4 (N—N), $(\text{CH}_3)_2\text{O}$ (C—O), etc. On the other hand, when the barrier height exceeds κT , the internal rotation is known as *torsional oscillation*, e.g. in C_2H_4 . Thus, free rotation and torsional oscillation are the limiting cases of internal rotation. Internal rotation appears when the atoms in a molecule form configurations separated by a potential-energy minima and just like inversion, the internal rotation is possible by the quantum mechanical tunneling effect.

As a result of internal rotation of methyl groups in simple molecules, the rotational lines in the pure rotational spectra of molecules split up into two components. The spacing between the doublets is of the order of a few megahertz. From the splitting, the barrier to internal rotation is determined. The error is of the order of 5 percent. The barrier to internal rotation about single bonds in some typical molecules is

C—C in $(\text{CH}_3)_2\text{O}$: 2.58, C—S in $(\text{CH}_3)_2\text{S}$: 2.10, C—Si in $(\text{CH}_3)_2\text{SiH}_2$: 1.83, C—O in CH_3OH : 1.07,
 C—C in $\text{CH}_3\text{—CCl}_3$: 2.70 and C—C in $\text{CH}_3\text{CH}_2\text{Cl}$: 3.68 kcal mole⁻¹.

The potential energy for C_2H_6 , CH_3OH type molecules is expressed as

$$U(\theta) = U\left(\theta \pm \frac{2}{3}\pi\right) \quad (2.151)$$

while for C_2H_4 type molecules, it is

$$U(\theta) = U(\theta + \pi) \quad (2.152)$$

where θ is the angle of torsion.

The plot of potential energy as a function of angle of torsion in C_2H_4 or in CH_3OH and C_2H_6 type molecules is presented in Fig. 2.32. The two identical minima in C_2H_4 correspond to the two energetically identical configurations of C_2H_4 while the three minima in C_2H_6 type molecules correspond to three energetically equivalent configurations of C_2H_6 . Thus, as a result of interaction among the energetically identical configurations, the torsional levels will split into sublevels depending upon the number of configurations. The separation between the torsional levels increases as the torsional quantum number increases. In case of C_2H_4 , each level of torsion oscillation splits into two sublevels while in C_2H_6 type molecules, each torsion oscillation level also splits into two sublevels but the sublevels are doubly degenerate as shown in Fig. 2.32 (b). The degenerate sublevels are alternately the upper and lower one. The energy level of torsion oscillation lies significantly below the potential energy barrier and is expressed as

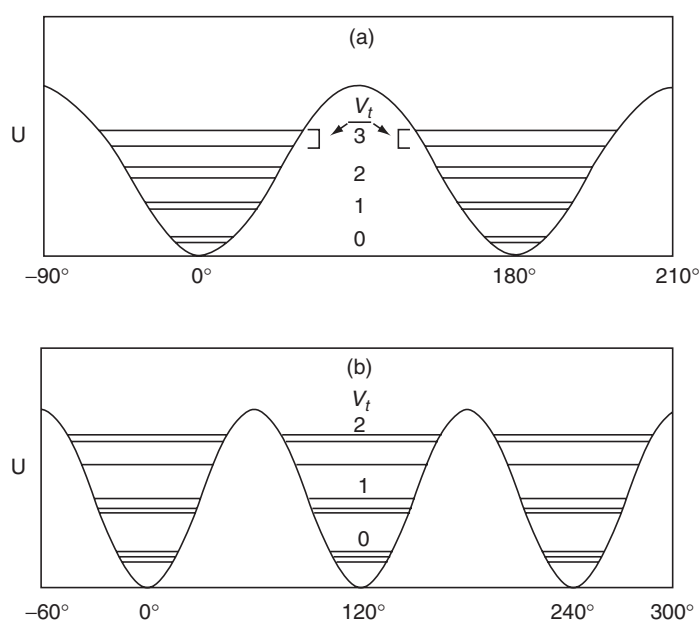


Fig. 2.32 Potential energy as a function of torsion angle in molecules of the (a) ethylene type C_2H_4 and (b) ethane type C_2H_6 or CH_3OH , etc.

$$E_t = \omega_t \left(V_t + \frac{1}{2} \right) \quad (2.153)$$

where E_t is the energy of the torsion oscillation level, ω_t is the frequency of torsion oscillation and V_t is torsional quantum number and can take on all integral values including zero, i.e. $V_t = 0, 1, 2, \dots$. The potential energy of torsion oscillation is expressed as

$$U = \frac{1}{2} U_0 (1 - \cos n\theta) \quad (2.154)$$

where n is the number of identical minima, and U_0 is the height of the potential hill separating the minima. For small oscillations, θ is small and hence,

$$\cos n\theta = 1 - \frac{n^2 \theta^2}{2} \quad (2.155)$$

Consequently, Eq. (2.154) reduces to

$$U = U_0 \left(\frac{n\theta}{2} \right)^2 \quad (2.156)$$

Thus, the frequency of torsion oscillation is given by

$$\omega_t = n \sqrt{\frac{U_0 A_1 A_2}{A}} \quad (2.157)$$

where A_1 and A_2 are the rotational constants of the two parts of the molecule that exhibit torsional motion relative to each other about the same axis. The respective moments of inertia are represented by I_A^1 and I_A^2 . A is the rotational constant of the whole molecule about the axis of torsion such that

$$\left. \begin{aligned} A &= A_1 + A_2 \\ I_A &= I_A^{(1)} + I_A^{(2)} \end{aligned} \right\} \quad \text{or} \quad (2.158)$$

$$\text{Here} \quad A_1 = \frac{h}{8\pi^2 I_A^{(1)} c} \quad (2.159)$$

and

$$A_2 = \frac{h}{8\pi^2 I_A^{(2)} c} \quad (2.160)$$

Combining Eqs (2.158), (2.159) and (2.160), we get

$$A = A_1 + A_2 = \frac{h}{8\pi^2 I_r c} \quad (2.161)$$

where

$$I_r = \frac{I_A^{(1)} I_A^{(2)}}{I_A^{(1)} + I_A^{(2)}} \quad (2.162)$$

and is called *reduced moment of inertia of the molecule*. Here A , A_1 , A_2 and U_0 are in cm^{-1} . Consequently, ω_t will also be in cm^{-1} .

For symmetric molecules of the type C_2H_4 , C_2H_6 , $\text{C}_2(\text{CH}_3)_2$, etc., $A_1 = A_2 = 2A$. Hence Eq. (2.157) for such type of molecules reduces to

$$\omega_t = 2n \sqrt{U_0 A} \quad (2.163)$$

Thus, from Eqs (2.157) and (2.163), we can determine the barrier to internal rotation from the observed value of torsional oscillation and the rotational constants of the molecule.

In case of symmetric molecules, the internal rotation and torsional oscillation will be microwave and infrared inactive respectively, since there will be no oscillating dipole moment. Hence, just like ordinary rotation spectrum, there will be no pure rotational spectrum of such molecules due to internal rotation.

For nearly asymmetric molecules, such as CH_3OH , the free internal rotation and torsional oscillation will be infrared active. The energy of internal rotational level (on the assumption of free rotation) as deduced quantum mechanically is given by the formula

$$E_{\text{int rot}} = E_{k_1, k} = h \frac{A_1 A_2}{A} \left[k_1 - k \frac{A}{A_1} \right]^2 \quad (2.164)$$

where $k = \pm K$, is the component of total angular momentum J about the top axis, also called unique axis, and k_1 , is quantum number of angular momentum of part '1' of the molecule.

$$k_1 = 0, \pm 1, \pm 2, \dots \quad (2.165)$$

Equation (2.164) may be expressed as

$$E_{k_1, k} = A_1 k_1^2 + A_2 (k - k_1)^2 - A k^2 \quad (2.166)$$

where, $k - k_1 = k_2$ is the quantum number of angular momentum of part '2' of the molecule about the top axis. Theoretical studies reveal that as the potential barrier grows from zero (free rotation) to large values in a molecule, the levels of free rotation expressed by Eq. (2.164) pass gradually into levels of torsional oscillations.

As stated earlier that for symmetric molecules, viz. C_2H_4 , C_2H_6 , etc., $A_1 = A_2 = 2A$. Consequently, the expression (2.166) reduces to

$$\begin{aligned} E_{k_1, k} &= A(2k_1 - k)^2 = A [k_1 + (k_1 - k)]^2 \\ &= A(k_1 - k_2)^2 = AK_i^2 \end{aligned} \quad (2.167)$$

Here $K_i = |k_1 - k_2|$ is the quantum number for internal rotation.

Since $K = |k_1 + k_2|$, therefore, $k_1 - k_2 = 0, \pm 2, \pm 4, \dots$ for even values of K and $k_1 - k_2 = \pm 1, \pm 2, \pm 3, \dots$ for odd values of K . The selection rules for internal rotation are $\Delta K_i = 0$ for $\Delta K = 0$ in case of $\parallel$ bands, i.e. K_i does not change for $\parallel$ bands, and $\Delta K_i = \pm 1$ for $\Delta K = \pm 1$ in case of $\perp$ bands, i.e. K_i changes by ± 1 for $\perp$ bands.

Combining (i) Eq. (2.167) with Eq. (2.97), and (ii) Eq. (2.97) with Eq. (2.166), we obtain the expressions for the total energy of the asymmetric and symmetric molecules, respectively. For symmetric molecules, viz. C_2H_4 , C_2H_6 , etc.,

$$E_{J, K, k_1, k_2} = BhcJ(J+1) + hc(A-B)K^2 + Ahc(k_1 - k_2)^2 \quad (2.168)$$

and for nearly symmetric molecules, viz. CH_3OH ,

$$E_{J, K, k_1, k_2} = BhcJ(J+1) - BhcK^2 + A_1 hck_1^2 + A_2 hck_2^2 \quad (2.169)$$

2.11.1 Selection Rules for Transition Between Two Adjacent Rotational Energy Levels in Slightly Asymmetric Molecules of the Type CH_3OH

In CH_3OH , the rotation of the OH group about the top axis is responsible for the transition dipole moment. The selection rules for the pure internal rotation spectrum are

$$\Delta J = 0, \pm 1, \Delta K = \pm 1, \Delta k_1 = \pm 1, \Delta k_2 = 0 \quad (2.170)$$

where $K_1 = |k_1|$ and $K_2 = |k_2|$. The subscripts '1' and '2' correspond to OH and CH_3 groups respectively.

Now if two sets of quantum numbers, i.e. (J', K', k_1', k_2') and (J'', K'', k_1'', k_2'') , correspond respectively to the lower and upper rotational energy levels then we can write from Eq. (2.169)

$$\begin{aligned} \bar{\nu}_{\text{rot}} &= \frac{\Delta E_{\text{rot}}}{hc} = \frac{E_{J'', K'', k_1'', k_2''} - E_{J', K', k_1', k_2'}}{hc} \\ &= 2B(J'' - J')(J'' + J' + 1) - B(K''^2 - K'^2) \\ &\quad + A_1(k_1'' - k_1')(k_1'' + k_1') + A_2(k_2'' - k_2')(k_2'' + k_2') \end{aligned} \quad (2.171)$$

Applying the selection rules expressed by Eq. (2.170), we obtain

$$\bar{\nu}_{\text{rot}} = A_1 - B \mp 2BK' \pm 2A_1 k_1' \text{ for } \Delta J = 0 \quad (2.172)$$

The upper signs correspond to positive ΔK and Δk_1 , while the lower signs correspond to negative ΔK and Δk_1 . The lines in the spectrum as deduced from Eq. (2.172) are recorded in the tabular form as follows:

State	Wave Number, $\bar{\nu}_{K, k_1}, \text{cm}^{-1}$
$K' = 0, k_1' = 0$	$\bar{\nu}_{0,0} = A_1 - B$
± 1	$\bar{\nu}_{0,\pm 1} = A_1 - B + 2A_1$
± 2	$\bar{\nu}_{0,\pm 2} = A_1 - B + 4A_1$
± 3	$\bar{\nu}_{0,\pm 3} = A_1 - B + 6A_1$
$K' = 1, k_1' = 0$	$\bar{\nu}_{1,0} = A_1 - B - 2B$
± 1	$\bar{\nu}_{1,\pm 1} = A_1 - B - 2B + 2A_1$
± 2	$\bar{\nu}_{1,\pm 2} = A_1 - B - 2B + 4A_1$
± 3	$\bar{\nu}_{1,\pm 3} = A_1 - B - 2B + 6A_1$

The table reveals that the Q lines of the free internal rotation spectrum consist of a series of bands of spacing $2A_1$, each of which consists of sub-bands whose zero lines have a spacing $2B$. It is to be noted that $A_1 \gg B$. Such a series of bands for large values of k_1 have been observed in the infrared spectrum of CH_3OH in the region 600–860 cm^{-1} .

The selection rules for the rotational–vibration spectrum are as follows:

(a) For $\parallel$ Bands ($\Delta K = 0$) $\Delta k_1 = 0, \Delta k_2 = 0$, i.e. the internal rotation does not influence the structure of a $\parallel$ band just as for molecules of the type C_2H_6 , provided there is no strong interaction between vibration and internal rotation.

(b) For $\perp$ Bands $\Delta k_1 = \pm 1, \Delta k_2 = 0$, or $\Delta k_1 = 0, \Delta k_2 = \pm 1$ depending on whether the dipole moment of the vibrational transition is in part ‘1’, i.e. OH or part ‘2’, i.e. CH_3 of the molecule in case of CH_3OH . With these selection rules for $\perp$ bands, it can be shown from the formula (2.171) that the $\perp$ bands have a double rotational structure as has been observed in case of molecules of the C_2H_6 type. Each sub-band with a given K and $\Delta K (= \pm 1)$ is made up of sub-sub-bands corresponding to different k_1 values and $\Delta k_1 = \pm 1$ (OH group) or to the different k_2 values and $\Delta k_2 = \pm 1$ (CH_3 group).

The spacing of the sub-sub-bands will be $\sim 2A_1$ or $2A_2$ while the spacing of the subbands will be $2B$. Since A_1 and $A_2 \gg B$, a number of sub-bands of spacing $2A_1$ or $2A_2$, each of which consists of lines with spacing $2B$ are possible.

Problem 2.28: From the Raman spectrum of C_2H_4 in the gaseous phase, the band at 825 cm^{-1} has been assigned to torsional oscillation about the $\text{C} = \text{C}$ bond. The infrared absorption spectrum of C_2H_4 , also in the gaseous phase, shows a fine structure of fundamental at 3.22μ . The spacing between the equidistant lines in the fine structure is 9.734 cm^{-1} . Determine the barrier to internal rotation about the $\text{C} = \text{C}$ bond.

Solution Given $2A = 9.734 \text{ cm}^{-1}$, $\omega_t = 825 \text{ cm}^{-1}$, $n = 2$

Therefore, $A = 4.867 \text{ cm}^{-1}$

From Eq. (2.163), we obtain the barrier to internal rotation,

$$U_0 = \frac{\omega_t^2}{4n^2 A} = \frac{825(\text{cm}^{-1}) \times 825(\text{cm}^{-1})}{4 \times 4 \times 4.867(\text{cm}^{-1})}$$

$$= 8740 \text{ cm}^{-1} = 25 \text{ kcal mole}^{-1}$$

Thus, barrier to torsional oscillation is about 25 kcal mole^{-1} .

Problem 2.29: The infrared spectrum of CH_3OH in the gaseous phase has been recorded in the $600\text{--}800\text{ cm}^{-1}$ region. The spacing between the successive lines has been found to be about 40 cm^{-1} . The strong band at 270 cm^{-1} in the infrared spectrum of gaseous CH_3OH is assigned to torsional oscillation about the C—O bond. Determine barrier to torsional or twisting oscillation.

Solution Here $n = 3$, $2A_1 = 40\text{ cm}^{-1}$, $\omega_t = 270\text{ cm}^{-1}$

From Problem (2.4), the moment of inertia due to CH_3 is

$$I_{\text{CH}_3} = I_A^{(2)} = 3.286\text{ au}$$

With the help of Eqs (2.34) and (2.160), we get

$$A_2 = \frac{16.8575}{3.286} = 5.130\text{ cm}^{-1}$$

Thus,

$$A = A_1 + A_2 = 20 + 5.130 = 25.130\text{ cm}^{-1}$$

The Eq. (2.157) may be written as

$$U_0 = \frac{\omega_t^2 A}{n^2 A_1 A_2}$$

Substituting the values of various parameters, we obtain

$$U_0 = \frac{270 \times 270 \times 25.130}{9 \times 20 \times 5.130} = 1984\text{ cm}^{-1} = 5.67\text{ kcal mole}^{-1}$$

2.12 ROTATIONAL SUM OVER THE STATES AND ROTATIONAL CONSTANTS

In statistical mechanics, the quantity $\sum_i g_i e^{-E_i/\kappa T}$ was originally known as *Zustandsumme* (in German), i.e. state sum or sum over the states, and is denoted by the symbol Z_{rot} as

$$Z_{\text{rot}} = \sum_i g_i e^{-E_i/\kappa T} \quad (2.173)$$

However, with time the term *state sum* became known as partition function which of course is a misnomer. Partition function indicates how at equilibrium, the systems are partitioned among the available energy states, although it is the individual term in the summation which gives us the information. It is denoted by Q . This function plays an important role in statistical mechanics. The formulae for rotational partition functions are different for linear, symmetric and asymmetric-top molecules.

2.12.1 Sum Over States for Diatomic and Linear Polyatomic Molecules

For diatomic and linear polyatomic rigid rotator molecules, the rotational partition function is given by

$$Z_{\text{rot}} = \sum_J \frac{(2J+1)e^{-BhcJ(J+1)/\kappa T}}{\sigma} \quad (2.174)$$

since for linear rigid rotators

$$E_J = BhcJ(J+1) \quad (\text{Eq. 2.33})$$

Here, σ is called the symmetry number (spin of identical nuclei is zero). It is equal to the number of indistinguishable positions into which a molecule can be turned by rigid rotations.

$\sigma = 2$ for homonuclear diatomics and $\sigma = 1$ in the case of heteronuclear diatomic molecules. The nuclear spin factor can be neglected in statistical calculations and hence is not incorporated in the formula.

At ordinary temperature, the number of rotational levels involved are very large, hence the asymptotic expansion is employed, i.e.

$$Z_{\text{rot}} = \frac{1}{\sigma} \left[\frac{\kappa T}{hcB} + \frac{1}{3} + \frac{1}{315} \cdot \frac{hcB}{\kappa T} + \frac{4}{315} \left(\frac{hcB}{\kappa T} \right)^2 + \frac{1}{315} \left(\frac{hcB}{\kappa T} \right)^3 + \dots \right] \quad (2.175)$$

When B is small and T is large, the higher terms may be omitted. Consequently, Eq. (2.175) reduces to

$$Z_{\text{rot}} = \frac{\kappa T}{\sigma h c B} = 0.6951 \frac{T}{\sigma B} \quad (2.176)$$

Equation (2.176) may also be deduced from Eq. (2.144) by replacing the summation by integration. By making use of the above formulae, we can determine the value of Z_{rot} from the observed value of rotational constant, B . It is to be noted that the influence of nuclear spin is omitted in the formula.

Problem 2.30: Determine the rotational partition function for CO and HCN at 500 K. The rotational constants for CO and HCN are 1.9319 and 1.4878 cm^{-1} respectively.

Solution The CO and HCN molecules are heteronuclear, hence $\sigma = 1$

Using Eq. (2.176)

$$Z_{\text{rot}}(\text{CO}) = 0.6951 \times \frac{500}{1.9319} = 179.9$$

$$Z_{\text{rot}}(\text{HCN}) = 0.6951 \times \frac{500}{1.4878} = 233.6$$

Problem 2.31: Determine the rotational component of the sum over states for CO_2 and CO_2^+ at 500 K. The rotational constants (in the ground state) for CO_2 and CO_2^+ are 0.3895 and 0.3806 cm^{-1} , respectively.

Solution The symmetry number in both the cases is 2.

$$B_0(\text{CO}_2) = 0.3895 \text{ cm}^{-1} \text{ and } B_0(\text{CO}_2^+) = 0.3806 \text{ cm}^{-1}$$

With the aid of Eq. (2.176), we get

$$Z_{\text{rot}}(\text{CO}_2) = 0.6951 \times \frac{500}{2 \times 0.3895} = 446.1$$

$$Z_{\text{rot}}(\text{CO}_2^+) = 0.6951 \times \frac{500}{2 \times 0.3806} = 456.5$$

2.12.2 Sum Over States for Symmetric-Top and Asymmetric-Top Molecules

The rotational partition function for symmetric tops is given by

$$Z_{\text{rot}} = \sum_{J=0}^{\infty} \sum_{K=-J}^{+J} \frac{(2J+1)}{\sigma} e^{-[BJ(J+1) + (A-B)K^2] \frac{hc}{\kappa T}} \quad (2.177)$$

since the energy of the rotational levels of symmetric-top molecules is expressed as

$$E_{J,K} = BhcJ(J+1) + (A-B)hcK^2$$

where $K = J, J-1, \dots, -J$.

For all cases except at very low temperatures, the following expansion of Eq. (2.177) is used.

$$Z_{\text{rot}} = \frac{e^{Bhc/(4\kappa T)}}{\sigma} \times \sqrt{\frac{\pi}{B^2 A} \left(\frac{\kappa T}{hc} \right)^3} \times \left[1 + \frac{1}{12} \left(1 - \frac{B}{A} \right) \frac{Bhc}{\kappa T} + \frac{7}{480} \times \left(1 - \frac{B}{A} \right)^2 \left(\frac{Bhc}{\kappa T} \right)^2 + \dots \right] \quad (2.178)$$

For small values of B/T , the higher terms in Eq. (2.178) are ignored. Consequently, Eq. (2.178) becomes

$$\begin{aligned} Z_{\text{rot}} &= (Z_{\text{rot}})_{\frac{B}{T} \rightarrow 0} = \frac{1}{\sigma} \sqrt{\frac{\pi}{B^2 A} \left(\frac{\kappa T}{hc} \right)^3} \\ &= \frac{1.02718}{\sigma} \sqrt{T^3 / B^2 A} \end{aligned} \quad (2.179)$$

Thus, knowing B and A from the rotational spectrum of symmetric tops, we can determine the value of Z_{rot} for these type of molecules.

For spherical-top molecules, the formula for rotational partition function can be obtained by substituting $A = B$ in the expression for symmetric-top molecules.

In case of asymmetric-top molecules if B and C are not too different, the constants A and B in Eq. (2.178) are replaced by A and $\sqrt{BC}$ respectively in order to obtain the formula for rotational partition function of asymmetric tops. Consequently, for asymmetric tops

$$Z_{\text{rot}} = \frac{e^{\sqrt{BC}hc/(4\kappa T)}}{\sigma} \times \sqrt{\frac{\pi}{ABC}} \left(\frac{\kappa T}{hc} \right)^3 \times \left[1 + \frac{1}{12} \left(1 - \frac{\sqrt{BC}}{A} \right) \frac{\sqrt{BC}hc}{\kappa T} + \dots \right] \quad (2.180)$$

For sufficiently high temperature or small rotational constants, Eq. (2.180) reduces to

$$\begin{aligned} Z_{\text{rot}} &= \frac{1}{\sigma} \sqrt{\frac{\pi}{ABC}} \left(\frac{\kappa T}{hc} \right)^3 = \frac{1.02718}{\sigma} \sqrt{\frac{T^3}{ABC}} \\ &= \frac{0.0148386}{\sigma} \sqrt{T^3 I_A I_B I_C} \end{aligned} \quad (2.181)$$

Problem 2.32: The rotational constants for halomethanes are given in the tabular form as follows: Determine their rotational partition functions at 500 K.

Variation Number	System	B_0 (cm ⁻¹)	A_0 (cm ⁻¹)
1	CH ₃ Cl	0.49	5.09
2	CH ₃ Br	0.31	5.08
3	CH ₃ I	0.28	5.07

Solution Using Eq. (2.179), we can determine the value of Z_{rot} . The calculated values of Z_{rot} at 500 K are recorded in the tabular form as follows.

Variation Number	System	σ	Z_{rot}	Z_{rot}/σ
1	CH ₃ Cl	3	10388.35	3462.78
2	CH ₃ Br	3	16436.45	5478.81
3	CH ₃ I	3	18215.44	6071.81

Problem 2.33: Determine the rotational partition functions for asymmetric-top molecules such as C₂H₄ and C₂D₄ at 500 K. The moments of inertia of the two systems are

System	I_A (au)	I_B (au)	I_C (au)
C ₂ H ₄	3.464	16.911	20.386
C ₂ D ₄	6.913	22.843	29.763

Solution $\sigma = 4$ in both the cases. Using Eq. (2.181), we get

$$\begin{aligned} Z_{\text{rot}}(\text{C}_2\text{H}_4) &= \frac{0.0148386}{4} \sqrt{500 \times 500 \times 500 \times 3.464 \times 16.911 \times 20.386} \\ &= \frac{5733.073}{4} = 1433.268 \\ Z_{\text{rot}}(\text{C}_2\text{D}_4) &= \frac{0.0148386}{4} \sqrt{500 \times 500 \times 500 \times 6.913 \times 22.843 \times 29.763} \\ &= \frac{11373.552}{4} = 2843.388 \end{aligned}$$

2.12.3 Partition Function for Spherical-Top Rigid Molecules

In case of spherical-top molecules, $A = B$. Consequently, Eq. (2.179) becomes

$$Z_{rot} = (Z_{rot})_{\frac{B}{T} \rightarrow 3} = \frac{1}{\sigma} \sqrt{\frac{\pi}{B^3} \left(\frac{\kappa T}{hc} \right)^3} = \frac{1.02718}{\sigma} \sqrt{\left(\frac{T}{B} \right)^3} \quad (2.182)$$

Problem 2.34: Determine the partition functions for CH_4 , CD_4 , SiH_4 and SiD_4 at 500 K if the values of the respective rotational constants are 5.252, 2.64, 2.96 and 2.87 cm^{-1} .

Solution Here, $\sigma = 12$ in all the cases. The partition functions as determined from the formula (2.182) are recorded in the tabular form as follows.

Variation Number	System	Z_{rot}	Z_{rot}/σ
1	CH_4	954.145	79.512
2	CD_4	2677.291	223.107
3	SiH_4	2255.090	187.924
4	SiD_4	2361.993	196.832

2.12.4 Sum Over States for Molecules with Internal Rotation

In case of polyatomic molecules having groups of atoms that are capable of rotating one with respect to another, the partition function is computed by employing the formula

$$Z_{\text{introt}} = \frac{1}{\sigma} \left(\frac{8\pi^3 \kappa T I_{\text{red}}}{h^2} \right)^{\frac{1}{2}} = \frac{0.359965}{\sigma} \sqrt{TI_{\text{red}}} \quad (2.183)$$

Here, σ is the degree of symmetry of a group of atoms, and I_{red} is the reduced moment of inertia (in au) of internal rotation. It is to be noted that for the rigid C_2H_6 molecule, the value of σ is 6. However, when there is free rotation, there are three indistinguishable positions for the two CH_3 groups relative to each other. For each of these three indistinguishable positions, we have the six positions as for rigid C_2H_6 .

Consequently, the total number of indistinguishable positions are $= 3 \times 6 = 18$.

Thus, $\sigma = 18$ in this case.

$$I_{\text{red}} = \frac{I_1 I_2}{I_1 + I_2} \quad (2.184)$$

I_2 is the moment of inertia of one half of the molecule about the top axis and I_1 is the moment of inertia of the whole molecule about an axis perpendicular to the top axis.

Problem 2.35: Determine the value of the free internal rotational component of the sum over states at 500 K in case of CH_3OH if $I_{\text{CH}_3} = 3.284$ au and $I_{\text{OH}} = 0.8136$ au.

Solution Here the symmetry number $s_{\text{CH}_3} \times s_{\text{OH}} = 3 \times 1 = 3$,

From Eq. (2.184) we get

$$I_{\text{red}} = \frac{I_{\text{CH}_3} \times I_{\text{OH}}}{I_{\text{CH}_3} + I_{\text{OH}}} = \frac{0.8136 \times 3.284}{0.8136 + 3.284} = 0.652 \text{ au}$$

Using the formula (2.183), we obtain

$$Z_{\text{introt}} = \frac{0.359965}{3} \times (500 \times 0.652)^{\frac{1}{2}} = 2.166.$$

2.13 APPLICATIONS OF MICROWAVE SPECTROSCOPY

Rotational spectroscopy is employed to estimate the relative abundance of isotopes and for the detection of conformational isomers since they have different moments of inertia and hence rotational spectra. The symmetry and geometry of molecules are also determined from microwave spectroscopy. It also serves as a potential tool to

determine the dipole moment of linear and symmetric-top molecules. The advantages of the microwave method over other methods of measuring dipole moments are its accuracy and sensitivity, which makes measurements possible even with small quantities of a sample. The sensitivity of the microwave method is especially significant in case of low-volatility substances whose dipole moments cannot be determined by methods based on dielectric constant and index of refraction measurements of these substances due to their low vapour pressure. The dipole moments when measured in solution by these methods are likely to be distorted due to the interaction of the sample under study with the solvent. The microwave method like other methods based on dielectric constant and index of refraction gives dipole moment of the molecule as a whole. The experimental method for determining the dipole moments of intramolecular bonds from intensities of the infrared vibrational spectra will be discussed in Chapter 3 on infrared vibrational spectroscopy. We know that as a result of interaction between the rotation of the molecule and reorientation of the nuclear spin, the rotational energy levels get perturbed. This effect appears in the rotational spectrum of the molecules. Thus, from the spectral features one can get information on the nuclear spin and about the symmetry of the electronic environment in the region of the nuclei. Microwave spectroscopy has also played a major role in the chemical study of interstellar space. A number of chemical species such as OH, CS, CH, CH⁺, CN radicals and molecules CO, SiO, CH₃CN, CH₃OH, HCOOH, HCN, HNCO, COS, NH₃, H₂O, etc., have been detected. In the light of these species, we can also look for other possible candidates in interstellar space, e.g. the existence of CN, HCN and HNCO led to infer that NC, NCO may also be searched. The presence of NH₃ and H₂O may throw light on the origin of biological molecules and hence the origin of life itself. Since the intensities of rotational lines are temperature dependent, the temperature of interstellar material can also be estimated. The temperature is generally determined from the temperature effect on the rotational spectrum of NH₃. It is to be remembered that the microwave spectrum of the molecule is observed as a whole. So just like vibrational and nuclear magnetic resonance spectra, it cannot be used for the study of functional groups, viz., CH₃, OH, SH, NH, CO, etc., present in the molecule.

PROBLEMS

1. Determine the atomic mass of the unknown atom say X, in the following diatomics from their rotational constants. Write the molecular formulae of the diatomics and calculate their bond lengths also.

Molecule	2B(cm ⁻¹)
X ⁷⁹ Br	0.195
X ⁷⁹ Br	0.188
X ³⁷ C1	21.32
³ HX	7.48
³⁵ C1X	1.03
X ¹⁹ F	1.01

2. Find the product of the moments of inertia, I_A , I_B and I_C of the water molecule if the equilibrium bond distance and bond angle are $r_e = 0.957 \text{ \AA}$ and $\theta = 104^\circ 31'$ respectively.
[Ans: $55.84 \times 10^{-142} \text{ kg}^3 \text{m}^6$]
3. Using the values of reduced moments of inertia from the book for SO₂ and H₂S, calculate their bond lengths and rotational constants.
4. Determine the relative population of the first five rotational levels of Br₂, BrCl, DF, and DI if their respective values of B_e are 0.0821, 0.152, 11.00 and 32.84 cm⁻¹.
5. The bond lengths of IO and FO molecules are 1.868 and 1.32 Å respectively. Estimate which is the most intense line in their pure rotational spectra at (a) 100 K, and (b) 1000 K. $B_e = 0.340 \text{ cm}^{-1}$ for IO and 1.104 cm^{-1} for FO.
6. Given the equilibrium bond lengths of the following rigid rotator diatomics; calculate the wave numbers of the first five lines in their rotational absorption spectra.

Molecule	¹² C ¹⁹ F	¹² C ³⁵ Cl	¹² C ³¹ P	²⁸ Si ¹ H	²⁸ Si ³⁵ Cl	¹⁴ N ² H	¹⁶ O ² H
$r_e(\text{\AA})$	1.267	1.645	1.558	1.521	2.058	1.038	0.971

7. The pure rotational spectrum of the CO molecule shows the following lines: 7.682, 11.508, 15.316, 19.100 cm⁻¹. Compute r_0 and D_0 for the molecule.
8. The number of lines in the pure rotational band of some molecule is given by

$$\bar{\nu}_{\text{rot}} = 1000(2n-1)\text{cm}^{-1} \text{ and } \bar{\nu}_{\text{rot}} = -1000(2n+1)$$

for positive and negative values of n respectively. Calculate the moment of inertia of the molecule.

• **Hint:** Show $B = 1000 \text{ cm}^{-1}$

9. Using the moments of inertia data from the book for F₂, H₂, HI, NO and OH diatomics, calculate (a) their bond lengths, (b) for $J = 5$, their angular momenta and velocities, and (c) determine the energy absorbed in the $J = 5 \rightarrow 6$ transition.

• **Hint:** Angular momentum = $l\omega = \sqrt{J(J+1)} (h/2\pi)$

[Ans: For OH, (a) 0.96 Å

(b) $5.77 \times 10^{-27} \text{ erg s}$, $3.90 \times 10^{13} \text{ rad s}^{-1}$ (c) 227 cm^{-1}]

10. Determine the energy of rotation and the rate of rotation for $J = 10$ for the following molecules from their microwave spectra.

Molecule	² H ³⁷ Cl	² H ⁷⁹ Br	² H ¹⁹ F	³ H ¹⁹ F	³⁵ Cl ¹⁹ F	³⁷ Cl ⁸¹ Br
2B(cm ⁻¹)	10.94	8.64	42.17	15.48	1.03	0.187

11. Calculate the rotational partition functions for the molecules listed in Problem 6 at 25°C and 100°C.
12. Calculate the energy in calories per mole needed to raise NO from its lowest rotational level to the level with $J = 4$. Given $r_0 = 1.151 \text{ \AA}$. [Ans: 97.42 cal mole⁻¹]
13. Estimate the values of centrifugal distortion constants from vibrational frequency and rotational constant data for the following nonrigid diatomic rotators. Also comment upon the values so obtained.

Molecule	H ₂	I ₂	IO	BrCl
$B(\text{cm}^{-1})$	60.86	0.037	0.340	0.152
$\omega(\text{cm}^{-1})$	4400.4	214.55	681.47	444.27

14. Frame different types of problems from the rotational constant data for the molecules given below:

Molecule	$2B(\text{cm}^{-1})$
¹ H ³⁵ Cl	21.35
² H ³⁵ Cl	10.97
³ H ³⁵ Cl	7.51
¹ H ¹⁹ F	42.22
² H ¹⁹ F	42.17
³ H ¹⁹ F	15.48
¹ H ⁸¹ Br	17.06
² H ⁸¹ Br	8.64
³ H ⁸¹ Br	5.83
³⁵ Cl ¹⁹ F	1.03
³⁷ Cl ¹⁹ F	1.01

15. Determine the H—C and C≡N bond lengths for HCN given

[Ans: 1.07, 1.15 Å]

¹ H ¹² C ¹⁴ N	$B_0 = 44316 \text{ MHz}$
² D ¹² C ¹⁴ N	$B_0 = 36208 \text{ MHz}$

16. The vibration-rotation constant for ⁶⁹Ga³⁵Cl is +0.004 cm⁻¹ and $2B_0 = 0.2972 \text{ cm}^{-1}$. Determine the value of r_e .
[Ans: 2.213 Å]
17. The atoms of CSI are separated by 3.31 Å. Calculate the reduced mass and the rotational inertia of the molecule.
[Ans: 105.6 amu; $7.7 \times 10^{-34} \text{ kg-m}^2$]
18. The rotational spectrum of ¹²C³²S gives the following data.
Determine the value of B_e and α_e from these data.
[Ans: $\alpha_e = 0.00592 \text{ cm}^{-1}$, $B_e = 0.82004 \text{ cm}^{-1}$]

V	$B_v(\text{cm}^{-1})$
0	0.81708
1	0.81116
2	0.80524
3	0.79932

19. The following spectroscopic constants are reported for pure samples of ⁷²Ge³²S and ⁷⁴Ge³²S:

Parameters	⁷⁴ Ge ³² S	⁷² Ge ³² S
$B_e(\text{MHz})$	5593.08	5640.06
$\alpha_e(\text{MHz})$	22.44	22.74
D (kHz)	2.349	2.388
$r_e(V=0)(\text{pm})$	0.20120	0.20120

Determine the frequency of the $J = 0$ to $J = 1$ transition for both the isotopic species in their ground vibrational state. The width of a microwave absorption line is of the order of one kHz. Could you distinguish a pure sample of ⁷⁴Ge³²S from a 50/50 mixture of the two isotopic species using microwave spectroscopy?

Ans : Molecule	$\bar{\nu}, J=0$ (cm ⁻¹)	$\bar{\nu}, J=1$ (cm ⁻¹)	$\Delta\bar{\nu}$ (cm ⁻¹)
⁷⁴ Ge ³² S	0.372372	0.744742	0.372370
⁷² Ge ³² S	0.375496	0.750990	0.375494
Yes			

20. The spectroscopic parameters of some diatomic molecules in the ground electronic state are indicated below. Determine the values of B_0 , B_1 , B_2 , and B_3 of the diatomics.

Molecule	$B_e(\text{cm}^{-1})$	$\alpha_e(\text{cm}^{-1})$
H ₂	60.8530	3.0622
¹⁶ O ¹⁶ O	1.4456	0.0159
¹² C ¹⁶ O	1.9313	0.0175
¹⁴ N ¹⁶ O	1.67195	0.0171
¹⁴ N ¹⁴ N	1.9982	0.01732
H ¹⁹ F	20.9557	0.798
H ³⁵ Cl	10.5934	0.3072
H ⁷⁹ Br	8.4649	0.2333
H ¹²⁷ I	6.5122	0.1689
³⁹ K ³⁹ K	0.05674	0.000165

APPENDIX 2.1A: ENERGY LEVELS OF A DIATOMIC RIGID ROTATOR

The two atoms, say 1 and 2, in a diatomic molecule form a rigid rotator, i.e. when the diatomic molecule rotates, the interatomic distance between the two atoms does not change. If m_1 and (x_1, y_1, z_1) and m_2 and (x_2, y_2, z_2) are the masses and coordinates of the atoms 1 and 2 respectively then the classical Hamiltonian in the Cartesian coordinates system will be

H = Kinetic energy due to both the masses + Potential energy. (2.1A-1)

Since in the case of rigid rotator, the interatomic distance remains fixed, the potential energy will be constant and can be considered as zero. Thus Eq. (2.1A-1) reduces to

H = Kinetic energy due to both the masses.

$$= \frac{1}{2} m_1 \left[\left(\frac{dx_1}{dt} \right)^2 + \left(\frac{dy_1}{dt} \right)^2 + \left(\frac{dz_1}{dt} \right)^2 \right] + \frac{1}{2} m_2 \left[\left(\frac{dx_2}{dt} \right)^2 + \left(\frac{dy_2}{dt} \right)^2 + \left(\frac{dz_2}{dt} \right)^2 \right] \quad (2.1A-2)$$

Also we know that

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned} \quad (2.1A-3)$$

So Eq. (2.1A-2) in terms of spherical coordinates can be expressed as

$$\begin{aligned} \hat{H} &= \frac{1}{2} m_1 \left[\left(\frac{dr_1}{dt} \right)^2 + r_1^2 \left(\frac{d\theta}{dt} \right)^2 + r_1^2 \sin^2 \theta \left(\frac{d\phi}{dt} \right)^2 \right] \\ &+ \frac{1}{2} m_2 \left[\left(\frac{dr_2}{dt} \right)^2 + r_2^2 \left(\frac{d\theta}{dt} \right)^2 + r_2^2 \sin^2 \theta \left(\frac{d\phi}{dt} \right)^2 \right] \end{aligned} \quad (2.1A-4)$$

If the distance r of the masses from the origin is fixed then the derivatives

$$\left(\frac{dr_1}{dt} \right) = \left(\frac{dr_2}{dt} \right) = 0$$

Thus Eq. (2.1A-4) reduces to

$$\hat{H} = \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) \left[\left(\frac{d\theta}{dt} \right)^2 + \sin^2 \theta \left(\frac{d\phi}{dt} \right)^2 \right] \quad (2.1A-5)$$

The first term within brackets of Eq. (2.1A-5) represents the moment of inertia (say I) of a rigid rotator. So

$$\hat{H} = \frac{1}{2} I \left[\left(\frac{d\theta}{dt} \right)^2 + \sin^2 \theta \left(\frac{d\phi}{dt} \right)^2 \right] \quad (2.1A-6)$$

Thus the solution of the Schrödinger wave equation of type

$$\hat{H} \Psi_{\text{rot}} = E_{\text{rot}} \Psi_{\text{rot}} \quad (2.1A-7)$$

will give the energy levels of the rigid rotator. We know that the rigid rotator behaves like a single particle of mass ' I ' placed at a fixed distance equal to unity (since $r = 1$) from the origin (which is the centre of mass). Consequently, Schrödinger wave equation for a rigid rotator is given by

$$\frac{\partial^2 \Psi_{\text{rot}}}{\partial x^2} + \frac{\partial^2 \Psi_{\text{rot}}}{\partial y^2} + \frac{\partial^2 \Psi_{\text{rot}}}{\partial z^2} + \frac{8\pi^2 I E_{\text{rot}}}{h^2} \Psi_{\text{rot}} = 0$$

and in spherical polar coordinates

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial \Psi_{\text{rot}}}{\partial \theta} \right] + \frac{1}{\sin^2 \theta} \frac{\partial^2 \Psi_{\text{rot}}}{\partial \phi^2} + \frac{8\pi^2 I E_{\text{rot}}}{h^2} \Psi_{\text{rot}} = 0 \quad (2.1A-8)$$

Equation (2.1A-8) indicates that Ψ_{rot} is a function of θ and ϕ , i.e.

$$\Psi_{\text{rot}} = \Psi_{\text{rot}}(\theta, \phi)$$

If Ψ_{rot} is a product of two functions and each function has one variable only then

$$\Psi_{\text{rot}}(\theta, \phi) = \Theta(\theta) \Phi(\phi)$$

$$\text{and } \frac{\partial \Psi_{\text{rot}}}{\partial \theta} = \Phi \frac{\partial \Theta}{\partial \theta}$$

$$\frac{\partial^2 \Psi_{\text{rot}}}{\partial \phi^2} = \Theta \frac{\partial^2 \Phi}{\partial \phi^2}$$

Substituting the values of the respective differentials into Eq. (2.1A-8) and rearranging the resultant equation, we get

$$\frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial \Theta}{\partial \theta} \right] + \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} + \frac{8\pi^2 I E_{\text{rot}}}{h^2} \sin^2 \theta = 0 \quad (2.1A-9)$$

Separating the variables, we obtain

$$\frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial \Theta}{\partial \theta} \right] + \lambda \sin^2 \theta = -\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} \quad (2.1A-10)$$

$$\text{where } \lambda = \frac{8\pi^2 I E_{\text{rot}}}{h^2}.$$

Now each side of Eq. (2.1A-10) contains one variable and they must be equal to the same constant. Let this constant be equal to m^2 so that

$$\frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial \Theta}{\partial \theta} \right] + \lambda \sin^2 \theta = m^2 \quad (2.1A-11)$$

$$\text{and } -\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = m^2 \quad (2.1A-12)$$

The solution of Eq (2.1A-12) is

$$\Phi_m(\phi) = C e^{\pm i m \phi}$$

$\Phi_m(\phi)$ must be of the well-behaved class, i.e. it must be a single-valued function. Therefore $\Phi_m(\phi)$ must have the same values for $\phi = 0$ and 2π , i.e.

$$\Phi_m(\phi) = C e^{\pm i m 0} = C$$

and $\Phi_m(\phi) = C e^{\pm i 2\pi m}$ should be the same. Therefore,

$$C = C e^{\pm i 2\pi m}$$

$$\text{or } C e^{\pm i 2\pi m} = 1$$

$$\text{or } \cos 2\pi m \pm i \sin 2\pi m = 1$$

which can be true only if m has integral values including zero, i.e. $m = 0, 1, 2, 3, \dots$. Such characteristics are those that would be expected of a quantum number.

Next, the solution of Eq. (2.1A-11) is obtained as follows:

Multiplying Eq. (2.1A-11) by $\frac{\Theta}{\sin^2 \theta}$ we get

$$\begin{aligned} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \lambda \Theta &= \frac{m^2 \Theta}{\sin^2 \theta} \\ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \left(\lambda - \frac{m^2}{\sin^2 \theta} \right) \Theta &= 0 \end{aligned} \quad (2.1A-13)$$

Let $x = \cos \theta$

$$\therefore \frac{\partial x}{\partial \theta} = -\sin \theta$$

So we can write $\frac{\partial \Theta}{\partial \theta}$ as

$$\frac{\partial \Theta}{\partial \theta} = \frac{\partial \Theta}{\partial x} \frac{\partial x}{\partial \theta} = -\sin \theta \frac{\partial \Theta}{\partial x}$$

Consequently, Eq. (2.1A-13) becomes

$$\frac{1}{\sin \theta} (-\sin \theta) \frac{\partial}{\partial x} \left[-\sin^2 \theta \frac{\partial \Theta}{\partial x} \right] + \left[\lambda - \frac{m^2}{\sin^2 \theta} \right] \Theta = 0$$

$$\text{or } \frac{\partial}{\partial x} \left[(1-x^2) \frac{\partial \Theta}{\partial x} \right] + \left[\lambda - \frac{m^2}{(1-x^2)} \right] \Theta = 0 \quad (2.1A-14)$$

which is the Legendre's differential equation. x can take on values from $\cos 0$ or $(+1)$ to $\cos \pi$ or (-1) . The solution of Eq. (2.1A-14) can be obtained by expressing Θ as:

$$\Theta = (1-x^2)^{|m|/2} L$$

Thus

$$\frac{\partial \Theta}{\partial x} = -mx(1-x^2)^{|m|/2-1} L + (1-x^2)^{|m|/2} \frac{\partial L}{\partial x}$$

or

$$(1-x^2) \frac{\partial \Theta}{\partial x} = -mx(1-x^2)^{|m|/2} L + (1-x^2)^{|m|/2+1} \frac{\partial L}{\partial x}$$

Hence the first term of Eq. (2.1A-14) is

$$\frac{\partial}{\partial x} \left[(1-x^2) \frac{\partial \Theta}{\partial x} \right] = \frac{\partial}{\partial x} \left[-mx(1-x^2)^{|m|/2} L + (1-x^2)^{|m|/2+1} L' \right]$$

where $L' = \frac{\partial L}{\partial x}$

or

$$\begin{aligned} \frac{\partial}{\partial x} \left[(1-x^2) \frac{\partial \Theta}{\partial x} \right] &= \left[-m(1-x^2)^{|m|/2} + m^2 x^2 (1-x^2)^{|m|/2-1} \right] L \\ &\quad - \left[2x(m+1)(1-x^2)^{|m|/2} \right] L' \\ &\quad + \left[(1-x^2)^{|m|/2+1} \right] L'' \end{aligned}$$

Here $L'' = \frac{\partial^2 L}{\partial x^2}$

Consequently, Eq. (2.1A-14) in terms of x can be written as

$$(1-x^2)L'' - 2(m+1)xL' + [\lambda - m(m+1)]L = 0$$

$$\text{or } (1-x^2)L'' - 2\alpha xL' + \beta L = 0 \quad (2.1A-15)$$

where $\alpha = m+1$, and $\beta = \lambda - m(m+1)$

The solution of Eq. (2.1A-15) can be obtained by the power series technique, i.e.

$$L(x) = \sum_{v=0,1,2,\dots}^{\infty} a_v x^v = a_0 + a_1 x + a_2 x^2 + \dots$$

Taking the first and second derivatives and proceeding as in the case of a harmonic oscillator, we arrive at the following recursion formula.

$$\frac{a_{v+2}}{a_v} = \frac{(v+m)(v+m+1) - \lambda}{(v+1)(v+2)} \quad (2.1A-16)$$

for the coefficients of a power series of $L(x)$. Here, v is a zero or an integer. This formula is analogous to Eq. (2.1A-15). For $L(x)$ to be a polynomial, the series $L(x)$ must break off after a finite number of terms which is possible only if

$$(v+m)(v+m+1) - \lambda = 0$$

$$\text{or } \lambda = (v+m)(v+m+1) = l(l+1)$$

Since v and m qualify the condition of a quantum number, the sum $(v+m) = l$ should also qualify the same condition, i.e.

$$l = 0, 1, 2, \dots$$

$$\text{We know that } \lambda = \frac{8\pi^2 I E_{\text{rot}}}{h^2}$$

$$\text{So } \frac{8\pi^2 I E_{\text{rot}}}{h^2} = l(l+1)$$

$$\text{or } E_{\text{rot}} = \frac{h^2}{8\pi^2 I} l(l+1)$$

Replacing l by J , we get

$$E_J / E_{\text{rot}} = \frac{h^2}{8\pi^2 I} J(J+1) \quad (2.1A-17)$$

where J is known as the *rotational quantum number*. Or

$$E_J / E_{\text{rot}} = B h c J(J+1); \quad J = 0, 1, 2, 3, \dots \quad (2.1A-17a)$$

$$\text{or the rotational term } F_J = \frac{E_J}{h c} = B J(J+1)$$

where $B = \frac{h}{8\pi^2 I c}$ cm^{-1} is called the *rotational constant*.

Equation (2.1A-17a) is the expression for the energy levels of a rigid rotator.

APPENDIX 2.2A: ENERGY LEVELS OF A RESTRICTED ROTATOR

The internal motions of complex molecules in crystals are the examples of a rigid rotator moving under the influence of a potential field.

Let us now consider a rigid rotator whose moment of inertia I , moving in a sinusoidal potential field of type

$$U(\theta) = \frac{U_0}{2} (1 - \cos n\theta) \quad (2.2A-1)$$

where θ is the angle of rotation. For a molecule made of light atoms, such as H_2 or O_2 , $n = 2$, $U = 0$ at $\theta = 0, \pi, 2\pi, \dots$ etc. Accordingly, the wave equation for this system is expressed as

$$\frac{d^2 \Psi(\theta)}{d\theta^2} + \frac{8\pi^2 I}{h^2} \left[E_r - \frac{U_0}{2} (1 - \cos n\theta) \right] \Psi(\theta) = 0 \quad (2.2A-2)$$

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Making substitutions:

$$x = n \frac{\theta}{2}; \quad n\theta = 2x$$

$$dx = \frac{n}{2} d\theta$$

$$dx^2 = \frac{n^2}{4} d\theta^2$$

into Eq. (2.2A-2), we obtain

$$\frac{d^2\Psi(x)}{dx^2} + \left[\frac{32\pi^2 I}{n^2 h^2} \left\{ E_r - \frac{U_0}{2} \right\} + \frac{16\pi^2 I U_0}{n^2 h^2} \cos 2x \right] \Psi(x) = 0 \quad (2.2A-3)$$

$$\text{or } \frac{d^2\Psi(x)}{dx^2} + (b_r + 2\Phi \cos 2x) \Psi(x) = 0 \quad (2.2A-4)$$

$$\text{in which } \Phi = \frac{8\pi^2 I U_0}{n^2 h^2} \quad (2.2A-5)$$

$$\text{and } b_r = \frac{32\pi^2 I}{n^2 h^2} \left(E_r - \frac{U_0}{2} \right) \quad (2.2A-6)$$

Equation (2.2A-4) is known as *Mathieu's differential equation*, the solution of which is hard and cumbersome. However the limiting cases of this equation correspond to the motion of a free rotator or that of harmonic oscillator:

Case I: For $b_r \gg 2\Phi$, Eq. (2.2A-4) reduces to

$$\frac{d^2\Psi(x)}{dx^2} + b_r \Psi(x) = 0 \quad (2.2A-7)$$

The solutions of this equation are

$$\Psi = e^{\pm i r x} = e^{\pm i r \frac{n\theta}{2}} \quad (2.2A-8)$$

where r is a positive integer including zero.

$$\frac{d^2\Psi}{dx^2} = i^2 r^2 e^{\pm i r x} = -r^2 \Psi \quad \text{or} \quad \frac{d^2\Psi}{dx^2} + r^2 \Psi = 0$$

So $b_r = r^2$

By the symmetry of the potential field,

$$\Psi(\theta) = \Psi\left(\frac{2\pi}{n} + \theta\right) \quad (2.2A-9)$$

According to Eq. (2.2A-2), only even integral values of r including zero are allowed, i.e. $r = 0, 2, 4, 6, \dots$. Since $b_r = r^2$, so the energy levels are deduced from Eq. (2.2A-6). These are.

$$E_r - \frac{U_0}{2} = \frac{n^2 h^2 r^2}{32\pi^2 I}, \quad r = 0, 2, 4, 6, \dots \quad (2.2A-10)$$

$$\text{or } \frac{E_r - \frac{U_0}{2}}{hc} = \frac{n^2 h r^2}{32\pi^2 I c} = \frac{n^2 r^2}{4} A \quad (2.2A-10a)$$

where $A = \frac{h}{8\pi^2 I c}$ is the rotational constant for the whole molecule. For the various values of n ; we obtain,

$$n = 1, \quad \frac{E_m - \frac{U_0}{2}}{hc} = A m^2, \quad m = 0, 1, 2, 3, 4, \dots$$

$$n = 2, \quad \frac{E_m - \frac{U_0}{2}}{hc} = A m^2, \quad m = 0, 2, 4, 6, \dots$$

$$n = 3, \quad \frac{E_m - \frac{U_0}{2}}{hc} = A m^2, \quad m = 0, 3, 6, 9, \dots$$

$$\text{where } m^2 = \frac{n^2 r^2}{4}$$

Thus for $n > 1$, only $\frac{1}{n}$ th of the energy levels for the free rotator are allowed. The connection between this fact and the origin of symmetry number in rotation partition function is obvious. These energy levels are doubly degenerate.

Case II: For $b_r \ll 2\Phi$, the wave function will have appreciable values only for $x \approx 0$. so Eq (2.2A-4) can be written as

$$\frac{d^2\Psi}{dx^2} + [b_r + 2\Phi (1 - 2x^2)] \Psi = 0 \quad (2.2A-11)$$

This is the equation for the harmonic oscillator and can be rewritten as

$$\frac{d^2\Psi}{dx^2} + [(b_r + 2\Phi) - 4\Phi x^2] \Psi = 0$$

$$\text{or } \frac{d^2\Psi}{dx^2} + [\lambda - \alpha x^2] \Psi = 0 \quad (2.2A-11a)$$

in which $\lambda = b_r + 2\Phi$ and $\alpha = 2\sqrt{\Phi}$. Equation (2.2A-11a) is analogue to Equation (2.2A-4) of the harmonic vibrator. Thus the energy levels are given by the relation

$$\lambda = (2r + 1) \alpha, \text{ i.e.}$$

$$b_r = 2(2r + 1) \sqrt{\Phi} - 2\Phi \text{ so that}$$

$$E_r = (r + 1/2) h \nu_0 \quad r = 0, 1, 2, 3, \dots \quad (2.2A-12)$$

$$\text{or } \frac{E_r}{hc} = \left(r + \frac{1}{2}\right) \frac{\nu_0}{c} \quad (2.2A-12a)$$

$$\text{where } \nu_0 = \frac{n}{2\pi} \sqrt{\frac{U_0}{2I}} \quad (2.2A-13)$$

For the intermediate case $b_r \sim \Phi$, the energy levels cannot be well approximated by either of the above relations.

CHAPTER 3 INFRARED SPECTROSCOPY

No hypothesis can lay claim to any value until it assembles many phenomena under one concept.

—Goethe

3.1 INTRODUCTION

Just like rotational motion, the vibrational motion of molecules is also quantised and the vibration of a molecule manifests itself in the heat capacity of gases and in the molecular vibrational spectra. The discrete nature of the vibrational spectra is an experimental evidence to the quantum nature of the vibrational motion of molecules. Since the energy of vibrational transitions lies in the infrared region of the electromagnetic radiation, the vibrational spectrum is also known as *infrared spectrum (IR)*. Thus, IR absorption spectroscopy deals with the absorption of photons in the $10\text{--}12,000\text{ cm}^{-1}$ frequency region of the spectrum. As a result of the absorption of photons, the vibrational, rotational or vibrational–rotational configuration of the molecules gets perturbed in contrast to visible/ultraviolet spectroscopy where, in addition, electronic configuration of the molecules also gets affected due to the absorption of visible/ultraviolet photons.

Since the energies involved in IR spectroscopy are of the order of tenths of electron volts, IR radiation affects only vibrational and rotational transitions within molecules. Indeed at normal temperatures, IR absorption usually arises primarily from vibrational rather than rotational transitions. Thus, the rotational–vibrational motions are usually found in gases. The change (ΔJ) in the total rotational quantum number gives rise to *P*, *Q* and *R* branches in the spectra of gases ($\Delta J = -1$ for *P*, $\Delta J = 0$ for *Q* and $\Delta J = +1$ for *R*). Since the rotational frequencies depend upon the moments of inertia of the molecules, the rotational–vibrational spectra are of help in the study of molecular structure. In condensed gases, liquids and solids, only the vibrational motions have been generally observed. The vibrational frequencies of polyatomic molecules depend upon (a) the masses of linked atoms, (b) their geometric interrelationships, and (c) the forces due to deviation from equilibrium bond configurations.

IR spectroscopy is divided into three major regions:

(a) Far IR ($10\text{--}200\text{ cm}^{-1}$) This region deals with pure rotational motion of the molecules. It is seldom used in chemical spectroscopy since it is difficult to generate and detect such low frequencies. The region from $200\text{--}670\text{ cm}^{-1}$ is also sometimes included in the far IR. The primary use of this region has been for the determination of the structures of inorganic and metal organic species based on absorption measurements. It is to be noted that heavy metal iodides generally absorb in the region below 100 cm^{-1} , while the bromides and chlorides have bands at higher wave numbers. Far IR studies of inorganic solids have also provided information about the lattice energies of crystals and transition energies of semiconducting materials.

(b) Mid IR ($200\text{--}4,000\text{ cm}^{-1}$) This is the most suitable and important region for qualitative as well as quantitative IR spectral investigations since most of the frequencies due to functional groups in molecules fall in this region. The studies in this region are based upon absorption, reflection and emission measurements of samples.

(c) Near IR ($4,000\text{--}12,000\text{ cm}^{-1}$) Almost all the bands in this region are due to either overtones or combination tones of A—H stretching vibrations where A = C, N, O, S, etc. The importance of this region is mainly from the point of view of quantitative determination of functional groups specially containing hydrogen atoms. This region also finds considerable use for the routine quantitative determination of certain species, such as water, carbon dioxide, sulphur dioxide, low-molecular-weight hydrocarbons, amine nitrogen and many other simple compounds that are of interest in agriculture and industry. These determinations are usually based upon diffuse reflectance measurements of untreated solid or liquid samples or transmission studies of gases.

3.2 MECHANISM OF IR ABSORPTION AND IR ACTIVITY

The inter-atomic distances within molecules fluctuate cyclically about average values through one or more simultaneous vibrational motions, viz. stretching, bending, torsion, etc. When such motions change the dipole moment of a given bond, its electric field oscillates at the same frequency as the bond vibration (10^{10} – 10^{11} Hz, corresponding to wavelengths 2–20 μ). Thus, when molecules are exposed to infrared radiations, they will experience its electric field. If the field is reversed periodically as it is in the environment of radiation then the dipole charges will experience forces alternately. As a result of this interaction, the dipole spacing will increase and decrease. Hence the net effect of the oscillating electric field of the IR photons will make the dipole moment of any molecule vibrate at the frequency of the photon. The pictorial view of the effect of electric field of radiations on the dipole is shown in Fig. 3.1.

The molecules have certain nuclear vibrational frequencies where the vibration causes an oscillation of the dipole moment. The photon will excite only those vibrations which cause dipole moment to oscillate, i.e. the absorption of IR radiation will occur if the frequency of photon matches or resonates with any one of the frequencies of the molecule. Since dipole moment (M) is defined in the case of a simple dipole as the product of magnitude of either charge (e) in the dipole and the charge spacing (r), i.e. $M = er$, therefore, if a nonvibrating molecule has a centre of symmetry and none of the vibrations alter the centre of symmetry at any moment will necessarily be infrared inactive. The dipole moment does not change since it is always zero. Thus, the gross selection rule for IR vibrational spectrum is that the molecule must have permanent dipole moment, i.e. $M \neq 0$, and must possess oscillating (also called transition) dipole moment M_r . Variation in dipole moment of a bond A—H with the internuclear distance is shown in Fig. 3.2. The two cases shown in the figure illustrate the possible differences in the sign of the slope (dM/dr). The homonuclear diatomic molecules such as H_2 , N_2 , O_2 , etc., are IR inactive since their dipole moment is zero. Vibrational data for such molecules are determined from Raman and electronic spectra. However, if the centre of symmetry of such molecules gets distorted some way or the other, the infrared inactive vibration becomes infrared active.

It is thus possible to observe infrared inactive frequencies at high pressures, when due to collisions, the symmetry of the molecule is perturbed, e.g. at pressures of 150 atmospheres and higher, we observe absorption bands for H_2 , N_2 and O_2 . At pressures up to 25 atmospheres, the absorption spectrum of C_2H_2 exhibits a band at 1974 cm^{-1} which is infrared inactive at ordinary conditions. The increase in intensity of the band is proportional to the square of the gas density which indicates that activity is due to deformation of the C_2H_2 molecule in collisions. Adsorption also causes deformation of the molecule since optically inactive frequency of H_2 observed at 4161 cm^{-1} in Raman spectrum also appears at 4131 cm^{-1} in IR spectrum during its adsorption on solid surfaces.

Further, molecular vibrations which are infrared active may or may not be Raman active. The necessary condition for a particular vibration in a molecule to be Raman active is that its polarisability should change when the molecule is exposed to an electromagnetic wave of light. The mechanism of change in polarisability of molecule will be explained in Chapter 4 on Raman spectroscopy. The vibrations which do not lead to change in polarisability or dipole moment are both IR and Raman inactive. Thus, from the foregoing discussion it is clear that in all the molecules which have centre of symmetry, the infrared active vibrations are Raman inactive and vice versa. This is called *exclusion principle*, e.g. CO_2 has centre of symmetry. Two of its fundamental vibrations are IR active only while the third one is Raman active. On the other hand, all the three normal modes of vibrations in H_2O are Raman as well as IR active. To summarise, we can say that Raman spectra significantly supplement IR spectra and simplify the problem of analysing the vibrational terms of complex molecules. The Raman spectrum of molecules will be discussed in detail in Chapter 4 on Raman spectroscopy.

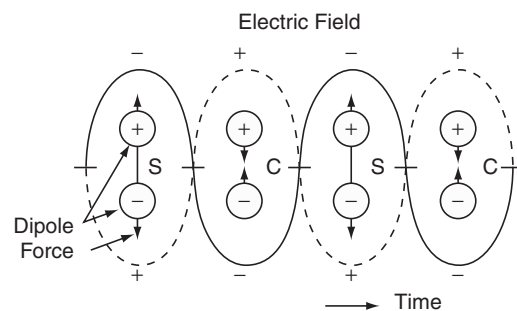


Fig. 3.1 The effect of electric field (reversed periodically) on the dipole increase (S)/decrease (C) of dipole spacing.

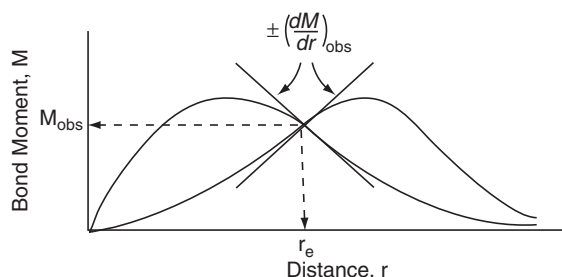


Fig. 3.2 Change in the dipole moment of a bond A—H with internuclear distance.

3.3 INSTRUMENTATION

The instrument employed for recording the spectra in the IR region is called an IR spectrophotometer. There are generally two types of spectrometers, viz single- and double-beam spectrometers. The block diagram of a single-beam spectrometer is shown in Fig. 3.3.

When a single-beam spectrometer is used for recording the spectrum, the IR absorption bands due to H_2O and CO_2 present in the air appear in the spectrum as shown in Fig. 3.4. The background spectrum due to CO_2 and H_2O is, therefore, to be subtracted from the spectrum of any sample under investigation in order to have the spectrum of the sample.

Since H_2O and CO_2 may create difficulties in the spectroscopic studies in their respective absorption regions, they should either be removed from air or ways and means should be found out to avoid overlapping due to CO_2 and H_2O of the spectrum. One way of dealing with this problem is the complete evacuation of the spectrometer. This is not an easy task because the volume of a modern spectrometer is of the order of 0.3 m^3 and even the chances of leakage in such a large instrument are not ruled out. Further, time limit is also a problem. The evacuation process needs a week's time for the complete desorption of water vapours from the surface of mirrors inside the instrument. The second method of tackling the problem is to flush the instrument either with dry nitrogen or dry CO_2 free air. But both these methods are not very effective since they are tedious and time consuming. However, the introduction of double-beam spectrometer proved very fruitful since it eliminates the problems which are encountered in a single-beam spectrometer. The block diagram of a double-beam spectrometer is presented in Fig. 3.5.

3.3.1 Working of a Double-Beam Spectrometer

The infrared radiation from the source is split into two beams, one passing through the sample and the other serving as reference. Therefore, when spectrum of a solution is to be recorded, the reference beam should be passed through the solvent. The function of the attenuator is to reduce the intensity to the required level. The two beams are fed alternately to the monochromator through the entry slits by an oscillating mirror assembly called alternator. The width of entry slits varies between about 10 and 100μ . After passing through the optical portion of the spectrometer, the radiation passes through the second set of slits, called exit slits (width $10\text{--}100 \mu$), to the detector and then to the analyser. The analyser records per cent transmission of the sample as a function of wavelength or wave number. It should be borne in mind that double-beam instrument only removes the spectral traces of CO_2 and H_2O . Therefore, for very accurate spectroscopic work, the instrument must be flushed thoroughly with some dry inert gas since the very strong absorption energy by CO_2 and H_2O still remains in both beams and reduces their energy.

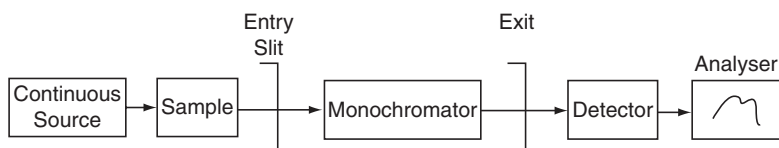


Fig. 3.3 Block diagram of a single-beam spectrometer.

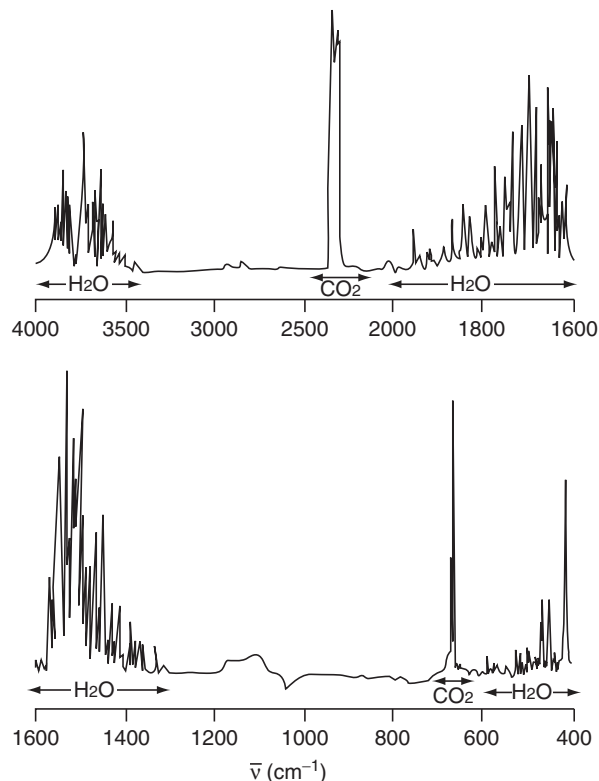


Fig. 3.4 The spectrum of atmospheric water vapour and carbon dioxide.

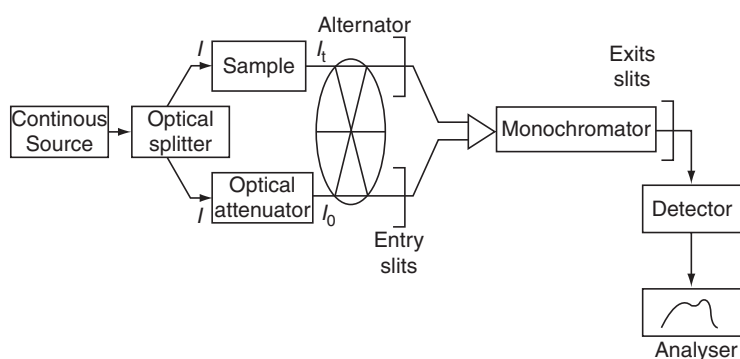


Fig. 3.5 Block diagram of a double beam spectrometer.

3.3.2 Sources

The two most common sources for IR radiations are the Nernst glower and the globar. The *Nernst glower* is a hollow rod of zirconium, yttrium and thorium oxides heated electrically around 1500°C. It gives an intense radiation of up to about 1000 cm⁻¹. Its normal life is several hundred hours. Globars are made from silicon carbide and operate at about 1400°C. They are more stable than Nernst glowers. The radiation emitted approximates that of a black body. Globar life is relatively short and power consumption is relatively high. The other sources are heated nichrome wire, heated alumina tube or Welshbach mantle which is good for below 400 cm⁻¹ and tunable lasers.

The wavelength of any black-body radiation is given by the Planck equation

$$W_{\lambda} = \frac{C_1}{\lambda^5 (e^{C_2/\lambda T} - 1)} \quad (3.1)$$

where W_{λ} is the amount of radiation emitted by the black body per unit surface area, T is the absolute temperature of the black body, λ is the wavelength of the emitted radiation in centimeters, and C_1 and C_2 are the constants; $C_1 = 3.7402 \times 10^{-12}$ watts/cm² and $C_2 = 1.43848$ cm deg⁻¹. The displacement of maximum intensity of emitted radiation with temperature is given by Wien's displacement law

$$\lambda_{\max} T = K \quad (3.2)$$

where the constant, $K = 2897 \mu \text{ deg}^{-1}$ when $\lambda_{\max}$ is in microns. At the lowest temperatures, the maximum lies in the infrared region. That is precisely why infrared radiation is also termed *thermal radiation*.

3.3.3 Monochromators

The polychromatic radiations emitted from or passed through the sample under investigation are dispersed into its constituent wavelengths with the help of monochromators. Prisms of suitable material as well as gratings or a combination of both are used for dispersion purposes. Gratings are especially useful for higher resolution. The suitable prisms along with their spectral ranges are listed in Table 3.1.

Table 3.1 Prism materials and their spectral ranges.

Prism Material	Spectral Range, cm ⁻¹
LiF	4000–1400
NaCl	1700–700
KBr	800–400
CsI	400–250
TlI-TlBr	5000–250
CaF ₂	50000–1200

3.3.4 Detectors

Thermocouples are the most common type of detectors employed. Photoconductive cells, i.e. PbS, PbTe and semiconductor types such as Bolometers and Golay pneumatic detectors, are generally employed.

3.4 SAMPLE PREPARATION AND SAMPLE CELLS

IR spectra are generally recorded in the gaseous, liquid (neat and solution) and solid phases. The most important part is the sample preparation. Any solvent is a chemical compound and will absorb in the IR region. Therefore, the choice of the solvent is decided by the region to be studied. Various solvents and their regions of transparency are known and the solvents employed are CCl₄, CS₂, or CHCl₃. 1 to 5 per cent solution of the compound whose spectrum is to be recorded is prepared in some suitable solvent. The sample cell of some suitable material of thickness 0.1 to 1 mm has been used. A sample whose spectrum is to be recorded should be dried before use since water absorbs at ≈3710 cm⁻¹ and 1630 cm⁻¹. If the compound is not soluble in some suitable solvent suggested then other methods are adopted. Liquid samples are held between plates of suitable window material. The liquid

film thickness varies and its values are 0.025, 0.1 and 0.5 mm. Cells in which path length can be adjusted are also available these days. Suitable gas cells fitted with optical windows are used to record the gaseous spectra. The path length of the gas cells varies from few centimetres to metres. Metal cells are used when spectra of gases are to be studied under high pressure.

Spectra of solids are not recorded because of the problem encountered due to scattering. The important factors in determining the infrared spectra of solids are (i) the differences in the refractive indices of the material under study and of the dispersion medium, and (ii) the dimensions of the individual particles under study. The second effect is especially important in the study of infrared spectra of adsorbed molecules, since excessive scattering by adsorbent causes a large reduction in I_0 value that can be obtained. Also the effect of large particle size is to reduce both the apparent intensity of absorption and resolution of spectrum. This can be demonstrated by recording the spectra of CaCO_3 (Calcite) in KBr discs as a function of particle size. According to Rayleigh, the amount of scattering, S , is related to the wavelength of incident radiation by the expression

$$S \propto \frac{d^3}{\lambda^4}$$

where d is the particle diameter.

Thus, as we move to higher frequencies, the amount of scattering also increases, e.g. surface OD groups ($\sim 2700 \text{ cm}^{-1}$) are preferred over surface OH groups ($\sim 3600 \text{ cm}^{-1}$) for infrared spectral studies. It is to be noted that while discussing the effect of particle size on light scattering it was assumed that the material was embedded in a medium of equal refractive indices which is not possible in practice. However, wherever possible, the material under investigation should be immersed in a liquid or solid whose refractive index is as close as possible to that of the particle under investigation. This reduces scattering and enhances the attainable resolution, e.g. when a pressed disk of silica gel is immersed in a fluorolube oil, the transmittance which initially may be 20 per cent is increased to about 80 per cent. This is because of the effectiveness of oil in reducing the light scattering. The use of such oil in surface studies is avoided since it may contaminate the surface.

It is seen that maximum transmission is obtained when particle size is less than one micron, i.e. less than the wavelength of incident light. As the particle size is increased, a stage may come where the particles become so large that they approach the bulk crystalline material in their absorption properties. The transmittance must go through a minimum. It is because of this effect that materials such as porous glass and silica-alumina gels are so unique in their light-transmitting qualities compared with pressed silica discs containing material of apparently similar fundamental particle size. Therefore, solids are studied in nujol mull which is a saturated paraffin hydrocarbon. The C—H region is lost since nujol absorbs in this region and spectrum of nujol is shown in Fig. 3.6. In that case perfluorinated hydrocarbon, fluorolube is used. Generally one milligram of the solid is homogenised in a drop of the liquid hydrocarbon. In some cases especially, inorganic, polymers, etc., KBr discs are used. The mixture of KBr and solid sample is in the ratio of 1:10 or 1:100 is pressed under pressure of the order of 20,000 lb/in² or $13.7894 \times 10^4 \text{ kN/m}^2$ into an optically acceptable disc using a special mould and a hydraulic press. The use of KBr eliminates the problems encountered in liquid paraffin but a band at 3450 cm^{-1} called K band due to the OH group of traces of water always appears.

Polarised infrared spectra of the sample can be recorded in liquid crystal solvents, provided the background absorption of the liquid crystal solvent does not interfere in the studies. When the absorption bands due to the sample fall outside the region of the liquid crystals, such studies can be carried out easily, e.g. p -(p' -ethoxybenzoxy) phenyl carbonate is a weak absorber in the frequency region $1900\text{--}2800 \text{ cm}^{-1}$ ($\text{OD} < 0.15$). The terminal $\text{C} \equiv \text{O}$ stretching bands usually occur in the region $1900\text{--}2200 \text{ cm}^{-1}$. Hence, this liquid crystal can be used to determine the orientation of $\text{C} \equiv \text{O}$ vibrations.

The major hurdle in the measurement of IR spectra of biologically important molecules is strong absorption due to water in the regions of spectrum that are of interest to the biochemist. However, the aqueous interference could be avoided by the following methods: (i) H_2O may be replaced by D_2O since it does not interfere in the

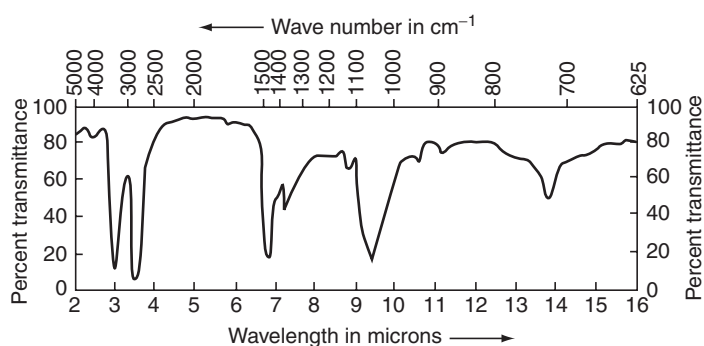


Fig. 3.6 The infrared spectrum of nujol mull.

Table 3.2 Infrared spectra (cm^{-1}) of H_2O and D_2O .

H_2O	D_2O	Assignment
Very broad band with two main maxima and a shoulder (sh) at 25°C		O—X str (ν_s)
3920 sh (0.83)	2900 sh (0.60)	
3490 (62.7)	2540 (59.8)	
3280 (54.4)	2450 (55.2)	
2125(3.23)	1515(1.74)	Association (ν_A)
1645(20.8)	1215(16.1)	X—O—X bend (ν_2)
Broad band between	300 cm^{-1} and 900 cm^{-1}	Libration (ν_L)
Prominent shoulder on	ν_L band at $\sim 190 \text{ cm}^{-1}$, 30°C	Hindered translation (ν_T)

str-stretch. The quantities within parentheses are the values of extinction coefficients (in units of $10^3 \text{ cm}^{-2} \text{ mole}$) at the absorption maximum.

regions of spectrum of biological importance. The IR spectra of H_2O and D_2O are compared in Table 3.2; (ii) evaporation to dryness of an aqueous layer on a disk of AgCl; (iii) formation of a KBr pellet or oil suspension with the dried sample. In addition, cooling of the sample to $\sim -180^\circ\text{C}$ sharpens water absorption bands and allows discrimination of otherwise obscured components. Multiple frustrated internal reflection and refined differential IR spectroscopy may also be employed to record the spectra of biological molecules.

Further, when recording the spectra, compensation should be allowed in the reference beam. A solvent is used in solution work while a plane window of the same thickness as that of the sample beam is put across the reference beam in the case of solid mulls or liquids. The optical windows generally used in recording the spectra in the various IR regions are listed in Table 3.3.

Table 3.3 Optical materials useful in infrared studies.

Material	Useful Range (cm^{-1})	Refractive Index at 0.54μ	Comments
NaCl	>500	1.54	Widely used, cheap and easily worked; must be kept dry, however.
KBr	>310	1.53	Soft and easily scratched. Similar to NaCl, but has greater range. Used as powder for pressed-disc technique.
CsBr	>240	1.69	Easily worked, but harder than other halides. Expensive. Not hygroscopic.
SiO_2	>2500	~ 1.5	Insoluble and easy to work in fused form. Useful for high-temperature work and in the overtone region.
Al_2O_3	>1600	1.77	Has high mechanical strength but is expensive.
MgO	>1200	1.74	Hard and costly. Can be sealed to high expansion glass.
LiF	>1200	1.38	Very useful in the near infrared because of good dispersion, Scratches easily.
CaF_2	>900	1.41	Inert to most chemicals, but tends to be costly. Good from -200°C to 1000°C . Has low solubility in all except NH_4^+ salts.
AgCl	>400	2.07	Soft material. Has low melting point, is corrosive and photosensitive.
MgF_2	>1333	1.38	Strong. Will withstand temperature of 900°C . Chemically durable.
ZnS	>714	2.37	Chemically durable, good up to 800°C . Strong, very useful.
ZnSe	>500	2.89	Useful up to 300°C . Soluble in acids.

3.5 CALIBRATION OF SPECTRA

For authentic IR results, the calibration of spectra, are important. The spectra are calibrated using standards such as methane, water, carbon monoxide, ammonia, indene, toluene and some substituted benzenes. The most commonly used calibrant is polystyrene with bands at 3.509, 6.238 and 11.035 microns.

3.6 BANDWIDTH

The shape of an IR curve may be approximated by a Lorentzian curve of the form

$$\ln \frac{I_0}{I_t} = \frac{a}{(v - v_0)^2 + b^2} \quad (3.3)$$

where $\ln I_0/I_t$ is the optical density, a and b are constants. For maximum optical density, $v = v_0$ at the band centre,

$$\ln \left(\frac{I_0}{I_t} \right)_{v_0} = \frac{a}{b^2} \quad (3.4)$$

Then, bandwidth (recall from Chapter 1) is defined as the full width of the absorption band at half the maximum absorbance or extinction (Fig. 3.7) and is given by

$$\Delta v_{1/2} = 2b \quad (3.5)$$

The above formulae hold if the instrumental inadequacies are ignored. If the slit function is incorporated in Eq. (3.3), a difference is noticed between the observed and theoretical values of $\Delta v_{1/2}$. $\Delta v_{1/2}$ is independent of the number of molecules particularly in an absorption process while peak height is dependent on it. Therefore, it is good to report $\Delta v_{1/2}$ for standard peak heights. Under standardised conditions, $\Delta v_{1/2}$ is as useful as the extinction coefficient in identifying the molecule.

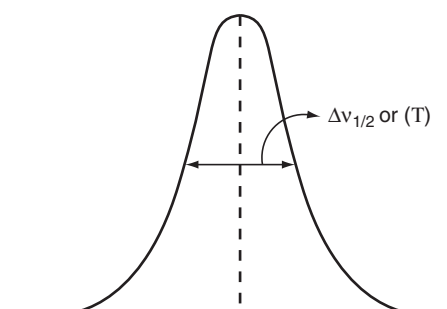


Fig. 3.7 Spectral band having width $\Delta v_{1/2}$ at half height.

3.7 POLARISATION OF INFRARED BANDS

The degree of absorption polarisation ρ_{ir} is measured in term of the ratio of the optical densities (OD)

$$\rho_{ir} = \frac{OD_{\parallel}}{OD_{\perp}} \quad (3.6)$$

where $OD_{\parallel}$ and $OD_{\perp}$ are the optical densities obtained if the polarisation direction of the measuring infrared radiation is oriented parallel and perpendicular to the optic axis or the electric field respectively. $\rho_{ir} > 1$ for parallel while < 1 for perpendicular bands.

3.8 VIBRATIONAL SPECTRA OF DIATOMIC MOLECULES

The observed infrared vibrational spectra of diatomic molecules such as HCl, CO, HBr, HI, NO, etc., consist of a series of equally distant lines but with diminishing intensity. The vibrational spectra may also be obtained theoretically, from mathematical models describing the vibrational motion of the molecules. The three well-known models to predict the vibrational spectra of diatomics, are (i) the classical harmonic vibrational model; (ii) the quantum mechanical harmonic vibrational model, and (iii) the quantum mechanical anharmonic vibrational model. Let us see how these models have been developed and what has led to their failure and success?

3.9 DIATOMIC MOLECULE AS A HARMONIC VIBRATOR

This problem is treated by considering the diatomic molecule to be always in one of its lowest vibrational state at room temperature, and on absorption of radiation, it behaves as a simple harmonic oscillator. Classically, assume the molecule to be a dumb bell and let r_e be the equilibrium distance between the atoms of masses m_1 and m_2 as shown in Fig. 3.8.

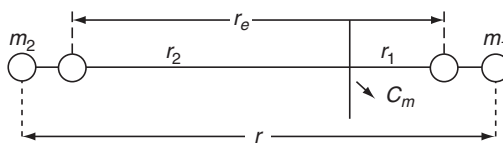


Fig. 3.8 The dumb-bell model of a diatomic molecule.

As a result of absorption, the atoms oscillate about their fixed mean positions and let $\pm \Delta r = r - r_e$ be the amount of bond-distance difference from the equilibrium distance.

The potential energy U of the system is then given by

$$U = \frac{1}{2} k (r - r_e)^2 \quad (3.7)$$

where k is a constant. Equation (3.7) represents a parabola shown in Fig. 3.9. From classical mechanics, the restoring force

$$f = \frac{-d \left[\frac{1}{2} k (r - r_e)^2 \right]}{d(r - r_e)} \quad (3.8)$$

$$f = -k (r - r_e)$$

Thus the constant k is the restoring force required to bring the molecule back to its equilibrium position and is called force constant. It is generally expressed in millidynes/Å.

If Δr_1 and Δr_2 are displacements of the masses from their equilibrium positions then

$$(r_2 - r_1) = r - r_e \text{ Since force = mass} \times \text{acceleration}$$

Therefore,

$$k (r_2 - r_1) = m_1 \frac{d^2 r_1}{dt^2} \text{ and } -k (r_2 - r_1) = \frac{m_2 d^2 r_2}{dt^2} \quad (3.9)$$

The force on m_1 and m_2 is in the positive and negative directions respectively when $r_2 - r_1$ is positive. The solutions of set of equations of motion given in Eq. (3.9) are

$$r_1 = A_1 \cos (2\pi\nu + \phi) \text{ and } r_2 = A_2 \cos (2\pi\nu + \phi) \quad (3.10)$$

These equations describe the simple harmonic motion for both masses, each oscillating with the same frequency ν and phase constant ϕ along the molecular axis, but with different maximum amplitudes A_1 and A_2 .

Combining Eqs (3.9) and (3.10),

$$k(A_2 - A_1) = -m_1 A_1 4\pi^2 \nu^2 \quad (3.11)$$

$$k(A_2 - A_1) = m_2 A_2 4\pi^2 \nu^2$$

Rearranging Eqs (3.11), we get

$$\frac{A_1}{A_2} = \frac{-k}{4\pi^2 m_1 \nu^2 - k} \text{ and } \frac{A_1}{A_2} = \frac{4\pi^2 m_2 \nu^2 - k}{-k} \quad (3.12)$$

Eliminating A_1/A_2 from the set of equations in Eq. (3.12)

$$\nu^4 - \nu^2 \left(\frac{k}{4\pi^2} \right) \left(\frac{m_1 + m_2}{m_1 m_2} \right) = 0$$

or

$$\nu^2 \left[\nu^2 - \frac{k}{4\pi^2} \left(\frac{m_1 + m_2}{m_1 m_2} \right) \right] = 0 \quad (3.13)$$

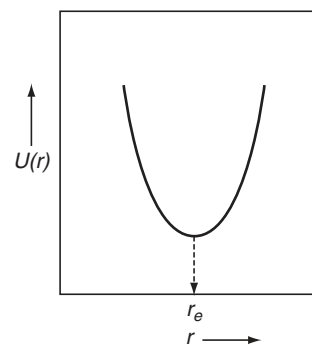


Fig. 3.9 Potential energy internuclear distance curve for simple harmonic oscillator.

Equation (3.13) has two solutions: (i) $v = 0$, i.e. $A_1 = A_2$ from Eq. (3.12) and for any time t , $r_1 = r_2$ from Eq. (3.10). This corresponds to translational motion of masses without vibration in the molecular axis direction.

$$(ii) \quad v = \frac{1}{2\pi} \sqrt{k \left(\frac{1}{m_1} + \frac{1}{m_2} \right)} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu_m}} \quad (3.14)$$

where

$$\mu_m = \frac{m_1 m_2}{m_1 + m_2}$$

It represents the vibration of masses without translational motion. Further, it is evident from Eq. (3.14) that v is independent of amplitude of vibration.

Combining Eq. (3.14) with Eqs (3.12) and (3.10)

$$\frac{A_1}{A_2} = -\frac{m_2}{m_1} \quad (3.15)$$

$$\text{or at any time } \frac{r_1}{r_2} = \frac{-m_2}{m_1}$$

This indicates that centre of gravity of nuclei remains stationary during the vibration. Thus, according to classical model of the harmonic diatomic vibrator, all energies are possible with frequency of vibration

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu_m}}$$

However, this is contrary to the experimental facts. The vibrational spectrum of diatomics is not continuous but has a discrete structure. The discrete character of the vibrational spectrum could be explained on the basis of quantum mechanical treatment of vibrational motion of the diatomics.

Quantum mechanically, the vibrational motion of the diatomic molecule is reduced to the motion of a single particle of reduced mass μ_m . Thus, the total energy of vibration

$$E_{\text{vib}} = \text{Kinetic energy} + \text{Potential energy}$$

$$= \frac{1}{2} \mu_m \frac{d(r - r_e)^2}{dt} + \frac{1}{2} k (r - r_e)^2 \quad (3.16)$$

The Schrödinger equation then takes the form

$$\frac{d^2 \Psi(r)}{dr^2} + \frac{8\pi^2 \mu_m}{h^2} \left[E_v - \frac{1}{2} k (r - r_e)^2 \right] \Psi(r) = 0 \quad (3.17)$$

The solution of Eq. (3.17) gives

[For solution see Appendix 3.1A]

$$E_v = h\nu \left(V + \frac{1}{2} \right) \quad (3.18)$$

$$= hc\omega_e \left(V + \frac{1}{2} \right) \left[\text{or } G = \frac{E_v}{hc} = \omega_e \left(V + \frac{1}{2} \right), \text{cm}^{-1} \right]$$

where

$$\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu_m}} \quad \text{and} \quad \omega_e (\text{cm}^{-1}) = 1303.16 \sqrt{\frac{k (\text{millidynes/\AA})}{\mu_m (\text{amu})}} \quad (3.19)$$

Here ν/ω_e , is the frequency of vibration in Hz/cm^{-1} and V , the vibration quantum number, and can have values 0, 1, 2, 3,....

3.9.1 Spacing Between Two Successive Vibration Levels

From Eq. (3.18), we write

$$E_{V+1} = kc\omega_e \left(V + 1 + \frac{1}{2} \right) \quad (3.20)$$

$$E_V = hc\omega_e \left(V + \frac{1}{2} \right) \quad (\text{Eq. 3.18})$$

From Eqs (3.20) and (3.18) we obtain

$$\Delta d = \frac{E_{V+1} - E_V}{hc} = \omega_e \quad (3.21)$$

Thus, the spacing between successive harmonic levels is always constant.

3.9.2 Selection Rules of Harmonic Vibrator

The selection rules have been deduced quantum mechanically from the solution of the integral.

$$M = \int (\Psi_i^* \hat{M} \Psi_j) d\tau \quad (3.22)$$

and are the following:

- (i) Diatomic molecules must possess permanent dipole moment, i.e. $M \neq 0$.
- (ii) The oscillating dipole moment should not be zero, i.e. $M_i \neq 0$.
- (iii) Only those transitions are permissible for which $\Delta V = \pm 1$.

(3.23)

Let the transition electric-dipole-moment integral be defined as

$$M_{ij} = \int \Psi_i^* \hat{M} \Psi_j d\tau \quad (3.22a)$$

Here, i corresponds to V'' and j corresponds to V' .

For pure rotational motion, M is constant while for vibrational motion it changes because of change in bond length, provided the molecule has a permanent dipole moment. Thus, the dipole moment of a oscillating molecule may be expressed by a Maclaurin series about $Q = 0$ by

$$M_Q = M_{Q=0} + \left(\frac{dM}{dQ} \right)_{Q=0} Q + \frac{1}{2!} \left[\frac{d^2 M}{dQ^2} \right]_{Q=0} Q^2 + \dots \quad (3.22b)$$

where Q is the weighted average Cartesian displacement coordinate Q , i.e. $Q = r - r_e$. Combining Eqs (3.22a) and (3.22b) and ignoring the third and higher terms of Eq. (3.22b), we get

$$\begin{aligned} M_{ij} &= \int \Psi_i^* \left[M_{Q=0} + \left(\frac{dM}{dQ} \right)_{Q=0} Q \right] \Psi_j d\tau \\ &= M_{Q=0} + \int \Psi_i^* \left(\frac{dM}{dQ} \right)_{Q=0} Q \Psi_j d\tau \end{aligned} \quad (3.22c)$$

Equation (3.22c) reveals that there will be no transition if the permanent dipole moment of molecule does not change during a vibration. The second term gives rise to the selection rule $\Delta V = \pm 1$ and is responsible for the fundamental vibrational mode in the IR spectrum of the molecule. The inclusion of higher terms, i.e. $\left(\frac{d^2 M}{dQ^2} \right)_{Q=0} \int \Psi_i^* Q^2 \Psi_j d\tau$,

etc., lead to the selection rules $\Delta V = \pm 2, \pm 3, \dots$. Since $\left(\frac{dM}{dQ} \right)_{Q=0} \gg \left(\frac{d^2 M}{dQ^2} \right)_{Q=0} \gg \left(\frac{d^3 M}{dQ^3} \right)_{Q=0} \dots$, the additional

lines due to overtones and combination bands will in general be very weak, i.e. $I(V=0 \rightarrow 1) \gg I(V=0 \rightarrow 2) \gg I(V=0 \rightarrow 3)$.

3.9.3 Transition Between Two Successive Vibrational Levels

Let V' and V'' be the vibrational quantum numbers of the lower and upper levels respectively and $E_{V'}$ and $E_{V''}$ be the energies of the respective levels. According to Eq. (3.18),

$$E_{V''} = hcw_e(V'' + 1/2) \quad (3.24)$$

$$E_{V'} = hcw_e(V' + 1/2) \quad (3.25)$$

Lumping together Eqs (3.24) and (3.25),

$$\Delta G = \frac{E_{V''} - E_{V'}}{hc} = w_e(V'' - V') \quad (3.26)$$

Applying the selection rule, $\Delta V = +1$ to Eq. (3.26) we obtain

$$\Delta G = w_e$$

Thus, the spectrum of energy values according to Eq. (3.18) is a discrete one, as distinct from the continuous spectrum permitted by classical harmonic oscillator. The difference between energy levels has always a constant value w_e . The other important result from quantum mechanical oscillator is that the lowest energy of vibrational level is $h\nu_0/2$ but not zero. This is called the zero point energy of the harmonic vibrator which means that the molecule is always vibrating.

To summarise, according to harmonic vibrator model of the diatomics, the vibrational spectrum consists of a single band as predicted by the selection rule $\Delta V = \pm 1$. Recalling that the experimentally observed spectrum of diatomics consists of a series of nearly equally spaced lines with diminishing intensity, the discrepancy between the experimental and theoretical spectra may be because of anharmonic nature of the diatomic vibrator.

Problem 3.1: Determine the force constant for CO vibrator provided $w_e = 2170 \text{ cm}^{-1}$.

Solution According to Eq. (3.19),

$$k = \frac{w_e^2}{(1303.16)^2} \times \frac{m_1 m_2}{m_1 + m_2} = \frac{(2170)^2}{(1303.16)^2} \times \frac{12 \times 16}{28} \\ = 19.01 \text{ millidynes/\AA}$$

Problem 3.2: Determine the frequency of OD vibrator if w_e for OH vibrator is 3738 cm^{-1} .

Solution According to Eq. (3.19), we write

$$w_e(OH) = 1303.16 \sqrt{k_{OH} \div \mu_{OH}}$$

$$w_e(OD) = 1303.16 \sqrt{k_{OD} \div \mu_{OD}}$$

Lumping together these expressions,

$$\frac{w_e(OD)}{w_e(OH)} = \sqrt{\frac{\mu_{OH}}{\mu_{OD}}} \quad [\text{since } k_{OH} = k_{OD}]$$

$$w_e(OD) = w_e(OH) \sqrt{\mu_{OH} \div \mu_{OD}}$$

$$= 3738 \sqrt{\frac{16}{17} \times \frac{18}{32}}$$

$$= 2720 \text{ cm}^{-1}$$

3.10 DIATOMIC MOLECULE AS AN ANHARMONIC VIBRATOR

The potential function of an anharmonic vibrator may be represented in several ways.

(i) The potential energy may be described by power series in k ,

$$U(r) = \frac{1}{2} k_1 (r-r_e)^2 + \alpha(r-r_e)^3 + \beta(r-r_e)^4 + \dots \quad (3.27)$$

where α and β are constants, and (ii) the potential energy is more or less adequately described by the Morse potential function. The Morse function gives an idea of the dependence of the potential energy of a molecule on the bond length as shown in Fig. 3.10. It is clear from Fig. 3.10 that $U(\infty) - U(0) = D_e$.

The Morse function for a diatomic vibrator may now be written as

$$U(r) = D_e [1 - \exp(-\alpha_a(r - r_e))]^2 \quad (3.28)$$

where D_e is the depth of potential well, α_a is adjustable constant and by changing α_a , the degree of curvature on the right-hand side of potential well can be changed.

$$D_e = \frac{hcw_e}{4x_e} \quad (3.29)$$

$$\alpha_a = \sqrt{8\pi^2 \mu_m w_e c x_e / h} \quad (3.30)$$

x_e is the anharmonicity constant.

$$U(r) = 0 \text{ at } r = r_e.$$

This is the reference point to measure U according to Eq. (3.28)

The Morse function may also be written as

$$U(r) = D_e \left[e^{-2\alpha_a(r-r_e)} - 2e^{-\alpha_a(r-r_e)} \right] \quad (3.31)$$

$$U(r) = 0 \text{ at } r = \infty$$

This is the reference point to measure U according to Eq. (3.31).

The Schrödinger wave equation for a diatomic anharmonic vibrator may now be written as,

$$\frac{d^2\Psi(\rho)}{d^2\rho} + \frac{8\pi^2 I_e}{h^2} [E_v - U(\rho)] \Psi(\rho) = 0, \quad \left[\rho = \frac{r-r_e}{r} \right] \quad (3.32)$$

The solution of the wave equation (3.32), gives the expression for the energy of the vibrational levels of an anharmonic oscillator. (Appendix 3.2A)

$$E_v = hcw_e \left(V + \frac{1}{2} \right) - hcw_e x_e \left(V + \frac{1}{2} \right)^2 + hcw_e y_e \left(V + \frac{1}{2} \right)^3 + \dots$$

$$G_v = w_e \left(V + \frac{1}{2} \right) - w_e x_e \left(V + \frac{1}{2} \right)^2 + w_e y_e \left(V + \frac{1}{2} \right)^3 + \dots \quad (3.33)$$

where $w_e \gg w_e x_e \gg w_e y_e \dots$, etc. In practice, only the first three terms are within the precession of the spectrometers.

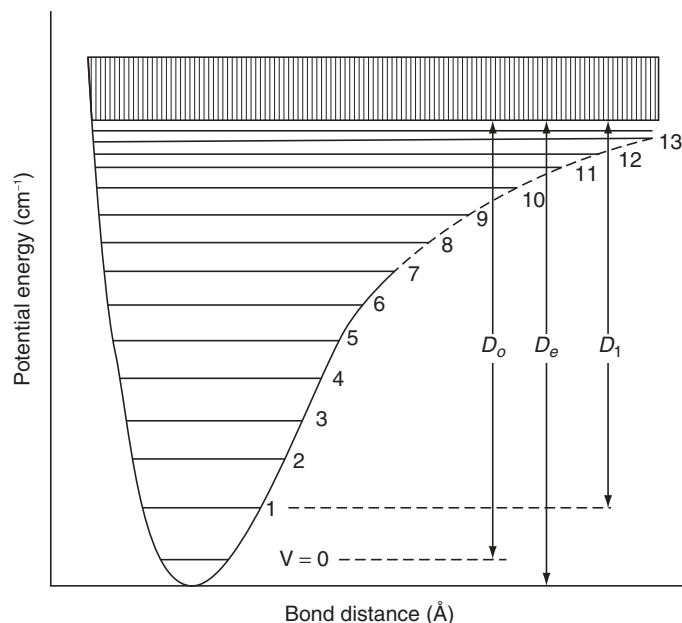


Fig. 3.10 Morse potential energy-internuclear distance curve for an anharmonic oscillator.

For $V = 0$

$$\begin{aligned} E_{V,0} &= \frac{hcw_e}{2} - \frac{hcw_e x_e}{4} + \frac{hcw_e y_e}{8} \\ &= \frac{hcw_e}{2} \left(1 - \frac{x_e}{2} + \frac{y_e}{4} \right) \end{aligned}$$

or

$$G_{V,0} = \frac{w_e}{2} \left(1 - \frac{x_e}{2} + \frac{y_e}{4} \right) \quad (3.34)$$

$E_{V=0}$ is termed as the zero point vibrational energy of the anharmonic vibrator.

Combining Eqs (3.33) and (3.34), we get the expression for the energy levels of the anharmonic oscillator with respect to the zero point energy.

$$G_{V(V,0)} = G_V - G_{V,0} = w_0 V - \omega_0 x_0 V^2 + w_0 y_0 V^3 \quad (3.35)$$

where

$$w_0 = w_e - w_e x_e + \frac{3}{4} w_e y_e + \dots \quad (3.36)$$

$$w_0 x_0 = w_e x_e - \frac{3}{2} w_e y_e + \dots \quad (3.37)$$

$$w_0 y_0 = w_e y_e + \dots \quad (3.38)$$

Problem 3.3 Using the Morse function,

$$U(\rho) = D(1 - e^{-a\rho})^2,$$

where $\rho = \frac{r - r_e}{r}$; prove that in case of a diatomic vibrator $w^2 \sim D$.

Solution Given $U(\rho) = D(1 - e^{-a\rho})^2$,

For small (ρ) (small vibrations), the function can be written as

$$U(\rho) = D \left[1 - \left\{ 1 - a\rho + \frac{(a\rho)^2}{2} - \dots \right\} \right]^2 = D(a\rho)^2 = Da^2 \rho^2$$

Thus, the quasi-elastic force

$$F = -2 Da^2 \rho / r_e = -k r_e \rho$$

where

$$k = 2Da^2 / r_e^2.$$

Comparing $U(\rho)$ and k , we get

$$U(\rho) = Da^2 \rho^2 = \frac{k r_e^2 \rho^2}{2}$$

Solution of Schrödinger wave equation for a diatomic vibrator gives

$$E_V = hcw \left(V + \frac{1}{2} \right)$$

where

$$\omega = \frac{1}{2\pi c} \sqrt{k / \mu_m}$$

Substituting the value of k , we write

$$w = \frac{1}{2\pi c} \sqrt{\frac{2Da^2}{\mu_m r_e^2}} = \frac{a}{2\pi c} \sqrt{2D/I_e}$$

or

$$w^2 = \frac{a^2}{2\pi^2 I_e c^2} D.$$

Since the factor $\frac{a^2}{2\pi^2 I_e c^2}$ is very small, the expression can safely be approximated to

$$w^2 \cong D.$$

The greater the D , the greater should be the vibrational frequency. Experimental observations show that the relationship is qualitatively fulfilled in practically all cases.

3.10.1 Spacing Between Two Adjacent Vibrational Energy Levels

From Eq. (3.33), the energy of the two successive vibrational levels of an anharmonic oscillator may be written as

$$\begin{aligned} E_V &= hcw_e \left(V + \frac{1}{2} \right) - hcw_e x_e \left(V + \frac{1}{2} \right)^2 \\ E_{V+1} &= hcw_e \left(V + \frac{3}{2} \right) - hcw_e x_e \left(V + \frac{3}{2} \right)^2 \end{aligned} \quad (3.39)$$

From Eqs (3.33) and (3.39), we write

$$\Delta d = \frac{E_{V+1} - E_V}{hc} = w_e [1 - 2x_e (V + 1)] \quad (3.40)$$

where Δd is the spacing between the two successive vibrational energy levels.

$$\begin{array}{ccc} \text{For } V & \Delta d & \\ \left. \begin{array}{l} 0 \\ 1 \\ 2 \end{array} \right\} & \left\{ \begin{array}{l} w_e(1 - 2x_e) \\ w_e(1 - 4x_e) \\ w_e(1 - 6x_e) \end{array} \right\} & \end{array} \quad (3.41)$$

Set of Eqs (3.41) indicates that the spacing between two consecutive anharmonic vibrational levels decreases as the vibrational quantum number grows.

3.10.2 Selection Rules

The selection rules worked out in the usual way, to predict the spectrum of real molecules, are (i) $M \neq 0$, (ii) $M_l \neq 0$, and (iii) $\Delta V = \pm 1, \pm 2, \pm 3, \dots, I_{\Delta V=\pm 1} \gg I_{\Delta V=\pm 2} \gg I_{\Delta V=\pm 3}$.

3.10.3 Transition Between Two Adjacent Vibrational Levels

Let V' and V'' be the vibrational quantum numbers of the lower and upper vibrational levels respectively and $E_{V'}$ and $E_{V''}$ be the respective energies. From Eq. (3.33) we may write

$$E_{V'} = hcw_e \left(V' + \frac{1}{2} \right) - hcw_e x_e \left(V' + \frac{1}{2} \right)^2 \quad (3.42)$$

$$E_{V''} = hcw_e \left(V'' + \frac{1}{2} \right) - hcw_e x_e \left(V'' + \frac{1}{2} \right)^2 \quad (3.43)$$

Using Eqs (3.42) and (3.43) we obtain,

$$\begin{aligned}\Delta G &= \frac{E_{V''} - E_{V'}}{hc} \\ &= (V'' - V')[w_e(1 - x_e) - w_e x_e (V'' + V')]\end{aligned}\quad (3.44)$$

Applying selection rule $\Delta V = +1$ we get

$$\Delta V = V'' - V' = +1, V'' = 1 + V'$$

Therefore, for $\Delta V = +1$, $\Delta G = w_e(1 - x_e) - w_e x_e (2V' + 1)$ Consequently for,

$$\left. \begin{array}{lll} V' & \text{Transition} & \Delta G \\ 0 & 0 \rightarrow 1 & w_e(1 - 2x_e) \\ 1 & 1 \rightarrow 2 & w_e(1 - 4x_e) \\ 2 & 2 \rightarrow 3 & w_e(1 - 6x_e) \end{array} \right\} \quad (3.45)$$

Thus, it is evident from the set of Eqs (3.45) that as the vibrational quantum number increases, the anharmonicity also increases as expected. The transitions $1 \rightarrow 2$, $2 \rightarrow 3$,... are observed only at higher temperatures. Therefore, vibrational bands due to such transitions are termed *hot bands*. At higher temperature, the intensity of $0 \rightarrow 1$ transition depletes because under these conditions, the molecules jump to higher levels. However, the band due to $0 \rightarrow 1$ transition will still be more intense as compared to the hot bands. A comparison of Eqs (3.41) and (3.45) suggests that separation between successive energy levels (cm^{-1}) is equal to the transition energy between the corresponding successive energy levels.

For $\Delta V = +2$, $V'' = V' + 2$,

$$\Delta G = 2w_e(1 - x_e) - 4w_e x_e (V' + 1) \quad (3.46)$$

Since $V' = 0, 1, 2, \dots$

Therefore, for $V' = 0$

$$\Delta G_{0 \rightarrow 2} = 2w_e(1 - 3x_e)$$

for $V' = 1$

$$\Delta G_{1 \rightarrow 3} = 2w_e(1 - 5x_e) \quad (3.47)$$

and for $V' = 2$,

$$\Delta G_{2 \rightarrow 4} = 2w_e(1 - 7x_e).$$

The $1 \rightarrow 3$ and $2 \rightarrow 4$ transitions occur only at higher temperatures and are termed as hot overtones. Similarly, we arrive at the following set of equations for $\Delta V = +3$.

$$\begin{aligned}\Delta G_{0 \rightarrow 3} &= 3w_e(1 - 4x_e) \\ \Delta G_{1 \rightarrow 4} &= 3w_e(1 - 6x_e) \\ \Delta G_{2 \rightarrow 5} &= 3w_e(1 - 8x_e)\end{aligned}\quad (3.48)$$

Thus, at room temperature, the following bands are observed in the vibrational spectrum of a diatomic molecule.

$$\bar{\nu}_1 = \Delta G_{0 \rightarrow 1} = w_e(1 - 2x_e)$$

$$\bar{\nu}_2 = \Delta G_{0 \rightarrow 2} = 2w_e(1 - 3x_e) \quad (3.49)$$

$$\bar{\nu}_3 = \Delta G_{0 \rightarrow 3} = 3w_e(1 - 4x_e)$$

Here, $\bar{\nu}_1$, $\bar{\nu}_2$, $\bar{\nu}_3$, are the wave numbers of the fundamental absorption band, first and second overtones respectively. For small values of V , the approximation of harmonic oscillator is quite good and becomes significant at large values of V . Thus, for small values of V , the bands will appear at w_e , $2w_e$, $3w_e$, ... The fundamental band is always intense as compared to overtones and intensity follows the trend, $I_{\Delta V = \pm 1} \gg I_{\Delta V = \pm 2} \gg I_{\Delta V = \pm 3}$.

3.10.4 Determination of Electrical Anharmonicity

The harmonic oscillator model can account for the fundamental vibration that occurs between nonvibrating state and the next vibrationally excited state, but it cannot account for the presence of overtones and combination bands. Overtones and combination bands may be explained by introducing mechanical anharmonicity into the potential energy, i.e. by expanding the potential energy of an anharmonic oscillator about the equilibrium position ($Q = 0$) in the Maclaurin series

$$U_Q = \frac{1}{2!} \left(\frac{d^2 U}{dQ^2} \right)_{Q=0} Q^2 + \frac{1}{3!} \left(\frac{d^3 U}{dQ^3} \right)_{Q=0} Q^3 + \dots \quad (3.50)$$

and in which the energy scale is chosen in such a way that $U_{(0)} = 0$. The quantum mechanics of an anharmonic oscillator has been described in Appendix 3.2 A and it expresses the total energy of the anharmonic oscillator by the expression

$$G_V = w_e \left(V + \frac{1}{2} \right) - w_e x_e \left(V + \frac{1}{2} \right)^2 + w_e y_e \left(V + \frac{1}{2} \right)^3 + \dots \quad (\text{Eq. 3.33})$$

$$G_{V(V,0)} = w_0 V - w_0 x_0 V^2 + w_0 y_0 V^3$$

where w_e is the harmonic oscillator frequency, $w_e x_e$ and $w_e y_e$ are anharmonicity constants, $w_e y_e \ll w_e x_e \ll w_e$.

The net effect of expressing the potential energy of anharmonic oscillator by Eq. (3.50) is that the instantaneous dipole moment, M_Q of an oscillating molecule may be expressed by a Maclaurin series about $Q = 0$ by

$$M_Q = M_{Q=0} + \left(\frac{dM}{dQ} \right)_{Q=0} Q + \frac{1}{2!} \left(\frac{d^2 M}{dQ^2} \right)_{Q=0} Q^2 + \dots \quad (3.51)$$

where Q is the weighted average Cartesian displacement coordinate.

The first term in Eq. (3.51) expresses the permanent dipole moment and is responsible for the pure rotational infrared spectrum only. The second term is responsible for the appearance of vibrational infrared spectrum while the higher terms provide intensities to overtones and combination bands.

The energy difference between two successive vibrational levels V and $V + 1$ is

$$\Delta G \left(V + \frac{1}{2} \right) = G_{(V+1)} - G_{(V)} = G_{(V+1)(V=0)} - G_{(V)(V=0)} \quad (3.52)$$

which because of Eq. (3.33) yields

$$\begin{aligned} \Delta G \left(V + \frac{1}{2} \right) &= w_e \left(V + 1 + \frac{1}{2} \right) - w_e x_e \left(V + 1 + \frac{1}{2} \right)^2 + \dots - w_e \left(V + \frac{1}{2} \right) + w_e x_e \left(V + \frac{1}{2} \right)^2 + \dots \\ &= w_e - 2w_e x_e - 2w_e x_e V \\ &= w_0 - 2w_0 x_0 - 2w_0 x_0 V \end{aligned} \quad (3.53)$$

Similarly, the energy difference between vibrational levels $V + 1$ and $V + 2$ would be

$$\Delta G(V + 3/2) = w_e - 4w_e x_e - 2w_e x_e V \quad (3.54)$$

so that

$$\begin{aligned}\Delta^2 G_{(V+1)} &= \Delta G_{(V+3/2)} - \Delta G_{(V+1/2)} \\ &= -2w_e x_e = -2w_0 x_0\end{aligned}\quad (3.55)$$

However, in most of the cases the frequency of the fundamental and first overtone is available. In such cases the energy corresponding to the lowest vibrational level ($V=0$) is taken as zero so that energy difference between the vibrational levels 0 and V is

$$\Delta G_{\left(V+\frac{1}{2}\right)} = G_{(V)} - G_{(V=0)} = w_e V - w_e x_e V^2 + \dots \quad (3.56)$$

Consequently, the frequency of the fundamental, $G_0(1)$ and first overtone $G_0(2)$ would be expressed by

$$G_0(1) = w_0 - w_0 x_0 \quad (3.57)$$

$$\text{and} \quad G_0(2) = 2w_0 - 4w_0 x_0 \quad (3.58)$$

Hence, both w_0 and $w_0 x_0$ can be obtained from Eqs (3.57) and (3.58) once the experimental values of $G_0(1)$ and $G_0(2)$ are known.

Problem 3.4: The laser Raman and infrared spectra of tribromoacetyl chloride reveal that the position of the C = O fundamental vibration is at 1772 cm^{-1} and that of its first overtone is at 3540 cm^{-1} . Calculate the anharmonicity constants for the C = O stretching frequency.

Solution

$$\text{Here} \quad G_0(1) = 1772 \text{ cm}^{-1}$$

$$\text{and} \quad G_0(2) = 3540 \text{ cm}^{-1}$$

Consequently, Eqs (3.57) and (3.58) yield

$$1772 \text{ cm}^{-1} = w_0 - w_0 x_0$$

$$3540 \text{ cm}^{-1} = 2w_0 - 4w_0 x_0$$

$$\text{Hence, } w_0 = 1774 \text{ cm}^{-1} \text{ and } w_0 x_0 = 2 \text{ cm}^{-1}.$$

Problem 3.5: The low-temperature infrared study of the self-association of thiolacetic acid reveals that the fundamental and the first overtone for a free and associated S—H vibrations appear at 2588 cm^{-1} and 5078 cm^{-1} and at 2530 cm^{-1} and 4910 cm^{-1} , respectively. Calculate the anharmonicity constants for both the free and the associated S—H groups.

Solution For free S—H group, we have

$$G_0(1) = 2588 \text{ cm}^{-1}$$

$$G_0(2) = 5078 \text{ cm}^{-1}$$

From expressions (3.57) and (3.58), we write

$$2588 = w_0 - w_0 x_0$$

$$5078 = 2w_0 - 4w_0 x_0$$

$$\text{Therefore, } w_0 x_0 = 49.5 \text{ cm}^{-1} \text{ and } w_0 = 2637 \text{ cm}^{-1}.$$

Similarly, the constants for associated S—H group have been found to be $w_0 x_0 = 75 \text{ cm}^{-1}$ and $w_0 = 2605 \text{ cm}^{-1}$.

Problem 3.6: Determine the values of anharmonic constants w_0x_0 and w_ex_e from the following infrared spectral data on HCl,

V	0	1	2	3	4
$\bar{\nu}(\text{cm}^{-1})$	0	2885.9	5668.2	8347.4	10923.7

Solution In order to determine w_0x_0 and w_ex_e , the infrared spectral data are arranged as follows.

V	$\bar{\nu}(\text{cm}^{-1})$	$\Delta G(\text{cm}^{-1})$	$-\Delta^2 G(\text{cm}^{-1})$
0	(0)		
1	2885.9	2885.9	103.6
2	5668.2	2782.3	103.1
3	8347.4	2679.2	102.9
4	10923.7	2576.3	

$\Delta^2 G$ is constant within the permissible limits. The average value of $\Delta^2 G = -103.2 \text{ cm}^{-1}$. Using Eq. (3.55)

$$w_ex_e = w_0x_0 = \frac{103.2}{2} = 51.6 \text{ cm}^{-1}$$

The value of w_0 can be obtained either graphically or analytically. Graphically, the intercept of the plot of V against $\Delta G_{V+1/2}$ [Eq. (3.53)] will correspond to w_0 . To determine w_0 analytically, use is made of Eqs (3.57) and (3.58), etc.

$$G_0(1) = w_0 - w_0x_0$$

$$G_0(2) = 2w_0 - 4w_0x_0$$

$$2885.9 = w_0 - 51.6$$

$$5668.2 = 2w_0 - 4 \times 51.6$$

$$w_0(1) = 2937.5 \text{ cm}^{-1}$$

$$w_0(2) = 2937.3 \text{ cm}^{-1}$$

$$w_0 = \frac{w_0(1) + w_0(2)}{2}$$

$$= 2937.4 \text{ cm}^{-1}$$

Therefore, from Eq. (3.36)

$$2937.4 = w_e - 51.6$$

$$w_e = 2989 \text{ cm}^{-1}$$

3.10.5 Maximum Value of Vibrational Quantum Number and Energy

The maximum value of the vibrational quantum number, $V_{\max}$ is calculated from Eq. (3.40) as follows.

$$\Delta d = w_e[1 - 2x_e(V+1)]$$

For the maximum value of quantum number, i.e. $V = V_{\max}$, Δd , the spacing between consecutive levels will tend to zero, i.e. $\Delta d \rightarrow 0$. Consequently,

$$V_{\max} = \frac{1 - 2x_e}{2x_e} \quad (3.59)$$

The distinct nature of the spectrum vanishes and continuous spectrum is obtained.

The vibrational energy of the maximal vibrational quantum level is determined from Eqs (3.59) and (3.33).

$$E_{V, \max} = \frac{hcw_e}{4x_e} (1 - x_e^2)$$

Since $x_e^2 \ll 1$

Therefore,

$$E_{V, \max} = \frac{hcw_e}{4x_e} = D_e \quad (3.60)$$

3.10.6 Bond Energy of Diatomic Molecule

The Bond Energy (BE) is the product of the difference between the vibrational energies on the maximal and zeroth vibrational levels and the Avogadro number, N_A .

Therefore, using Eqs (3.60) and (3.34),

$$\begin{aligned} \text{BE} &= (E_{V, \max} - E_{V, 0})N_A \\ &= \left[\frac{hcw_e}{4x_e} - \frac{hcw_e}{2} \left(1 - \frac{x_e}{2} \right) \right] N_A \\ &= \frac{hcw_e}{4} N_A \left(x_e + \frac{1}{x_e} - 2 \right) \end{aligned} \quad (3.60a)$$

Problem 3.7: (a) Calculate the maximal vibrational quantum number for C1F, if $w_e = 786.15 \times 10^2 \text{ m}^{-1}$.

$$x_e = 7.84 \times 10^{-3} \text{ and } r_e = 1.63 \times 10^{-10} \text{ m}$$

(b) Using the data from part (a) determine the vibrational energy of molecule ClF on the zeroth and maximal vibrational quantum levels. Determine also the bond energy. (c) With the aid of data from part (b), find the vibrational energies of the molecule ClF on the vibrational levels $V = 0, 1, 2, 3, 5, 8, 12, 20, 30$ and 63; (d) Using the data from part (c) compute the minimal and maximal distances between the atoms Cl and F on the vibrational levels $V = 0, 1, 2, 3, 5, 8, 12, 20, 30$ and 63.

Solution (a) According to Eq. (3.59)

$$\begin{aligned} V_{\max} &= \frac{1 - 2x_e}{2x_e} = \frac{1 - 2 \times 7.84 \times 10^{-3}}{2 \times 7.84 \times 10^{-3}} \\ &= \frac{0.9843}{0.01568} = 63 \end{aligned}$$

(b) The maximum value of vibrational energy corresponding to $V_{\max} = 63$ can be determined from Eq. (3.60).

$$E_{V, \max} = \frac{hcw_e}{4x_e} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8 \times 786.15 \times 10^2}{4 \times 7.84 \times 10^{-3}} = 49.786 \times 10^{-20} \text{ J}$$

The zero point vibrational energy is determined from Eq. (3.34).

$$\begin{aligned} E_{V, 0} &= \frac{hcw_e}{2} \left[1 - \frac{x_e}{2} \right] = \frac{6.62 \times 10^{-34} \times 3 \times 10^8 \times 786.15 \times 10^2}{2} \left[1 - \frac{7.84 \times 10^{-3}}{2} \right] \\ &= 0.777 \times 10^{-20} \text{ J} \end{aligned}$$

Therefore, by definition from Eq. (3.60a)

$$\begin{aligned}\text{BE} &= (49.786 - 0.777) \times 10^{-20} \times 6.023 \times 10^{23} \\ &= 295.18 \times 10^3 \text{ J mole}^{-1} = 295.18 \text{ kJ mole}^{-1}\end{aligned}$$

(c) Here

$$w_e = 786.15 \times 10^2 \text{ m}^{-1}$$

$$x_e = 7.84 \times 10^{-3}$$

$$c = 3 \times 10^8 \text{ m/s}$$

$$h = 6.62 \times 10^{-34} \text{ J s}$$

In order to determine the vibrational energies on the different vibrational levels, determine the terms $hc\omega_e$ and $hc\omega_e x_e$.

$$\begin{aligned}hc\omega_e &= 786.15 \times 10^2 \times 3 \times 10^8 \times 6.62 \times 10^{-34} \\ &= 156.12 \times 10^{-22} \text{ J}\end{aligned}$$

$$hc\omega_e x_e = 156.12 \times 10^{-22} \times 7.84 \times 10^{-3} = 1.22 \times 10^{-22} \text{ J}$$

Now by making use of Eq. (3.33), i.e.

$$E_V = \left(V + \frac{1}{2}\right) hc\omega_e - \left(V + \frac{1}{2}\right)^2 hc\omega_e x_e$$

E_V for different values of V have been determined and are listed in Table 3.4.

Now we see from Table 3.4 that as the vibrational quantum number increases the contribution of anharmonicity also increases. Also, we see that for the vibrational quantum numbers 0 and 1, the vibrations are almost harmonic.

(d) Solve Eqs (3.33) and (3.28) together.

$$\left(V + \frac{1}{2}\right) hc\omega_e - \left(V + \frac{1}{2}\right)^2 hc\omega_e x_e = D_e [1 - \exp(\alpha_a(r - r_e))]^2$$

Compute the constants D_e and α_a , using Eqs (3.29) and (3.30), respectively.

Table 3.4 Vibrational energy of CIF vibrator on different vibrational levels.

V	$\left(V + \frac{1}{2}\right) hc\omega_e \times 10^{+22} \text{ J}$	$\left(V + \frac{1}{2}\right)^2 hc\omega_e x_e \times 10^{+22} \text{ J}$	$E_V \times 10^{+22} \text{ J}$
0	78.06	0.3060	77.76
1	234.19	2.75	233.44
2	390.32	7.65	392.67
3	546.45	14.99	531.46
5	858.71	37.02	821.69
8	1327.09	88.43	1231.66
12	1951.61	191.25	1760.36
20	3200.65	514.40	2686.25
30	4761.94	1138.67	3623.27
63	9913.62	4919.34	4994.27

$$D_e = \frac{hcw_e}{4x_e} = \frac{156.12 \times 10^{-22}}{4 \times 7.84 \times 10^{-3}} = 4.97 \times 10^{-19} \text{ J}$$

$$\alpha_a = \sqrt{\frac{8\pi^2 cw_e x_e \mu_m}{h}} = \sqrt{\frac{8 \times (3.14)^2 \times 3 \times 10^8 \times 786.15 \times 10^2 \times 7.84 \times 10^{-3} \times 20.42 \times 10^{-27}}{6.62 \times 10^{-34}}} = 2.1213 \times 10^{10} \text{ m}^{-1}$$

Transform Eq. (3.33) to $1 - e^y = \sqrt{\frac{E_v}{D_e}}$

where $y = -\alpha_a(r - r_e)$.

The values of each factor in the transformed equation are recorded in Table 3.5. In Columns 7 and 8 of Table 3.5,

$$r_1 = r_e - \frac{y_1}{\alpha_a} \text{ and } r_2 = r_e - \frac{y_2}{\alpha_a}$$

are the maximal and minimal distances between the atoms Cl and F on the different vibrational levels respectively.

Table 3.5 Maximal and minimal distances between Cl and F atoms on the different vibrational levels.

V	$\pm(1 - e^y)$	e^{y_1}	e^{y_2}	y_1	y_2	$r_1 \times 10^{10} \text{ m}$	$r_2 \times 10^{10} \text{ m}$
0	0.125	0.8749	1.1251	-0.1336	0.1178	1.6927	1.5745
1	0.216	0.7833	1.2167	-0.2442	0.1961	1.7446	1.5381
2	0.281	0.7189	1.2811	-0.3300	0.2477	1.7851	1.5136
3	0.327	0.6730	1.3270	-0.3960	0.2829	1.8167	1.4971
5	0.406	0.5934	1.4066	-0.5219	0.3412	1.8751	1.4697
8	0.497	0.5022	1.4978	-0.6888	0.4040	1.9539	1.4400
12	0.595	0.4049	1.5951	-0.9041	0.4669	2.0557	1.4103
20	0.735	0.2648	1.7352	-1.3288	0.5511	2.2560	1.3703
30	0.853	0.1462	1.8538	-1.9228	0.6172	2.5337	1.3396
63	1.000	0	2.0		0.6931		1.3033

where $r_1 = r_e - \frac{y_1}{\alpha_a}$, $r_2 = r_e - \frac{y_2}{\alpha_a}$ and $r_e = 1.63 \times 10^{-10} \text{ m}$.

3.10.7 Determination of Dissociation Energy of Diatomics

The dissociation energy of diatomic molecules can be determined from the spectroscopic data by the following three methods:

(i) The values of D_0 and D_e can be determined from the vibration constants of the diatomic molecule, i.e. (Eq. 3.60).

$$D_e = \frac{w_e^2}{4w_e x_e}; D_0 = \frac{w_0^2}{4w_0 x_0}$$

These relations do not give accurate values of D_e and D_0 .

Problem 3.8: Determine the values of D_e and D_0 for FO molecule if

$$w_e = 1060 \text{ cm}^{-1} \text{ and } x_e = 14.6 \times 10^{-3}$$

Solution From Eq. (3.60)

$$D_e = \frac{1060 \times 1060}{4 \times 1060 \times 14.6 \times 10^{-3}} = 18.15 \times 10^3 \text{ cm}^{-1}$$

$$= (18.15 \times 10^3 \text{ cm}^{-1}) \times (3 \times 10^{10} \text{ cm/s}) \times (6.62 \times 10^{-34} \text{ Js}) \times (6.023 \times 10^{23} \text{ mole}^{-1})$$

$$= 2171.12 \times 10^2 \text{ J mole}^{-1} = 217.112 \text{ kJ mole}^{-1}$$

By Eq. (3.36)

$$w_0 = w_e - w_e x_e = 1060 - 1060 \times 14.6 \times 10^{-3} = 1045 \text{ cm}^{-1}$$

Since

$$w_e x_e = w_0 x_0 \text{ (By Eq. 3.37)}$$

Therefore,

$$D_0 = \frac{1045 \times 1045}{4 \times 1045 \times 14.6 \times 10^{-3}} = 17.64 \times 10^3 \text{ cm}^{-1} = 211.018 \text{ kJ mole}^{-1}$$

(ii) *The band convergence method* is the most accurate method since the discrete spectrum is joined by the continuous spectrum. The position of convergence limit corresponds to D_e and D_0 . The method fails if convergence limit is not achieved. In such cases, the Birge–Sponer method is used.

We have already proved that the maximum value of vibrational quantum number is given by

$$V_{\max} = \frac{1 - 2x_e}{2x_e} \quad (\text{Eq. 3.59})$$

The vibrational energy corresponding to $V_{\max}$ will then correspond to D_e as shown earlier.

$$E_{V,\max} = \frac{hcw_e}{4x_e} (1 - x_e^2) \quad (3.60b)$$

$$= \frac{hcw_e}{4x_e} = D_e \quad (3.60c)$$

It is evident from this expression that vibrational energy of a diatomic molecule cannot exceed its dissociation energy.

(iii) *The Birge–Sponer method* gives accurate values of D_0 and D_e if large number of vibrational bands is observed. This method is based on the transition energy between two successive quantum vibration levels.

$$\Delta G = w_e - 2x_e w_e (V+1) \quad (\text{Eq. 3.44})$$

A graph is plotted between $\Delta G \text{ (cm}^{-1}\text{)}$ and V . If the molecule is a Morse oscillator, such a plot will be a straight line. Otherwise it is always curved as shown in Fig. 3.11.

The linear extrapolation to X'_m always overestimates $V_{\max}$ and hence dissociation energy. The curve is extrapolated to meet the X-axis at X_m . This point corresponds to maximum value of vibrational quantum number, i.e. $V_{\max}$, since at this point $\Delta G = 0$. To determine D_e , substitute the value of $V_{\max}$ into the energy expression (3.33) for the vibrational level.

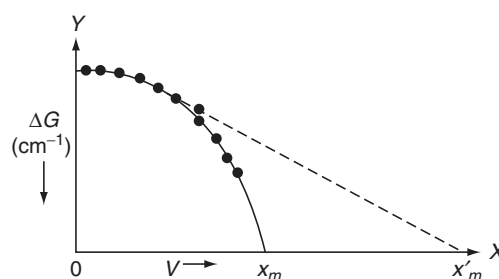


Fig. 3.11 Plot of ΔG versus V .

Problem 3.9: (a) The following data are obtained from the electronic spectrum of ClO radical:

Band V', V''	$\bar{\nu}, \text{cm}^{-1}$	Band V', V''	$\bar{\nu}, \text{cm}^{-1}$
5	33406.6	17	37264.8
6	33844.4	18	37425.1
9	35053.6	19	37561.9
10	35415.8	20	37678.7
11	35754.5	21	37772.9
12	36066.5	22	37849.5
13	36355.8	23	37917.8
14	36619.5	24	37960.0
15	36864.3	25	37997.4
16	37072.8	—	—

(i) Compute the values of the constants w_e, x_e for the upper level and determine the dissociation energy from these constants, and (ii) calculate the value of dissociation energy from Birge–Sponer plot and compare it with the one determined in Part (i).

(b) The average value of Δ^2G as deduced from the electronic spectrum of BrO radical is -16.40 cm^{-1} . ΔG for the first band is 477 cm^{-1} . The value of $V_{\max}$ found from the Birge–Sponer plot is 24. Calculate the energy of the vibrational state for $V_{\max} = 24, w_0, w_e, D_0$ and D_e .

Solution (a) In order to determine the constants w_e, x_e and the dissociation energy, the values of ΔG and Δ^2G mentioned in Eqs (3.53) and (3.55) respectively have been calculated and recorded in the tabular form as follows.

Band	$\bar{\nu}, \text{cm}^{-1}$	$\Delta G, \text{cm}^{-1}$	$-\Delta^2G, \text{cm}^{-1}$
5	33406.6		
6	33844.4	437.8	
9	35053.6	not allowed	
10	35415.8	362.2	23.5
11	35754.5	338.7	26.7
12	36066.5	312.0	22.7
13	36355.8	289.3	25.6
14	36619.5	263.7	18.9
15	36864.3	244.8	36.3
16	37072.8	208.5	16.5
17	37264.8	192.0	31.7
18	37425.1	160.3	23.5
19	37561.9	136.8	20.0
20	37678.7	116.8	22.6
21	37772.9	94.2	17.6
22	37849.5	76.6	8.3
23	37917.8	68.3	26.1
24	37960.0	42.2	4.8
25	37997.4	37.4	

The average value of $-\Delta^2G$ has been found to be 21.65 cm^{-1} . (i) Proceeding as in Problem 3.5, we get

$$w_e x_e = w_0 x_0 = \frac{21.65}{2} = 10.83 \text{ cm}^{-1}$$

With the aid of Eq. (3.53), for $V = 5$, we obtain

$$\Delta G_{(V+1/2)} = w_0 - w_0 x_0 - 2w_0 x_0 \times 5 \text{ or } 437.8 = w_0 - 10.83 - 5 \times 21.66$$

Hence, $w_0 = 546.88 \text{ cm}^{-1}$

From Eq. (3.36) we get

$$546.88 = w_e - 10.83; w_e = 567.71 \text{ cm}^{-1}$$

Since

$$w_e x_e = w_0 x_0, \text{ therefore}$$

$$x_e = 19.07 \times 10^{-3}$$

$$\text{and } D_e = \frac{w_e}{4x_e} = \frac{567.71 \times 10^3}{4 \times 19.07} = 7442.45 \text{ cm}^{-1} = 88.98 \text{ kJ mole}^{-1}$$

(ii) In order to determine dissociation energy from the Birge–Spencer method, the maximum value of vibrational quantum number, i.e. $V_{\max}$, is determined from the plot of ΔG against V shown in the diagram.

Here

$$V_{\max} = 28$$

Using Eq. (3.33) we get

$$\begin{aligned} G(28) &= 567.71 \left(\frac{57}{2} \right) - 10.83 \left(\frac{57}{2} \right)^2 \\ &= 7383.06 \text{ cm}^{-1} \\ D_e &= 88.27 \text{ kJ mole}^{-1} \end{aligned}$$

The error with respect to $G(28)$

$$= \frac{|88.27 - 88.98|}{88.27} \times 100 = 0.79 \text{ per cent}$$

(b) Proceeding as in Problem 3.5

$$w_e x_e = w_0 x_0 = \frac{16.4}{2} = 8.20 \text{ cm}^{-1}$$

From Eq. (3.53), for $V = 1$, we get

$$\begin{aligned} \Delta G_{(V+1/2)} &= G_{(1+1)} - G_{(1)} \\ 477 &= w_e - w_e x_e - 2 w_e x_e \\ &= w_0 - 8.20 - 16.4 \\ w_0 &= 501.6 \text{ cm}^{-1} \end{aligned}$$

So from Eq. (3.36)

$$501 = w_e - 8.2, w_e = 509.8 \text{ cm}^{-1}$$

The energy corresponding to the maximum value of vibrational quantum number, i.e. 24, is determined from Eq. (3.33).

$$G(24) = 509.8 \left(\frac{49}{2} \right) - 8.2 \left(\frac{49}{2} \right)^2 = 7568 \text{ cm}^{-1}$$

$$D_0 = \frac{w_0^2}{4w_0 x_0} = \frac{(501.6)^2}{4 \times 8.2} = 7670.80 \text{ cm}^{-1} = 91.70 \text{ kJ mole}^{-1}$$

$$D_0 = \frac{w_e^2}{4w_e x_e} = \frac{(509.8)^2}{4 \times 8.2} = 7923.65 \text{ cm}^{-1} = 94.73 \text{ kJ mole}^{-1}$$

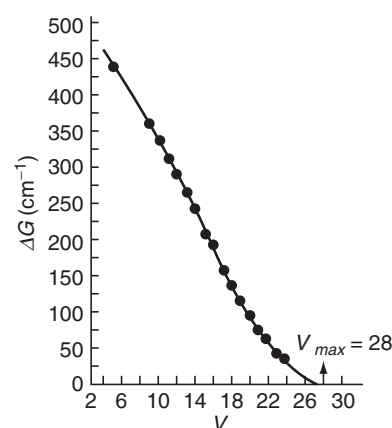


Fig. 3.12 Plot of V against ΔG .

3.11 THE VIBRATIONAL PARTITION FUNCTIONS OF MOLECULES

The vibrational component of partition function for diatomic molecules is expressed as

$$Z_{\text{vib}} = \frac{1}{1 - e^{-hcw_e/\kappa T}} = \frac{1}{1 - e^{-\theta/T}} \quad (3.61)$$

where w_e is the frequency of vibration (in cm^{-1}) and θ is the characteristic temperature,

$$\theta = \left(\frac{hc}{\kappa} \right) w_e = 1.4387 w_e \quad (3.62)$$

The same function for polyatomic molecules is

$$Z_{\text{vib}} = \prod_{i=1}^{3n-6(5)} \frac{1}{1 - e^{-\theta_i/T}} \quad (3.63)$$

Problem 3.10: Calculate the vibrational partition function for NO molecule at 500 K if the frequency of vibration is 1904 cm^{-1} ,

Solution Using Eq. (3.62),

$$\theta = 1.4387 \times 1904 = 2738$$

$$\frac{\theta}{T} = \frac{2738}{500} = 5.476$$

$$\text{From Eq. (3.61)} \quad Z = \frac{1}{1 - e^{-5.476}} = \frac{1}{1 - 0.0041} = 1.0041$$

Similarly, we can determine Z_{vib} for other diatomics such as CO (2170 cm^{-1}), OH (3738 cm^{-1}), FO (1060 cm^{-1}), Cl_2 (560 cm^{-1}) etc.

3.12 POPULATION DISTRIBUTION AMONG THE VARIOUS VIBRATIONAL STATES

The relative population of molecules at a particular temperature on any vibration state is governed by Boltzmann law of the form

$$\frac{N_V}{N_A} = \frac{g_V}{Z_{\text{vib}}} e^{-E_V/\kappa T} \quad (3.64)$$

where g_V , the degree of degeneracy of any vibrational state, is unity. The relative population varies as $e^{-E_V/\kappa T}$ and is shown in Fig. 3.13.

Problem 3.11: Using Boltzmann law for the population distribution among the vibrational states, derive the expression for the maximum value of vibration quantum number.

Solution Lumping together Eqs (3.64) and (3.33),

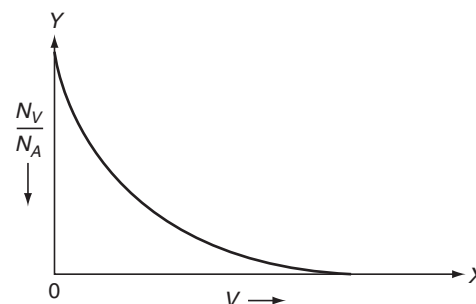


Fig. 3.13 Plot of N_V/N_A versus V .

$$\frac{N_V}{N_A} = \frac{g_V}{Z_{\text{vib}}} \exp [-hc\omega_e(V+1/2) + hc\omega_e x_e(V+1/2)^2]/\kappa T \quad (3.65)$$

Differentiating Eq. (3.65) with respect to V at constant temperature and applying the condition maxima, i.e.

$$\left(\frac{dN_V}{dV} \right)_T = 0$$

we get $-1 + x_e(2V_{\max} + 1) = 0$

$$V_{\max} = \frac{1 - x_e}{2x_e} \quad (3.66)$$

Problem 3.12: Determine the value of $V_{\max}$ for OH, if $w_e = 3738 \text{ cm}^{-1}$, $x_e = 29.7 \times 10^{-3}$.

Solution Using Eq. (3.66)

$$V_{\max} = \frac{1 - 29.7 \times 10^{-3}}{2 \times 29.7 \times 10^{-3}} = 16$$

Problem 3.13: Find the fraction of FO molecules at 1000 K on the vibrational quantum level $V = 1$ and on the zeroth rotational quantum level if $w_e = 1060 \text{ cm}^{-1}$ and $x_e = 14.6 \times 10^{-3}$.

Solution To determine the fraction of FO on the vibrational level $V = 1$, the vibrational partition function needs to be defined first. Using Eqs (3.61) and (3.62)

$$\theta = 1.4387 \times 1060 = 1525$$

$$\frac{\theta}{T} = \frac{1525}{1000} = 1.525$$

$$Z_{\text{vib}} = \frac{1}{1 - e^{-1.525}} = \frac{1}{1 - 0.2176} = 1.278$$

To find the FO molecules on the vibrational level $V = 1$, use Eq. (3.64). To do this, calculate the value of exponent

$$\begin{aligned} \frac{E_V}{kT} &= \frac{1.5hcw_e - 2.25hcw_ex_e}{1.38054 \times 10^{-23} \times 1000} \\ &= \frac{6.62 \times 10^{-34} \times 3 \times 10^8 \times 1060 \times 10^2 (1.5 - 2.25 \times 14.6 \times 10^{-3})}{1.38054 \times 10^{-20}} \\ &= 2.2372 \\ \frac{N_1}{N_A} &= \frac{e^{-2.2372}}{Z_{\text{vib}}} = \frac{0.1067}{0.3646} = 0.2925 \end{aligned}$$

3.13 ROTATION-VIBRATION SPECTRA OF DIATOMIC MOLECULES

The rotational spectra can be observed in pure form while the purely vibrational spectra are possible only in extremely rare and special cases (except liquids and solids). There is a simultaneous change in the vibrational and rotational states of the molecule. The spectrum produced due to change in both forms of energy—vibrational and rotational—of the molecule is known as rotation-vibration spectrum and generally appears in the region $1\text{--}23 \mu$.

3.13.1 Selection Rules

The transition dipole moment integral for a vibrating rotator is defined as

$$M_{v''v'} = \int \Psi_{v''}^*(V'') \hat{M} \Psi_{v'}(V') d\tau$$

where $\Psi_{v'}$ is given by

$$\Psi_{v'} = \Psi_{\text{vib}} \frac{r - r_e}{r} \Psi_{\text{rot}}(\theta, \varphi)$$

and $\hat{M}$ is the transition dipole moment operator and is related to the permanent dipole moment M . The expanded form of the dipole moment integral is

$$M_{V''J''M''_J V'J'M'_J} = \int \Psi_{\text{vib}}^*(V'') \hat{M}(r) \Psi_{\text{vib}}(V') dr \int \int_{\theta, \phi} \Psi_{\text{rot}}(J''M''_J) \hat{M}(\theta, \phi) \Psi_{\text{rot}}(J'M'_J) d\tau$$

where $d\tau = \sin \theta d\theta d\phi$ and M_J 's are the components of J the direction of an external field.

In polar coordinates, we have

$$M(r, \theta, \phi) = M(r) M(\theta, \phi).$$

Neglecting the anharmonicity of M or the vibration, we obtain the following selection rules.

$$\Delta V = \pm 1, \Delta J = \pm 1, \Delta M_J = 0, \pm 1$$

3.13.2 Transition Between two Adjacent Rotation–Vibration States

Ignoring the interaction of vibrations with rotations, the total energy E of a molecule can be written as

$$E = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} \quad (3.67)$$

where E_{elec} , E_{rot} and E_{vib} have their usual meanings. Since the total electronic energy of the molecule does not change in the rotation–vibration spectrum, we can write Eq. (3.67) as

$$E_{V,J} = E_V + E_J \quad (\text{or } T = G_V + F_J \text{ cm}^{-1}) \quad (3.68)$$

or $T_{V,J} = (G_V + F_J)$, cm^{-1} , and is called the vibrating rotator term value. It can be obtained from the solution of Schrödinger wave equation. (For solution see Appendix 3.3A).

$$\bar{\nu} = \frac{E_{V''} - E_{V'}}{hc} + \frac{E_{J''} - E_{J'}}{hc} = \bar{\nu}_{\text{rot}} + \bar{\nu}_{\text{vib}} \quad (3.69)$$

The single and double primes here stand for lower and upper vibrational and rotational states respectively.

If the anharmonicity of diatomic vibration is taken into account and the rotational constant is dependent on the vibrational state of the molecule, the energy of the rotation-vibration levels may be expressed as the minimum in the potential curve.

$$B_V = B_e - \alpha_e \left(V + \frac{1}{2} \right) + \gamma_e \left(V + \frac{1}{2} \right)^2$$

$$D_V = D_e - \beta \left(V + \frac{1}{2} \right) \quad (3.70)$$

Here, B_e and D_e are the rotational constant and dissociation energy respectively for the hypothetical vibrationless molecule and correspond to the position represented by

$$E_{V,J} = hcw_e \left(V + \frac{1}{2} \right) - hcw_e x_e \left(V + \frac{1}{2} \right)^2 + B_V hcJ(J+1)$$

$$G_{V,J} = w_e \left(V + \frac{1}{2} \right) - w_e x_e \left(V + \frac{1}{2} \right)^2 + B_V J(J+1) \quad (3.71)$$

Taking into account the anharmonicity of the oscillations, and assuming rotational constant to be independent of vibrational state, it follows from Eq. (3.71) that for a simultaneous vibrational and rotational transitions from V'' to V' and J'' to J' .

$$\Delta E = E_{V'',J''} - E_{V',J'} \quad (3.72)$$

$$= hcw_e(V'' - V') + B_e hcJ''[(J'' + 1) - J'(J' + 1)]$$

For a fundamental band $V'' - V' = 1$, $J'' - J' = 1$ or $J'' - J' = -1$

Therefore, for $J'' - J' = 1$, we get from Eq. (3.72)

$$\Delta E = hc(w_e + 2B_e J'') \quad (3.73)$$

where $J'' = 1, 2, 3, \dots$ but not zero.

The corresponding frequency is, therefore

$$\bar{\nu} = w_e + 2B_e J'' \quad [\text{R-branch}] \quad (3.74)$$

Similarly for $J'' - J' = -1$, we have

$$\Delta E = hcw_e - 2B_e hc (J' + 1) \quad (3.75)$$

$$\text{and } \bar{\nu} = w_e - 2B_e (J' + 1) \quad [\text{P-branch}] \quad (3.76)$$

where $J' = 0, 1, 2, 3, \dots$

The second term in Eqs (3.74) and (3.76) yields the rotational fine structure of the vibration-rotation band. For definite values of numbers V'' and V' , i.e. w_e = constant, therefore, only the second term is responsible for the fine rotational structure of the band. Hence if $J'' = 1, 2, 3, \dots$ we get a group of lines called positive or R-branch of the band and is characterised by the values $\bar{\nu} > w_e$. Similarly when $J' = 0, 1, 2, 3$, a group of lines called negative or P-branch is observed and is characterised by the values $\bar{\nu} < w_e$. We thus obtain the following lines that form R- and P-branches of the given band.

The lines of R-branch begin with $J' = 0$ while for P-branch $J' = 1$ because $J' = 0$ corresponds to $J'' = J' - 1 = -1$, which has no physical meaning. Thus, the following lines form the P- and R-branches of the given vibration-rotation band.

J'	0	1	2	3
P	—	$w_e - 2B_e$	$w_e - 4B_e$	$w_e - 6B_e$
R	$w_e + 2B_e$	$w_e + 4B_e$	$w_e + 6B_e$	$w_e + 8B_e$

The band, therefore, consists of equally spaced lines with a zero gap w_e , except when the molecule has an angular momentum about the internuclear axis, called the zero line of the band. The distance between adjacent lines is of the order of $2B$. The graphical representation of the expected vibration-rotation spectrum is shown in Fig. 3.14. In reality due to interaction between rotation and vibration, the straight lines become curved.

If anharmonicity and nonrigidity of a diatomic oscillator and rotator respectively are taken into account, then for the P-branch we shall have

$$\bar{\nu} = w_e - 2w_e x_e - 2B_e J - 1.5\alpha_e J(J-1) \quad (3.77)$$

and for the R-branch

$$\bar{\nu} = w_e - 2w_e x_e + 2B_e (J+1) - 1.5\alpha_e (J+1)(J+2) \quad (3.78)$$

The spectrum of HCl under moderate resolution is shown in Fig. 3.15. The spectrum consists of two peaks of different intensities and shapes of the peaks are temperature dependent. The high resolution spectrum suggests that

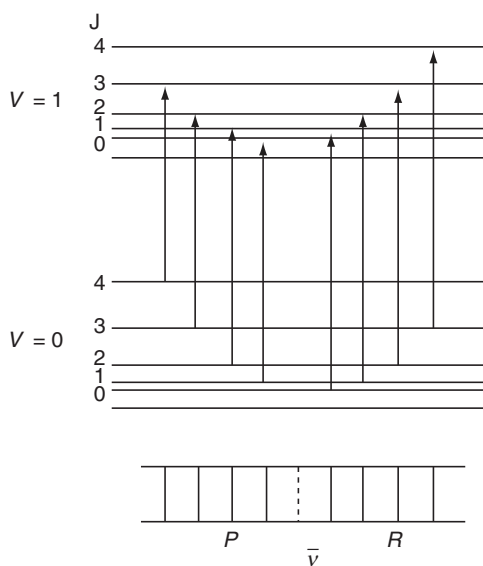


Fig. 3.14 Vibrational-rotational energy level diagram for a diatomic molecule.

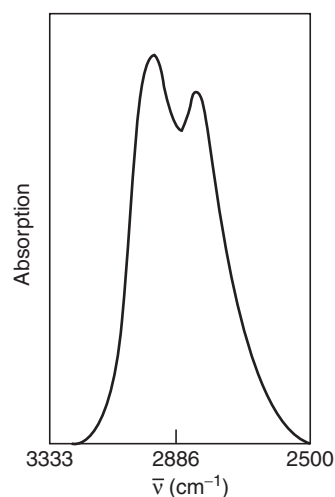


Fig. 3.15 The fundamental absorption band of HCl in the near infrared under moderate dispersion.

these peaks are simply the envelop of a series of approximately equally spaced lines apart from the gap in middle as shown in Fig. 3.16.

Let us now consider transition between the ground and first excited vibrational level of the molecule. Then, from Eq. (2.33) we have

$$E_0 = B_0 J(J+1) \quad (3.79)$$

and

$$E_1 = \bar{\nu}_{\text{vib}} + B_1 J(J+1) \quad (3.80)$$

where B_0 and B_1 have their usual meanings.

Since, for P-branch $J' = J'' + 1$ and for R-branch $J' = J'' + 1$, the energy terms of Eqs (3.79) and (3.80) can be written as

$$\text{For P-branch,} \quad E_0 = J(J+1)B_0 \quad (3.81)$$

$$E_1 = \bar{\nu}_{\text{vib}} + (J-1)JB_1 \quad (3.82)$$

$$\text{For R-branch,} \quad E_0 = J(J+1)B_0 \quad (3.83)$$

$$E_1 = \bar{\nu}_{\text{vib}} + (J+1)(J+2)B_1 \quad (3.84)$$

Thus, the frequencies of the lines in P- and R-branches of the spectrum can be obtained from the expressions

$$P(J) \dots \bar{\nu}_{\text{vib}} + (J-1)JB_1 - J(J+1)B_0 \text{ for } J \geq 1 \quad (3.85)$$

$$\text{and} \quad R(J) \dots \bar{\nu}_{\text{vib}} + (J+1)(J+2)B_1 - J(J+1)B_0 \text{ for } J \geq 0 \quad (3.86)$$

Thus,

$$R(J) - P(J) = 4 \left(J + \frac{1}{2} \right) B_1 \quad (3.87)$$

and similarly we can deduce

$$R(J-1) - P(J+1) = 4 \left(J + \frac{1}{2} \right) B_0 \quad (3.88)$$

$$\text{and} \quad P(J) + R(J-1) = 2 \bar{\nu}_{\text{vib}} - 2(B_0 - B_1) J^2 \quad (3.89)$$

B_1 and B_0 can be obtained from Eqs (3.87) and (3.88) respectively and hence the corresponding moments of inertia, i.e. I and I_0 .

The value of $\bar{\nu}_{\text{vib}}$ is determined graphically by means of Eq. (3.89). The plot of $P(J) + R(J-1)$ versus J^2 will yield a straight line with intercept $= 2 \bar{\nu}_{\text{vib}}$ and slope $= -2(B_0 - B_1)$. The value of $\bar{\nu}_{\text{vib}}$ can thus be evaluated from the intercept.

The internuclear distance (r_e) is determined from the relation

$$I = \mu_m r_e^2$$

and force constant from

$$w_e = 1303.16 \sqrt{k / \mu_m}$$

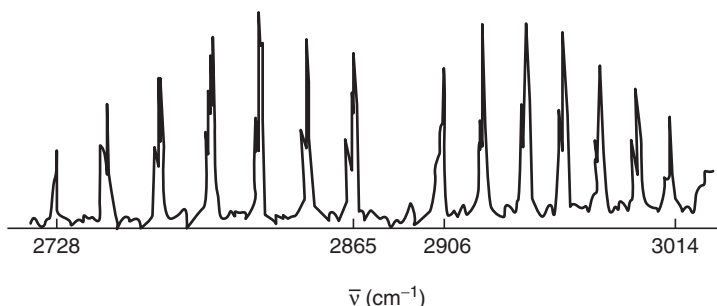


Fig. 3.16 High-resolution spectrum of the fundamental vibrational band of HCl showing rotational fine structure and isotopic splitting due to $H^{35}\text{Cl}$ and $H^{37}\text{Cl}$.

Problem 3.14: Calculate the number of absorption maxima in the purely rotational spectrum of CO.

$$w_e = 2170 \text{ cm}^{-1}, x_e = 6.11 \times 10^{-3}, B_e = 1.931 \text{ cm}^{-1}.$$

Solution Using Eq. (3.49), the wave number of fundamental band of CO is

$$\begin{aligned}\bar{\nu} &= w_e(1-2x_e) = 2170(1 - 0.01222) \\ &= 2143 \text{ cm}^{-1}\end{aligned}$$

The rotational quantum number of maxima in the pure rotational spectrum with wave number $\bar{\nu} = 2143 \text{ cm}^{-1}$, is

$$\bar{\nu} = 2B_e(J+1), 2143 = 2 \times 1.931(J+1), J = 554$$

Problem 3.15: The wave numbers of the lines in the P-branch of the rotation-vibration spectrum of methane are 3032.30, 3043.15, 3054.00, 3064.85 and 3075.70 cm^{-1} . Determine the moment of inertia and bond distance of methane.

Solution The average value of spacing between the successive lines in the P-branch of the rotation-vibration spectra of methane is 10.85 cm^{-1} , i.e.

$$2B = 10.85 \text{ cm}^{-1}$$

or

$$B = 5.42 \text{ cm}^{-1}$$

Using Eq. (2.34)

$$I = \frac{16.8575}{5.42} = 3.11 \text{ au}$$

From Eqs (2.17) and (2.18)

$$r_1 = \sqrt{3.11} = 1.763 \text{ Å}$$

$$r_2 = \sqrt{3/8} r_1 = 1.079 \text{ Å}$$

Thus, C—H bond length of CH_4 is 1.079 Å. The literature value is of the order of 1.09 Å.

Problem 3.16: Determine the wave numbers of the first three lines in the P- and R-branches of the rotation-vibration absorption spectrum of ClF if $w_e = 786.15 \text{ cm}^{-1}$; $x_e = 7.84 \times 10^{-3}$, $B_e = 0.516 \text{ cm}^{-1}$.

Solution The wave numbers of P- and R-branches are calculated from Eqs (3.77) and (3.78), respectively.

$$\bar{\nu} = w_e - 2w_ex_e - 2B_eJ - 1.5\alpha_e(J-1)J$$

$$\bar{\nu} = w_e - 2w_ex_e + 2B_e(J+1) - 1.5\alpha_e(J+1)(J+2)$$

$$w_e - 2w_ex_e = 786.15 - 2 \times 786.15 \times 7.84 \times 10^{-3} = 773.83 \text{ cm}^{-1}$$

Ignoring the contribution of α_e , the wave numbers for the first five levels are recorded in the tabular form as follows.

<i>J</i>	<i>P-branch</i>		<i>R-branch</i>	
	$2B_eJ, \text{cm}^{-1}$	$\bar{\nu}, \text{cm}^{-1}$	$2B_e(J+1), \text{cm}^{-1}$	$\bar{\nu}, \text{cm}^{-1}$
0	—	—	1.032	774.862
1	1.032	772.798	2.064	775.894
2	2.064	771.766	3.096	776.926
3	3.096	770.734	4.128	777.958
4	4.128	769.702	5.160	778.990
5	5.160	768.670	6.192	780.022

Problem 3.17: The frequencies (in cm^{-1}) of HI lines arranged in order of their magnitudes, starting with the highest value in the region $2200\text{--}2300\text{ cm}^{-1}$ are 2117.7, 2132.7, 2147.5, 2161.7, 2176.7, 2176.0, 2190.0, 2203.6, 2216.7, 2242.2, 2254.3, 2266.1, 2277.5 and 2288.5. Calculate the moment of inertia, internuclear distance and bond strength of HI.

Solution The division of the branches on the basis of gap between the lines at 2216.7 and 2242.2 cm^{-1} is as follows.

J	$R(J), \text{cm}^{-1}$	$P(J), \text{cm}^{-1}$
0	2242.2	—
1	2254.3	2216.7
2	2266.1	2203.6
3	2277.5	2190.0
4	2288.5	2176.0
5	—	2161.7
6	—	2147.5
7	—	2132.7
8	—	2117.7

The values of a_0 , b_0 and c_0 are calculated from Eqs (3.87), (3.88) and (3.89) in order to determine B_1 , B_0 and $\bar{\nu}_{\text{vib}}$,

where
$$a_0 = \frac{R(J) - P(J)}{\left(J + \frac{1}{2}\right)}; \quad b_0 = \frac{R(J-1) - P(J+1)}{\left(J + \frac{1}{2}\right)}; \quad \text{and} \quad c_0 = P(J) + R(J-1)$$

The calculated values of B_1 and B_0 , a_0 , b_0 and c_0 (in cm^{-1}) are

J	a_0	B_1	b_0	B_0	c_0
1	25.06	6.27	25.73	6.43	4458.9
2	25.00	6.25	25.72	6.43	4457.9
3	25.00	6.25	25.74	6.44	4456.1
4	25.00	6.25	25.73	6.43	4453.6
5	—	—	25.64	6.41	4450.2

The difference in the values of B_0 and B_1 is due to centrifugal stretching. Taking $B_0 = 6.43$ and $B_1 = 6.26\text{ cm}^{-1}$, we get

$$I_0 = \frac{h}{8\pi^2 c B_0} = \frac{6.624 \times 10^{-27} (\text{g cm}^2 \text{s})}{8\pi^2 \times 2.998 \times 10^{10} (\text{cm s}^{-1}) \times 6.43 (\text{cm}^{-1})} = 4.36 \times 10^{-40} \text{ g cm}^2 = 2.625 \text{ au}$$

and

$$I_1 = \frac{h}{8\pi^2 c B_1} = \frac{6.624 \times 10^{-27} (\text{g cm}^2 \text{s})}{8\pi^2 \times 2.998 \times 10^{10} (\text{cm s}^{-1}) \times 6.26 (\text{cm}^{-1})} = 4.48 \times 10^{-40} \text{ g cm}^2 = 2.698 \text{ au}$$

Then plot between $P(J) + R(J-1) = c_0$ and J^2 is shown in Fig. 3.17.

The intercept at $J = 0$ is 4459.3 cm^{-1} . From the intercept we get

$$\bar{\nu}_{\text{vib}} = \frac{1}{2} \times 4459.3 = 2229.7\text{ cm}^{-1}$$

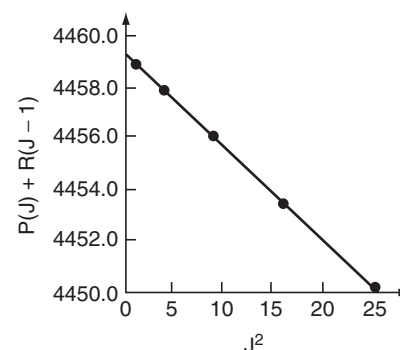


Fig. 3.17 The fundamental vibrational frequency of HI.

The bond lengths in both the states are determined from the expression $I = \mu_m r^2$ as follow.

We know $m_H = 1.663 \times 10^{-24} \text{ g} = 1 \text{ amu}$

and $m_I = 126.92 \times 1.663 \times 10^{-24} \text{ g} = 126.92 \text{ amu}$

Hence, $\mu_{HI} = 1.6486 \times 10^{-24} \text{ g} = 0.99218 \text{ amu}$

Thus, from

$$I_0 = \mu_m r_0^2$$

$$2.625 = 0.99218 r_0^2$$

$$r_0 = 1.63 \text{ \AA}$$

and

$$I_1 = \mu_m r_1^2$$

$$2.698 = 0.99218 r_1^2$$

$$r_1 = 1.65 \text{ \AA}$$

Force constant is evaluated from Eq. (3.19).

Since $\bar{\nu}_{vib} = (1 - 2x_e)w_e$, where

$$x_e = 0.0172 \text{ and } \bar{\nu}_{vib} = 2229.7 \text{ cm}^{-1}$$

Therefore,

$$w_e = \frac{2229.7}{(1 - 2 \times 0.0172)} = 2309 \text{ cm}^{-1}$$

and

$$2309.1 = 1303.16 \sqrt{\frac{k}{0.99218}}$$

Therefore,

$$k = \left(\frac{2309.1}{1303.16} \right)^2 \times (0.99218) = 3.12 \text{ millidynes/\AA}$$

3.13.3 Intensity Distribution in Rotation–Vibration Absorption Spectrum

The maxima in the rotation–vibration absorption spectra of diatomics are because of intensity distribution of rotational lines. The maxima can be determined from population distribution among the rotational levels and the probabilities of appropriate transitions between the levels.

Recall from Chapter 2 that the relative population among the rotational levels is governed by the Boltzmann law of the form

$$\frac{N_J}{N_A} = \frac{(2J+1) e^{-B_e h c J(J+1)/kT}}{\sigma Z_{rot}} \quad (3.90)$$

The intensity of the absorption line is measured in terms of its absorption coefficient,

$$A_v = A_v^0 N_J \quad (3.91)$$

where A_v^0 is a constant proportional to the probability of the appropriate transition. Combination of Eqs (3.90) and (3.91) yields

$$A_v = A_v^0 N_J = A_v^0 \frac{2J+1}{\sigma} \frac{e^{-B_e h c J(J+1)/kT}}{Z_{rot}} N_A \quad (3.92)$$

The relative probabilities in which we are mainly interested can easily be worked out in case of the terms $^1\Sigma$. In this case two transitions, $J \rightarrow J+1$ with probability P_+ and $J \rightarrow J-1$ with probability P_- except for $J=0$ are possible.

The total probability due to these two transitions may be expressed as

$$P_0 = P_+ + P_- \quad (3.93)$$

Theoretically, P_0 remains constant within the limits of a given band.

The relative probabilities of transitions are expressed in terms of intensity factor; and is determined from the equality;

$$iP_0 = (2J + 1)P \quad (3.94)$$

It follows from Eq. (3.94) that

$$\sum i = i_+ + i_- = 2J + 1 \quad (3.95)$$

Combining Eqs (3.92) and (3.95), we get

$$A_v \sim \frac{1}{\sigma} \frac{e^{-B_e hc J(J+1)/\kappa T}}{Z_{rot}} i N_A \quad (3.96)$$

$J' - J''$ and $J'' - J'$ belong to the same value of intensity factors because J'' and J' enter symmetrically into the expression of the appropriate quasi-moments. Due to this reason, we must assign intensity factors to the transitions. The assigned values to different transitions are as follows:

Transition	Intensity Factor
$0 \rightarrow 1', 1' \rightarrow 0$	$i(0) = i_+(0) = 1$ (i_- in this case is zero)
$1 \rightarrow 0', 0' \rightarrow 1$	$i(1) = i_-(1) = 1$
$[1 \rightarrow 2]$ is also possible in this case from $J = 1$	$[i_+(1) = 3 - 1 = 2]$
$2 \rightarrow 1'$	$i_-(2) = 2$
$2 \rightarrow 3', 3 \rightarrow 2'$	$i_+(2) = i_-(3) = 5 - 2 = 3$

From the above data, the general expressions deduced for the intensity factors of the lines belonging to the P- and R-branches of the band are

$$P: i_-(J) = J \quad (3.97)$$

$$R: i_+(J) = J + 1$$

Taking advantage of Eqs (3.97) we can, from expression (3.96), find the value of J and consequently, the frequency (or wavelength) to which at the given temperature, there corresponds a maximum of intensity in each branch of the band.

The following conditions of maxima have been deduced from Eq. (3.96)

$$\left(\frac{di}{dJ} \right)_T = i(2J + 1) \frac{B_e hc}{\kappa T} \quad (3.98)$$

which for the R- and P-branches will be written in the form

$$\text{R-branch: } 2J_+^2 + 3J_+ + 1 = \frac{\kappa T}{B_e hc} \quad (3.99)$$

and

$$\text{P-branch: } 2J_-^2 + J_- = \frac{\kappa T}{B_e hc} \quad (3.100)$$

Assuming that at room and higher temperature $B_e hc/\kappa T \ll 2$, and solving Eqs (3.99) and (3.100) for J_+ and J_- respectively, we arrive at the following expressions:

$$J_+ + J_- + 1 = \sqrt{\frac{2\kappa T}{B_e hc}} \quad (3.101)$$

For different molecules at room temperature, the value of $B_e hc/\kappa T$ lies in the range of 0.1 – 0.001.

Solution of Eqs (3.99) and (3.100) gives the values of J_+ and J_- that correspond to the maximum intensity of the line in the R- and P-branches of the band, respectively. From these values we can find the frequencies ν_+ and ν_- that correspond to the maximum intensity.

From Eqs (3.74) and (3.76), we write

$$\nu_+ = \bar{\nu}_{vib} + 2B_e(J_+ + 1) \quad (3.102)$$

$$\nu_- = \bar{\nu}_{vib} - 2B_e J_- \quad (3.103)$$

$$\text{Thus,} \quad \Delta\nu_{\max} = \nu_+ - \nu_- = 2B_e(J_+ + J_- + 1) \quad (3.104)$$

where $\Delta\nu_{\max}$ is the distance between maxima.

Combining Eqs (3.301) and (3.104)

$$\Delta\nu_{\max} = 2B_e \sqrt{\frac{2\kappa T}{B_e h c}} = \sqrt{\frac{8B_e \kappa T}{h c}} \quad (3.105)$$

$$\text{Since} \quad B_e = \frac{h}{8\pi^2 I_e c} \quad (\text{From Chapter 2})$$

$$\text{Therefore,} \quad \Delta\nu_{\max} = \frac{1}{\pi c} \sqrt{\frac{\kappa T}{I_e}} \quad (3.106)$$

Using Eq. (3.106), we can determine the moment of inertia of a molecule (I_e) from the distance between the maxima of the bands.

Bjerrum also proposed an identical formula to determine moment of inertia from $\Delta\nu_{\max}$.

$$I_e = \frac{\kappa T}{(\pi c \Delta\nu_{\max})^2}$$

Due to this reason, the bands with a double maximum in rotation–vibration spectra of diatomics are called Bjerrum doublets. Since $\Delta\nu_{\max}$ cannot be measured very accurately, the accuracy of determination of moment of inertia by this method is very low. However, we can have a tentative value of moment of inertia by this method without analysing the fine structure of the bands.

Problem 3.18: The observed distance between the maxima in the P- and R-branches of the rotation-vibration spectrum for the $\lambda = 3.5\mu$. (2857 cm^{-1}) band of HCl is 125.19 cm^{-1} (0.15μ). Calculate the moment of inertia of HCl at 273 K and compare it with the literature value.

Solution Using Eq. (3.106)

$$I_e = \frac{8.3142 \times 10^{23} (\text{amu } \dot{A}^2 \text{ s}^{-2} \text{ deg}^{-1}) \times 273 \text{ K}}{\left[3.14 \times 125.19 (\text{cm}^{-1}) \times 3 \times 10^{10} (\text{cm} / \text{s}) \right]^2} = 1.63 \text{ lau} = 2.71 \times 10^{-46} \text{ kg}^2$$

This value of moment of inertia is in agreement with the literature value, i.e. $2.71 \times 10^{-46} \text{ kg}^2$.

Problem 3.19: (a) Predict the wave numbers of the lines with maximum intensities at 500 K in the P- and R-branches of the rotation-vibration spectrum of HI. $w_e = 2309.01 \text{ cm}^{-1}$, $x_e = 17.2 \times 10^{-3}$ and $B_e = 65.11 \text{ cm}^{-1}$. (b) Using the data from Part (a), determine the moment of inertia of HI and compare it with the literature value.

Solution (a) In order to determine the wave numbers of the lines with maximum intensities, $J_{\max}^{s'}$ for the P- and R-branches need to be defined.

To define J_+ and J_- from Eqs (3.99) and (3.100) respectively, let us first calculate the value

$$\frac{\kappa T}{B_e h c} = \frac{1.3805 \times 10^{-23} \times 500}{65.11 \times 6.6252 \times 10^{-34} \times 3 \times 10^{10}} = 5.33$$

Substituting the value of $\kappa T/B_e hc$ in Eqs (3.99) and (3.100), we get

$$2J_+^2 + 3J_+ - 4.33 = 0$$

$$2J_-^2 + J_- - 5.33 = 0$$

Solution of these quadratics results in

$$J_+ = 1$$

$$J_- = 1$$

Consequently, from Eqs (3.102) and (3.103)

$$\nu_+ = 2309.01 + 2 \times 65.11(1+1) = 2569.44 \text{ cm}^{-1}$$

$$\nu_- = 2309.01 - 2 \times 65.11 \times 1 = 2188.79 \text{ cm}^{-1}$$

$$\therefore \Delta\nu_{\max} = (2569.44 - 2188.79) = 380.65 \text{ cm}^{-1}$$

(b) The tentative value of

$$I_e = \frac{8.314 \times 10^{23} \times 500}{[3.14 \times 3 \times 10^{10} \times 380.65]^2} = 3.230 \text{ au}$$

The value of I_e from $B_e = 2.59 \text{ au}$.

Molecular constants of some diatomic molecules are given in Appendix 3.4A and the reciprocal table for the conversion of microns (μ) to wave numbers (cm^{-1}) is given in Appendix 3.5A.

3.14 NATURE AND NUMBER OF VIBRATIONAL MOTIONS IN POLYATOMIC MOLECULES

Atoms in a molecule are bound together through chemical bonds and oscillate about their mean positions which results in the change of molecular shape. Depending upon these type of motions of atoms in molecules relative to each other, different-natured vibrations result, e.g. in a diatomic molecule (say HCl), only one type of vibrational motion exists while in linear and bent triatomic molecules (say CO_2 and H_2O) additional vibrations are possible as shown in Fig. 3.18. Thus, it is evident from Fig. 3.18 that in polyatomic molecules there are several ways in which the molecules may vibrate. However, the number of vibrations, in which each atom vibrates about its equilibrium position with the same frequency but with different amplitude and motions of all atoms are in phase called

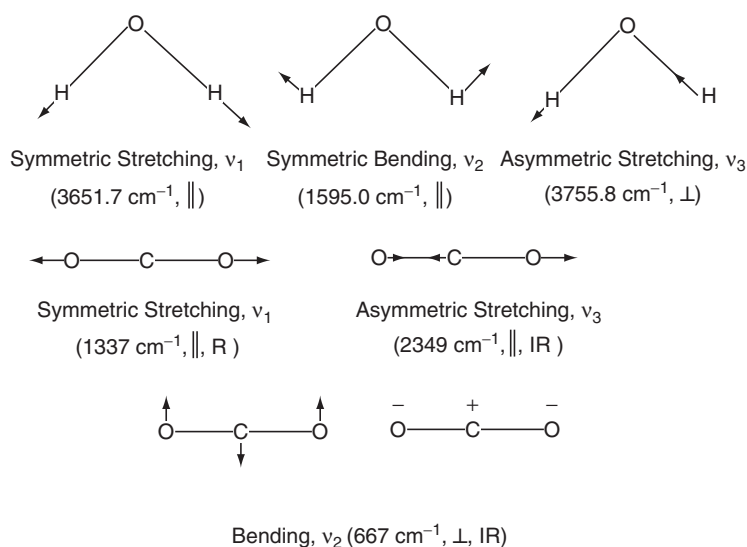


Fig. 3.18 Normal modes of vibration of (a) water molecule, and (b) the carbon dioxide molecule; (+) and (–) signify displacements in and out of the plane of the paper.

fundamental or normal modes of vibration, are fixed. When two atoms move in opposite directions, a stretching or valence vibration results while their movement at an angle results in bending vibration. The various types of stretching and bending vibrational modes are listed in Table 3.6.

Any molecule thus may have different set of frequencies each of which may cause IR absorption. If a nonlinear molecule has n atoms, it has $3n$ total degrees of freedom of which 3 are translations and 3 are rotations and the remaining $3n - 6$ are vibrational degrees of freedom. However, in case of linear molecules the number of vibrational modes will be $3n - 5$ since the rotation about molecular axis does not displace any nuclei which results in only 2 rotational degrees of freedom. Thus $n - 1$ and $2n - 5$ will be the number of stretching and bending vibrations respectively in nonlinear molecules and $n - 1$ and $2n - 4$ in linear molecules. The three translations along the three coordinate axes or rotations about two or three suitable axes are also termed as null or non-genuine vibrations because there is no restoring force for these motions, the vibrational frequency is zero.

Table 3.6 Various types of stretching and bending vibrational modes in polyatomic molecules.

Fundamental Stretching Vibration	ν_{st}	
Symmetric Stretching Vibration	ν_{sym}	
Asymmetric Stretching Vibration	ν_{asym}	
In-Plane Bending Vibration	δ_b	
Out-of-Plane Bending Vibration	γ_b	
Symmetric Bending Vibration	b_s	
Asymmetric Bending Vibration	b_a	
In-Plane Rocking Vibration	ρ_r	
Out-of-Plane Wagging Vibration	χ_w	
Twisting Vibration	τ_t	
Ring Deformation in Plane	d	
Ring Deformation Out-of-Plane	d	

It should be noted that in symmetric molecules such as CO_2 , C_2H_2 , CH_4 , CCl_4 , etc., certain frequencies coincide due to which the total number of different frequencies observed is less than the expected from the formula $3n - 5$ or $3n - 6$. The frequencies which coincide with one another vibrate in mutually perpendicular planes and the vibration corresponding to the observed frequency is said to be doubly degenerate, e.g. in case of CO_2 , the coincidence frequencies are the two identical frequencies that correspond to the vibrating ν_2 of the molecule in two mutually perpendicular planes. Triply degenerate vibrations can also occur in some molecules.

Further, in polyatomic except diatomic molecules, the fundamental vibrations are slightly anharmonic due to their delocalisation effect but their components are fundamental and consisting of simple integral multiples of the fundamental vibrational frequency called overtones are harmonic. Thus, overtones corresponding to $\Delta V = \pm 2, \pm 3, \dots$ are possible for each normal mode. The two or more vibrational normal modes may also combine to give combination (sum or difference) tones, e.g. the normal frequencies ν_1 and ν_2 may give $\nu_1 + \nu_2$, $\nu_1 + 2\nu_2$ and $\nu_1 - \nu_2$, etc., combination bands. Therefore, a molecule which vibrates anharmonically causes a dipole moment to oscillate with harmonic frequencies and their overtones and combination tones. It is, therefore, possible for molecules to absorb radiation in the over- and combination-tones region also. This results in the appearance of additional bands in the IR spectra. The intensity of these bands is weak in comparison to fundamental bands and depends upon the amount of anharmonicity in the molecule, e.g. the intensity ratio of carbonyl normal mode to its first overtone is of the order of 100/1.

The vibrational transitions in polyatomic molecules are generally abbreviated as follows: For fundamental bands all $V_i = 0$ except one which is equal to unity, e.g. $V(0, 0, 0, \dots) \rightarrow V(1, 0, 0, \dots)$. In case of overtone transitions all $V_i = 0$ except one which is greater than unity, e.g. $V(0, 0, 0, \dots) \rightarrow V(0, 2, 0, \dots)$, while for combination bands, various combinations of V_i exists, e.g. $V(0, 0, 0, \dots) \rightarrow V(0, 1, 1, \dots)$, etc.

3.14.1 Fermi Resonance

Sometimes it so happens that the energies of the different normal vibrational modes or combinations of vibrations of polyatomic molecule coincides closely with one another. This characteristic feature of the vibrational modes of molecules is known as *accidental degeneracy*. Depending upon the type of symmetry, they may interact, if they have the same type of symmetry, resulting in the mutual perturbation of each other and hence displacement of frequencies in opposite directions. This type of interaction is due to the fact that two close molecular vibrational frequencies resonate and exchange energy and this phenomenon is known as Fermi resonance. This is similar to vibrational perturbations of diatomic molecules. The only essential difference is that for diatomic molecules only vibrational levels of different electronic states can have nearly the same energy and thus perturb one another whereas in Fermi resonance, two vibrational levels of the same electronic level can have the same energy and perturb each other, e.g. in case of CO_2 the levels $V_1 = 0$, $V_2 = 2$, $V_3 = 0$ has almost the same energy as the levels $V_1 = 1$, $V_2 = 0$, $V_3 = 0$, since $\nu_1 = 1337$ and $2\nu_2 = 667 \times 2 = 1334 \text{ cm}^{-1}$. In diatomics, the perturbation is because of the interaction of vibration and electronic motions whereas in polyatomics, the perturbation is due to interaction between different vibrations when two levels happen to lie very close together. Further, in the case of complex molecules having so many fundamentals and combination tones, chances of accidental degeneracy becomes bright. However, it should be borne in mind that not all such degeneracies lead to resonance. In these types of interactions, the overtone or combination band gains intensity at the expense of the fundamental and the higher frequency shifts in the higher direction while the lower one gets depressed. Fermi resonance is also detected in COS , CS_2 , COSe , ICN , C_2H_2 but not in H_2O , even though two of its vibrations have close frequencies at $\nu_1 = 3651.7 \text{ cm}^{-1}$ and $\nu_2 = 3755.8 \text{ cm}^{-1}$, since these vibrations belong to different types of symmetry.

Though we have already described the effect of Fermi resonance on the intensities and energies of the two interacting transitions, it is nice to elaborate it quantum mechanically. The intensity of overtone or combination transitions is generally less than one tenth, the intensity of fundamental transitions. If ν_i , ν_j and ν_k are the three fundamental vibrational frequencies of a molecule such that $(\nu_i + \nu_j) \approx \nu_k$ then the magnitude of interactions is given by

$$E_{ij,k} = \int \psi_{ij} \hat{E} \psi_k d\tau$$

The interaction operator $\hat{E}$ is nonzero because the vibrations are anharmonic. It is also totally symmetric and for this reason the two states ψ_{ij} and ψ_k must belong to the same symmetry otherwise the integral will not have finite value. This interaction displaces the two expected frequencies away from each other. Moreover, the interaction between ψ_{ij} and ψ_k which affects the actual energies, also gives rise to new wave functions which are linear combinations of these two. Thus, actual excited state whose energy is very close to $(\nu_i + \nu_j)$ will be described by a wave function

$$\Psi'_{ij} = C(\Psi_{ij} + x\Psi_k)$$

where C is a normalisation factor and $x \leq 1$. the actual excited state whose energy is very close to ν_k is expressed by the wave function.

$$\Psi'_k = C(\Psi_k + x\Psi_{ij})$$

Thus a transition from the ground state ψ_0 to ψ_{ij} will have low intensity and is proportional to the small integral

$$\int \psi_0(x, y, z) \psi_{ij} d\tau$$

and transition to the actual excited state, Ψ'_{ij} , has an intensity proportional to

$$\int \psi_0(x, y, z) \psi_{ij} d\tau + x \int \psi_0(x, y, z) \psi_k d\tau$$

where the second integral must be large, because $\psi_0 \rightarrow \psi_k$ transition is intense. The weak overtone transitions 'borrow' intensity from the strong fundamental transition because it is close to it and has an excited state with the same symmetry. The closer the energies $(\nu_i + \nu_j)$ and ν_k , the larger the sharing of total intensity equally between $(\nu_i + \nu_j)$ and ν_k . The schematic diagram depicting Fermi resonance is shown in Fig. 3.19.

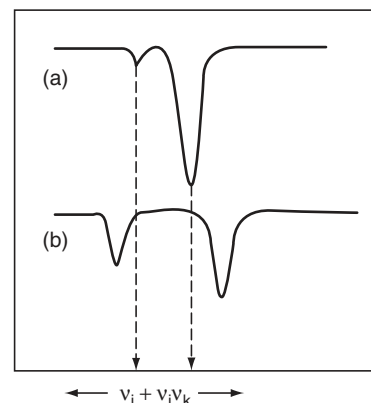


Fig. 3.19 The schematic diagram depicting Fermi resonance. (a) The spectrum (infrared or Raman) expected for the combination, $(\nu_i + \nu_j)$ and ν_k in the absence of Fermi resonance. (b) The actual spectrum where two bands diverge and share intensity because of Fermi interaction.

3.14.2 Coriolis Force

Further, in addition to Fermi resonance, Coriolis force and the phenomenon of inversion also influence the vibrational and rotational spectra of molecules. In the nonrigid rotator model of the diatomic molecule, a constant term, called the *centrifugal distortion constant*, is introduced in order to narrow down the discrepancies between the observable experimental and theoretical data. The constant term appears because of the centrifugal force given by

$$F_{\text{centrifugal}} = mr\omega^2 \quad (3.107)$$

The centrifugal force is exerted on particles which are stationary in the rotating system. The magnitude of centrifugal force depends upon the distance of the particle from the axis of rotation, C_m . However, if the particle is moving with certain velocity because of the oscillation of a particle in a rotating system, a new force called Coriolis force becomes operative and is given by

$$F_{\text{coriolis}} = 2m v_x \omega \sin \phi \quad (3.108)$$

Here in Eqs (3.107) and (3.108), m is the mass of the nucleus, v_x is the velocity of the particle due to the vibration of the particle, r is the distance from the axis of rotation, ω is the angular velocity and ϕ is the angle between the axis of rotation and the direction of v_x . This force is independent of the position of the particle but depends upon the velocity v_x , i.e. not only by its magnitude but also by its direction with respect to the axis of rotation. When the particle moves along the axis of rotation, coriolis force is zero. The greater the value of ϕ , the greater will be the Coriolis force, and has maximum value when motion of the particle is at right angles to the direction of rotation.

The Coriolis force leads to an additional interaction between rotation and vibration which in general is much larger than the effect of centrifugal force since velocity due to vibration (v_x) is much larger than that because of rotation ($r\omega$). Such type of interaction occurs only in the vibrating molecule and is measured in terms of a constant called the *Coriolis coupling constant*. It is denoted by the symbol ζ . It is the magnitude of the vibrational angular momentum in units of $h/2\pi$ for the particular vibrational state and is to be taken positive or negative depending on whether or not the direction of rotation of the electric dipole moment of the molecule coincides with the direction of the angular momentum of vibration. It is different for different vibrations and its value lies between +1 and -1. Thus, in the case of diatomic molecules, the variation α of the rotation constant B with the vibrational quantum number is because of the following three reasons: (i) for harmonic vibration, the mean value of $(1/I)_{\text{average}} \neq 1/I_e$ although $(r)_{\text{average}} = r_e$, (ii) for anharmonic oscillation, $(r)_{\text{average}} > r_e$, and (iii) the Coriolis coupling constant. In other words, we can say that,

$$\alpha_i = \alpha_i(\text{harm.}) + \alpha_i(\text{anharm}) + \alpha_i(\text{Cor.}) \quad (3.109)$$

α_i for different types of molecules have been expressed in terms of potential constants and internuclear distances. The formulae for the linear XY_2 molecules are

$$\alpha_1(\text{harm.}) = \frac{-6B_e^2}{w_1}$$

$$\alpha_2(\text{harm.}) = \frac{+B_e^2}{w_2}$$

$$\alpha_3(\text{harm.}) = \frac{+2B_e^2}{w_3}$$
(3.110)

$$\alpha_1(\text{anharm.}) = \frac{24B_e^3 I_e^{3/2} \alpha_{111}}{w_1^3 hc}$$

$$\alpha_2(\text{anharm.}) = \frac{-8B_e^3 I_e^{3/2} \alpha_{122}}{w_1^2 w_2 hc}$$

$$\alpha_3(\text{anharm.}) = \frac{-8B_e^3 I_e^{3/2} \alpha_{133}}{w_1^2 w_3 hc}$$
(3.111)

$$\alpha_{I(\text{Cor.})} = 0$$

$$\alpha_2(\text{Cor.}) = \frac{4B_e^2 w_2}{(w_3^2 - w_2^2)}$$

$$\alpha_3(\text{Cor.}) = \frac{-8B_e^2 w_3}{(w_3^2 - w_2^2)}$$
(3.112)

Here, α_{111} , α_{122} and α_{133} are the anharmonic potential constants and w_1 (symmetric stretch), w_2 (bend) and w_3 (asymmetric stretch) are the fundamental modes of vibration of linear XY_2 type of molecules. Knowing the values of the various constants, w_1 , w_2 and w_3 ; the values of different types of α_i s can be estimated.

Further, since Coriolis coupling constant is proportional to the speed of rotation, a splitting that grows with J is expected and indeed l -type splitting in Π , Δ -vibrational levels of linear polyatomic molecules has been observed. The l -type splitting in a vibrational state Π is given by

$$\Delta v = qJ(J+1)$$
(3.113)

where $q = \alpha_i(\text{harm.}) + \alpha_i(\text{Cor.})$ and the subscript i stands for the $\perp$ vibration that is excited in the Π state. The sum of the ζ_i values for all vibrations of the same species is independent of the potential constants and hence can be expressed in terms of the moments of inertia. The sum rule is valid provided no resonance occurs and harmonicity is ignored. For planar or pyramidal molecules:

$$\zeta_3 + \zeta_4 = \frac{I_A}{2I_B} - 1$$
(3.114)

For planar molecules, since

$$I_A = 2I_B$$

Therefore, $\zeta_3 = -\zeta_4$

For the two F_2 vibrations ν_3 and ν_4 of XY_4 molecules, $\zeta_3 + \zeta_4 = 1/2$ since here $B = A$. $\zeta_2 = 0$ for the E vibration of XY_4 .

The general rule specifying the vibrational states between which a Coriolis interaction can take place is due to Jahn, i.e. two vibrations will interact in consequence of Coriolis force in the rotating molecule only when the product of their species contains the species of a rotation. In case of symmetric top molecules, the Coriolis forces that occur in the rotating molecule may produce an interaction between mutually degenerate vibrations, which in turn results in splitting of the degeneracy. There are three species of degenerate vibrational levels in tetrahedral molecules, i.e. E , F_1 and F_2 . The fundamentals of Y_4 and XY_4 have only species E and F_2 . No Coriolis splitting arises for the doubly degenerate vibrational states since $E \times E = A_1 + A_2 + E$, i.e. does not contain the species of

rotation which is F_1 in this case, The rotational energy levels are the same as for the non-degenerate vibrational states. However, for the triply degenerate vibrational states, the Coriolis interaction causes a splitting. The rotational energy values for the three levels which are similar to that for symmetric top molecules (Fig. 3.20) are given by the formulae:

$$F^+(J) = B_v J(J+1) + 2B_v \zeta_i (J+1) (\Delta J = -1) \quad (3.115)$$

$$F^0(J) = B_v J(J+1) (\Delta J = 0) \quad (3.116)$$

$$F^-(J) = B_v J(J+1) - 2B_v \zeta_i J (\Delta J = +1) \quad (3.117)$$

The formulae hold good for vibrational states of species F_1 as well as of F_2 , the former occurring only as upper states of certain overtone and combination bands of the XY_4 molecules. The fine structure of rotation-vibration bands of tetrahedral molecules for the $F_2 - A_1$ transitions is well understood. The spacing in different bands is different. The reason for this is, as for symmetric top molecules, the Coriolis coupling between rotation and vibration in the upper degenerate vibration state. Consequently, the upper states of corresponding lines of the P-, Q- and R-branches are somewhat different. Using Eqs (3.115), (3.116) and (3.117) and applying the selection rules, for the F^+ , F^0 and F^- substates, we obtain for the R-branch

$$R(J) = \nu_0 + 2B_v'' - 2B_v' \zeta_i + (3B_v'' - B_v' - 2B_v' \zeta_i)J + (B_v'' - B_v')J^2 \quad (3.118)$$

for the Q-branch,

$$Q(J) = \nu_0 + (B_v'' - B_v')J + (B_v'' - B_v')J^2 \quad (3.119)$$

and for the P-branch,

$$P(J) = \nu_0 - (B_v'' + B_v' - 2B_v' \zeta_i)J + (B_v'' - B_v')J^2 \quad (3.120)$$

The P- and R-branches form one series of lines represented by the formulae:

$$\nu = \nu_0 + (B_v'' + B_v' - 2B_v' \zeta_i)m + (B_v'' - B_v')m^2 \quad (3.121)$$

where $m = J+1$ for R, $m = -J$ for P-branch and where one line $m = 0$ is missing. For fundamentals $B_v'' - B_v' = 0$, therefore, the separation of successive lines in this series is nearly constant and is equal to $2B(1 - \zeta_i)$, and all lines of the Q-branch coincide at the zero line ν_0 . Since ζ_i is different for different vibrations, the spacing of the lines in different infrared bands may differ widely. The moment of inertia of tetrahedral molecule, therefore, cannot be determined from the fine structure of one infrared band alone. However, because of the sum rule for ζ_i , it is possible to determine the moment of inertia if the spacing in all infrared-active fundamentals is known. For XY_4 molecules there are two such fundamentals, ν_3 and ν_4 for which $\zeta_3 + \zeta_4 = 1/2$. Therefore, the sum of spacings in ν_3 and $\nu_4 = 3B$. Thus, B , I_B and the bond distance $X-Y$ in XY_4 can be determined. The fundamental bands of CH_4 are observed at $\nu_1(A_1) = 2914.2$, $\nu_2(E) = 1520$, $\nu_3(F_2) = 3020.3$ and $\nu_4(F_2) = 1306.2 \text{ cm}^{-1}$.

Recall from Chapter 2 that inversion in case of nonplanar XY_3 type molecules manifests itself in the vibrational spectrum of such molecules. The doubling of all the vibrational energy levels occurs because of two potential minima corresponding to inversion. In the infrared only sublevels of opposite parity combine with one another ($+\leftrightarrow -$) while in the Raman effect only sublevels of the same parity combine with one another ($+\leftrightarrow +$, $-\leftrightarrow -$). When the inversion doubling of the vibrational levels is unobservably small, the selection rules have no observable effect on the spectrum. Only the selection rules for one potential minimum are considered. However when the inversion doubling is observable as in the case of NH_3 , the selection rules for sublevels are also taken into account. All the infrared and Raman transitions are then double as shown in Figs 3.21(a) and (b). The doublet splitting of the bands in the infrared and Raman spectra is different because of different selection rules in the respective

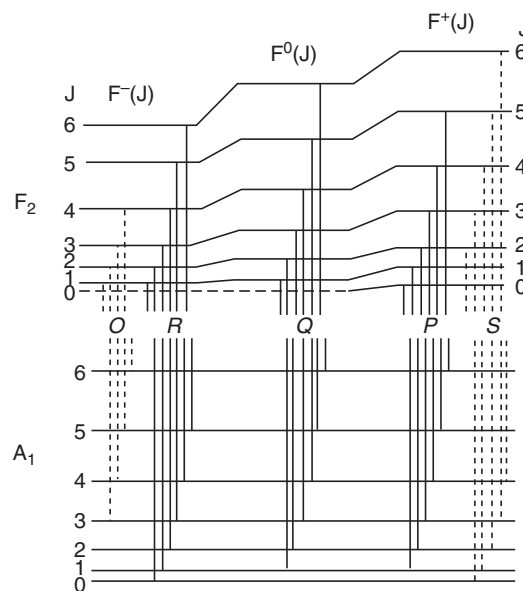


Fig. 3.20 Rotational energy levels of a spherical top molecule in a triply degenerate (F_2) and totally symmetric (A_1) vibrational states. The broken lines do not occur.

Table 3.7 The energy states $(0, V_2, 0, 0)$ of NH_3 and ND_3 .

State (V_2)	$\text{NH}_3(\text{cm}^{-1})$	$\text{ND}_3(\text{cm}^{-1})$
0^+	0	0
0^-	0.66	~ 0
1^+	932.24	745.6
1^-	968.08	749.0
2^+	1597.4	1359
2^-	1910	1429
3^+	2380	1830
3^-	2861	2113
4^+		2495
4^-		2868

spectra. The doublet splitting of the upper and lower levels is the sum in the infrared [Fig. 3.21(a)], whereas it is the difference in the Raman spectrum [Fig. 3.21(b)]. Totally symmetric ν_1 and ν_2 bands of NH_3 are double, i.e. ν_1^{IR} ($3335.9, 3337.5 \text{ cm}^{-1}$), ν_2^{IR} ($931.58, 968.08$); ν_2^{R} ($934.0, 964.3 \text{ cm}^{-1}$). In case of ND_3 , ν_2^{IR} ($748.6, 749.0 \text{ cm}^{-1}$).

The doublet splitting of ν_2 band in case of ND_3 is small in comparison to that of NH_3 . The energy states $(0, V_2, 0, 0)$ of NH_3 and ND_3 are recorded in Table 3.7.

Problem 3.20: Write shorthand notation for the following bands: (i) $2\nu_2$; $3n - 6 = 3$ (ii) $\nu_2 + \nu_3 + \nu_6$; $3n - 6 = 6$ and (iii) $2\nu_2 + \nu_3 + 2\nu_4$; $3n - 5 = 4$.

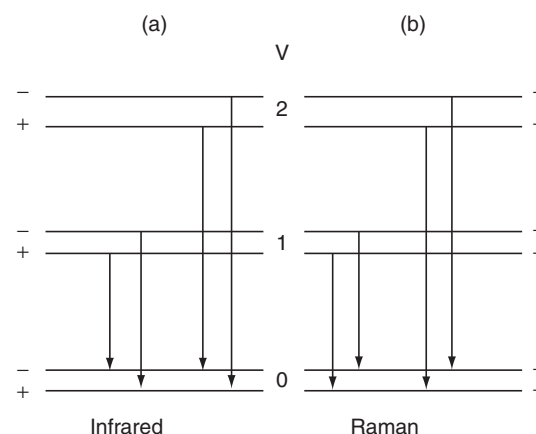
Solution The shorthand notation for (i) $2\nu_2$ band is $(0, 0, 0) \rightarrow (0, 2, 0)$, (ii) $\nu_2 + \nu_3 + \nu_6$ band is $(0, 0, 0, 0, 0, 0) \rightarrow (0, 1, 1, 0, 0, 1)$, and (iii) $2\nu_2 + \nu_3 + 2\nu_4$ band is $(0, 0, 0, 0) \rightarrow (0, 2, 1, 2)$. This also suggests that molecule is linear.

Problem 3.21: State the meaning of the following vibrational transitions in a polyatomic molecule: (i) $(0, 0, 0) \rightarrow (0, 0, 2)$; (ii) $(0, 2, 0, 0) \rightarrow (0, 1, 1, 1)$; (iii) $(0, 0, 0, 0) \rightarrow (0, 2, 1, 1)$; and (iv) $(0, 1, 1, 1, 2) \rightarrow (0, 2, 1, 2, 0)$.

Solution (i) The transition $V(0, 0, 0) \rightarrow V(0, 0, 2)$ means that the vibration ν_3 is excited from $V_3 = 0 \rightarrow$ vibration $V_3 = 2$ and this is the first overtone with frequency $2\nu_3$. In total there are three modes of vibrations. (ii) By transition $V(0, 2, 0, 0) \rightarrow V(0, 1, 1, 1)$, we mean that the vibration ν_2 is de-excited from $V_2 = 2 \rightarrow V_2 = 1$ while the vibrations ν_3 and ν_4 are excited from $V_3 = 0 \rightarrow V_3 = 1$ and $V_4 = 0 \rightarrow V_4 = 1$, respectively. The band corresponding to this transition is a combination with frequency $\nu_2 + \nu_3 + \nu_4$. In all, there are four modes of vibrations. (iii) The transition $(0, 0, 0, 0) \rightarrow (0, 2, 1, 1)$ is a combination band with frequency, $2\nu_2 + \nu_3 + \nu_4$. Overall there are four vibrational degrees of freedom. (iv) The transition $(0, 1, 1, 1, 2) \rightarrow (0, 2, 1, 2, 0)$ is a combination band with frequency $\nu_2 + \nu_4 + 2\nu_5$. In all, there are five vibrational degrees of freedom.

Problem 3.22: The frequencies of three fundamental modes of vibration of CO_2 have been observed at $667, 1337$ and 2349 cm^{-1} . Calculate the frequencies of the absorption bands for the following arbitrary transitions: (i) $V(0, 0, 0) \rightarrow V(2, 0, 0)$; (ii) $V(0, 0, 0) \rightarrow V(0, 1, 2)$; (iii) $V(0, 0, 2) \rightarrow V(1, 1, 0)$; and (iv) $V(0, 0, 2) \rightarrow V(2, 1, 0)$.

Solution The frequencies for (i) $V(0, 0, 0) \rightarrow V(2, 0, 0)$ transition = $667 \times 2 = 1334 \text{ cm}^{-1}$; (ii) $V(0, 0, 0) \rightarrow V(0, 1, 2)$ transition = $1337 + 2 \times 2349 = 6035 \text{ cm}^{-1}$; (iii) $V(0, 0, 2) \rightarrow V(1, 1, 0) = 667 + 1337 + 2 \times 2349 = 6702 \text{ cm}^{-1}$; and (iv) $V(0, 0, 2) \rightarrow V(2, 1, 0) = 2 \times 667 + 1337 + 2 \times 2349 = 7369 \text{ cm}^{-1}$.

**Fig. 3.21** Effect of inversion doubling on (a) infrared, and (b) Raman spectra.

Problem 3.23: Determine the value of $\alpha_i(\text{Cor.})$ in case of CO_2 if $w_1 = 1337$, $w_2 = 667$ and $w_3 = 2349 \text{ cm}^{-1}$, $B_e = 0.3906 \text{ cm}^{-1}$, and $I_e = 18.816 \times 10^{-40} \text{ g cm}^2$.

Solution The value of $\alpha_i(\text{Cor.})$ can be calculated by substituting the values of different given constants into Eq. (3.112).

$$\alpha_1^{(\text{Cor.})} = 0; \alpha_2^{(\text{Cor.})} = \frac{4(0.3906)^2 \times 667}{(2349 - 667)(2349 + 667)} = 8.02 \times 10^{-5} \text{ cm}^{-1}$$

and

$$\alpha_3^{(\text{Cor.})} = \frac{-8(0.3906)^2 \times 2349}{(2349 - 667)(2349 + 667)} = -5.65 \times 10^{-4} \text{ cm}^{-1}$$

Problem 3.24: For CH_4 , the spacing of lines in the band ν_3 at 3020 cm^{-1} near the origin is 9.93 cm^{-1} and in the band ν_4 at 1306 cm^{-1} is 5.74 cm^{-1} . Determine the values of Coriolis constants for the two F_2 vibrations ν_3 and ν_4 .

Solution For XY_4 molecules,

$$\zeta_3 + \zeta_4 = \frac{1}{2} \text{ and sum of spacings in } \nu_3 \text{ and } \nu_4 = 3B$$

Therefore, $3B = 9.93 + 5.74 = 15.67 \text{ cm}^{-1}$, and $B = 5.223 \text{ cm}^{-1}$.

This is an average of the B values of the upper and lower states. For fundamentals, the separation of successive lines in the series $= 2B(1 - \zeta_i)$

Therefore for ν_3 ,

$$2B(1 - \zeta_3) = 9.93$$

$$2 \times 5.223(1 - \zeta_3) = 9.93$$

$$\zeta_3 = \frac{10.446 - 9.93}{10.446} = \frac{0.516}{10.446} = 0.05$$

and, for ν_4 ; $\zeta_4 = 0.45$.

3.15 ROTATION-VIBRATION SPECTRA OF POLYATOMIC MOLECULES

When the molecule has an angular momentum about the internuclear axis, the vibrational change is then calculated theoretically by rotational transitions. However, due to large difference between the moments of inertia in the initial and final levels, very small changes actually occur in the rotational energy due to which a series of very closely spaced lines, called the Q-branch appears at the centre of the branch, e.g. nitric oxide or polyatomic ($n > 2$) molecules. This is shown in Figs 3.22 and 3.23.

Further, it is inferred that the rotational selection rules depend upon whether the *vibration* is accompanied by a change in dipole moment perpendicular or parallel to the symmetry axis. The selection rules for parallel vibrations of linear molecules such as HCN , N_2O , CO_2 , C_2H_2 , etc., are the same as for diatomic molecules, i.e.

$$\Delta J = \pm 1 \text{ and } \Delta V = \pm 1, (\pm 2, \pm 3, \dots)$$

for anharmonic motion. The selection rules for perpendicular vibrations

$$\Delta J = 0, \pm 1 \text{ and } \Delta V = \pm 1, (\pm 2, \pm 3, \dots)$$

reveal that a vibrational change can occur without simultaneous rotational transition. Consequently, the Q-branch is observed along with the P- and R-branches in perpendicular bending mode of HCN . Further, the fine structure of nonlinear polyatomic molecules depends upon whether the molecule has symmetric or asymmetric rotation. In spite of the fact that the fine structure is complex in pure rotational spectra, the Q-branch will always be observed in parallel and perpendicular bands of the molecules since in all cases $\Delta J = 0, \pm 1$.

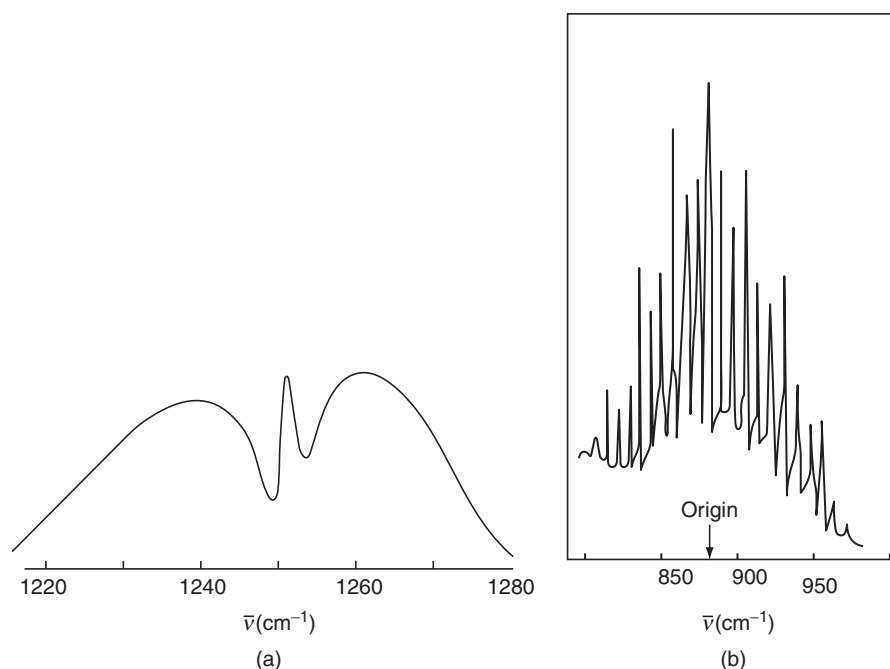


Fig. 3.22 (a) Parallel, and (b) perpendicular modes of methyl iodide.

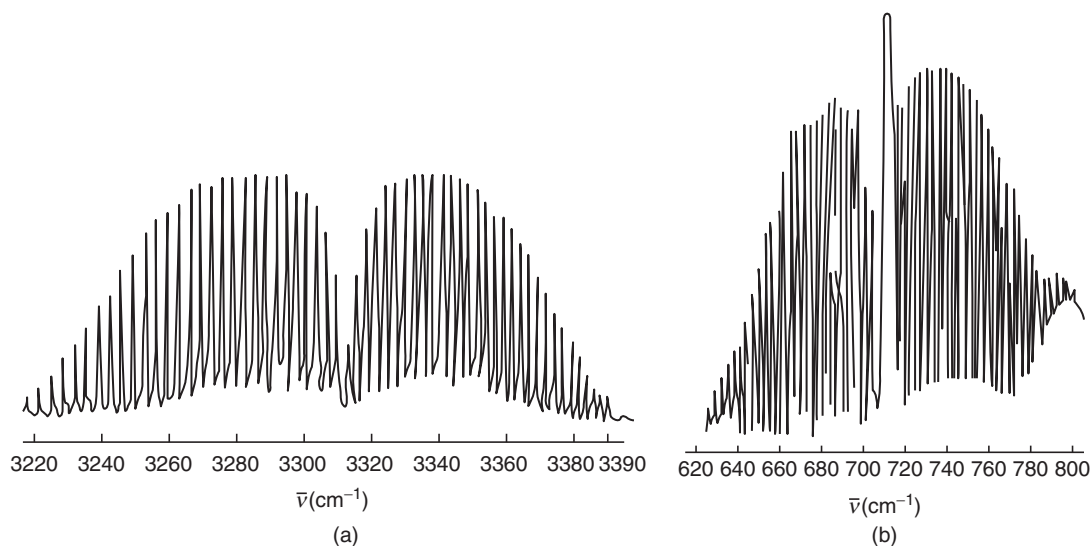


Fig. 3.23 The spectrum of (a) parallel symmetric stretch, and (b) perpendicular bending modes of HCN. Note the P-, R-branches in (a) P-, Q-, R-branches in (b).

3.15.1 Structure and Characteristics of Rotation–Vibration Bands in Polyatomic Molecules

For a vast majority of molecules, the rotational constants are so small that the infrared spectra taken at even the highest resolution do not show individual rotational lines, the expected line spacings being smaller than Doppler half widths. However, envelopes of their vibration–rotation bands possess distinctive features, which depend uniquely on the rotational constants of the molecule and the direction of change of dipole moment (parallel, perpendicular or hybrid bands). The observables involved are (i) the separation of P- and R-branch peaks ($\Delta\nu_{PR}$); (ii) the relative intensity of the Q-branch as compared to the integrated intensity of the whole band (I_Q/I_{Total}) (Fig. 3.24); and (iii) the actual shape of the band contour. If explicit relations could be established between these observables and the molecular parameters, one could use band contour analysis to deduce these parameters. The situation is, however, quite complex both from theoretical and experimental standpoints.

3.15.2 The Band Types

Recalling the definitions of the rotational constants (A , B and C) and the principal moments of inertia (I_A , I_B and I_C) as given in Chapter 2, one can easily define the momental ellipsoid (ME). The ME is an ellipsoid with the principal axes a , b and c such that

$$a = 2(I_A)^{-1/2}, b = 2(I_B)^{-1/2} \text{ and } c = 2(I_C)^{-1/2}$$

Here, a is the 'major', b the 'intermediate', and, c the 'minor' axis of inertia.

For linear and prolate symmetric top molecules, a band is referred to as parallel ($\parallel$) or perpendicular ($\perp$) when it corresponds to a dipole change parallel or normal to the unique (major) a -axis of inertia. For oblate symmetric top molecules, a band is referred to as parallel or perpendicular depending on whether it corresponds to electrical oscillations parallel or perpendicular to the unique (minor) c -axis of inertia. However, for asymmetrical top molecules, the letters A-type, B-type and C-type are used to qualify the bands, denoting that the transition dipole moments are parallel to the a -, b - and c -axis respectively. Type A bands exhibit a fairly strong central maximum, corresponding to the Q-lines, with two accompanying maxima on either side, corresponding to the P- and R-lines, for any value of ρ ($\rho = B/A \rightarrow 1$ or $C/A \rightarrow 1$), the Zumbalt parameter. The contour of such type of band is shown in Fig. 3.25(a). Type C bands have similar envelopes, except for small ρ values when the central branch no longer stands out, so that only one broad maximum results. The type C band contour is shown in Fig. 3.25(b). The P and R maxima in type C bands are broad and are not as pronounced as in the case of type A bands. Type B bands have no central maximum but, the Q lines form two maxima, i.e. QQ' or QQ'' on either side and fairly close to zero line, in addition to the P and R maxima. A contour of type B band is presented in Fig. 3.25(c). These Q maxima are prominent particularly for the larger ρ values. For small moments of inertia the intensity distribution is not quite symmetrical about the band origin. Sometimes instead of QQ' maxima only a single maxima is observed with P- and R-maxima on either side of Q as shown in Fig. 3.25(d). For pure B-type bands the Q positions are obtained from the positions of minimum between the P- and R-branches. I_Q/I_{Total} may also be fixed as a criterion to characterise the type of bands in the spectra of molecules. The range of intensity ratio of different types of virgin bands is different. It is to be noted that in the spectrum of molecules, it is not always possible to examine all the bands for $\Delta\nu_{PR}$ and I_Q/I_{Total} values due to either the complex structure resulting from overtones, binary combinations, Fermi resonance, hot bands, etc., or their very feeble intensities, especially in isotopically labelled molecules. For all practical purposes, only those bands are chosen which exhibit no overlapping with other bands.

PQR thus implies that the band consists of three branches with the P($\Delta J = -1$) on the low-frequency side and the R-branch ($\Delta J = +1$) on the high-frequency side of the Q branch ($\Delta J = 0$). PQQR or PQQ'R means that the band structure with four maxima is seen. By PR separation we mean the interval (in cm^{-1}) between the intensity maxima of P- and R-branches.

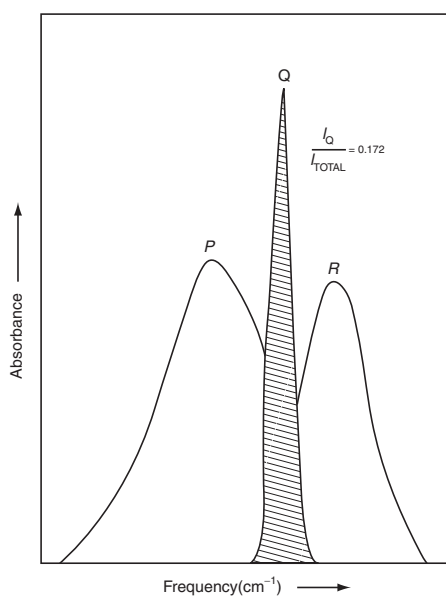


Fig. 3.24 Representative curve for calculating I_Q/I_{TOTAL} in an A-type band. Shaded portion indicates the area attributed to Q-branch.

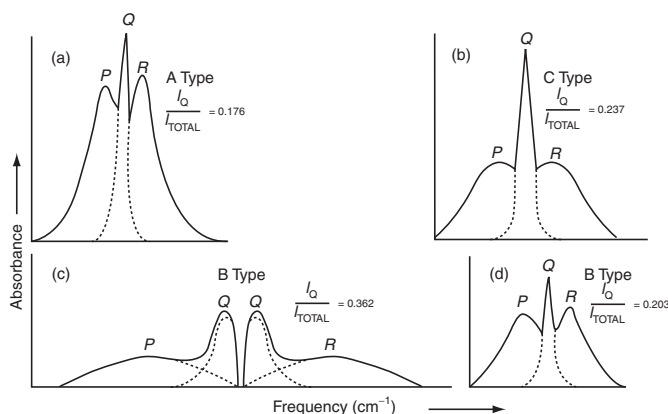


Fig. 3.25 Nature of typical (a) A -, (b) C -, and (c, d) B-type infrared bands.

3.15.3 Theoretical Aspects of PR-separation and I_Q/I_{Total} in Different Types of Molecules

(a) Linear Molecules For a linear molecule the PR separation, δ in a vibration-rotation vapour phase band contour at TK is given by

$$\Delta\nu_{PR} \equiv \delta = \left(\frac{8B\kappa T}{hc} \right)^{\frac{1}{2}} = 2.358\sqrt{TB} (\text{cm}^{-1}) \quad (3.122)$$

where B is the rotational constant and other symbols have their usual meanings. In the derivation of this formula, the change of rotational constants in different vibrational states, the centrifugal distortion effects and the complications resulting from Coriolis interaction have been neglected; and it has also been assumed that the intensity of rotational transition is primarily governed by the product of the statistical weight and the Maxwell-Boltzmann distribution function for the particular energy level from which the absorption is taking place.

(b) Symmetric-Top Molecules For symmetric-top molecules, the expression for PR separation in parallel bands can be represented as

$$\Delta\nu_{PR}(\parallel) = S(\beta) \cdot \delta \quad (3.123)$$

where parameter β is defined as

$$\beta = (A/B) - 1 \text{ or } (C/B) - 1 \quad (3.124)$$

for prolate or oblate molecules respectively and the function $S(\beta)$ is given by an empirical relation

$$\log_{10} S(\beta) = \frac{0.721}{(\beta + 4)^{1.13}} \quad (3.125)$$

which is found to hold good within 0.5 per cent for β in the range -0.5 to $+100$. The expression for the ratio I_Q/I_{Total} in the parallel-type bands is given by

$$\frac{I_Q}{I_{\text{Total}}} = \frac{\ln[\beta^{1/2} + (1 + \beta)^{1/2}] - [\beta/(1 + \beta)]^{1/2}}{\beta[\beta/(1 + \beta)]^{1/2}} \quad (3.126)$$

for $\beta > 0$, a case in which molecules are all near prolate symmetric tops. Thus, I_Q/I_{Total} is a function of parameter ' β ' alone. It tends to ~ 0.5 for disc-shaped molecules ($\beta = -1/2$), ~ 0.33 for a spherical-top molecule ($\beta = 0$), and falls to 0 for a linear molecule ($\beta = \infty$).

For the perpendicular bands in symmetric-top molecules, there are no general formulae for $\Delta\nu_{PR}$ or for I_Q/I_{Total} . For ($\perp$) bands, (i) the Q-branch gets stronger with β increasing from -0.5 to ~ 1 , beyond which the bands rapidly cease to show PQR structure, and (ii) $\Delta\nu_{PR}$ decreases monotonously with increasing β .

(c) Asymmetric-Top Molecules For the asymmetric-top molecules, the energy level scheme becomes more complex, being expressed (for a near prolate molecule) by

$$F(J, \tau) = \bar{B}J(J+1) + (A - \bar{B})E_{\tau}(\kappa_a) \quad (3.127)$$

$\bar{B}$ is defined by

$$\bar{B} = \frac{1}{2}(B + C) \quad (3.128)$$

The asymmetry parameter κ_a is defined by

$$\kappa_a = \frac{B - \frac{1}{2}(A + C)}{\frac{1}{2}(A - C)} \quad (3.129)$$

and the parameter l is defined as

$$l = (A - C)/B \quad (3.130)$$

Since large J values are involved in heavy molecules, one can obtain approximate solutions for the $(2J + 1)$ values of $F(J, \tau)$ in terms of κ_a and l to obtain band contours. $E_{\tau}(\kappa_a)$ represents the $(2J + 1)$ solutions.

For both parallel and perpendicular-type bands of the prolate and oblate asymmetric-top molecules, general sets of empirical expressions for PR separations applicable in various ranges of κ and l are available. For parallel bands of near prolate symmetric tops, the expression used for determination of PR separation is in the form

$$\Delta\nu_{PR}A(\parallel) = S(\bar{\beta}) \cdot \bar{\delta} \quad (3.131)$$

where $\bar{\delta}$ and $S(\bar{\beta})$ are obtained on replacing B by $\bar{\beta}$ in the expressions for δ and $S(\beta)$ respectively.

For $B(\perp)$ and $C(\perp)$ bands in the range $3/4 < l < 3$,

$$\Delta\nu_{PR}B(\perp) = \bar{\delta} \quad (3.132)$$

and

$$\Delta\nu_{PR}C(\perp) = \frac{3}{2} [S(\bar{\beta}) \cdot \bar{\delta}] \quad (3.133)$$

Expressions are not available for the ratio I_Q/I_{Total} for bands of asymmetric top molecules. However, we can extend the application of relation (Eq. 3.126) to asymmetric top molecules just by replacing β with $\bar{\beta}$.

(d) Hybrid Bands PR separation in hybrid bands can be obtained from the empirical formula

$$\Delta\nu_{PR}(\alpha\beta) = \frac{\Delta\nu(A)\cos\alpha + \Delta\nu(B)\cos\beta}{\cos\alpha + \cos\beta} \quad (3.134)$$

where α and β are the angles between the oscillating dipole and the a and b axes of the molecule, and $\Delta\nu(A)$ and $\Delta\nu(B)$ are the PR separations for pure A -type and pure B -type bands, respectively. The uncertainties in measurement of $\Delta\nu_{PR}$ values (in hybrid bands in particular) are so large that relation (Eq. 3.134) can at best be used to check hybrid character but not for deducing the direction of dipole oscillation within a narrow range. In fact, a simple formula like

$$\Delta\nu_{PR}(\alpha\beta) = \frac{\alpha\Delta\nu(A) + \beta\Delta\nu(B)}{\alpha + \beta} \quad (3.135)$$

gives as good a fit as the formula (3.134) in almost all cases.

Problem 3.25: The vapour-phase spectrum of methylthiolformate shows resolved rotational contours. The PR separations as determined from the $C=O$ stretching ($1708, 1698, 1688 \text{ cm}^{-1}$) and CH_3 symmetric stretching ($2954, 2945, 2937 \text{ cm}^{-1}$) bands, both of type A have been found to be 20 and 19 cm^{-1} respectively. Determine (a) the moment of inertia of the molecule, (b) the values of the parameters l and κ_a and (c) the configuration of the molecule if the rotational constants of the *cis*- and *trans*- configurations are

Rotational Constants (MHz)	<i>cis</i>	<i>trans</i>
A	11149.9	19392.8
B	5009.7	3577.9
C	3533.2	3078.9

Solution (a) Moments of inertia are determined from the rotational constants by making use of the conversion factor.

$$\frac{h}{8\pi^2} = 5.0537 \times 10^5 (\text{amu})^{-1} (\text{\AA})^2$$

$$\text{Moment of inertia (MI)} = \frac{h}{8\pi^2 \times \text{Rotational constant}}$$

MI (au)	<i>cis</i>	<i>trans</i>
I_A	45.3258	26.0601
I_B	100.8800	141.2501
I_C	143.0371	164.1427

(b) Using expressions (3.129) and (3.130), we obtain

$$\kappa_a(cis) = \frac{5009.7 - \frac{1}{2}(11149.9 + 3533.2)}{\frac{1}{2}(11149.9 - 3533.2)} = -0.6123$$

$$\kappa_a(trans) = \frac{3577.9 - \frac{1}{2}(19392.8 + 3078.9)}{\frac{1}{2}(19392.8 - 3078.9)} = -0.9388$$

$$I_{cis} = \frac{(11149.9 - 3533.2)}{5009.9} = 1.5203$$

$$I_{trans} = \frac{(19392.8 - 3078.9)}{3577.9} = 4.5596$$

(c) In order to determine the *PR* separations of Type-*A*, -*B* and -*C* band contours, the parameters, $\bar{B}$, $\bar{\beta}$ and $S(\bar{\beta})$ need to be defined.

Using Eqs (3.128), (3.124) and (3.125) we get

<i>cis</i>	<i>trans</i>
$\bar{B}_{cis} = \frac{1}{2}(5009.7 + 3533.2)$	$\bar{B}_{trans} = \frac{1}{2}(3577.9 + 3078.9)$
$= 4271.45 \text{ MHz}$	$= 3328.4 \text{ MHz}$
$\bar{\beta}_{cis} = \frac{11149.9}{4271.45} - 1$	$\bar{\beta}_{trans} = \frac{19392.8}{3328.4} - 1$
$= 1.6103$	$= 4.8264$
$\log S(\bar{\beta})_{cis} = \frac{0.721}{(1.6103 + 4)^{1.13}}$	$\log S(\bar{\beta})_{trans} = \frac{0.721}{(4.8264 + 4)^{1.13}}$
$= 0.102$	$= 0.0615$
$S(\bar{\beta})_{cis} = 1.2667$	$S(\bar{\beta})_{trans} = 1.1521$

Substituting the values of B_{cis} and B_{trans} into Eq. (3.122) we get $\delta_{cis} = 16.6 \text{ cm}^{-1}$ and $\delta_{trans} = 14.0 \text{ cm}^{-1}$ respectively.

Now the *PR* separations for the *cis*- and *trans*-configurations are determined from Eqs (3.131), (3.132) and (3.133) and are as follows.

Band Type	<i>cis</i>	<i>trans</i>
<i>A</i>	21.0	16.1
<i>B</i>	16.6	14.0
<i>C</i>	31.5	24.1

The theoretical value of *PR* separation for the type *A* band for the *cis* configuration conforms to the *PR* separations observed experimentally for the C = O (19 cm^{-1}) and CH_3 (20 cm^{-1}) stretching bands both of type *A*. Thus, in methylthiolformate, the methyl group is *cis* to the carbonyl group.

Problem 3.26: The absorption band at 920 cm^{-1} in the vapour-phase infrared spectra of methylthiolformate has a type *C* contour with a strong Q-branch and is assigned to CH (formyl) out-of-plane wagging. Using the data from Problem (3.25), find the spacing of the Q-branch fine structure on the P and R shoulders of a type *C* contour.

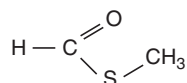
Under the operating condition of the instrument, the rotational fine structure of the lines with a separation of 1 cm^{-1} or greater is observable.

Solution The presence of such a C-type contour suggests that the molecule has either planar or near planar molecular geometry. The spacing of such a Q-branch fine structure of a type C band is determined from the expression

$$\Delta\nu = \frac{2}{c} \left[A - \frac{(B+C)}{2} \right] \text{cm}^{-1} \quad (3.136)$$

The values of $\Delta\nu_{\text{cis}}$ and $\Delta\nu_{\text{trans}}$ are found to be of the order of 0.46 and 1.07 cm^{-1} respectively.

Under the operating conditions of the spectrometer, the absence of rotational fine structure lines suggests that the molecule most probably exists in cis-configuration as shown below.



3.16 APPLICATIONS OF IR SPECTROSCOPY

The applications of infrared spectroscopy have been discussed under three parts, viz. qualitative, quantitative and biological applications.

3.16.1 Qualitative Applications

By qualitative applications in infrared spectroscopy, we mean functional group identification, skeleton identification and structural elucidation on the basis of spectral observations and any other additional information if available. Infrared spectroscopy is of great help, if information on elemental analysis is also available. This method enjoys advantage over all other methods, in that it supplies information of whole molecule, composite and whole, but not about protons as in nuclear magnetic resonance, electronic transitions as in ultraviolet/visible and about a free radical as in electronic spin resonance spectroscopy. Thus, IR spectroscopy is used in almost every possible way to study chemical systems. It is generally an easy matter to place a sample in a spectrometer and examine its absorption spectrum and see whether it has changed due to some change in conditions or not. Some of the typical qualitative applications of IR spectroscopy are discussed here.

(a) Structural Elucidation The spectra of compounds is divided mainly into two parts: (i) above 1500 cm^{-1} , and (ii) below 1500 cm^{-1} . The region above 1500 cm^{-1} is mainly due to the normal vibrations of functional groups while below 1500 cm^{-1} , called the *fingerprint region* contains mainly skeletal motions due to normal bending vibrations and fundamental stretching vibrations of bonds like C—X where X = C, N, O, Cl, Br, I, F. The fingerprint bands are widely used as means of identifying structural units within polyatomic molecules. Further, isotopic substitution plays a major role in structural elucidation since it helps in sorting out the skeletal and functional group vibrations in complex molecules. These days, different detailed and comprehensive correlation tables in which the region and exact positions of the frequencies due to different modes of vibrations are available. The infrared spectra-structure correlations by regions given by NB Colthup and the characteristic infrared frequencies of some functional groups are given in Table 3.8. Thus, simply by matching the spectral data of unknown compounds with the standard ones reported in the tables, one can propose a tentative structure to the compound. However, it should be borne in mind that the changes in the group frequencies in different molecules may be better understood if the interaction between the groups and the environment is specifically considered. Some of the important factors which affect the frequencies are explained here.

(i) Mass Distribution The vibrational frequency of any vibrator is usually governed by its mass and force constant. A change in the mass distribution in a group of molecules alters the form as well as the frequency of vibration; an increase in mass usually causes a decrease in frequency.

The effect of nature of mass on the C = O vibrational band is shown in Fig. 3.26. It is estimated that these mechanical changes in the nature of C = O vibration lowers its frequency by about 15 wave numbers, when heavier substituent on the carbonyl carbon [Fig. 3.26(a)] is replaced by the lighter atom, i.e. hydrogen [Fig. 3.26(b)]. Thus, the lowering in frequency of C = O is mainly controlled by mass effect while an increase of 15 cm^{-1} in going from ketones to aldehydes is mainly due to the fact that aldehydes have larger C = O force constant than ketones.

Table 3.8 Infrared spectra-structure correlations (in cm^{-1}).

Correlations by regions					
3700–3100		OH, NH, $\equiv\text{C—H}$			
3100–3000		olefinic, aromatic, three membered ring CH			
3000–2700		aliphatic CH			
2300–1900		$\text{X} \equiv \text{Y}$, $\text{X} = \text{Y} = \text{Z}$			
1900–1550		$\text{C} = \text{O}$			
1700–1550		$\text{C} = \text{C}$, $\text{C} = \text{N}$			
1600 and 1500		aromatic ring			
1460		CH_2 , CH_3			
1375		C—CH_3			
1300–1000		C—O			
1000–600		olefinic, aromatic CH wag			
Aliphatic groups					
CH_3		2960, 2870 and 1460 (± 10)			
C—CH_3		1375			
$\text{C}(\text{CH}_3)_2$		1385 m and 1370 m			
$\text{C}(\text{CH}_3)_3$		1394 w and 1370 s			
$\text{O} = \text{C—CH}_3$		1370 s			
CH_2		2925, 2850 and 1460			
$\text{CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2$		724			
$\text{O} = \text{C—CH}_2$, $\text{N} \equiv \text{C—CH}_2$		1420			
Olefins					
$\text{C} = \text{C}$			1680–1630		
Conjugated $\text{C} = \text{C—C} = \text{C}$			1650 and	1600	
$\text{R—CH} = \text{CH}_2$	3080 w	1820 w	1645 m	1415 m	990 s, 910 s
$\text{R}_2\text{C} = \text{CH}_2$	3080w	1780 w	1645 m	1415 m	890 s
$\text{R—CH} = \text{CH—R}$	cis	3030 w	1645 m	1415	730–650 m
$\text{R—CH} = \text{CH—R}$	trans	3030 w	1670 w		970 s
$\text{R}_2\text{C} = \text{CHR}$		3030 w	1670 w		840–790
(R-hydrocarbon group)					
Aromatics					
aromatic CH			3100–3000		
aromatic ring			frequencies	1600,1580,1500.and 1450	
5 adjacent,			H780–730	mono 710–680	
4 adj.			H770–735		
3 adj.			H 795–770	meta 710–680	
2 adj.			H850–795		
1 lone			H890–835		
Overtones and combinations					2000–1700
in plane CH bend					1200–1000
Triple and cumulated double bonds					
$\text{C—C} \equiv \text{C—H}$		2140–2100		$\equiv\text{C—H}$ 3340–3267	
$\text{C} = \text{C} = \text{CH}_2$		2000–1900			
$\text{CH}_2\text{—C} \equiv \text{N}$		2260–2240		$\text{CH}_2\text{—CN}$ 1420	
conj— $\text{C} \equiv \text{N}$		2235–2220			

(Continued)

Table 3.8 Infrared spectra-structure correlations (in cm^{-1}) —Cont'd.

$\text{—S—C}\equiv\text{N}$	2170–2135	
—N=C=S	2150–2050	
—N=C=O	2275–2263	
<i>Carbonyls</i>		
R—CO—N		1695–1630 NH_2 3350, 3180 and 1630 NH ; 3300 and 1550
R—CO—OH		1720–1680 OH ca 3000 broad
R—CO—R		1725–1705, singly conjugated 1700–1670; doubly conj. 1680–1640
R—CO—H		1740–1720 conj. 1710–1685 CH 2900–2800 and 2775–2695
R—CO—O—R		1750–1735 conj. 1735–1715
strained ring		C=O 1850–1750
R—O—CO—Cl		1785–1775 C—O 1172–1134
R—CO—Cl		1810–1795 aryl- CO—Cl 1785–1765 and 1750–1735
R—CO—O—CO—R		1825–1815 s and 1755–1745 m
cyclic anhydride		1870–1845 w and 1800–1775 s
C—O		
$\text{CH}_2\text{—O—CH}_2$		1140–1085
$\text{CH}_2=\text{CH—O—CH}_2$		1225–1200
Aryl- O—CH_2		1310–1210 and 1050–1010
epoxy		950–815, 880–805 ca 3050
alcohol ca		3300 broad
$\text{CH}_2\text{—OH}$		1075–1000
$\text{R}_2(\text{CH—OH})$		1125–1090
$\text{R}_3(\text{C—OH})$		1210–1100
Aryl- OH		1260–1180
<i>Nitrogen compounds</i>		
NH_2		3370 3300 3200 (w) 1600
NH		3350
$\text{CH}_2\text{—NH}_2$		1080
$\text{CH}_2\text{—NH—CH}_2$		1130
Aryl- NH_2		1300
N—R_3		2800
C=N		1690–1630
C=N—O		1000–900
O=N—O—C		1650 trans, 1610 cis and 814–751
$\text{O}_2\text{N—O—C}$		1640, 1280 and 870–840
$\text{CH}_2\text{—NO}_2$		1550 and 1375
$\text{CH}_3\text{—C—NO}_2$		1550, 1390 and 1360
Cl—C—NO_2		1570 1350
arom. NO_2		1515 1350
$\text{R—C}\equiv\text{N}$		2240–2260 (m)
<i>Halogens</i>		
C—Cl		830–560
$\text{C—CH}_2\text{—CH}_2\text{—Cl}$		725 and 650
$\text{CH}_2\text{—Cl}$		1300–1240

Table 3.8 Infrared spectra-structure correlations (in cm^{-1})—Cont'd.

cyclic C—Cl	742 eq, 688 ax
aryl C—Cl	1094–1035 p→ m → o
C—Br	700–515
C—CH ₂ —CH ₂ —Br	644 and 563
CH ₂ —Br ca.	1240
cyclic C—Br	685 eq, 658 ax
aryl C—Br	1075–1025 p→ m → o
C—F	1000–1400 (s)
C—I	~500 (s)
<i>Sulphur</i>	
SH	2590–2540w
C—SO ₂ —C	1320–1140
C—SO ₂ —N	1340–1160
C—SO ₂ —OH	1350–1160
C—SO ₂ —O—C	1350–1180
C—SO ₂ —Cl	1375–1180
C—SO ₂ —F	1400–1205
C—SO ₃ ⁻ H ₃ O ⁺	1200–1050
C—SO ₃ ⁻ Na ⁺	1200–1050
C—S	600–800 (w)
C=S	1050–1200 (s)
<i>Boron</i>	
BH	2640–2350
B .. H .. B	2220–1540
B—O	1380–1310
B—N	1465–1330
B—OH	3300–3200
<i>Phosphorus</i>	
PH	2440–2275
P=O	1300–1140
P—OH	2700–2200 very broad
P—O—C	1050–970
P—O—C ₂ H ₅	2990, 1485, 1450, 1395, 1375, 1160
P—O—CH ₃	2960, 1460, 1180
<i>Silicon</i>	
Si—H	2250–2100
Si—O	1100–1000
SiCH ₃	1265–765
Si(CH ₃) ₂	1265–860 and 800
Si(CH ₃) ₃	1265–840 and 765
<i>Inorganic ions</i>	
CO ₃ ²⁻	1410–1450(v.s.) 860–880(m)
SO ₄ ²⁻	1080–1130 (v.s.) 610–680 (m)
NO ₃ ⁻	1350–1380 (v.s.) 815–846 (m)

(Continued)

Table 3.8 Infrared spectra-structure correlations (in cm^{-1}) —Cont'd.

NO_2^-		1320–1380 1230–1250 (v.s.) 800–840(w)
NO_2	Fund. frequencies	1618, 1320, 750
NO_2^-		1328, 1261, 828
NO_2^{2-}		1298, 1238, 880
NH_4^+		3030–3300 (v.s.) 1390–1430 (w)
$\text{PO}_4^{3-}, \text{HPO}_4^{2-}, \text{H}_2\text{PO}_4^-$		1000–1100 (s)
$\text{CN}^-, \text{SCN}^-, \text{OCN}^-$		2000–2200 (s)
Silicates		900–1100 (s)

v.s. = very strong; s = strong; m = medium; w = weak; b = broad.

(ii) Electronegativity The intrinsic power of an atom to attract the electrons within the molecule is called its electronegativity. A covalent bond between C and F develops an ionic character, because a partial negative charge at F and equivalent positive charge on C are produced due to higher electronegativity of F than C. The coulombic attraction between opposite charges makes the bond stronger than a purely covalent one. Thus, the position and intensity of the corresponding band in the spectrum will be affected due to the ionic character of the bond.

For example, the C—H stretching frequency in HCN is observed at 3312 cm^{-1} while that of F—C in FCN is observed at 1250 cm^{-1} . This lowering of frequency is not mainly due to mass effect but due to higher ionic character of F—C bond (~43 per cent). The relatively higher ionic character makes F—C bond stronger and hence large value of F—C force constant (9.2 millidynes/Å in comparison to that of C—H bond where the value of force constant has been estimated to be of the order of 5.8 millidynes/Å). Percentage of ionic character = $100[1 - \exp\{-0.25(X_A - X_B)^2\}]$ where X_A and X_B are the electronegativities of atoms A and B respectively on the Pauling scale.

(iii) Inductive Effect The action of one group of a molecule to affect electrostatically the electron distribution in the other groups is described as the inductive effect. It may act across space as well as through bond. Due to the change in the charge distribution in the molecule, the frequencies of many bonds may be altered. The inductive effects on C = O stretching frequencies are shown in Fig. 3.27. It is inferred from Fig. 3.27 that electron attracting groups tend to raise while electron repelling groups tend to lower the frequency of the C = O stretching band.

(iv) Resonance Splitting As a rule the vibrations of different symmetries, e.g. the in-plane and out-of-plane vibrations in a planar molecule do not interact with each other. However, when each of the two bonds oscillates with a common atom having nearly the same individual frequency, they interact very strongly. The resulting

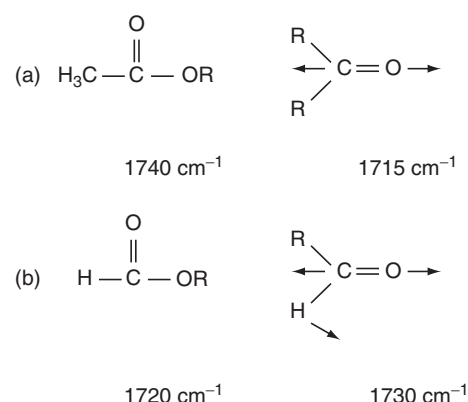


Fig. 3.26 The C=O mass effect: (a) in acetates/ketones, and (b) in formates/aldehydes.

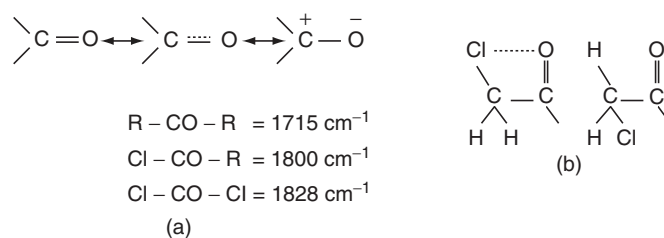


Fig. 3.27 Inductive effects on C = O stretching frequencies (a) through bond, and (b) across the space (field effect).

frequencies are displaced from their original positions, depending upon the relative phasing and coupling of two oscillators, e.g. in allene ($\text{CH}_2 = \text{C} = \text{CH}_2$), because of the common atom, the coupling between the two $\text{C} = \text{C}$ stretching vibrations is so strong that the in- and out-of-phase $\text{C} = \text{C}$ stretching vibrations will be in the single (1071 cm^{-1}) and triple (1980 cm^{-1}) bond regions respectively.

(v) Mesomeric Effect This is a resonance effect and may be affected by electron-loving and hating groups or due to conjugation. Consequently, the group frequencies may shift due to this effect. It can be shown mathematically from wave mechanics that when an electron exchange is possible and does take place, the energy of resonating structures is less than that of the molecule without exchange. Thus, resonance energy leads to an increase in stability of the resulting structures. Resonance may arise from oscillations of electrons from one position in the molecule to another. This is what happens in the case of $\text{C}_6\text{H}_5\text{CHO}$, or $\text{C}_6\text{H}_5\text{OH}$ and we get resonance structures. In $\text{C}_6\text{H}_5\text{CHO}$, the exchange of π -electrons takes place between $\text{C} = \text{O}$ bond and benzene ring and we call it by the name of *conjugation*. For effective conjugation, the two parts should be planar or nearly planar.

The influence of this effect on the stretching vibration of the carbonyl group in some typical molecular systems is shown in Figs 3.28(a) to (c). The decrease of carbonyl double bond character, i.e. carbonyl stretching frequency in amides, esters and acid chlorides due to this effect follows the order: amides > esters > acid chlorides [Fig. 3.28(a)]. It conforms to the expected trend on the basis of mesomeric electron donation of heteroatoms, i.e. nitrogen, oxygen and chlorine to the $\text{C} = \text{O}$ group, i.e. $\text{N} > \text{O} > \text{Cl}$. Further, when electron withdrawing group is present on the ester oxygen or amide nitrogen, the mesomeric electron donation decreases, thereby the carbonyl frequency for esters or amides having such groups increases, [Fig. 3.28(b)]. Figure 3.28(c) exhibits another type of mesomeric effect, i.e. conjugation. When $\text{C} = \text{O}$ is conjugated with $\text{C} = \text{C}$ or aromatic ring, the delocalisation of electrons results in lowering of the $\text{C} = \text{O}$ frequency.

(vi) Hydrogen Bonding When a proton is attached to a more electronegative atom, say A (= Cl, O, F, etc.), forms a partial bond with a neighbouring electronegative atom, say B (= Cl, O, F, etc.) or a π -bond, e.g. $\text{C} = \text{O}$, $\text{C} = \text{C}$, aromatic ring, etc., it is known as hydrogen bonding. It may be intramolecular or intermolecular; the former being stronger than the latter.

The strongest hydrogen bonds are formed when the atomic centres A, H and B are collinear. The energy of a hydrogen bond is of the order of a few kilocalories ($10 \text{ kcal mole}^{-1}$); weaker by a factor of 10 than the covalent bond between atoms and stronger by almost the same factor than the Van der Waals bond.

The vibrations of the H-bonded complex $\text{A}-\text{H} \cdots \cdots \text{B}$ useful in H-bonding studies are; (i) the fundamental $\text{A}-\text{H}$ stretching frequencies, $\nu(\text{A}-\text{H})$; (ii) $\text{A}-\text{H}$ in-plane deformation (bending) frequencies, $\delta(\text{A}-\text{H})$;

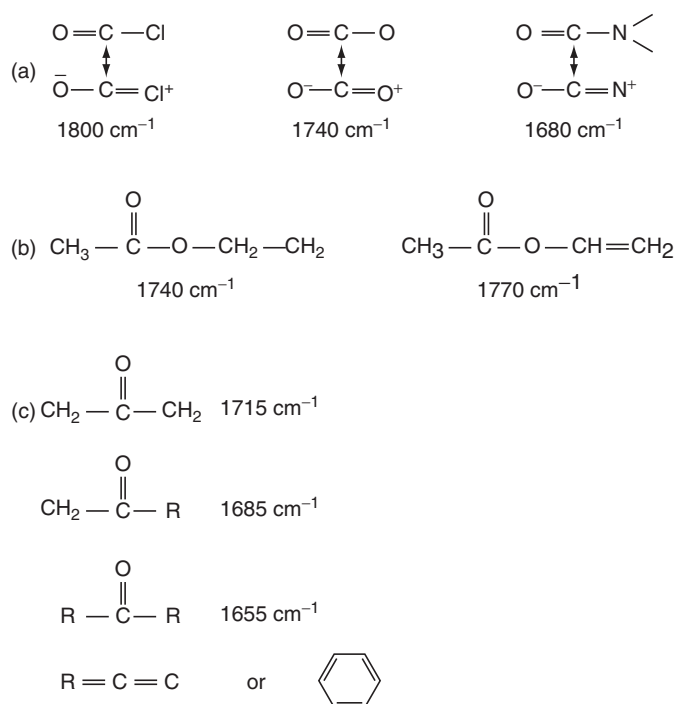


Fig. 3.28 (a)-(c) Mesomeric effect on carbonyl stretching frequencies.

(iii) A—H out-of-plane deformation (bending) frequencies, $\gamma(\text{A—H})$; (iv) AH ... B fundamental stretching frequencies, $\nu(\text{H... B})$; (v) AH... B deformation (bending) frequencies, $\delta(\text{H... B})$ and $\gamma(\text{H... B})$. These are represented in Fig. 3.29.

The main effects of hydrogen bonding on the vibrations of the participants are as follows:

- The absorption bands due to the A—H stretching vibrations (fundamentals and overtones) are shifted to lower frequencies. These shifts range from about 30 cm^{-1} to several hundred cm^{-1} or more. This effect is due to the weakening of the force constant for the A—H stretching mode caused by the formation of the H bond.
- The shifted absorption bands due to the H bonded A—H stretching vibration are much broader than the corresponding bands of the non-H bonded A—H groups. The change in band width ($\Delta\nu_{1/2}$) varies from $\sim 30\text{ cm}^{-1}$ to 100 cm^{-1} or more. The breadth and structure of H bonded A—H stretching vibrations are affected very little by change in phase or temperature.
- In addition to the broadening, the integrated intensity of fundamental A—H stretching bands grows sometimes by factors of up to ten or more. However the corresponding overtones decrease slightly in integrated intensity. The reasons for these intensity effects are probably related to the fact that H bonds have substantial electrostatic character and the intensity of absorption due to IR active vibrations is directly proportional to the rate of change of the electrostatic dipole moment with internuclear distance.
- The A—H deformation modes are shifted to higher frequencies. These shifts are appreciably smaller as compared to that of A—H stretching vibrations. Formation of H bonds constraints the deformation vibrations and therefore increases the force constants for these modes.
- The A—H deformation modes do not show any substantial band broadening or intensity change when H bonding occurs.
- New vibrational modes corresponding to H...B stretching and deformation are found at low frequencies in the far IR region.
- The vibrational modes of the H bond acceptor, B are shifted by H bonding. These shifts may be either to longer or shorter wavelengths, and are generally much smaller than those found for the donor A—H vibrations.

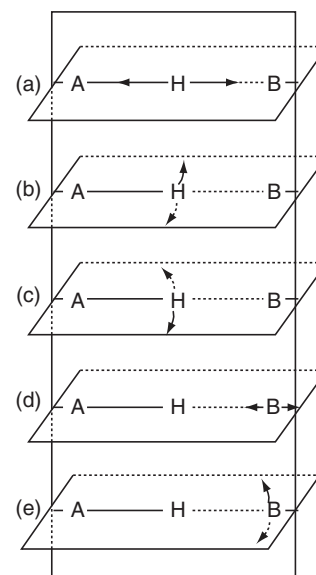


Fig. 3.29 Vibrations of hydrogen bonded complex A—H ... B.

(vii) Dielectric Constant The stretching frequencies of polar groups of molecules in nonpolar solvents depend on the dielectric constant D of the solvent. The frequency ν_s in the solution phase is related to dielectric constant of the solvent by the Kirkwood–Bauer–Magat equation, i.e. $(\nu_0 - \nu_s)/\nu_0 = K(D - 1)/(2D + 1)$. Here ν_0 is the frequency in the vapour phase and K is a proportionality factor.

(viii) Bond Angle Ring Strain The observed C = C frequency shift with bond angle ring strain in alicyclic systems is caused by a change in interaction between C = C and C—C stretching vibrations rather than by a large change in the force constant. In cycloalkenes, $(\text{CH}_2)_n\text{—}2\text{H}$ where $n = 3, 4, 5, 6$, when C = C—C angle is 90° , the interaction between C—C and C = C stretching vibrations is nearly zero. As a result, the C = C frequency is expected to be minimum when C = C—C angle is 90° and progressively grows as the angle gets larger or smaller. On the other hand in alkylidene substituted cycloalkanes, $[(\text{CH}_2)_n\text{—}2\text{H}] = \text{C}$, the exocyclic C = C stretching frequency progressively increases with the bond angle strain, i.e. decreases as the cyclic C = C—C angle decreases. In 1, 2-dialkyl-cycloalkenes; $\text{C—}[(\text{CH}_2)_n\text{—}4\text{H}]\text{—C}$; a decrease in cyclic C—C = C angle (which lowers the frequency) is compensated by increase in exocyclic C—C = C angle (which raises frequency). The C = C stretching frequency, therefore, remains unchanged until the ring angle becomes smaller than 90° . A further decrease in the cyclic C—C = C angle then raises the frequency.

In lactones, the C = O and C—O frequency shifts with ring size are primarily caused by the mechanical effects rather than by large changes in force constants. As the ring size decreases, the C = O stretching frequency increases whereas C—O decreases. The divergence in the C = O and C—O stretching frequencies with ring size is caused by the change in interaction between C—O and C = O stretching vibrations.

Since all these factors affect the characteristic group frequencies to different extent, one must be very careful while assigning a particular band unequivocally in an unknown spectrum. In large molecules, the assignment of normal modes, their overtones, combinations (sum or difference), bands becomes fairly complicated. However, if the point group for the molecule in vapour phase is known by any other method, the vibrations can be divided into various symmetry species of the group. The selection rules from the character table will provide information

about the allowed and forbidden transitions which will ultimately help the vibrational assignments, e.g. the data on the IR vibrational frequencies (in cm^{-1}): 3380 m, 3020 m, 2970 m, 2585 vw, 1735 vst, 1425 m, 1365 s, 1287 m, 1225 w, 1128 vst, 1072 w, 1000 s, 860 w, 830 m and 628 vst (in Raman only) and elemental analysis, C = 31.57, H = 5.26 and S = 42.10 per cent correspond to the structure CH_3COSH . The absence of any band in the OH stretching and bending regions rules out the possibility of structure CH_3CSOH . Deuteration effect also conforms to these conclusions.

Polarised infrared spectra of $\text{Re}_2(\text{CO})_{10}$ when recorded in a suitable liquid crystal solvent show three bands at 2070 m, 2010 vs and 1970 w cm^{-1} as shown in Fig. 3.30.

$\text{Re}_2(\text{CO})_{10}$ molecules orient with their long molecular axis which is parallel to the direction of infrared incident beam. Thus, the two bands at 2070 and 1970 cm^{-1} are polarised parallel ($\rho_{\text{ir}} > 1$) to the long molecular axis whereas the band at 2010 cm^{-1} is polarised perpendicular ($\rho_{\text{ir}} < 1$) to the long molecular axis as expected. $\text{Me}_2(\text{CO})_{10}$ molecule belongs to D_{4d} symmetry and hence have three allowed C = O stretching normal modes of vibrations, i.e. $2B_1 + E_1$. According to group theory, E_1 vibration is polarised perpendicular and B_2 vibrations are polarised parallel to the molecular axis.

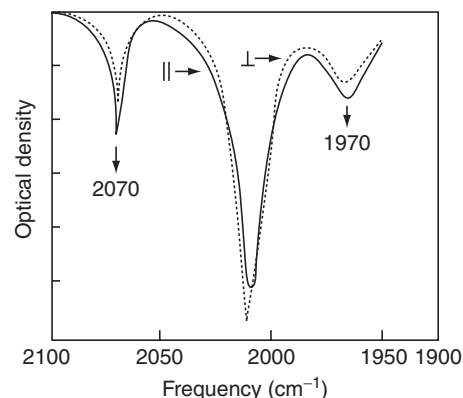


Fig. 3.30 Polarised infrared spectra of $\text{Re}_2(\text{CO})_{10}$ in a liquid crystal in the 1900-2100 cm^{-1} region.

(b) Identification of Molecular Species Since IR spectra are differentiable for many different species, one can easily make use of this property for the identification of molecular species in a mixture and also molecular species of the same compound in the solution. The presence of three bands at 3638, 3632 and 3627 cm^{-1} in the OH stretching region in the high resolution spectrum of 1-propanol in dilute CCl_4 indicate the presence of three OH groups in conformationally distinct environments. The spectrum of 1-propanol in the OH stretching region and equilibria between its rotamers are shown in Figs 3.31 and 3.32 respectively.

Recently, IR spectroscopy, low and high resolution in conjunction with other spectroscopic and non-spectroscopic techniques has proved to be a boon to the space chemists for the detection of various molecular species in space, e.g. spectral analysis has revealed the presence of CO_2 (97 per cent), N_2 (< 2 per cent), H_2O vapours (~1 per cent) and O_2 (~0.1 per cent) in the atmosphere of Venus. The absence of amide bands in Venus material due to the peptide linkages in proteins rules out the possibility of life on this planet as expected earlier.

(c) Study of Environmental Effects of Molecular Systems Since molecules are generally affected by their environments, the IR spectral shifts can give valuable information about the inter- as well as intramolecular interactions. This is demonstrated with the aid of the following examples. The IR spectroscopic studies on acetic acid reveal that it exists mainly as dimer due to intermolecular H-bonding at room temperature while at 150°C it is predominantly monomeric. The broad OH band at 3000 cm^{-1} observed at room temperature appears at 3580 cm^{-1} as a narrow band when temperature is raised to 150°C. The in-plane and out of plane bending vibrations of

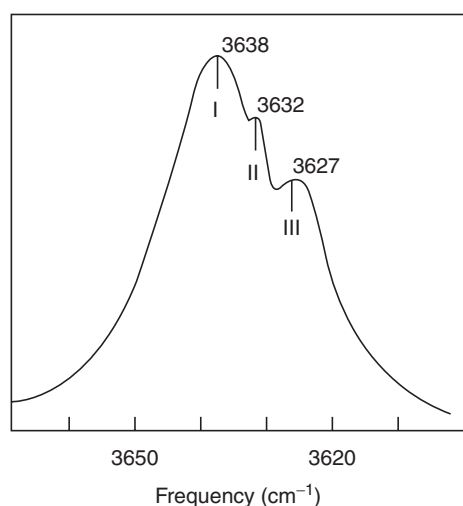


Fig. 3.31 The $\nu_{\text{OH}}(\text{O—H})$ band of 1-propanol in CCl_4 .

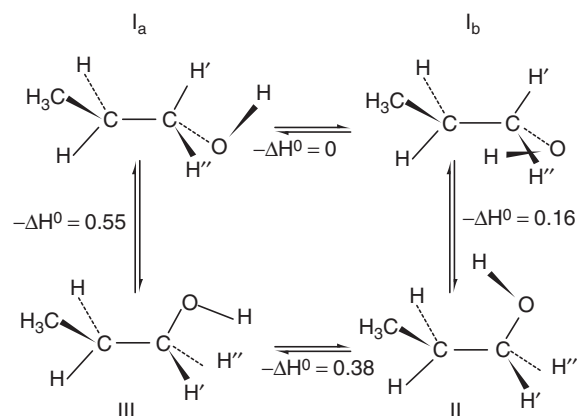
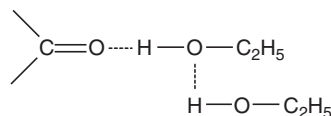


Fig. 3.32 Equilibria between the rotamers of 1-propanol (ΔH° in kcal mole^{-1}).

the OH group at 1400 and 1000 cm^{-1} shift to higher frequencies at low temperatures where acetic acid is more associated. These results are supported by deuteration effect also.

Spectra of ethyl acetate in ethanol and ethanol + water show three bands at 1740 , 1725 and 1705 cm^{-1} . They may be due to (a) the free C = O group of ethyl acetate, (b) 1 : 1 bond complex $\text{>C=O} \cdots \text{H-O-C}_2\text{H}_5$, and (c) 1:2 H bonded complex.



The IR spectra of thiolacetic acid and thiolbenzoic acids in both the fundamental and first overtone regions of the S—H stretching vibration in a mixture of CCl_3F and $\text{C}_2\text{F}_4\text{Br}_2$ in the temperature range 20 to -190°C reveal that S—H...O type bonds are formed at low temperature or at high concentration of solute. The existence of two associated bands (2570 cm^{-1} , 2530 cm^{-1}) in the S—H stretching region and the virtual absence of the free S—H and C = O bands at low temperature seems to show that only the cyclic structure (I) remains at the lowest temperature but the possibility of having open structure (II) is likely at intermediate temperatures. Chain and cyclic

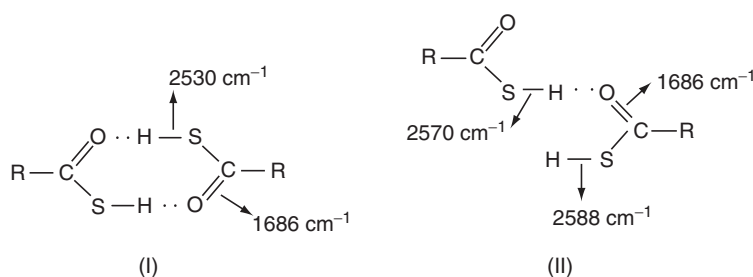


Fig. 3.33 The cyclic and open-chain structures of aliphatic and aromatic thiolacids.

structures are shown in Fig. 3.33.

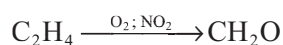
If the molecule is physically adsorbed it is subjected only to weak intermolecular forces of the van der Waals type and thus its symmetry is only slightly perturbed from that of the gas phase. Accordingly, the infrared spectrum is altered only slightly, and small frequency shifts, usually less than 1 per cent are observed (some Raman vibrations inactive in IR become IR active because of adsorption). During the chemisorption process, however, the symmetry of the adsorbed species is completely different from that of the gaseous molecule, the surface bond is very strong, and the adsorption may be dissociative in nature. In this case, a completely new infrared spectrum is observed and band shifts and intensities are far removed from those of the gaseous adsorbate.

C—O stretching frequency observed in gaseous carbon monoxide at 2143 cm^{-1} , is shifted to 2000 – 2100 cm^{-1} after monodentate ligand formation with transition-metal compounds of Ni, Fe, Co, Mn and Re. Bidentate ligand formation causes a greater shift in frequency, the C—O stretch usually is observed below 2000 cm^{-1} . Thus, the bands above 2000 cm^{-1} are attributed to a 'linear' CO group on the surface, $\text{Ni}_s\text{—C}=\text{O}$ (type A), and those below 2000 cm^{-1} to a 'bridged' CO structure, $(\text{Ni}_s)_2\text{C}=\text{O}$ (type B). CO chemisorbed on silica supported Fe, i.e. Fe/SiO_2 gives rise to two bands at 1950 and 850 cm^{-1} . They are attributed to C—O and Fe—C stretching vibrations respectively. The force constants for the C—O and Fe—C bonds are of the order of 14 and 4 millidynes/Å, respectively. The Fe—C bond distance as computed from the application of Pauling electronegativity data has been found to be 1.67 Å and the bond is estimated to have 12 percent ionic character. The bond order of both of the C—O and Fe—C bond is ~ 2 . In view of this, the surface species is written as $\text{Fe}_s=\text{C}=\text{O}$.

Adsorption of ammonia on well-dried silica–alumina surfaces reveals that coordinately bonded ammonia gives bands at 3335 , 3280 and 1610 cm^{-1} and the adsorbed NH_4^+ ions exhibit bands at 3270 and 1440 cm^{-1} .

Adsorption of the isotopic species $^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}$ and $^{15}\text{N}_2$ on Ni– SiO_2 surface gives rise to separate distinctive bands in the spectrum at 2195 , 2160 and 2123 cm^{-1} respectively, thereby suggesting that dissociation of the nitrogen molecule does not take place during the adsorption process. The force constants determined from the isotopic shifts are found to be of the order of 19.1×10^{-5} and 3×10^{-5} dynes/cm for the N—N and Ni—N bonds respectively.

Reaction product obtained on oxidation of ethylene depends upon the nature of catalyst used and there is a correlation between ethylene frequency and catalyst frequency. NO_2 exhibits three vibrational modes ν_1 , ν_2 and ν_3 at 1321 , 648 and 1621 cm^{-1} . In the presence of NO_2 , ethylene is oxidised by molecular oxygen to formaldehyde, i.e.

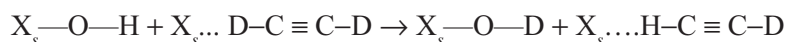


The loss of oxygen from the NO_2 molecule proceeds via the ν_3 vibration (1621 cm^{-1}) since C_2H_4 also exhibits an identical frequency at 1625 cm^{-1} . Thus, only the vibrations of catalyst and reactant having identical frequencies will cause fragmentation. Hydrolysis of ethylene in presence of Al_2O_3 yields ethanol. The ethylene frequency at 950 cm^{-1} corresponds to the AlO frequency of the catalyst at 964 cm^{-1} . Ethylene oxide is obtained as an oxidised product when AgO is used as a catalyst. The first overtone of AgO at 962 cm^{-1} corresponds to the ethylene frequency at 950 cm^{-1} .

The stretching frequency of NO is observed at 1843 cm^{-1} whereas those of NO^+ and NO^- falls in the range $1575\text{--}1940\text{ cm}^{-1}$ and $1040\text{--}1200\text{ cm}^{-1}$ respectively. The adsorption of NO on nickel surface exhibits bands at 1840 (N—O) , 650 and 625 (Ni—N) cm^{-1} . The force constants for the respective bands are 13.0 and 5.7 millidynes/ $\text{\AA}$. On both the Fe and Ni surface, NO is partially decomposed to give $\text{N}_2(\text{g})$ and O , i.e. $2\text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{O}_{\text{ads}}$. An absorption band due to nickel oxide formed by this process has also been observed and at this stage the surface potential is found to be negative, due to adsorbed oxygen. Adsorption of more NO imparts positive potential to the surface which may be due to the presence of NO_{ads}^+ . At this stage the reaction $\text{NO}(\text{g}) + \text{NO}_{\text{ads}} \rightarrow \text{N}_2\text{O}(\text{g}) + \text{O}_{\text{ads}}$, further complicates the interpretation of the spectra. Neither hydrogen nor oxygen at room temperature reacts with adsorbed species.

CO_2 chemisorbed on alumina at room temperature exhibits strong bands at 1770 , 1640 , 1480 and 1232 cm^{-1} . The physically adsorbed CO_2 on silica is observed at 2350 and $1800\text{--}1870\text{ cm}^{-1}$.

The normal and combination modes of vibration of C_2H_2 are $\nu_1[\nu_{\text{sym}}(\text{C—H})]$, R , 3374 cm^{-1} , $\nu_2[\nu(\text{C} \equiv \text{C})]$, R , 1974 cm^{-1} , $\nu_3[\nu_{\text{asym}}(\text{C—H})]$, R , IR , 3287 cm^{-1} , $\nu_4[\delta_{\alpha}(\text{C—H})]$, R , 612 cm^{-1} , $\nu_5[\delta_{\beta}(\text{C—H})]$, IR , 729 cm^{-1} and $\nu_4 + \nu_5$ (1341 cm^{-1}). Adsorption of C_2H_2 on alumina gives a spectrum in which two species can be identified. One species can be completely removed from the surface by a 5-second evacuation at room temperature, is observed only at pressures above 0.5 cm and is characterised by bands at 3220 and 1950 cm^{-1} . The former band is attributed to the (ν_3) C—H stretching vibration and the latter to the (ν_2) $\text{C} \equiv \text{C}$ stretching mode. The strongly adsorbed acetylene is stable up to 300°C and shows a $\text{C} \equiv \text{C—H}$ stretching mode at 3300 cm^{-1} and a $\text{—C} \equiv \text{C—}$ stretching vibration at 2007 cm^{-1} . The $\nu_4 + \nu_5$ combination band does not appear in the spectrum. The value of the ν_3 vibration (3300 cm^{-1}) lies between the value for gaseous C_2H_2 (3287 cm^{-1}) and methylacetylene (3334 cm^{-1} , gas; 3305 cm^{-1} , liquid). This in conjunction with the asymmetry implied by the presence of $\text{—C} \equiv \text{C—}$ vibration and the lack of $\nu_4 + \nu_5$ combination band suggests that C_2H_2 is adsorbed in an end-to end position: $\text{X}_s \dots \text{H—C} \equiv \text{C—H}$ or $\text{X}_s \dots \text{C} \equiv \text{C—H}$. Further, the addition of C_2D_2 to a hydroxylated surface shows that the intensity of the OH band at the highest frequency diminished and a new single band at 2785 cm^{-1} due to OD appears. This exchange may be represented as



The surface O—D groups can be removed by evacuation at 900°C . This leads to infer that the sites responsible for C_2H_2 adsorption are not hydroxyl groups.

The vibrational spectra of molecules undergoing rotational isomerism and keto-enol tautomerism are most likely to be affected on adsorption, because the free rotation of molecules is restricted upon adsorption. The *cis/trans* ratio as determined from spectral data on dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$) adsorbed on silica gel is 1.9 as compared to 1 in chloroform solution and 1.4 in the neat liquid. The keto/enol ratio in acetylacetone adsorbed on silica gel has been found to be of the order of 8.6 . This ratio in chloroform solution and for pure liquid is 1 and 2.4 respectively.

The rotational motion of surface functional groups can also be studied. In the IR adsorption studies of $\text{H}_2\text{O}/\text{D}_2\text{O}$ on silica surface, P (very weak), Q (strong), R (very weak) branches of surface silanol, i.e. >Si—OH/OD has been observed. The separation of the band maxima of P- and R- branches are $200/140\text{ cm}^{-1}$. The relation between the separation of the P- and R- branches, i.e. $\Delta\nu$ due to Peri and Herzberg is given by the expression:

$$\Delta\nu = \frac{8kTB}{hc} = 2.358 TB\text{ cm}^{-1},$$

where the terms and symbols have their usual meanings.

If the Si—O—H bond angle is θ and if ϕ is the angle between the axis of rotation and the O—H axis, then

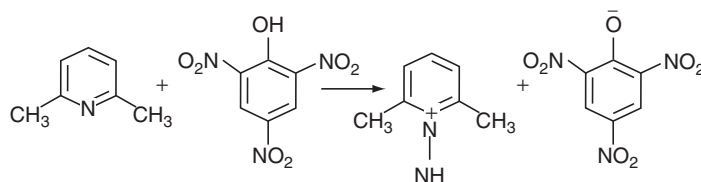
$$I_B = \mu_m r^2 \cos^2(\phi - 90^\circ)$$

Thus if $r_{\text{OH}} = 0.958$ (from water), the angle ϕ can be calculated. The true Si—O—H bond angle θ is slightly less than ϕ and is calculated to be 113° .

In view of the foregoing examples on the adsorption of different type of chemical species on different adsorbing surfaces, it is concluded that the spectra of adsorbed species is pressure, temperature and nature of the adsorbing surface dependent.

(d) Study of Charge-Transfer Complexes Molecular complex of charge-transfer type is formed between an electron donor with low ionisation potential, i.e. an electron-rich molecule and an electron acceptor with high electron affinity, i.e. an electron-deficient molecule. Charge transfer occurs primarily in the excited state and is stabilised relative to the ground state by electrostatic interaction between the separated charges on the donor and acceptor whereas in H-bonded adducts, the electrostatic contribution is predominantly to the ground state of the complex. When the infrared spectra of charge transfer complexes are compared with those of isolated molecules which form the complexes, four types of changes may occur:

- (i) The vibrational frequencies in donor or acceptor (or both) may be shifted. The spectra of complexes clearly resemble the summation of spectra of both the donor and acceptor portions if there is weak interaction between the components. Some of the differences which are observed in the solid state may be because of *crystal packing*. Sometimes, the vibrational frequencies are shifted as much as 150 cm^{-1} . In such a case, the initial bonding within the constituents is disturbed by complex formation, as to be expected, but only enough to change a certain fraction of bond order. The decrease in energy of a particular bond also provides information about the particular site of a charge transfer interaction, for instance, the interaction of sulphur dioxide with N,N-dimethylaniline is through the nitrogen atom since the C–N stretching frequency of free amine decreases on complex formation. The decrease in C = O stretching energy of N, N-dimethylacetamide on complexation with iodine is an evidence for the interaction of iodine with oxygen atom of the amide. The band shift on complex formation may be fixed as a criterion for the classification of donor-acceptor complexes, e.g. the infrared spectra of the solid complex of o-phenylenediamine with 7, 7, 8, 8-tetracyano-quinodimethane with molecular composition 1 : 1 are similar to the spectra of components and hence the complexes are characterised as of nonbonded type. However, in the spectra of 2:1 composition, the C = N and the ring C = C stretching bands get shifted with variation in intensity and the complexes are classified as of ionic type. The general lack of change in the infrared spectrum on complex formation is used to distinguish between weak charge transfer complex and the products of electron transfer or proton transfer reactions. In case of complete electron transfer from donor to the acceptor in the ground state, the spectrum corresponds closely to the sum of the spectra of the two ions. On the other hand, in case of proton transfer, a new band due to the formation of a protonated group may also appear, e.g. when the infrared spectrum of an addition compound of 2,6-dimethylpyridine with picric acid with molecular ratio 1 : 1 is recorded in KBr, the band due to OH group of picric acid at 3110 cm^{-1} is not observed. Instead, a new band at 3080 cm^{-1} characteristic for the —NH^+ group is observed. The expected range for the —NH^+ group vibrational band is $2900\text{--}2500\text{ cm}^{-1}$. Thus, one can safely assume that the bonding in the complex occurs essentially through the proton transfer and consequently electrostatic attraction between positive and negative ions as shown in the following scheme.



- (ii) The intensities of the bands may be influenced considerably. The changes in energy and intensity of the vibrational bands on charge transfer complexation are generally larger in complexes involving σ -donors and σ -acceptors than in the π - π interactions.
- (iii) New low-energy bands may appear due to the fundamental stretching vibrations of the intermolecular bonds formed between the isolated molecules involved in the complexation, e.g. two bands at 145 and 184 cm^{-1} in the infrared spectra of iodine-trimethylamine solid complex in nujol mull have been assigned to intermolecular vibration mode of N...I and intramolecular I—I stretching vibration respectively, N...I distance in the complex is $2.27\text{ \AA}$. The I—I bond distance in the free acceptor is 2.67 while $2.84\text{ \AA}$ in the complex. The N...I vibration modes for iodine-pyridine, iodine-3, methylpyridine, iodine-3, chloropyridine and iodine-3, bromopyridine complexes in cyclohexane solution appear at 94 , 89 , 73 and 65 cm^{-1} respectively.
- (iv) The infrared vibration may become active with decrease in energy, e.g. the infrared inactive stretching vibrations of the homopolar diatomic halogen acceptors such as I_2 , Br_2 or Cl_2 become infrared active but with decrease in energy on complexation with an electron donor, e.g. the Cl—Cl fundamental vibration band of liquid $^{35}\text{Cl}^{37}\text{Cl}$ which appears at 541 cm^{-1} in the Raman spectrum has been observed at 513 cm^{-1} in the infrared spectrum of $\text{Cl}^{35}\text{Cl}^{37}$ in benzene. The Raman spectra of bromine and iodine gases exhibit bands at 317 and 213 cm^{-1} respectively. However, in toluene solutions, the respective bands appear at 300 and 204 cm^{-1} in the infrared spectra.

(e) Study of Polymers Infrared spectroscopy has been employed to characterise chain structure of polymer and has led to the explanations of the reactions of multifunctional monomers including rearrangement and isomerisation. End group, cross links, branches and many other structural characteristics are studied by this technique. This method is also used as a tool to measure end groups, isomeric composition, stereoregularity, copolymer composition, additives, fillers, plastisizers.

Infrared spectra of pure polymers show only a few bands, e.g. only five infrared bands are observed in spectrum of polythene. Two types of distinct relations have been observed between spectra of monomer and polymer: (i) spectrum of a polymer that has a complicated monomer structure is similar to the spectrum of monomer, e.g. cellulose; (ii) spectrum of a polymer that has a simple monomer structure is different from the spectrum of monomer. Monomer spectrum in such a case is more complex than polymer spectrum, e.g. polythene.

Spectra of polymers could best be understood on the basis of coupled vibrators. Let us consider a chain of n identical vibrators coupled together and having identical frequency. Then the single identical frequency is split into n components given by

$$\nu_m^2 = \nu_0^2 + w_c^2(1 + \cos \theta)$$

where $\theta = \frac{m\pi}{n+1}$ and $m = 1, 2, 3, \dots, n$ are the modified and ν_0 is the unmodified frequencies and w_c is the coupling parameter. Thus one frequency should split into n frequencies closely spaced since n is always small. The characteristic group frequency of a monomer is retained in the polymer, e.g. C—H frequency in polythene. When w_c is large, a wide range of frequencies can occur and gives rise to skeletal vibrations. Square of observed frequency when plotted as a function of $(1 + \cos \theta)$ gives rise to straight line. When n becomes infinite, only one band is active in infrared while all others are IR inactive, so one shifted frequency is observed, e.g. C = O in polyvinyl formate is observed at 1740 cm^{-1} while at 1765 cm^{-1} in the monomer. Large shift in frequencies of some of the modes of vibrations has been observed for large value of w_c , e.g. methylene rocking mode in polythene moves from 716 to 1107 cm^{-1} . It is to be noted that structure frequency correlations are valid for few bands. When the chemical repeat unit is complex, w_c is small and the spectrum of polymer is very similar to monomer where no characteristic frequency exists, the extrapolation is done from relationship in frequency shift and units in chain.

It is thus apparent that the identification of a polymer is done by comparison of an unknown spectrum. In case of copolymers, it is the superposition of the spectra of homopolymers. Since functional-group frequencies depend on environmental factors, a random copolymer may not have same spectrum as block copolymer or superimposed homopolymers.

One can also determine quantitatively: (a) copolymer ratios, (b) functional groups, (c) monomer impurities, (d) end groups, and (e) additives in polymers by this technique.

End-group determination is done by studying the polymer of different degree of polymerisation. The band that shows maximum variation of intensity is the one arising from the number of end groups in the polymer. The structure of the end group determines the nature of polymerisation reaction. These are least influenced by the nature of the rest of the polymer.

The analysis is done by dissolving the polymer or by using film-by-absorbance ratio method. Sometimes internal standard is added, and it may be disperse dye before casting the film. The visible absorption gives the thickness and acts as an internal standard for the infrared region.

Let us now see how methyl groups of polyethylene are estimated. A band which is independent of crystallinity is chosen, i.e. C—H band of CH_3 group at 7.25μ . But it is interfered by 7.31 and 7.39μ bands which are compensated by polymethylene wedge. Calibrate with n -hexadecane or other standards, compensate by polymethylene and determine absorption coefficient (specific absorbance)

$$\epsilon = \frac{A}{d \times t}$$

where d is the density in g/mL and t is the thickness.

A graph is then plotted between specific absorbance and number of methyl groups per 1000 carbon atoms. Now place the analytical film and measure the number of CH_3 groups per 1000 carbon atoms.

Isomerisation may give rise to (i) new bands, (ii) shifting of frequencies, and (iii) band broadening. Any of these can be used to determine composition of stereoisomers.

In PVA, the bands at 916 and 1141 cm^{-1} are characteristic of syndiotactic structure. In PVC a ratio of 635 – 692 cm^{-1} bands has been found to be proportional to isotactic syndiotactic ratio. The crystallinity in polymers induces some changes in the infrared spectra, viz., (i) some new bands may appear, (ii) bands may split into two with same polarisation, (iii) split bands may have mutually perpendicular dichroism. The last alternative is usually

seen in bands from helical conformation. Double helix exhibits three bands for a single bond. In polystyrene, the 1070 cm^{-1} band is split into two components with same polarisation on crystallisation.

The film of nylon-6 exhibits variation of crystallinity on various heat treatments. Crystallisation is followed by growth of bands at 935 , 970 , 1030 cm^{-1} whereas the amorphous band at 990 cm^{-1} diminishes on heat treatment. One can deduce extinction coefficient if the material is highly crystalline or a single crystal.

Polarised infrared radiation is also helpful in the study of polymer spectra. When an amorphous solid is exposed to unpolarised infrared radiation, the probability of radiation interaction with all the possible modes of vibration is equal. When a beam of plane polarised radiation is passed through an oriented film, the absorption band whose dipole moment change is parallel to the vibrating electric vector of radiation will be absorbed most and if it is perpendicular, the absorption will be minimum. The dichroic ratio given by $A_{\parallel}/A_{\perp}$ may be correlated with the orientation function or degree of orientation of a given sample.

Stabilisers and fillers can be separated from resinous material after soxhlet extraction, by dissolving in a suitable solvent, say tetrachloroethane, and washing with tetrahydropyran. The solid fillers, etc., are separated by centrifugation. Only inorganic stabilisers and fillers will separate. The usual stabilisers are lead carbonate, sulphate, phthalate, etc. The bands recommended for estimation are at 1410 cm^{-1} for lead carbonate, 877 cm^{-1} for calcium carbonate, 741 cm^{-1} for antimony oxide and 1535 cm^{-1} for phthalate. It is necessary to first calibrate for a given component.

(f) Study of Bridged Inorganic Complexes The infrared spectra aid in providing information about the presence of bridge in inorganic molecules. There are three types of partial assignments concerned with the bridge frequencies.

(i) ν_{asym} is about $50\text{--}100\text{ cm}^{-1}$ greater than ν_{sym} , e.g.

System	ν_{asym}	ν_{sym}	δ
$\text{P}_2\text{O}_7^{4-}$	940	909	201
$\text{H}_2\text{S}_2\text{O}_7$	806	732	—
$\text{S}_2\text{O}_5\text{Cl}_2$	773	716	486
$\text{P}_2\text{O}_3\text{Cl}_4$	806	713	—

(ii) ν_{asym} is about 200 cm^{-1} greater than ν_{sym} and the bending frequency is $1/3$ to $1/2$ of ν_{sym} , e.g.

System	ν_{asym}	ν_{sym}	δ
$\text{Mn}_2\text{P}_2\text{O}_7$	964	743	—
$\text{P}_2\text{O}_7^{4-}$ (calc)	978	727	—
$\text{K}_2\text{Cr}_2\text{O}_7$	797, 764	566, 556	220
$\text{Na}_4\text{As}_2\text{O}_7$	735	550	245
Cl_2O_7	695	495	—

(iii) ν_{asym} is about twice as great as ν_{sym} which in turn is about twice as great as the bending frequency, e.g.

System	ν_{asym}	ν_{sym}	δ
$\text{Si}_2\text{O}_7^{6-}$	1029	503	169
$\text{H}_2\text{S}_2\text{O}_7$	809	328	155
Ge—O—Ge	880–830	458	—
$\text{S}_2\text{O}_5\text{Cl}_2$	760	298	147
Cl_2O_7	695	280	—
$\text{P}_2\text{O}_3\text{Cl}_4$	962	425	159

3.16.2 Quantitative Applications

The quantitative applications of IR spectroscopy are based mainly on the exploitation of frequency, intensity and width of the band of the vibrational mode to determine the quantities such as concentration, thermodynamic functions, solvation number, bond strengths and distances, etc. In the present part, the theory of methodology is discussed prior to its application for estimating the quantities. Some of the quantitative aspects of IR spectroscopy have been discussed here in two sections: (a) problems based on intensity data; and (b) problems based on vibrational frequency and band width data.

(a) Problems Based on Intensity Data The earlier spectroscopic studies were mainly concerned with the use of vibrational frequency bands but these days intensity of vibrational bands has become a very useful parameter in spectroscopic studies. It gives fundamental information regarding the nature of bonds between the atoms since absolute intensity is related to the change in the dipole moment of the bond between, the two atoms during the vibrating process.

(i) Absorption Intensity The intrinsic absorption corresponding to a transition from the ground state, m to an excited state, n may be expressed in terms of transition probability coefficient, B_{mn} by the expression

$$\Delta I = -hc W_{mn} B_{mn} l_{mn} N_m \Delta X \quad (3.137)$$

where $cl_{mn} = I$ gives the intensity of the incident beam. ΔI is the amount absorbed in traversing a layer of thickness ΔX , N_m is the number of molecules per unit volume in state, m and the population, N_n is considered negligibly small.

The Einstein coefficient, B_{mn} is related with the matrix element, R_{mn} of the electric moment, M_Q between the states m and n . We have

$$R_{mn} \equiv \int \psi_n^* M_Q \psi_m d\tau \quad (3.138)$$

and then B_{mn} is given by

$$B_{mn} = \frac{8\pi^3}{3ch^2} |R_{mn}|^2 \quad (3.139)$$

The matrix element R_{mn} is also called the transition moment between the given states m and n . For an allowed transition R_{mn} is nonzero.

Formula (3.138) may be used to determine the interaction of electromagnetic wave with (a) electric dipole moment, (b) magnetic dipole moment, (c) quadrupole or higher moments, (d) induced dipole moments (in case of Raman scattering), etc., by substituting the appropriate moment in place of M_Q . In particular, R_{mn} turns out to be zero for all cases where the product of the two wave functions involved does not have the symmetry of one of the components of M_Q .

In general, the instantaneous dipole moment, M_Q for an oscillating molecule may be expressed by a Maclaurin series about $Q = 0$.

$$M_Q = (M)_{Q=0} + \left(\frac{dM}{dQ} \right)_{Q=0} Q + \frac{1}{2!} \left(\frac{d^2M}{d^2Q} \right)_{Q=0} Q^2 + \dots \quad (3.140)$$

As has already been stated that the first term in the expression gives the permanent dipole moment which is responsible only for the pure rotational infrared spectrum, the second term is responsible for the appearance of vibrational infrared spectrum while the quadratic and higher terms are effective in providing intensity to overtones and combination bands. When M_Q given by Eq. (3.140) is substituted in Eq. (3.138), the integral corresponding to the permanent dipole moment $(M)_{Q=0}$ becomes zero in view of the orthogonality of functions and R_{mn} comes out to be

$$R_{mn} = \frac{1}{\sqrt{2}\alpha} \left(\frac{dM}{dQ} \right)_{Q=0} \quad (3.141)$$

with the well-known relations

$$\alpha = \frac{2\pi(\mu_m k)^{1/2}}{h} \quad (3.142)$$

and

$$\frac{1}{2\pi c} (k/\mu_m)^{1/2} = W_{mn} \quad (3.143)$$

The extinction coefficient A' is given by

$$A' = -\frac{1}{\Delta X} \frac{\Delta I}{I} = h W_{mn} B_{mn} N_m \quad (3.144)$$

and using relations (3.137), (3.139) and (3.144), we get

$$A' = \frac{\pi N}{3c^2 \mu_m} \left(\frac{dM}{dQ} \right)^2 \quad (3.145)$$

where N_m is put equal to N as a close approximation.

• **Relation with Experimental Measurements** In actual experiments, if L cm path of the solution containing C g moles of absorbing sample per liter transmits intensity, I_t , out of the incident intensity, I_0 (Fig. 3.34), we get

$$A' = \frac{1}{LC} \ln \frac{I_0}{I_t} \text{ and } N = \frac{CN_A}{1000} \quad (3.146)$$

where N_A is Avogadro's number. Substitution in Eq. (3.145) gives the molar extinction coefficient

$$A' = \frac{1}{LC} \ln \frac{I_0}{I_t} = \frac{\pi C}{3c^2 \mu_m} \frac{N_A}{1000} \left(\frac{dM}{dQ} \right)^2 \quad (3.147)$$

The relation (3.147) is one of the forms of Beer–Lambert–Bouguer equation.

$$T = \frac{I_t}{I_0} = e^{-\epsilon Cl}$$

Recall from Chapter 1 that, although the transmittance is neither directly nor inversely proportional to concentration, $\ln(1/T)$ is related to concentration as shown by the more familiar version of exponential relation

$$A = \ln \frac{I_0}{I_t} = \ln \left(\frac{1}{T} \right) = kC$$

where $k = \epsilon l$ and A is the absorbance.

Absorbance is the greatest where transmittance is least. The Beer–Lambert–Bouguer equation predicts that if the concentration of the absorbing species is varied, the transmittance and absorbance will vary as shown by the dotted and dark lines in Fig. 3.35 respectively. Routinely it is easier to work with straight line behaviour of A when making quantitative determination from spectra.

At high concentration of solute, deviations from Beer's law have been noticed. These can be removed by calibration with a series of solutions of known concentration. The plot of absorbance versus concentration may not only be concave downward (negative deviation) or upward (positive deviation), it may have intercept on the axis of zero concentration, at a finite value, corresponding to background absorption. This quantity can be found by extrapolation and subtracted from all values of apparent absorbance, if a true value for the absorptivity is desired.

Further, it is to be noted that actually the transition mn is not a sharp transition. Apart from natural width in gases, the absorption band spreads due to Doppler and pressure broadening. In liquids various other physiochemical effects make the bands very broad. Added to these is the effect of finite slit width of the spectrometer. Thus, extinction coefficient values have not proved very useful, since these depend very much on the instrumental factors. Hence, in using the relation (3.147) to deduce (dM/dQ) , one must obtain integrated absorption coefficient A' or I_{abs} over the complete band corresponding to the given transition mn . If A_v is the molecular extinction coefficient of frequency in an absorption band, we define $\bar{A}$ or I_{abs} by

$$\bar{A} = \int_{\text{entire band}} A_v dv = \frac{1}{Cl} \int_{\text{entire band}} \ln \left(\frac{I_0}{I_t} \right) dv \quad (3.148)$$

In practice, Eq. (3.148) is integrated between two arbitrary values ν_1 and ν_2 on either side of ν_0 . If the curve is symmetrical,

$$\nu_0 = \frac{1}{2}(\nu_1 + \nu_2)$$

Consequently,

$$A = \frac{1}{Cl} \int_{\nu_1}^{\nu_2} \ln(I_0/I_t) dv \quad (3.149)$$

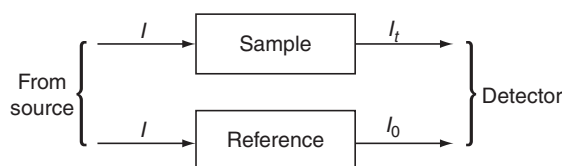


Fig. 3.34 Intensity relations in a double beam spectrometer. I , the intensity from the source, I_0 is passed by the reference, I_t by the sample solution.

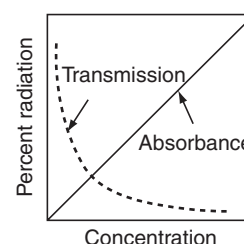


Fig. 3.35 The behaviour of transmittance and absorbance as concentration of the absorbing species is varied.

Experimentally, a graph between A_v against ν is plotted. Subsequently, either the squares on the graph paper are counted or the paper profile is weighed or the band areas are evaluated by using a planimeter to obtain the quantity A . Its unit is cm mole^{-1} or cm^2/moles . Some data on the integrated absorption intensities of series of compounds that could not be distinguished on the basis of their frequencies are listed in Table 3.9.

Table 3.9 Absolute absorption Intensities for several group vibrations.

Group	Position of Bands (cm^{-1})	Integral Absorption ($\text{cm}^2/\text{mole-s} \times 10^7$)
C = O	1720	
Esters		13
Alkylketones		8
Ketosteroids		9-20
C—O	1200	
Esters		15
Alkylketones		2.5
Acetoxy steroids		21
N—H	3400	
Dialkylamines		0.05
Alkylanilines		1.7
Diarylamine		2.2
Pyrroles, carbazoles		5.4
Indoles		6.6
C $\equiv$ N	2250	
Alkylcyanides		0.25
CH ₃	2900	
Hydrocarbons		4.4
—COCH ₃		0.74
—COOCH ₃		2.54
CH ₃	1460	
Hydrocarbons		0.54
—COCH ₃		1.3
—COOCH ₃		2.0
CH ₂	2900	
Hydrocarbons		3.8
—COCH ₂		0.5
CH ₂	1460	
Hydrocarbons		0.23
—COCH ₂ —		1.17
—COOCH ₂		0.65

It is quite evident from Table 3.9 that there is a wide variation in absolute intensities of the same group present in different molecules. This variation is due to the effect of structural environments of the molecule on the group. Hence, absolute intensity can be considered an additional parameter for the identification of molecules. Therefore, in times to come, the characteristic intensity tables similar to group frequencies tables will be available for identification of molecules.

• **Effect of Various Factors on Intensity** The intensity of spectral band depends mainly on: (i) transition probability, and (ii) the difference in the population in states m and n , provided the density of radiation of frequency is kept constant.

Theoretically, intensity is directly related to change in dipole moment of the bond between the two atoms during the vibratory process. The absolute intensity of the absorption band is given by $I_{\text{abs}} = a(dM/dr)^2$, where a is a constant. Therefore, for a more certain and better characterisation of an absorption band, in addition to its position, the bandwidth and intensity should also be recorded. The measurement of intensities in the solid phase is not reliable due to scattering or reflection losses. Intensities of solid samples are mostly restricted to the determination of ϵ_{max} which is markedly dependent on the particle size. In spite of these limitations and anomalies in solid state spectra, quantitative analysis of components in mixtures can still be carried out.

Infrared band intensities in gas phase will be different from those in the liquid phase because of perturbations due to neighbouring molecules in the latter case. The absolute intensity of a group vibration can be determined only in gas phase but it is more convenient to measure intensities in solution. The difference between the band intensity in solution and in gas phase may be ascribed to be due to several factors. In solution phase, specific interaction between solute and the solvent molecules like hydrogen bonding and dipole-dipole interactions will occur if solvents are polar. A solute molecule resides in a cavity associated with a solute dielectric constant which in turn is surrounded by the solvent medium of a particular dielectric constant. The packing of solvent molecules around the solute molecules varies with the molecular shape of the solute. In addition to these effects, several other effects of smaller magnitude like short range intermolecular forces, anisotropic character of polarisabilities and shapes of solvent molecules also contribute to the change in band intensity in solution as compared to the gas phase.

The intensity of the band is also affected by temperature. As the temperature increases, the population of rotational energy level changes. The population of vibrationally excited levels is very small at room temperature (say around 25°C) and intensity is not significantly affected by the redistribution among rotational levels. Temperature is not an important factor in gas phase measurements. In the case of solutions, however, the absorption at the band maximum decreases with increase in temperature, accompanied by the increase in bandwidth. This is due to the change in band shape resulting from an increased rate of collision of the solute molecules with the walls of the solvent cage. Integrated band intensity also seems to decrease with increase in temperature. An alternate explanation of intensity variation with temperature has been offered in terms of the coupling of vibrational modes in the liquid state. It may be concluded that wide variations in temperature must be avoided in band intensity measurements.

(ii) Concentration Determination The most important advantage of IR quantitative analysis is its specificity. This enables one to perform the analysis with practically very little pretreatment of the sample. This technique is particularly useful for the estimation of chemical species which are closely related structurally, e.g. *o*, *m* and *p*-cresol and isomers of similar type which is not possible in ultraviolet/visible because of close similarity of the spectra. Secondly, since there are many bands characteristic of a particular isomer, one can choose proper band which is free from the interference and is capable of maximum sensitivity. The basic theory of quantitative analysis is based on Lambert–Beer–Bouguer law.

The absorbance in IR spectroscopy is measured from the band under consideration by the baseline method. In this method a tangent, i.e. baseline is drawn from the shoulders on either side of the peak as shown for a hypothetical band in Fig 3.36. Baseline should be chosen carefully because a second component absorbing near the analytical wavelength may raise or lower the baseline if its concentration also varies. In this situation, certainty of results could be confirmed by analysing several absorption bands in the same spectrum. The consistency in results would prove the validity of the method.

Further, Fig. 3.36 reveals that at the band maximum the difference between the levels I_0 and I_t , where these are the percentage transmissions, will give the contribution

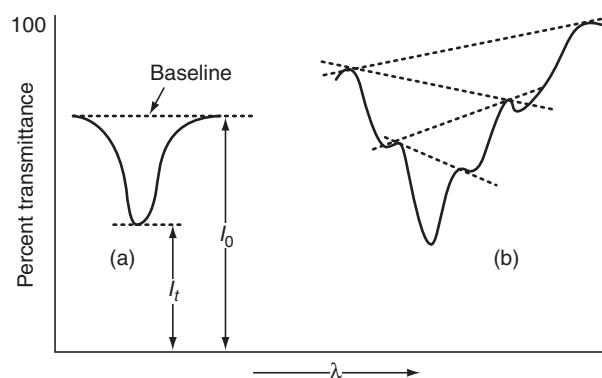


Fig. 3.36 Hypothetical infrared absorption spectra (a) illustrating the use of the baseline measurement technique; and (b) showing uncertainty as to where to draw the baseline.

of the solute to the absorption. Since $A = \log(I_0/I_t)$, one can determine the concentration of chemical species either by the direct application of Beer's law in case it is followed or by plotting working curves. In addition to Lambert-Beer-Bouger law, the other methods employed for concentration determination are explained here:

• **Slope Ratio Method or Method of Variable Path Length** This method eliminates the effect due to other interfering absorption or the correctness of I_0 . The equation of Beer's law $\log(I_0/I_t) = \epsilon Cl$ can be expressed in the form

$$\log \frac{I_0}{I_t} = \epsilon Cl + K \quad (3.150)$$

where K is absorbance due to cell and other absorbers in the path. Equation (3.150) can also be written as

$$\log I_t = -\epsilon Cl - K + \log I_0 \quad (3.151)$$

Thus, if we measure the transmitted intensity for different path lengths, and plot $\log I_t$ versus l , a straight line results with slope $= -\epsilon C$ and intercept $= \log I_0 - K$. The experiment is then repeated on sample solution for similar value of path lengths. Then again we will have

$$\log I_t = -\epsilon l C' - K + \log I_0 \quad (3.152)$$

This will give a straight line with slope $= -\epsilon C'$ and intercept $= \log I_0 - K$. Therefore, by simply taking the ratio of slope, i.e. $\epsilon C/\epsilon C' = m_1/m_2$ we can get the concentration of $C' = C \times m_2/m_1$ of the unknown sample.

• **Absorbance Ratio Method** This method is based on the use of some internal standard and is used for solid samples in KBr disc. In this method, the ratio of absorbances, i.e. A_1/A_2 is plotted against concentration. This technique is used for salts of organic acids, e.g. sodium valerate, disodium adipate, etc. One can also use absorbance ratio method in case of films or pellets. Suppose we have mixtures of two compounds x and y . Since the thickness is the same then,

$$R = \frac{A_x}{A_y} = \frac{\epsilon_x C_x}{\epsilon_y C_y} = m \frac{C_x}{C_y} \quad (3.153)$$

A standard curve is first drawn for synthetic mixtures of R against C_x/C_y and then unknown is determined from that. This method finds wide applications in copolymer analysis. Some quantitative analysis has also been done in aqueous medium. BaF₂ windows are used and work is restricted to 6.5 to 9 μ region, since other region is strongly absorbed by water. This is useful in biological systems and especially direct analysis of water phase of an organic water two layers system.

The additivity of absorbance is important in multiple analysis, the simultaneous determination of two or more absorbing species in the same solution. We can write

$$A = \sum_i A_i = l \sum_i \epsilon_i C_i$$

The relation can be understood by reference to Fig. 3.37 for two components analysis. Curves 1 and 2 are the absorption spectra of the pure components. Curve 3 is the spectrum of a mixture. The maxima in the mixture do not exactly match with the respective maxima of the pure components. It is assumed that no other substance present absorbs in this region. It will be seen that both substances contribute to absorption at both wavelengths λ_u and λ_v . Let C_1 and C_2 be the concentrations of the two components in the mixture and let A_{1v} represents absorbance of substance 1 at wavelength λ_v , etc. Then the absorbance of Curve 3 at λ_u will be given by,

$$A_{3u} = A_{1u} + A_{2u} = \epsilon_{1u} l C_1 + \epsilon_{2u} l C_2$$

and at λ_v by

$$A_{3v} = A_{1v} + A_{2v} = \epsilon_{1v} l C_1 + \epsilon_{2v} l C_2$$

Since A_{3u} and A_{3v} can be determined from the experimental observations on the mixture and ϵ s are obtained in advance from the formula $A = \epsilon Cl$, then the above equations can be solved simultaneously for C_1 and C_2 . For accurate results, ϵ_{1v} and ϵ_{2u} should be as low as possible

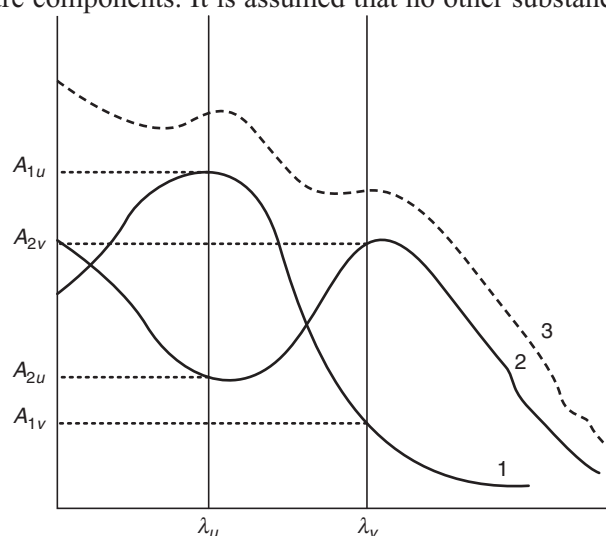


Fig. 3.37 Hypothetical figure exhibiting two-component analysis.

while ϵ_{1u} and ϵ_{2v} should be high. When ϵ_{2u} and ϵ_{1v} are negligibly small as compared to ϵ_{1u} and ϵ_{2v} respectively, the above expressions may be written as

$$A_{3u} = \epsilon_{1u} l C_1$$

and

$$A_{3v} = \epsilon_{2v} l C_2$$

However, in spite of all these facts, the quantitative aspects of IR spectroscopy in relation to concentration determination of chemical species have diminished in importance partly because of their inherent difficulties and largely due to the emergence of quicker and convenient methods of quantisation like gas chromatography for volatile substances, etc. The role of IR spectroscopy after quantitative separation by gas chromatography is only to identify each component qualitatively.

Problem 3.27: The following observations have been reported for the apparent absorbance of cyclohexanone in cyclohexane solution at 5.83μ .

Concentration (g/lit.)	Absorbance
5.00	0.190
10.00	0.244
15.00	0.293
20.00	0.345
25.00	0.390
30.00	0.444
35.00	0.487
40.00	0.532
45.00	0.562
50.00	0.585

Plot these data: (a) Over what range is Beer's law followed after necessary background correction is made?
(b) Compute the value of ϵ , the molar absorptivity.

Solution The plot between apparent absorbance and concentration is shown in Fig. 3.38. From Fig. 3.38, the background correction is found to be of the order of 0.14. After applying the background correction, the real values of absorbance at different concentrations are given in the following tabular form.

Concentration g/lit.	True Absorbance
5.00	0.050
10.00	0.104
15.00	0.153
20.00	0.205
25.00	0.250
30.00	0.304
35.00	0.347
40.00	0.392
45.00	0.422
50.00	0.445

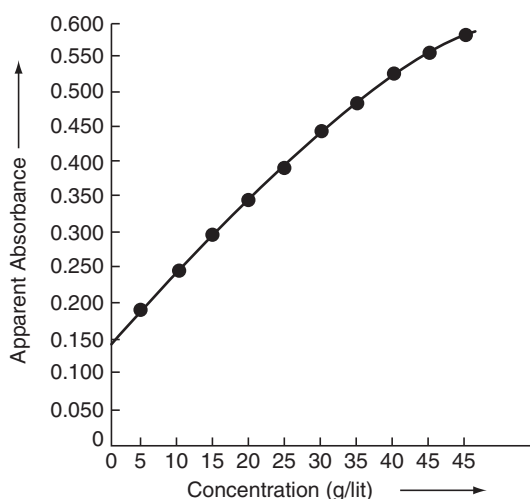


Fig. 3.38 The behaviour of apparent absorbance as the concentration of cyclohexanone is varied.

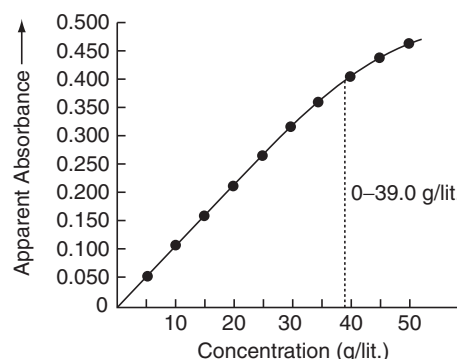


Fig. 3.39 The behaviour of true absorbance as the concentration of cyclohexanone is varied.

The graph based on concentration and true absorbance is presented in Fig. 3.39 from which it is evident that Beer's law holds good in the concentration range 0–39.0 g/lit beyond which negative deviation is observed.

The value of ϵ , the molar absorptivity is then determined from the relation

$$\epsilon = \frac{AM}{Cb}$$

From $A = 0.05$, $C = 5\text{ g/lit.}$ and $b = 0.096\text{ mm.}$ we have

$$\epsilon = \frac{0.05}{0.0096(\text{cm}) \times \left(\frac{5}{98}\right) \text{ mole/lit}} = 1.02 \times 10^2 \text{ lit mole}^{-1} \text{ cm}^{-1}$$

Problem 3.28: A sample of ethyl bromide suspected of containing trace amounts of water, ethanol and benzene was examined in an infrared spectrophotometer. The following relative absorbances were obtained by a baseline method: at 2.65μ , $A = 0.110$, at 2.75μ , $A = 0.220$, at 14.7μ , $A = 0.008$. Calculate the amounts of water and ethanol in parts per million and of benzene in 100 mL.

Name of Compound	A	Conc. (%), Length (mm)	Wavelength (μ)
Water	5.240	100,3.0	2.65
Ethyl alcohol	2.670	100,3.0	2.75
Benzene	0.830	100,0.1	14.70

Solution In order to determine the concentration of benzene, water and ethyl alcohol in a given sample of ethyl bromide, we must know the molar absorptivity of the respective impurities in ethyl bromide. Thus, using the reference data and the formula

$$\epsilon = \frac{AM}{bC}$$

we will have $\epsilon_{H_2O} = \frac{A}{b(C/M)} = \frac{5.24}{0.3(\text{cm}) \times 1(\text{mole})} = 17.46 \text{ mole}^{-1} \text{ cm}^{-1}$

Similarly, for C_2H_5OH and C_6H_6 , we get

$$\epsilon_{C_2H_5OH} = 8.90 \text{ mole}^{-1} \text{ cm}^{-1} \text{ and } \epsilon_{C_6H_6} = 83.00 \text{ mole}^{-1} \text{ cm}^{-1}$$

Now by using values of absorptivities, the concentration of H_2O , $\text{C}_2\text{H}_5\text{OH}$ and benzene are evaluated as follows. We know that

$$C = \frac{AM}{b}.$$

Therefore,
$$C_{\text{H}_2\text{O}} = \frac{0.110 \times 18}{0.3 \times 17.46} \text{ g/lit} = 37.8 \times 10^{-2} \text{ g/lit}$$

Hence, the amount of water in the sample of ethyl bromide

$$= 37.8 \times 10^{-2} \times 10^3 \text{ mg/lit} = 378 \text{ ppm}$$

Similarly,
$$C_{\text{C}_2\text{H}_5\text{OH}} = \frac{0.220}{8.9 \times 0.3} \times 46 \text{ g/lit} = 378.99 \times 10^{-2} \text{ g/lit}$$

Thus, the amount the ethyl alcohol in ethyl bromide

$$= 378.99 \times 10^{-2} \times 10^3 \text{ mg/lit} = 3790 \text{ ppm}$$

Similarly,

$$\begin{aligned} C_{\text{C}_6\text{H}_6} &= \frac{0.008 \times 78}{0.01 \times 83} \text{ g/lit} = 7.518 \times 10^{-1} \text{ g/lit} = 0.7518 \text{ g/lit} \\ &= 0.7518 \times 10^3 \text{ mg/lit} \\ &= 751.8 \text{ mg/lit} \end{aligned}$$

Therefore, the amount of benzene in ethyl bromide

$$= \frac{751.8 \times 100}{1000} = 75.18 \text{ mg/100 mL}$$

(iii) Detection of a Vibrational Band The vibrational bands due to different groups present in the molecule will be recorded by the spectrometer up to a value of $I_t/I_0 = 0.99$. However, at these high values of I_t/I_0 , i.e. close to 0.99, the sensitivity of the instrument is much reduced and weaker bands might not be observed in the spectrum. Thus, simply from the value of I_t/I_0 , one can infer whether a band due to a particular vibrational mode would be observed in the spectrum or not.

Problem 3.29: Carbon monoxide gas (effective area $17 \text{ \AA}^2/\text{CO}$ molecule) was adsorbed on a silica gel disc of 0.01 cm thickness and 1 cm^2 area. If the internal surface area and bulk density of silica is $100 \text{ m}^2 \text{ g}^{-1}$ and 2 g cm^{-3} respectively and if the extinction coefficient of a >C=O vibration is $3.3 \times 10^5 \text{ cm}^2 \text{ mole}^{-1}$, show that the absorption band due to >C=O absorption for 0.1 monolayer coverage on silica gel can easily be resolved by an IR spectrometer. Each gram of porous adsorbent has $\approx 100 \times 10^{20} \text{ \AA}^2$ surface available for adsorption.

Solution 1 g of silica gel has $100 \times 10^{20} \text{ \AA}^2$ of the surface available for adsorption. Since the effective area for CO molecule is $17 \text{ \AA}^2$, it follows that $100 \times 10^{20} \text{ \AA}^2 / 17 \text{ \AA}^2 = 6 \times 10^{20}$ CO molecules can be adsorbed on 1 g of silica. Each gram of porous adsorbent has $\approx 100 \times 10^{20} \text{ \AA}^2$ surface available for adsorbent.

Now, 6×10^{23} CO molecules (Avogadro's number) occupy 22400 mLs at NTP.

Therefore, 6×10^{20} CO molecules occupy $(22400 / 6 \times 10^{23}) \times 6 \times 10^{20} = 22.4 \text{ mLs}$ at NTP or 2.24 mLs for 0.1 monolayer coverage.

But 2.24 mLs of CO molecules at NTP contains

$$\frac{6 \times 10^{23} \times 2.24}{22400} = 6 \times 10^{19} \text{ CO molecules.}$$

Since $l = 0.01 \text{ cm}$.

Therefore, the number of molecules of CO absorbing/unit area of the IR beam $= 6 \times 10^{19} \times 0.01 = 6 \times 10^{17}$, also ϵ per CO molecule is,

$$\epsilon = \frac{3.3 \times 10^5}{6 \times 10^{23}} = 0.55 \times 10^{-18} \text{ cm}^2/\text{CO group}$$

Therefore, $\epsilon Cl = 6 \times 10^{17} \times 0.55 \times 10^{-18} = 0.33$

Since $I_t/I_0 = e^{-\epsilon Cl}$

Therefore, $\log_{10} \frac{I_t}{I_0} = \frac{-\epsilon Cl}{2.303} = \frac{-0.33}{2.303} = -0.1432 = \bar{1}.8568$

or transmittance $= I_t/I_0 = 0.72$ which can easily be resolved by an IR spectrometer. It is well-known that carbonyl groups are very strongly absorbing and easily detected in the spectrum.

Problem 3.30: Ethylene was adsorbed on a silica gel disc of thickness 0.01 cm and 1 cm² in area. If for —CH₂ group the absorptivity is of the order of 4000 cm²/g, show that the absorption band due to —CH₂ group for 0.1 monolayer coverage on silica gel can be recognised by an IR spectrometer.

Solution The extinction coefficient of a —CH₂ vibration can be written,

$$\begin{aligned}\epsilon &= \frac{4 \times 10^3 \times 14}{6 \times 10^{23}} = \text{cm}^2/\text{CH}_2 \text{ group} \\ &= 9.333 \times 10^{-20} \text{ cm}^2/\text{CH}_2 \text{ group}\end{aligned}$$

Since $l = 0.01$ cm.

Therefore, as in Problem 3.29, the number of CH₂ groups/cm² of the infrared beam $= 6 \times 10^{19} \times 0.01 = 6 \times 10^{17}$ for a monolayer coverage of 0.1.

$$\epsilon Cl = 9.333 \times 10^{-20} \times 6 \times 10^{17} = 0.0559$$

$$\log_{10} \frac{I_t}{I_0} = \frac{-0.0559}{2.303} = -0.0242 = \bar{1}.9758$$

or $\frac{I_t}{I_0} = 0.94$

Thus —CH₂ group can be resolved by a spectrometer, but to a lesser extent than the carbonyl group. It is also evident from the absolute absorption intensity data of these groups that the integral absorption of the CH₂ group is small than that of the >C=O group (Table 3.9).

(iv) Ratio of Z and E Isomers in a Given Molecule The IR spectra of mixture of conformations will contain vibrational bands characteristic of these states with intensities proportional to the concentration of each of the isomers present. It follows that by choosing two corresponding bands one belonging to each isomer

$$I_Z = \alpha_Z C_Z l \quad (3.154)$$

$$I_E = \alpha_E C_E l \quad (3.155)$$

where I_s' denote the band areas proportional to the band intensities of isomers Z and E , α_s' represent the integrated absorption coefficient and l is the cell path length. For all practical purposes we assume $\alpha_Z = \alpha_E = 1$. Therefore, from Eqs (3.154) and (3.155)

$$\frac{I_Z}{I_E} = \frac{C_Z}{C_E} \quad (3.156)$$

Thus, it is evident from Eq. (3.156) that simply by measuring the areas under the bands corresponding to Z and E isomers, one can find the percentage of the respective conformers.

Problem 3.31: The spectrum of secondary bands at 3425/3388 and 3417/3381 cm⁻¹ were assigned to the N—H stretching vibrations of Z and E conformers of N-isobutylthioformamide respectively. From the IR spectrum of N-isobutylthioformamide in Fig. 3.40, determine the percentage of Z and E isomers.

Solution The ratio of areas under the vibrational bands at 3425 and 3417 cm⁻¹ is 3.5:1 (Fig. 3.40).

We know that

$$\frac{I_Z}{I_E} = \frac{C_Z}{C_E}$$

Therefore $\frac{C_Z}{C_E} = \frac{3.5}{1}$ or $\frac{C_Z + C_E}{C_E} = \frac{3.5 + 1}{1}$ or $C_E = \frac{100}{4.5} = 22$ per cent

and

$$C_Z = 100 - 22 = 78 \text{ per cent}$$

(v) Evaluation of the Energy Difference between Isomeric States We know from the preceding problem,

$$I_A = \alpha_A C_A l \quad (3.154)$$

$$I_B = \alpha_B C_B l \quad (3.155)$$

where terms and symbols have their usual meanings. The equilibrium constant for the preceding problem,

$$A \xrightleftharpoons{K} B \quad (3.157)$$

can be expressed as

$$K = \frac{C_B}{C_A} = \frac{I_B \alpha_A}{I_A \alpha_B} \quad (3.158)$$

But, according to Van't Hoff isochore

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (3.159)$$

Consequently,

$$\ln \left(\frac{I_B \alpha_A}{I_A \alpha_B} \right) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

$$\ln \left(\frac{I_A}{I_B} \right) = \frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R} + \ln \left(\frac{\alpha_A}{\alpha_B} \right) \quad (3.160)$$

Accordingly if the intensities of the corresponding bands at different temperatures are known, ΔH^0 the energy difference between the isomeric states A and B can be determined from the slope of the plot $\ln(I_A/I_B)$ against $1/T$. This treatment assumes that ΔH^0 , ΔS^0 and $\ln(\alpha_A/\alpha_B)$ are independent of temperature which is usually assumed to be valid for the process of rotational isomerism.

Problem 3.32: The thermal equilibrium of equatorial and axial conformations of methylcyclohexane by means of infrared absorption spectra have been studied. The fundamental frequencies of the IR bands at 547 and 607 cm^{-1} are assigned to the equatorial and axial conformations. If the ratio of the respective band areas for these two conformations at 25 , 50 and 110°C are 8.0 , 5.0 and 4.25 respectively, calculate ΔH^0 and ΔS^0 for these isomeric species.

Solution Now $\ln(I_A/I_B)$ at different temperatures are

$\ln(I_A/I_B)$	T, K	$1/T \times 10^3$
2.0790	298.15	3.35
1.6090	323.15	3.09
1.4469	383.15	2.61

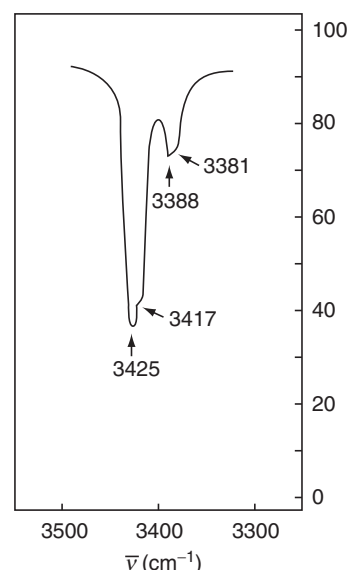


Fig. 3.40 The spectrum of *N*-isobutyl-thioformamide in CCl_4 in the NH stretching region.

The slope and intercept of the plot of the ratio of the axial and equatorial band areas for methylcyclohexane against $1/T$ can be determined from Fig. 3.41.

$$\text{Slope} = 0.781; \text{Intercept} = -0.875$$

But slope according to Eq. (3.160) is $\Delta H^0/R$

Therefore, $\Delta H^0 = +1552 \text{ cal/mole}$

Also intercept

$$= -\frac{\Delta S^0}{R} = -0.875$$

So, $\Delta S^0 = 1.738 \text{ cal/mole deg}$ (it is being assumed that $\alpha_B = \alpha_A = 1$).

(vi) Solvation Number Most of the surfactants are hardly soluble in nonpolar solvents, slightly soluble in nonhydrogen-bonding polar solvents and highly soluble in hydrogen-bonding polar solvents. The high solubility of surfactants in hydrogen-bonding polar solvents has been attributed to the existence of some intermolecular interactions between the solute and the solvent molecules. Actually, the infrared spectrum of the solvent shows remarkable changes in the fundamental bands of the solvent and bands of a particular stretching vibration corresponding to the free and the bonded states are observed separately. Since the ratio of the intensities of the bonded states to that of the free state can be regarded as a measure of the strength of the solute-solvent interaction, quantitative analysis of the absorption intensities can provide a valuable information regarding the process of dissolution of the surfactants. It can also provide a convenient method to determine the number of solvent molecules that combine with one molecule of the solute. In actual practice, sample solutions containing various amounts of the solute (surfactant) are prepared by weighing the solute and the solvent in the sample flask and recording their infrared spectra. This procedure is, however, modified for those surfactants that are insoluble in a given solvent. This is based on the observation that a surfactant which is insoluble in a given solvent (A) can be rendered soluble in this solvent by the addition of a small quantity of another hydrogen bonding polar solvent (B). In this case binary solutions of $A-B$, in which the molecular concentrations of A and B are C_A^0 and C_B^0 , are first made. The ratio of C_A^0/C_B^0 is called a dilution ratio and for a given dilution ratio, various amounts of surfactants are added and the change in intensity of a particular stretching band is observed. The procedure is repeated for various dilution ratios. The molar concentrations of A , B and the surfactants (S) in the solution are determined from the observed weight concentration and the density of the solution while the number of solvent molecules that combine with one molecule of the surfactant (S) can be calculated in the following manner.

The relative intensities in cm^{-1} of the free, I_f and bonded, I_b bands may be defined as

$$I_f = \frac{1}{l} \int_{\text{band}} \ln \left(\frac{I_0}{I_t} \right) d(\ln \nu) \quad (3.161)$$

and

$$I_b = \frac{1}{l} \int_{\text{band}} \ln \left(\frac{I_0}{I_t} \right) d(\ln \nu) \quad (3.162)$$

where l is the thickness of the sample, I_0 the energy of the incident radiation, I_t the energy of the transmitted radiation and ν the frequency of the radiation.

Normally the relative intensities defined by Eqs (3.161) and (3.162) are first corrected for local field effect and then reduced to the values at the molar concentration of the pure solvent C_B^0 by means of the expressions

$$I_f^* = f_d f_c I_f \quad (3.163)$$

$$I_b^* = f_d f_c I_b \quad (3.164)$$

where

$$f_d = \frac{9n_D}{(n_D^2 + 2)^2}$$

$$f_c = \frac{C_B^0}{C_B}$$

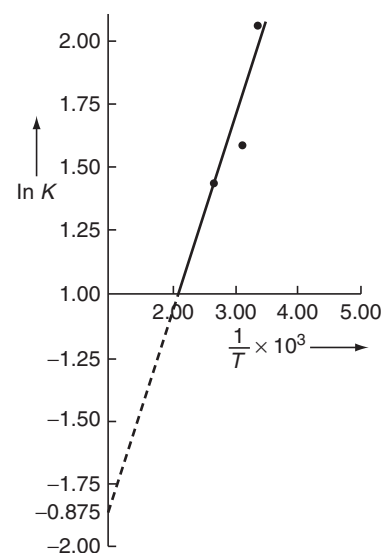


Fig. 3.41 Variation of equilibrium constant with temperature.

and n_D = refractive index of the solution. The solvent in such a solution exists in bonded and free states so that the molar concentration, C_B^0 of the solvent in solution can be expressed as

$$C_B^0 = C_b + C_f \quad (3.165)$$

where C_b and C_f are the molar concentrations of the solvent in the bonded and free states respectively. The absolute intensities τ of the bonded and free states are related to the corresponding I^* by means of

$$C_b^* \tau_b = I_b^* \quad (3.166)$$

$$C_f^* \tau_f = I_f^* \quad (3.167)$$

where

$$C_b^* = f_c C_b \quad (3.168)$$

and

$$C_f^* = f_c C_f \quad (3.169)$$

so that

$$\frac{I_b^*}{\tau_b} + \frac{I_f^*}{\tau_f} = C_b^* + C_f^* = f_c (C_b + C_f) = f_c \cdot C_B^0 \quad (3.170)$$

which on rearrangement yields

$$I_b^* = - \left[\frac{\tau_b}{\tau_f} \right] I_f^* + \tau_b C_B^0 f_c \quad (3.171)$$

Once τ_b and τ_f are known, the relative intensity for the bonded state (I_b) is calculated using Eq, (3.164) and concentration C_b so that solvent in the bonded state is evaluated from expressions (3.164), (3.166) and (3.168), i.e.

$$C_b = f_d \cdot \frac{I_b}{\tau_b} \quad (3.172)$$

The solvation number is then calculated from

$$n = \frac{C_B}{C_S} \quad (3.173)$$

Problem 3.33: The relative intensities of the C-D stretching vibration for the chloroform-d-dodecyl-dimethylamine oxide ($C_{12}AO$) system and the relevant data are

$C_S = C_{12}AO$ (wt percent)	n_D	d	I_b^* (cm^{-1})	I_f^* (cm^{-1})
0	1.4470	1.480	0	1.032
0.2569	1.4471	1.478	0.186	1.279
1.0106	1.4472	1.472	0.629	1.262
1.4062	1.4473	1.469	0.886	1.252
1.7816	1.4474	1.465	1.064	1.216
2.8574	1.4476	1.457	1.709	1.209
2.8608	1.4476	1.457	1.647	1.189
5.2304	1.4481	1.438	2.943	1.120
6.4981	1.4486	1.428	3.610	1.068
8.7316	1.4486	1.411	5.029	1.010

Calculate the solvation number for $C_{12}AO$ at various concentrations of $C_{12}AO$ provided it is soluble in chloroform-d and $C_{CDCl_3}^0 = 12.3$ M.

Solution In, order to calculate τ_b and τ_f according to Eq. (3.171), I_b^* is first plotted against I_f^* for different values of C_s . Such a plot for this system is shown in Fig. 3.42 and it yields $(I_f^*)_{I_b^*=0} = 1.30 \text{ cm}^{-1}$.

Further, since the plot of I_b^* against I_f^* is linear, the slope of the line yields $\tau_b / \tau_f = 16$. But $(I_f^*)_{I_b^*=0} = C_B^0 \tau_f = C_{CD_3Cl}^0 (= 12.3 \text{ M}) \tau_f$

$$\text{Therefore, } \tau_f = \frac{1.3}{12.3 \times 10^{-3}} \frac{\text{cm}^{-1}}{\text{mole/cm}^3} = 106 \text{ cm}^2/\text{mole}$$

which when combined with $\tau_b / \tau_f = 16$ yields $\tau_b = 1696 \text{ cm}^2/\text{mole}$.

Now for $C_s = 0.2569 \text{ wt per cent}$ $C_{CDCl_3} = 99.7431 \text{ wt. per cent}$, $I_b^* = 0.186 \text{ cm}^{-1}$, and $n_D = 1.4471$.

Consequently, from Eq. (3.164)

$$0.186 \text{ cm}^{-1} = \frac{9 \times 1.4471}{\left[(1.4471)^2 + 2\right]^2} \frac{12.3 M I_b}{\left(\frac{997.431}{120.5}\right) M}$$

or

$$I_b = 0.1584 \text{ cm}^{-1}$$

Further, from expression (3.172)

$$C_b = \frac{9 \times 1.4471}{\left[(1.4471)^2 + 2\right]^2} \frac{0.1584}{1696} = 0.7773 \times \frac{0.1584}{1696} = 0.0726 \times 10^{-3} \text{ mole/cm}^3$$

and so from Eq. (3.173)

$$n \left(\text{for } C_s = 0.2569 \text{ wt per cent} = 0.017 \times 10^{-3} \text{ mole/cm}^3 \right) = \frac{0.0726 \times 10^{-3}}{0.017 \times 10^{-3}} = 4.2$$

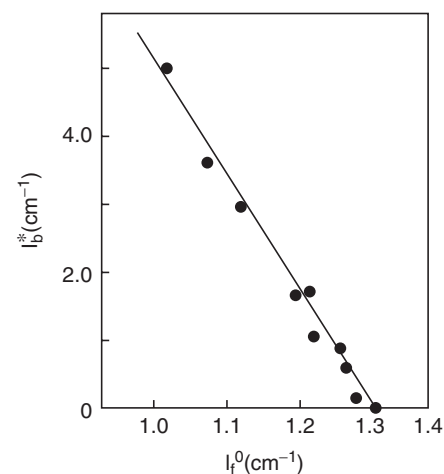


Fig. 3.42 I_b^* versus I_f^* plot for the chloroform- d - $C_{12}AO$ system.

Problem 3.34: The relative intensities of the C-D stretching vibration for the chloroform-d-cetyl trimethylammonium chloride (CTACl)-carbon-tetrachloride system have been studied. Their relative intensity data at dilution ratios $C_{CCl_4}^0 / C_{CDCl_3}^0$ of 0 and 7.49 are given below.

$C_{CCl_4}^0 / C_{CDCl_3}^0$	$C_s \times 10^3$ (mole/cm ³)	n_D	d	I_b^* (cm ⁻¹)	I_f^* (cm ⁻¹)
0	0	1.4470	1.480	0	1.311
	0.048	1.4480	1.465	0.428	1.278
	0.096	1.4489	1.463	0.810	1.269
	0.127	1.4493	1.458	1.070	1.255
	0.157	1.4499	1.453	1.331	1.234
	0.195	1.4507	1.446	1.594	1.223
	0.283	1.4514	1.431	2.475	1.169
	0.366	1.4529	1.416	3.126	1.141
7.49	0	1.4591	1.565	0	0.0769
	0.010	1.4591	1.563	0.033	0.0760

(Continued)

$C_{\text{CCl}_4}^0 / C_{\text{CDCl}_3}^0$	$C_S \times 10^3$ (mole/cm ³)	n_D	d	I_b^* (cm ⁻¹)	I_f^* (cm ⁻¹)
	0.016	1.4591	1.562	0.053	0.0758
	0.025	1.4593	1.560	0.080	0.0746
	0.028	1.4592	1.560	0.095	0.0748

Calculate the solvation number of CTACl at its various concentrations provided it is insoluble in CDCl_3 but rendered soluble in CDCl_3 by the addition of CCl_4 and $C_{\text{CDCl}_3}^0 = 12.3\text{M}$.

Solution We first consider the data for the dilution ratio 0.0. From the plot of I_b^* against I_f^* (Fig. 3.43) we get

$$(I_f^*)_{I_b^*=0} = 1.311 \text{ cm}^{-1} \text{ But } (I_f^*)_{I_b^*=0} = C_{\text{CDCl}_3}^0 (= 12.3\text{M}) \tau_f, \text{ which yields}$$

$$\begin{aligned} \tau_f &= \frac{1.311}{12.3 \times 10^{-3}} (\text{cm}^{-1}/\text{mole/cm}^3) \\ &= 106.58 \text{ cm}^2/\text{mole} \sim 107 \text{ cm}^2/\text{mole} \end{aligned}$$

Further, the slope of the I_b^* against I_f^* (Fig. 3.43) is -18 and so according to Eq. (3.171), $-\tau_b/\tau_f = -18$ which gives $\tau_b = 1930 \text{ cm}^2/\text{mole}$.

Now for $C_S = 0.048 \times 10^{-3} \text{ mole/cm}^3$, $I_b^* = 0.428 \text{ cm}^{-1}$, $C_{\text{CDCl}_3}^0 = 12.3 \text{ M}$, $n_D = 1.448$.

Consequently, from Eq. (3.164)

$$\begin{aligned} 0.428 \text{ cm}^{-1} &= \frac{9 \times 1.448}{\left[(1.448)^2 + 2\right]^2} \frac{12.3 I_b}{12.3} \\ I_b &= 0.55119 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Further, } C_b &= f_d \cdot \frac{I_b}{\tau_b} = 0.7765 \times \frac{0.5512 \text{ cm}^{-1}}{1930 \text{ cm}^2/\text{mole}} \\ &= 0.0002218 \text{ mole/cm}^3 \end{aligned}$$

and so

$$n = \frac{C_b}{C_S} = \frac{0.2218 \times 10^{-3}}{0.048 \times 10^{-3}} = 4.62$$

Similarly, for the dilution ratio 7.49, the relevant data for $C_S = 0.010 \times 10^{-3} \text{ mole/cm}^3$ are

$$\begin{aligned} I_b^* &= 0.033 \text{ cm}^{-1} \\ n_D &= 1.4591 \\ f_d &= \frac{9 \times 1.4591}{\left[(1.4591)^2 + 2\right]^2} = 0.7702 \\ f_c &= \frac{C_B^0}{C_B} = \frac{12.3\text{M}}{12.3\text{M}} = 1.0 \\ I_b &= \frac{0.033}{0.7702} = 0.04285 \text{ cm}^{-1} \end{aligned}$$

Similarly,

$$\begin{aligned} C_b &= f_d \cdot I_b / \tau_b \\ &= \frac{0.7702 \times 0.04285 (\text{cm}^{-1})}{2709 (\text{cm}^2/\text{mole})} \\ &= 0.0122 \times 10^{-3} \text{ mole/cm}^3 \end{aligned}$$

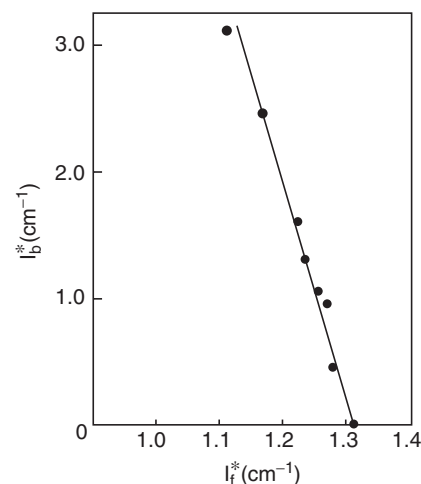


Fig. 3.43 I_b^* versus I_f^* plot for the Chloroform-d-CTACl-carbon tetrachloride system

and so,

$$n = \frac{C_b}{C_s} = \frac{0.0122 \times 10^{-3} \text{ mole/cm}^3}{0.010 \times 10^{-3} \text{ mole/cm}^3} = 1.2$$

(vii) Equilibrium Constants and Energetics of Hydrogen Bonding Hydrogen bonding between a donor ($A-H$) and an acceptor (B) may result in the formation of series of compounds with the general formula $(A-H)_m \cdots B_n$ where m and n are integral numbers. Once the equilibrium constant for the complexation reaction represented by



is known, free energy can easily be determined and enthalpy and entropy value can be obtained from the temperature variation of the equilibrium constants. We illustrate this for two different cases.

Case 1: When a Donor ($A-H$) and an Acceptor (B) form a 1 : 1 complex The complexation reaction is represented by



The equilibrium constant for the complexation reaction (3.175) is

$$K = \frac{C_{A-H \cdots B}}{C_{A-H} C_B} \quad (3.176)$$

where $C_{A-H \cdots B}$, C_{A-H} and C_B represent the equilibrium concentration of the H-bonded donor, free donor and acceptor respectively in solution. (It is assumed that the concentration of the proton donor is sufficiently low to avoid self-association.). If C_{A-H} and C_B denote the total concentration of the donor and the acceptor respectively in the solution, then the material balance equation yields

$$C_{A-H}^0 = C_{A-H} + C_{A-H \cdots B} \quad (3.177)$$

and

$$C_B^0 = C_B + C_{A-H \cdots B} \quad (3.178)$$

The equilibrium concentrations of the donor ($A-H$) and the H-bonded $A-H \cdots B$ complex in the solution can easily be determined for a solution of a given C_{A-H}^0 and C_B^0 from a measurement of its absorbance at the frequencies characteristic of either the donor ($A-H$) or of the donor and the complex $A-H \cdots B$ species in the following manner.

The absorptivity (extinction coefficient) of the proton donor ($A-H$) is first determined from measurement of the absorbance $A_{\nu(A-H)}$ of a very dilute solution of the donor in an inert solvent at a frequency characteristic of the donor. The absorbance of the solution at other concentrations of the solution is next measured at frequencies of the donor and the equilibrium concentration C_{A-H} evaluated from

$$A_{\nu(A-H)} = a_{A-H}^0 C_{A-H} \cdot l \quad (3.179)$$

where l is the cell length in cm. The Eq. (3.179) is the well-known Beer–Lambert law. The equilibrium concentrations $C_{A-H \cdots B}$ and C_B at a particular total concentrations C_{A-H}^0 and C_B^0 of the donor and the acceptor respectively are then calculated from Eqs (3.177) and (3.178). Alternatively, the equilibrium concentration of the complex $C_{A-H \cdots B}$ can also be independently calculated by first determining its absorptivity $a_{A-H \cdots B}^0$ in the manner described above for the donor for a solution that contains very large excess of the acceptor. Once $a_{A-H \cdots B}^0$ is known, the absorbance of the solution at any concentration of the donor is next measured at wave numbers that are characteristic of the complex. The equilibrium concentration of the complex is evaluated from Eq. (3.177) while that of C_B from Eq. (3.178). Equilibrium constant is then determined from the expression (3.176).

Case 2: Hydrogen Bonding due to Self-association When a solute, say, A , undergoes self-association due to hydrogen bonding to give molecular species of the general formula A_n , the complexation reaction is represented by



The equilibrium constant is given by

$$K_n = \frac{C_{A_n}}{(C_A)^n} \quad (3.181)$$

We illustrate this for the case of a simple reaction denoted by



for which the dimerisation constant is

$$K_d = \frac{C_{A_2}}{(C_A)^2} \quad (3.183)$$

where C_{A_2} and C_A represent the equilibrium concentrations of the dimer and monomer respectively. Since A in solution now exists both as A and A_2 , the material balance equation yields

$$C_A^0 = C_A + 2 C_{A_2} \quad (3.184)$$

where C_A^0 is the total concentration of A in the solution. If it is now assumed that the dimer does not contribute to the absorbance at the frequency characteristic of the monomer and that the Beer law is valid for the monomer, then employing the procedure as outlined for the Case (1) above, the equilibrium C_A of the monomer is evaluated from

$$A_{v(A)} = a_A^0 C_A l \quad (3.185)$$

where $A_{v(A)}$ is the absorbance of a solution at a frequency characteristic of the monomer, a_A^0 is its absorptivity and l the cell length in cm. This gives rise to

$$C_{A_2} = \frac{1}{2}(C_A^0 - C_A) = \frac{1}{2}\left(C_A^0 - \frac{A_{v(A)}}{a_A^0 l}\right) \quad (3.186)$$

Substitution of C_A and C_{A_2} values in Eq. (3.183) yields

$$K_d = \frac{1}{2}\left[C_A^0 - \frac{A_{v(A)}}{a_A^0 l}\right] \left/ \left[\frac{A_{v(A)}}{a_A^0 l}\right]^2 \right. \quad (3.187)$$

which on rearrangement yields

$$A_{v(A)} = \frac{a_A^0 l^2}{2K_d} \left[\frac{C_A^0}{A_{v(A)}} \right] - \frac{a_A^0 l}{2K_d} \quad (3.188)$$

Thus, a plot of $A_{v(A)}$ versus $C_A^0/A_{v(A)}$ yields straight line of

$$\text{Slope } (m) = \frac{a_A^0 l^2}{2K_d} \quad (3.189)$$

$$\text{and intercept } (b) = -a_A^0 \frac{l}{2K_d} \quad (3.190)$$

so that

$$K_d = \frac{m}{2b^2} \quad (3.191)$$

(viii) Evaluation of ΔG^0 , ΔH^0 and ΔS^0 from Equilibrium Constants The free energy change, ΔG , for the H-bonded systems is given by

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

$$\Delta G = (G_{\text{products}}^0 - G_{\text{reactants}}^0) + RT \ln \frac{C_{\text{products}}}{C_{\text{reactants}}} \quad (3.192)$$

where G_{products}^0 and $G_{\text{reactants}}^0$ denote the standard free energies while C_{products} and C_{reactant} represent the equilibrium concentrations. Further, as these reactions are at equilibrium, $\Delta G = 0$, so that Eq. (3.192) becomes

$$\Delta G^0 = -RT \ln K \quad (3.193)$$

where

$$K = C_{\text{products}} / C_{\text{reactants}}$$

Furthermore, for an isothermal (at constant temperature) process

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (3.194)$$

where
$$\Delta H^0 = \Sigma H_f^0(\text{products}) - \Sigma H_f^0(\text{reactants}) \quad (3.195)$$

is the difference between the enthalpies of the products and the reactants, similarly

$$\Delta S = \Sigma S^0(\text{products}) - \Sigma S^0(\text{reactants}) \quad (3.196)$$

Combination of expressions (3.193) and (3.194) yields

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (3.197)$$

Thus, a plot of $\ln K$ against $1/T$ would give a straight line of

$$\text{Slope } (m) = -\frac{\Delta H^0}{R}$$

$$\text{and intercept } (b) = \frac{\Delta S^0}{R}$$

Hence ΔH^0 and ΔS^0 can be evaluated.

Problem 3.35: The concentrations of free, non-hydrogen bonded pyrrole in pyrrole-pyridine-acyl mixtures from measurements of the intensity of the $\nu_{01}(\text{N-H})$ band at 3498 cm^{-1} have been determined. The total concentration of pyrrole (Table 3.10) presents the initial concentration C_{AH}^0 and C_B^0 of pyrrole and pyridine respectively and the measured equilibrium concentration C_{AH} of pyrrole (a) assuming that only 1:1 H-bonded complex is formed, calculate the equilibrium concentration C_B and $C_{A-H...B}$ of pyridine and of the complex respectively and the equilibrium constant K for the formation of the 1:1 complex (b). Calculate ΔH^0 , ΔS^0 and ΔG^0 at 298.15 K.

Solution (a) Consider the data at 12°C .

We know that $C_{AH}^0 = C_{A-H} + C_{A-H...B}$ and $C_B^0 = C_B + C_{A-H...B}$

Table 3.10

C_{AH}^0	C_B^0	C_{AH}	C_{AH}^0	C_B^0	C_{AH}
	A. 47°			B. 40°	
0.00667	0.0835	0.006	0.00675	0.0787	0.00583
0.00667	0.0125	0.00566	0.00675	0.0984	0.00552
0.00667	0.167	0.00547	0.00675	0.148	0.00506
0.00667	0.209	0.00512	0.00675	0.197	0.00485
			0.00675	0.246	0.00440
	C. 33°			D. 30°	
0.00645	0.0426	0.00593	0.00678	0.0813	0.00565
0.00645	0.0532	0.00575	0.00678	0.102	0.00546
0.00645	0.0798	0.00555	0.00678	0.153	0.00498
0.00645	0.133	0.00505	0.00678	0.203	0.00467
			0.00678	0.254	0.00424
	E. 20°			F. 12°	
0.00672	0.0813	0.00554	0.00677	0.0632	0.00565
0.00672	0.102	0.00527	0.00677	0.0790	0.00536
0.00672	0.153	0.00477	0.00677	0.119	0.00493
0.00672	0.203	0.00435	0.00677	0.158	0.00457
0.00672	0.254	0.00401	0.00677	0.197	0.00424

so that for $C_{AH}^0 = 0.00677$, $C_B^0 = 0.0632$ and $C_{AH} = 0.00565$ we get

$$\begin{aligned} C_{A-H...B} &= C_{AH}^0 - C_{AH} \\ &= 0.00677 - 0.00565 = 0.00112 \end{aligned}$$

and

$$C_B = C_B^0 - C_{A-H...B} = 0.0632 - 0.00112 = 0.06208$$

Consequently, K is given by

$$\begin{aligned} K &= \frac{C_{A-H...B}}{C_{AH} \times C_B} \\ &= \frac{0.00112}{0.06208 \times 0.00565} = 3.21 \end{aligned}$$

Similarly, K for different values of C_{AH}^0 , C_B^0 and C_{AH} are evaluated and then averaged. The average value of K determined in this manner for different temperatures are

$T^\circ\text{C}$	K
12	3.21
20	2.71
30	2.39
33	2.14
40	2.17
47	1.40

(b) In order to calculate ΔG^0 at 298.15 K, ΔH^0 and ΔS^0 have first to be evaluated. This is achieved by plotting $\ln K$ against $1/T$ (see Fig. 3.44). The slope and intercept of this line are: slope $= 3.375 \times 10^3$, intercept $= -0.17$.

But according to Eq. (3.197), the slope $= -\Delta H^0/R$ and intercept $= \Delta S^0/R$.

Therefore, $\Delta H^0 = -3.375 \times 10^3 \times 1.987 = -6.706 \text{ kcal/mole}$

and $\Delta S^0 = -0.17 \times 1.987 = -0.337 \text{ cal/deg/mole}$

Now ΔG^0 at 298.15 K is given by

$$\begin{aligned} \Delta G^0 &= \Delta H^0 - 298.15 \Delta S^0 \\ &= -6.706 + \frac{298.15 \times 0.337}{10^3} \\ &= -6.606 \text{ kcal/mole} \end{aligned}$$

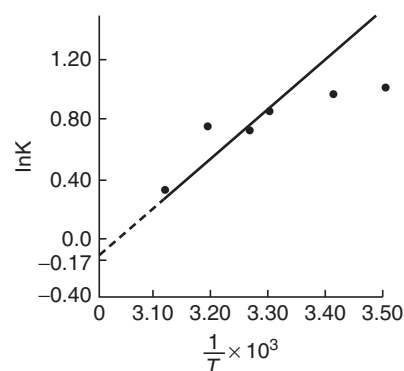


Fig. 3.44 Variation of equilibrium constant of 1:1 complex with temperature.

Problem 3.36: The self-association of 2-pyridone in CCl_4 has been studied by IR spectroscopy. From the data at 41.6°C presented in Table 3.11. (a) Calculate the equilibrium constant K_d for the cyclic dimerisation, (b) determine the absorptivity a , of the monomer at infinite dilution, (c) Calculate ΔH^0 , ΔG^0 and ΔS^0 for 2-pyridone at 41.6°C from the following data.

Temperature $^\circ\text{C}$	$K_d \times 10^{-3} (M^{-1})$
16.2	10.43
30.3	6.27
35.3	4.49
41.6	2.71
45.9	2.80

Table 3.11

$C_A^0 \times 10^4$ (mole/lit)	$A(3412 \text{ cm}^{-1})$ ($l = 1 \text{ cm}$)
1.999	0.118
3.191	0.162
4.423	0.193
5.305	0.217
6.638	0.243
6.643	0.247
9.040	0.296
9.947	0.315
12.847	0.379
15.402	0.419
16.347	0.418
19.714	0.484
24.163	0.555

Solution (a) The equilibrium constant, K_d for the cyclic dimerisation is calculated from the slope and intercept of the C_A^0 / A_v vs A plot (Fig. 3.45).

The slope and intercept of this line according to Eq. (3.188) are

$$\text{slope } (m) = \frac{a_A^0 l^2}{2K_d} = 1.5 \times 10^2 \text{ M}$$

$$\text{intercept } (b) = -\frac{a_A^0 l}{2K_d} = -0.16 \text{ M}$$

Now according to (3.191), K_d is given by

$$K_d = \frac{\text{Slope}}{2(\text{intercept})^2} = \frac{1.5 \times 10^2 \text{ M}}{2(0.16)^2 \text{ M}^2} = 2.93 \times 10^3 \text{ M}^{-1}$$

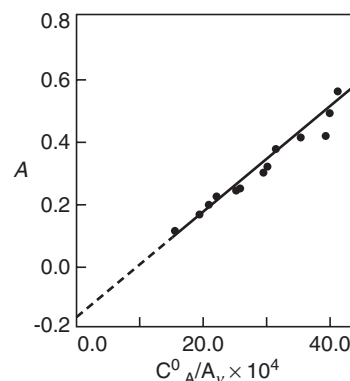


Fig. 3.45 Plot between C_A^0 / A_v and A .

(b) The absorptivity a , of the monomer of infinite dilution is determined from Eq. (3.190), i.e.

$$\text{intercept } (b) = -\frac{a_A^0 l}{2K_d}$$

Since

$$K_d = 2.93 \times 10^3 \text{ M}^{-1}$$

$$l = 1 \text{ cm}$$

$$b = -0.16 \text{ M}$$

$$a_A^0 = \frac{2 \times 0.16 \text{ M} \times 2.93 \times 10^3 \text{ M}^{-1}}{1 \text{ cm}} = 0.9376 \times 10^3 \text{ cm}^{-1}$$

(c) The values of ΔH^0 and ΔS^0 are first evaluated by plotting $\ln K_d$ vs $1/T$ (see Fig. 3.46). The slope and intercept of this line are

$$\text{slope} = 4.16 \times 10^3$$

$$\text{intercept} = 0.80$$

But according to Eq. (3.197),

$$\text{Slope} = \frac{-\Delta H^0}{R} \text{ and intercept} = \frac{\Delta S^0}{R}$$

Therefore, $\Delta H^0 = -1.987 \times 4.16 \times 10^3 = -8.265 \text{ kcal/mole}$

and $\Delta S^0 = 0.80 \times 1.987 = 1.589 \text{ cal/deg/mole}$

Consequently ΔG^0 at 41.6 °C is given by

$$\Delta G^0 = \Delta H^0 - 314.75 \times \Delta S^0 = -8.265 - 0.500 = -8.765 \text{ kcal/mole}$$

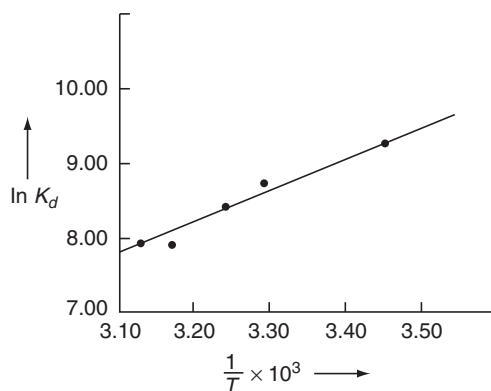


Fig. 3.46 Variation of equilibrium constant of dimerisation with temperature.

(ix) Dipole Moments of Intramolecular Bonds Recall from the foregoing chapter on microwave spectroscopy that the microwave spectroscopic and refractive index measurements yield the dipole moments of the molecule as a whole. The dipole moments of intramolecular bonds can be determined from the intensities of infrared absorption bands.

Quantum mechanically, the intensity of the infrared absorption band corresponding to the $V' \rightarrow V''$ transition is related to the square of the quasimoment $M_{V',V''}$, by the expression.

$$[M_{V',V''}]^2 = \frac{3hc}{8\pi^2\nu} \int_{\text{entire band}} A_\nu d\nu \quad (3.198)$$

$$[M_{V',V''}]^2 = \frac{3hc}{8\pi^2\nu} \int_{\text{entire band}} A_\nu d\nu = \frac{\left| \int \psi_{V''}^* p \psi_{V'} dr \right|^2}{\int |\psi_{V'}|^2 dr \int |\psi_{V''}|^2 dr} \quad (3.199)$$

Here, the dimensions of charge are $(\text{Length})^{3/2} (\text{Mass})^{1/2} (\text{Time})^{-1}$, ν is the frequency, single and double primed ψ_V are the wave functions for lower and upper vibrational states of the molecules respectively, p is the electric moment of the chemical bond whose valence vibrations give rise to the given absorption band. It is thus fundamentally possible to determine the electric moment of the bonds from the area of the absorption band provided we know the wave functions $\psi_{V'}(r)$ and $\psi_{V''}(r)$ and the variation of the dipole transition moment with the interatomic distance r , i.e. in the form of function $p(r)$. The wave functions can be found from the solution of the Schrodinger wave equation for normal vibrations of the molecule. The dependence of p upon r can be solved only semiempirically, i.e. by correlating the computed values of dipole moment on the assumption of a certain p - r relationship with directly measured values of the moments of the simplest molecules. The dipole moments of Cl-H, O-H, C-H, C-F and Si-F bonds, etc., can be determined from the intensities in the infrared spectra of HCl, H₂O, CHCl₃, CF₄ and SiF₄ respectively. The bond moments of C-H and C-D bonds in C₂H₂ and in C₂D₂ and others can also be determined. The dipole moments of some diatomic molecules are CO(0.11), HCl(1.04), OH(1.54), IC(0.50), HI(0.38), HBr(0.79) and NO(0.16 Debyes; 1D = 10⁻¹⁸ absolute unit). The dipole moments of some typical linkages are: 2.5 (—C=O); 0.9 (—C—O), 3.3 (—C≡N) and 1.5 D(—N—H).

The absorption frequency and integrated intensity data on the —C=O, —C—O, —C≡N and —N—H linkages (Table 3.9) yield very poor results on dipole moment of the respective linkages suggesting the limited applicability of the method.

(b) Problems Based on Vibrational Frequency and Bandwidth Data In this part, use has been made of the vibrational frequency and width of bands to determine the quantities such as force constant, anharmonicity constant, thermodynamic functions, intermediations, etc.

(i) Strength of Chemical Bonds When a molecule is formed, atoms are bound together by a certain amount of binding energy which is commonly called the bond strength. The binding energy arises from the electrostatic interaction of electrons and nuclei. Thus, if it is assumed that the X — Y bond has a strength of k dynes/cm, it means that there is a force of attraction between X and Y and it takes certain energy to tear them apart, which is the dissociation energy. If such a system is imagined and if one can say X is displaced from its equilibrium

position and left, the system begins to vibrate with a frequency approximate to the force constant and masses. The frequency and force constant in case of diatomics are related to each other by the expression (3.19).

$$w_e = 1303.16 \sqrt{\frac{k}{\mu_m}}$$

Thus, we can estimate the force constant for a particular bond if the corresponding vibrational frequency is known. The value of force constant for a specific bond in any molecule under the same environment is the same, therefore, one can predict the vibrational frequency of similar vibrators present in different molecules. As the vibrational frequency of normal modes depends upon a large number of factors, such as mass distribution, inductive effect, mesomeric effect, etc., hence effect of these factors on force constant could also be examined. In higher and complex molecules, in addition to stretching force constants, we have to fix the values of force constants for bending vibrations also, which is not possible with Eq. (3.19). Moreover, in complex molecules the normal modes of vibration are intermixed with each other due to delocalisation effects, and therefore, it is not proper to apply Eq. (3.19) even to evaluate the stretching force constants from the vibrational frequencies. Presently, the mathematical tool of normal coordinate analysis in conjunction with group theory has proved fruitful for fixing the force constants from vibrational frequencies of normal modes.

In this technique, the frequencies of the normal vibrations in terms of $\lambda = 4\pi^2\nu^2$ are given by solving the secular equation

$$\det|GF - E\lambda| = 0 \quad (3.200)$$

where G is the kinetic energy matrix, F the potential energy matrix and E the unitary matrix. The G matrix elements are generated by the method due to Wilson et al. [Wilson, Decius and Ross, *Molecular Vibrations*, McGraw-Hill, New York, 1955].

In actual practice, the kinetic energy matrix elements are not generated by this method since tables of elements are available in the literature for all common cases: (i) for linear molecules by Ferigle and Meister [Ferigle and Meister, *Am J. Phys.*, 20 (1952), 421]; and (ii) for planar molecules by Shimanouchi [Shimanouchi, *J. Chem Phys.*, 25(1956), 660]. However, the most comprehensive treatment is due to Decius and the expressions reported are applicable even where the valence angles are 90° ; $109^\circ 28'$; and 120° [Decius, *Chem. Phys.*, 16(1948), 1025].

The elements of F -matrix are obtained from different type of force fields available in the literature and the most commonly potential fields are Central Force Field (CFF), Simple Valence Force Field (SVFF), Urey–Bradley Force Field (UBFF), Modified Urey–Bradley Force Field (MUBFF), General Valence Force Field (GVFF), Orbital Valence Force Field (OVFF), and Most General Harmonic Force Field (MGHFF). The preferentiability of one field over the other and assignment of vibrational bands on the basis of potential energy distribution has been discussed in detail by Ross [Ross, *Inorganic Infrared and Raman spectra*, McGraw-Hill, London, 1972]. Further, the force constants have significance only with respect to the potential field in which they appear. In general, the field in which the number of interaction constants is minimum and transferable in similar molecules is considered to be the best and UBFF and MUBFF meet these requirements to the maximum extent. Although the potential energy distribution is a better quantity than normalised amplitudes of vibration for band assignments, but they have their own significance since they give additional information about force constants. The mean vibrational amplitudes are generally determined by the method of Cyvin [Cyvin, *Molecular Vibrations and Mean Square Amplitudes*, Elsevier, Amsterdam, 1968].

Problem 3.37: HCl gas is known to have a H—Cl stretching frequency at 2886 cm^{-1} . Calculate (i) the stretching force constant, (ii) the vibrational frequency due to DC1 molecule, and (iii) the ratio of amplitude of vibration of the nuclei.

Solution We know that for diatomic molecule

$$\bar{\nu} = 1303.16(k/\mu_m)^{1/2}$$

(i) Since $\bar{\nu} = 2886 \text{ cm}^{-1}$, and

$$\mu_m = \frac{1.008 \times 35.5}{1.008 + 35.5} = \frac{35.784}{36.508} = 0.980 \text{ amu}$$

Therefore,

$$k = \frac{(2886)^2 \times 0.98}{(1303.16)^2} = 4.80 \text{ millidynes/\AA}$$

- (ii) Since deuteration does not affect the electronic configuration of the molecule, the force constant can safely be transferred to DCl molecule. Here,

$$\mu_m = \frac{2.016 \times 35.5}{2.016 + 35.5} = \frac{71.568}{37.516} = 1.907 \text{ amu}$$

$$k = 4.80 \text{ millidynes/\AA}$$

Hence,
$$\bar{\nu} = 1303.16 \left(\frac{4.80}{1.907} \right)^{1/2} = 1303.16 \times 1.568 = 2067 \text{ cm}^{-1}$$

- (iii) The ratio of vibrational amplitude of nuclei is

$$\frac{A_H}{A_{Cl}} = \frac{m_{Cl}}{m_H} = \frac{33.5}{1.008} = 35.21$$

(ii) Effect of Adsorption on Force Constant The adsorption of a molecule on the surface of an adsorbent while it severely restricts the rotational movements of the adsorbate, it affects its vibrational movements also. This would consequently affect a particular vibrational frequency ($\bar{\nu}$) of the adsorbate and hence can be utilised to get an estimate of the strength of the bond with the adsorbent that gives rise to that particular vibration. The vibrational frequency for a diatomic molecule (assumed as simple harmonic oscillator) is given by

$$\bar{\nu} = 1303.16(k/\mu_m)^{1/2}$$

The adsorption of this molecule on the surface of an adsorbent would result in a change in its vibrational frequency $\bar{\nu}$ or its force constant. If the value of k decreases as compared to that in the gaseous state, it suggests a weakening of the bond that holds the adsorbate on the surface of the adsorbent.

Problem 3.38: Gaseous CO is known to have a force constant of the order of 18.53 millidynes/\AA. When the molecule is adsorbed on the surface of metal iridium, the C = O stretching bond is observed at 2050 cm^{-1} , show that the strength of C = O bond is weakened as a result of adsorption on metal surface.

Solution We know that

$$\bar{\nu} = 1303.16(k/\mu_m)^{1/2}$$

$$\bar{\nu} = 2050 \text{ cm}^{-1}$$

and

$$\mu_m = \frac{m_1 m_2}{m_1 + m_2} = \frac{16 \times 12}{28} = \frac{192}{28} = 6.857 \text{ amu}$$

Thus, the molar force constant, k , of CO after adsorption is

$$k_{ad} = \frac{(2050)^2 \times 6.857}{(1303.16)^2} = 16.95 \text{ millidynes/\AA}$$

Since $k_{ad} < k$, i.e. $16.96 < 18.53$, the strength of CO bond decreases as a result of adsorption of CO molecule the surface of metal.

(iii) Molar Heat of Evaporation of Water from Infrared Frequency of the Intramolecular Vibration of the Water Molecules Derived from Vapour Pressure Data The activity a_u , of non-H-bond water is proportional to the vapour pressure. Thus, $a_u = \text{constant} \times p$ and $a_B a_u = C$ and

$$\frac{d \ln a_u}{dT} = -\frac{d \ln a_B}{dT} = \frac{d \ln p}{dT} = \frac{\lambda}{RT^2} \quad (3.201)$$

The frequency of the intramolecular vibration of the water molecules, which are in immediate equilibrium with the molecules without hydrogen bond is related to the molar heat of evaporation λ , by the relation

$$\lambda = N_A h\nu \quad (3.202)$$

Here, N_A is Avogadro's number, h is Planck's constant and ν the frequency of vibration.

In very dilute solutions of water, if α is the fraction of the H-bonded water molecules and N_u the number of non-H-bonded water molecules, then the frequency of the band through which the hydrogen bonding is taking place is given by Maxwell-Boltzmann law, i.e.

$$\alpha N_u = \exp\left(\frac{-h\nu}{\kappa T}\right) \quad (3.203)$$

Equation (3.203) can also be written as

$$\ln \alpha + \ln N_u = \frac{-h\nu}{\kappa T}$$

Since α is constant, we get

$$\frac{d \ln N_u}{dT} = \frac{h\nu}{\kappa T^2} \quad (3.204)$$

Since $N_A \kappa = R$, the gas constant, therefore, Eq. (3.204) reduces to

$$\frac{d \ln N_u}{dT} = \frac{N_A h\nu}{RT^2} \quad (3.205)$$

Comparing Eqs (3.205) and (3.201), we get

$$\frac{d \ln N_u}{dT} = \frac{d \ln p}{dT} = \frac{\lambda}{RT^2} = \frac{N_A h\nu}{RT^2} \quad (3.206)$$

In not very dilute solutions of water

$$\alpha a_u = \exp\left(\frac{-h\nu}{\kappa T}\right) \quad (3.207)$$

Taking logarithm and differentiating with respect to temperature, Eq. (3.207) yields

$$\frac{d \ln a_u}{dT} = \frac{d \ln p}{dT} = \frac{h\nu}{\kappa T^2} = \frac{N_A h\nu}{RT^2} = \frac{\lambda}{RT^2} \quad (3.208)$$

where $\lambda = N_A h\nu = N_A h\bar{\nu}c$, c is the velocity of light and $\bar{\nu}$ the wave number. Integrating Eq. (3.208) and applying the limits of pressure and temperature

$$\begin{aligned} \int_{p_1}^{p_2} d \ln p &= \frac{\lambda}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \\ [\ln p]_{p_1}^{p_2} &= \frac{\lambda}{R} \left[-\frac{1}{T} \right]_{T_1}^{T_2} \\ \ln \frac{p_2}{p_1} &= \frac{\lambda}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \\ \lambda &= \frac{R \ln \frac{p_2}{p_1}}{\left[\frac{1}{T_1} - \frac{1}{T_2} \right]} \end{aligned} \quad (3.209)$$

Since

$$\lambda = N_A h\nu = N_A hc\bar{\nu}$$

Hence,

$$\bar{\nu} = \frac{R \ln p_2 / p_1}{N_A hc \left[\frac{1}{T_1} - \frac{1}{T_2} \right]} \quad (3.210)$$

Thus, by measuring the vapour pressure of dilute solutions of water at different temperatures one can determine the frequency $\bar{\nu}$ of the intramolecular vibration of water molecules which are in immediate equilibrium with the molecules without hydrogen bonding. Since $\bar{\nu}$ is related to molar heat of evaporation λ , one can determine λ also from $\bar{\nu}$, and hence from the vapour pressure data by the formula (3.210).

Problem 3.39: The vapour pressure data in the temperature range 0–100°C is given in Table 3.12.

Table 3.12

Temperature (°C)	P.atm
0	0.006028
10	0.012110
20	0.023070
25	0.031250
30	0.04186
40	0.07279
60	0.19660
70	0.30750
80	0.46740
90	0.69200
100	1.0000

Using the data in Table 3.12, (a) find the temperature intervals between 0–100°C, in which only one of the known frequencies of water is in a simple relation to the molar heat of evaporation in which there is no overlapping of vibrations and hence (b) calculate the molar heat of evaporation from the frequencies thus obtained in the temperature intervals between 0–100°C. $N_A = 6.0225 \times 10^{23}/\text{mole}$, $h = 6.6256 \times 10^{-27}$ erg s, $c = 2.998 \times 10^{10}$ cm/s, $R = 8.3143 \times 10^7$ erg/mole deg. and $1 \text{ cal} = 4.186 \times 10^7$ erg.

Solution Substituting the values of vapour pressure of water at 0 and 10°C from Table 3.12 in the Eq. (3.210),

$$\bar{\nu} = \frac{R}{N_A hc} = \frac{\ln p_2 / p_1}{\left[\frac{1}{T_1} - \frac{1}{T_2} \right]}$$

Table 3.13

Temperature (°C)	$\bar{\nu}(\text{cm}^{-1})$
0 – 10	3746
10 – 20	3714
20	
25 – 30	3654
30 – 40	3647
40 – 60	3599
60 – 70	3551
70 – 80	3524
80 – 90	3495
90 – 100	3465

$$= \frac{8.3143 \times 10^7}{6.025 \times 10^{23} \times 6.6256 \times 10^{-27} \times 2.998 \times 10^8} \times [-4.41472 - (-5.11134)] \times 772$$

$$= 0.6950115 \times 0.69762 \times 7225.9 = 3745.91 \sim 3746 \text{ cm}^{-1}$$

Similarly, the value of $\bar{\nu}$, in the different temperature intervals are determined and are given in Table 3.13.

From Table 3.13, only those frequencies, in which there is no overlapping of vibrations, are chosen by making use of experimental frequencies of water and are tabulated in Table 3.14.

The molar heat of evaporation λ can, thus be computed by using the data in Table 3.14 and equation, $\lambda = N_A h c \bar{\nu}$ and are given in Table 3.15.

Table 3.14

Temperature Interval ($^{\circ}\text{C}$)	$\bar{\nu}$, cm^{-1} from Vapour pressure Data (from infrared and Raman spectra)
0–10	3746(3755.8)
25–40	3654(3650, 3651.7)
60–70	3551(3550)
90–100	3465(3450)

Table 3.15

Temperature ($^{\circ}\text{C}$)	kcal/mole
0–10	10.70
25–40	10.44
60–70	10.44
90–100	9.90

(iv) Thermodynamic Functions from Spectroscopic Data by Statistical Methods Although the need for accurate thermodynamic quantities such as entropy S° , heat capacity C_p° , enthalpy H° and Gibbs energy G° is actually felt in such problems as in calculating the temperature and composition of rocket exhausts and flames, etc., it is not possible to determine the same at such high temperatures in laboratory. However, all these thermodynamic functions for a chemical species can be easily and precisely determined from its relevant spectroscopic data (which is available in most of the cases). Further, a comparison of the calculated and observed quantities provides an additional evidence for the validity of the vibrational assignments.

Evaluation of the thermodynamic properties of any chemical species requires the knowledge of a quantity called ‘Zummerstang, Z or partition function, Q . Literally speaking, this indicates how at equilibrium the systems are partitioned among the available energy states. Mathematically, however, partition function is expressed as

$$Z = \sum_i g_i \exp\left(\frac{-E_i}{\kappa T}\right) \quad (3.211)$$

where the summation is taken over all the energy levels and g_i and E_i represent the degeneracy and energy respectively of the i th energy level. Since chemical species possess translational, rotational, vibrational and electronic energies, the total partition of the chemical species is expressed by

$$Z = \sum_i g_i \exp\left[-(E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}})/\kappa T\right]$$

$$= \sum_i g_i \exp\left(\frac{-E_{\text{trans}}}{\kappa T}\right) \sum_i g_i \exp\left(\frac{-E_{\text{rot}}}{\kappa T}\right) \sum_i g_i \exp\left(\frac{-E_{\text{vib}}}{\kappa T}\right) \sum_i g_i \exp\left(\frac{-E_{\text{elec}}}{\kappa T}\right)$$

$$= Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} Z_{\text{elec}} \quad (3.212)$$

In most cases at moderate temperatures only the ground electronic level is populated so that

$$Z = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} \quad (3.213)$$

Further,

$$Z_{\text{trans}} = V \left(\frac{2\pi m \kappa T}{h^2} \right)^{\frac{3}{2}} \quad (3.214)$$

$$Z_{\text{rot}} = \frac{(\pi I_A I_B I_C)^{\frac{1}{2}}}{\sigma} \left(\frac{8\pi^2 \kappa T}{h^2} \right)^{\frac{3}{2}} \quad (\text{for asymmetric tops}) \quad (3.215)$$

and

$$Z_{\text{vib}} = \prod_i \left[1 - \exp\left(\frac{-hcw_i}{\kappa T}\right) \right]^{-g_i} \quad (3.216)$$

where V is the total volume of the system, m , I_A , I_B and I_C denote the molecular mass (in grams) and the three principle moments of inertia respectively of the chemical species. Further, σ is the symmetry factor, w_i is its i th vibrational frequency (in cm^{-1}).

The various thermodynamic quantities are related to Z by means of the well-known relations.

$$G^0 = E_0^0 - RT \ln\left(\frac{Z}{N}\right) \quad (3.217)$$

$$H^0 = E_0^0 - RT^2 \left[\frac{d}{dT} (\ln Z) \right] + R \quad (3.218)$$

$$C_p^0 = \frac{d}{dT} \left[RT^2 \frac{d}{dT} (\ln Z) \right] + R \quad (3.219)$$

and

$$S^0 = \frac{(H^0 - G^0)}{T} \quad (3.220)$$

where R is the gas constant, E_0^0 is the zero point energy and T is the absolute temperature.

For the purpose of actual calculations, however, these thermodynamic functions are expressed in the following form.

$$\begin{aligned} \frac{G^0 - E_0^0}{T} &= -R \ln Z + R \\ &= -R \ln \left[\left\{ \frac{(2\pi\kappa)^{3/2} R M^{3/2} T^{5/2} p^{-1} e}{h^3 N_A^{5/2}} (= Z_{\text{trans}}) \right\} \right. \\ &\quad \times \left\{ \frac{8\pi^2}{\sigma} \left(\frac{2\pi\kappa T}{h^2} \right)^{3/2} (I_A I_B I_C)^{1/2} (= Z_{\text{rot}}) \right\} \\ &\quad \times \left. \left\{ \sum_i^{3n-6/3n-5} [1 - \exp(-x_i)] \right\}^{-g_i} \right] + R \\ &\quad [M = mN_A; p = 1.0133 \times 10^5 \text{ Pa}] \end{aligned} \quad (3.221)$$

$$\frac{H^0 - E_0^0}{T} = R \left[\frac{4 + \sum_i g_i x_i}{(\exp x_i - 1)^2} \right] \quad (3.222)$$

$$C_p^0 = R \left[4 + \sum_i \frac{g_i (x_i)^2 \exp x_i}{(\exp x_i - 1)^2} \right] \quad (3.223)$$

where

$$x_i = \frac{hc\omega_i}{\kappa T} = 1.4388\omega_i / T.$$

Substituting the values of various constants, for an ideal gas at one atmospheric pressure Eq.(3.221) may be simplified to

$$\frac{G^0 - E_0^0}{T} = -R \left[\begin{aligned} &(3.45391 \log M + 5.7565 \log T - 2.3026 \log p + 8.8612) \\ &+ (0.5 \times 2.3026 \log(I_A I_B I_C) + 3.4539 \log T \\ &- 2.3026 \log \sigma - 4.2105) - g_i \ln \sum_i [1 - \exp(-x_i)] \end{aligned} \right] + R \quad (3.224)$$

$$= -R \left[\begin{aligned} &9.2104 \log T - 2.306 \log p + 1.1513 \log(I_A I_B I_C) \\ &+ 3.45391 \log M - 2.3026 \log \sigma + 4.6507 \end{aligned} \right] \\ + R g_i \ln \prod_i [1 - \exp(-x_i)] + R$$

where M is the mass of the molecule in amu and I_A , I_B and I_C are the principal moments of inertia in amu Å².

• **Isotopic Species** If the system contains isotopically substituted molecules, then the thermodynamic functions for mixtures are calculated using the formula

$$K = \sum_i N_i K_i \quad (3.225)$$

where K is any one of the thermodynamic functions for the mixture, N_i represents the mole fraction for the i th species for which the value of the function is K_i .

• **Entropy and Free Energy of Mixing** The entropy and free energy changes due to mixing of non-interacting ideal gases (for a total of 1 mole of the mixture of ideal gases) are given by

$$\Delta S^0 = -R \sum_i N_i \ln N_i \quad (3.226)$$

$$\frac{\Delta G^0}{T} = R \sum_i N_i \ln N_i \quad (3.227)$$

where N_i is the mole fraction of i th species.

• **Heat, Free Energy and Equilibrium Constant of Formation** The heat (ΔH_f^0), free energy (ΔG_f^0), entropy (ΔS_f^0) and equilibrium constant K_p in terms of pressure, of formation of any molecule can be computed at the desired temperatures using the following relation.

$$\begin{aligned} \Delta H_f^0 &= \Delta H_{298.15}^0 \\ &= (H_T^0 - H_{298.15}^0)_{\text{compound}} - \sum (H_T^0 - H_{298.15}^0)_{\text{elements}} \end{aligned} \quad (3.228)$$

$$\Delta G_f^0 = \Delta H_f^0 - T \Delta S_f^0 \quad (3.229)$$

$$\text{where} \quad \Delta S_f^0 = S_T^0(\text{compound}) - \sum S_T^0(\text{elements}) \quad (3.230)$$

$$\log_{10} K_p = \frac{-\Delta G_f^0}{0.004575845T} \quad (3.231)$$

Problem 3.40: The vapour-phase infrared spectra of chlorobenzene have been recorded and the following frequencies (in cm⁻¹) are assigned to its thirty normal modes of vibration, 416.8, 706.5, 1003.7, 1025.7, 1092.6, 1153, 1482.3, 1586.4, 3031, 3054, 3082, 294.7, 614.9, 1067.6, 1167.1, 1271.8, 1326.6, 1447.2, 1598.2, 3067, 3096, 197.5, 467.1, 683.9, 741.4, 902.5, 981.5, 403.4, 831.2, 961.7. The moments of inertia in amu Å² along the a , b and c axes are 89.113, 320.611 and 409.7775, and for ³⁵ClC₆H₅ and for ³⁷ClC₆H₅ 89.119, 329.811 and 418.9816 respectively. Calculate (a) $C_p^0(H_0 - E_0^0)/T$, $(G_0 - E_0^0)/T$, S^0 for chlorobenzene at 298.15 K and $p = 1.0133 \times 10^5$ Pa, (b) $(G_0 - E_0^0)/T$, for chlorobenzene at 298.15 K if it contains the two isotopes of chlorine of 35 and 37 amu in the ratio 3 : 1 and molecular mass in amu for ³⁵ClC₆H₅ is 112.07560 for ³⁷ClC₆H₅ is 114.07265, (c) the entropy (ΔS^0) and free energy ($\Delta G^0/T$) of mixing of C₆H₅Cl³⁵ and C₆H₅Cl³⁷ and (d) The heat (ΔH_f^0), free energy ($\Delta G^0/T$), and the equilibrium constant in terms of pressure ($\log_{10} K_p$), for the formation of chlorobenzene at 298.15 K. ($\Delta H_f^0_{298.15} = 12.39$ kcal mole⁻¹)

Solution The exponential terms used in the determination of thermodynamic functions from Eqs (3.222), (3.223) and (3.224) have been computed and are recorded in Table 3.16.

Table 3.16 The exponential terms determined from the vibrational frequencies.

$w_i(\text{cm}^{-1})$ (1)	x_i (2)	$\text{Exp } x_i$ (3)	$A = \frac{\exp x_i}{(\exp x_i - 1)^2}$ (4)	$x_i^2 A$ (5)	$\frac{x_i}{(\exp x_i - 1)^2}$ (6)	$1 - \exp(-x_i)$ (7)	$\ln[1 - \exp(-x_i)]$ (8)
416.8	2.0113763	7.4735961	0.1783358	0.7214813	0.0479957	0.8661956	-0.1436445
706.5	3.4093986	3.0247049×10^1	0.0353605	0.4110309	0.0039858	0.9669389	-0.0336200
1003.7	4.8436142	1.2692725×10^2	0.0080042	0.1877822	0.0003154	0.9921215	-0.0079097
1025.7	4.9497808	1.4114403×10^2	0.0071864	0.1760692	0.0002520	0.9929150	-0.0071102
1092.6	5.2726241	1.9492680×10^2	0.0051832	0.1440952	0.0001402	0.9948699	-0.0051433
1153.0	5.5640999	2.6089028×10^2	0.0038626	0.1195825	0.0000823	0.9961670	-0.0038404
1482.3	7.1532223	1.2782182×10^3	0.0007836	0.0400939	0.0000043	0.9992177	-0.0007826
1586.4	7.6555838	2.1124081×10^3	0.0004738	0.0277709	0.0000017	0.9995266	-0.0004735
3031	14.6268751	2.2509774×10^6	0.0000004	0.0000950	$2.8867534 \times 10^{-12}$	0.999996	-0.0000004
3054	14.7378675	2.5152117×10^6	0.0000004	0.0000863	$2.3296245 \times 10^{-12}$	0.9999996	-0.0000004
3082	14.8729888	2.8791013×10^6	0.0000003	0.0000768	$1.7942570 \times 10^{-12}$	0.9999997	-0.0000003
294.7	1.4221511	4.1460295	0.4188966	0.8472241	0.1436879	0.7588054	-0.2760099
614.9	2.9673591	1.9440512×10^1	0.0571692	0.5033874	0.0087262	0.9485610	-0.0528092
1067.6	5.1519801	1.7277327×10^2	0.0058555	0.1554225	0.0001746	0.9942121	-0.0058047
1167.1	5.6321431	2.7925997×10^2	0.0036067	0.1144075	0.0000727	0.9964191	-0.0035873
1271.8	6.1374001	4.6284865×10^2	0.0021699	0.0817351	0.0000287	0.9978395	-0.0021629
1326.6	6.4018517	6.0296051×10^2	0.0016640	0.0681968	0.0000176	0.9983415	-0.0016599
1447.2	6.9838382	1.0790520×10^3	0.0009285	0.0452847	0.0000060	0.9990733	-0.0009272
1598.2	7.7125278	2.2361877×10^3	0.0004476	0.0266246	0.0000015	0.9995528	-0.0004473
3067	14.8006024	2.6780578×10^6	0.0000004	0.0000817	$2.0636680 \times 10^{-12}$	0.9999996	-0.0000004
3096	14.9405494	3.0803365×10^6	0.0000003	0.0000724	$1.5746011 \times 10^{-12}$	0.9999997	-0.0000003
197.5	0.9530874	2.5937051	1.0211856	0.9276201	0.3752466	0.6144511	-0.4870259
467.1	2.2541120	9.5268293	0.1310308	0.6657697	0.0310028	0.8950333	-0.1108944
683.9	3.3003365	2.7121763×10^1	0.0397478	0.4329417	0.0048367	0.9631292	-0.0375677
741.4	3.5778176	3.5795336×10^1	0.0295654	0.3784607	0.0029551	0.9720634	-0.0283343
902.5	4.3552474	7.7886089×10^1	0.0131754	0.2499137	0.0007367	0.9871607	-0.0129224

Table 3.16 The exponential terms determined from the vibrational frequencies—Cont'd.

$w_i(\text{cm}^{-1})$ (1)	x_i (2)	$\text{Exp } x_i$ (3)	$A = \frac{\exp x_i}{(\exp x_i - 1)^2}$ (4)	$x_i^2 A$ (5)	$\frac{x_i}{(\exp x_i - 1)^2}$ (6)	$1 - \exp(-x_i)$ (7)	$\ln[1 - \exp(-x_i)]$ (8)
981.5	4.7364823	1.1403236×10^2	0.0089253	0.2002324	0.0003707	0.9912306	-0.0088081
403.4	1.9467111	7.0056089	0.1942369	0.7360966	0.0539743	0.8572572	-0.1540172
831.2	4.0111708	5.5211472×10^1	0.0187865	0.3022660	0.0013649	0.9818878	-0.0182782
961.7	4.6409323	1.0364092×10^2	0.0098376	0.2118852	0.0004405	0.9903513	-0.0096955
				7.7757872	0.6764115		-1.4134782

Now

$$\sum_{i=1}^{30} \frac{g_i x_i}{(\exp x_i - 1)^2} = \sum_{i=1}^{30} \frac{x_i}{(\exp x_i - 1)^2} = 0.6764$$

$$\sum_{i=1}^{30} g_i \ln[1 - \exp(-x_i)] = \sum_{i=1}^{30} \ln[1 - \exp(-x_i)] = -1.4135$$

and

$$\sum_{i=1}^{30} \frac{g_i x_i^2 \exp x_i}{(\exp x_i - 1)^2} = \sum_{i=1}^{30} x_i^2 A = 7.7757$$

Consequently,

$$(a) \quad \frac{H^0 - E_0^0}{T} = R \left[4 + \sum_{i=1}^{30} \frac{g_i x_i}{(\exp x_i - 1)^2} \right]$$

$$= 1.987 [4 + 0.6764] \\ = 9.29 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$C_p^0 = R \left[4 + \sum_{i=1}^{30} \frac{g_i x_i^2 \exp x_i}{(\exp x_i - 1)^2} \right]$$

$$= 1.987 [4 + 7.77571] = 23.39 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\frac{G^0 - E_0^0}{T} = -1.987 [9.2104 \log 298.15 - 2.306 \log 1.0133 \times 10^5 \\ + 1.1513 \log (89.113 \times 320.611 \times 409.777) \\ + 3.4539 \log 112.07560 - 2.3026 \log 2 + 4.65071] \\ + 1.987(-1.4135) + 1.987 = -61.30 \text{ cal deg}^{-1} \text{ mole}^{-1}.$$

and

$$S^0 = \frac{H^0 - E_0^0}{T} + \frac{G^0 - E_0^0}{T} = 61.30 + 9.29$$

$$= 70.59 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

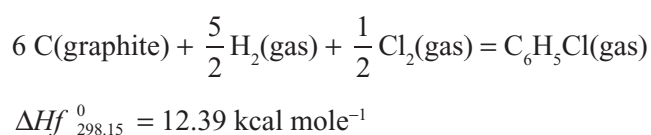
(b) In order to calculate $(G^0 - E_0^0)/T$ chlorobenzene having isotopes of chlorine 35 and 37 amu, we must first calculate the value of $(G^0 - E_0^0)/T$ for $^{37}\text{C}_6\text{H}_5$. From Part (a), we can show that

$$\frac{G^0 - E_0^0}{T} = -61.40 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

Therefore $(G^0 - E_0^0)/T$ for chlorobenzene containing isotopes ^{35}Cl and ^{37}Cl in the ratio 3 : 1

$$\begin{aligned}
 &= \sum_i N_i K_i \quad (\text{from 3.225}) \\
 &= \left(\frac{3}{4} \times -61.30 + \frac{1}{4} \times -61.40 \right) \\
 &= -61.32 \text{ cal deg}^{-1} \text{ mole}^{-1}
 \end{aligned}$$

The values of energy parameters computed for $^{35}\text{ClC}_6\text{H}_5$ together with those of C(graphite), $\text{H}_2(\text{gas})$, $\text{Cl}_2(\text{gas})$ and the experimental value of the heat of formation of chlorobenzene gas have been used to calculate ΔH_f^0 , ΔG_f^0 and $\log_{10} K_p$ from relations (3.228) to (3.231) for the reaction



The absolute values of entropy in cal deg⁻¹ for elements involved in the reaction are

$\text{Cl}_2(\text{g}) = 53.286$, $\text{H}_2(\text{g}) = 31.211$, $\text{C}(\text{graphite}) = 1.3609$

Thus,

$$\begin{aligned}
 \Delta S_f^0_{298.15} &= S^0_{298.15}(\text{compound}) - S^0_{298.15}(\text{elements}) \\
 &= 70.59 - \left(6\text{C} + \frac{5}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 \right) \\
 &= 70.59 - \left(6 \times 1.3609 + \frac{5}{2} \times 31.211 + \frac{53.286}{2} \right) \\
 &= 70.59 - 112.84 = -42.25 \text{ cal deg}^{-1} \text{ mole}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \Delta G_f^0_{298.15} &= \Delta H_f^0_{298.15} - T \Delta S_f^0_{298.15} \\
 &= 12.39 - 298.15 \times (-42.25 \times 10^{-3}) \\
 &= 24.98 \text{ kcal mole}^{-1}
 \end{aligned}$$

and

$$\begin{aligned}
 \log_{10} K_p &= \frac{-\Delta G_f^0_{298.15}}{0.004575845T} \\
 &= -\frac{24.98}{0.004575845 \times 298.15} = -18.31
 \end{aligned}$$

or

$$K_p = 2.04 \times 10^{18}$$

(c) The entropy and free energy changes due to mixing of $^{35}\text{ClC}_6\text{H}_5$ and $^{37}\text{ClC}_6\text{H}_5$ in the ratio 3:1

$$\begin{aligned}
 \Delta S^0 &= -R \sum_i N_i \ln N_i \\
 &= -R(0.75 \ln 0.75 + 0.25 \ln 0.25) \\
 &= -1.987 \times -0.250 \\
 &= 0.497 \text{ cal deg}^{-1} \text{ mole}^{-1}
 \end{aligned}$$

and

$$\begin{aligned}\frac{\Delta G^0}{T} &= R \sum_i N_i \ln N_i \\ &= 1.987 \times -0.250 \\ &= -4.497 \text{ cal deg}^{-1} \text{ mole}^{-1}\end{aligned}$$

In order to facilitate calculations by computer, simplified expressions for contribution to the corresponding thermodynamic quantity, owing to various types of degree of freedom are summarised below.

For diatomic and polyatomic molecules, the contribution to thermodynamic quantity due to translational motion is

$$(C_p^0)_{\text{trans}} = \frac{3}{2}R + R = \frac{5}{2}R = 4.968 \quad (3.232)$$

$$\begin{aligned}S_{\text{trans}}^0 &= \frac{3}{2}R \ln M + \frac{5}{2}R \ln T - R \ln p + \frac{5}{2}R - 7.282 \\ &= 6.8635 \log M + 11.4391 \log T - 4.5756 \log p - 2.313 \\ &= 6.8635 \log M + 11.4391 \log T - 2.313 \quad (p = 1 \text{ atm})\end{aligned} \quad (3.233)$$

$$\begin{aligned}\left(\frac{G^0 - E_0^0}{T}\right)_{\text{trans}} &= -\frac{3}{2}R \ln M - \frac{5}{2}R \ln T + R \ln p + 7.282 \\ &= -6.8635 \log M - 11.4391 \log T + 7.282\end{aligned} \quad (3.234)$$

$$\left(\frac{H^0 - E_0^0}{T}\right)_{\text{trans}} = \frac{3}{2}R + R = \frac{5}{2}R = 4.968 \quad (3.235)$$

For C_2H_4 ($\sigma = 4$) at 298.15 K and 1 atm pressure, we get from Eqs (3.232) to (3.235).

$$(C_p^0)_{\text{trans}} = 4.968 \text{ cal mole}^{-1} \text{ K}^{-1}$$

$$S_{\text{trans}}^0 = 35.924 \text{ cal mole}^{-1} \text{ K}^{-1}$$

$$\left(\frac{G^0 - E_0^0}{T}\right)_{\text{trans}} = -30.960 \text{ cal mole}^{-1} \text{ K}^{-1}$$

$$\left(\frac{H^0 - E_0^0}{T}\right)_{\text{trans}} = 4.968 \text{ cal mole}^{-1} \text{ K}^{-1}$$

For diatomic and linear polyatomic molecules, the contribution owing to rotational motion is

$$(C_p^0)_{\text{rot}} = R \quad (3.236)$$

$$S_{\text{rot}}^0 = R \ln T + R \ln I - R \ln \sigma + 177.67 \quad (3.237)$$

$$\left(\frac{G^0 - E_0^0}{T}\right)_{\text{rot}} = -R \ln T - R \ln I + R \ln \sigma - 175.683 \quad (3.238)$$

$$\left(\frac{H^0 - E_0^0}{T}\right)_{\text{rot}} = R \quad (3.239)$$

For polyatomic nonlinear molecules,

$$(C_p^0)_{\text{rot}} = \frac{3}{2}R \quad (3.240)$$

$$S_{\text{rot}}^0 = \frac{3}{2}R \ln T + \frac{1}{2}R \ln(I_A I_B I_C) - R \ln \sigma + 267.54 \quad (3.241)$$

$$\left(\frac{G^0 - E_0^0}{T} \right)_{\text{rot}} = -\frac{3}{2}R \ln T - \frac{1}{2}R \ln(I_A I_B I_C) + R \ln \sigma - 264.559 \quad (3.242)$$

$$\left(\frac{H^0 - E_0^0}{T} \right)_{\text{rot}} = \frac{3}{2}R \quad (3.243)$$

For C_2H_4 , $I_A = I_B = I_C = 17.33 \times 10^{-40} \text{ g cm}^2$ and at 298.15 K and 1 atm pressure; we obtain from Eqs (3.240) to

$$(3.243): S_{\text{rot}}^0 = 15.758 \text{ cal mole}^{-1} \text{ K}^{-1}, (C_p^0)_{\text{rot}} = 2.981 \text{ cal mole}^{-1} \text{ K}^{-1}, \left(\frac{G^0 - E_0^0}{T} \right)_{\text{rot}} = -12.848 \text{ cal mole}^{-1} \text{ K}^{-1}, \text{ and } \left(\frac{H^0 - E_0^0}{T} \right)_{\text{rot}} = 2.983 \text{ cal mole}^{-1} \text{ K}^{-1}.$$

The contribution due to vibrational degrees of freedom is

$$(C_p^0)_{\text{vib}} = R \sum_{i=1}^{3n-6/3n-5} \left[\frac{x_i^2 \exp(x_i)}{(\exp(x_i) - 1)^2} \right] \quad (3.244)$$

$$S_{\text{vib}}^0 = R \sum_{i=1}^{3n-6/3n-5} \left[\frac{x_i}{\exp(x_i) - 1} - \ln(1 - \exp(-x_i)) \right] \quad (3.245)$$

$$\left(\frac{G^0 - E_0^0}{T} \right)_{\text{vib}} = R \sum_{i=1}^{3n-6/3n-5} \ln(1 - \exp(-x_i)) \quad (3.246)$$

$$\left(\frac{H^0 - E_0^0}{T} \right)_{\text{vib}} = R \sum_{i=1}^{3n-6/3n-5} \left[\frac{x_i}{\exp(x_i) - 1} \right] \quad (3.247)$$

For numerical calculation, x_i is expressed as

$$x_i = \frac{hcw_i}{\kappa T} = \frac{w_i}{0.6951T} = 1.439 \frac{w_i}{T}$$

where w_i is in cm^{-1} .

Summation for polyatomic linear molecules covers $3n - 5$ vibrations and for polyatomic nonlinear molecules $3n - 6$ vibrations, where n is the number of atoms in the molecule.

For C_2H_4 the values of $\theta_i (= hcw_i/\kappa)$ are 4344, 2335, 1931, 1187, 4424, 1581, 1365, 1357, 4469, 1432, 4302, 2078. Using this data, we obtain from Eqs (3.244) to 3.247).

$$(C_p^0)_{\text{vib}} = 2.422 \text{ cal mole}^{-1} \text{ K}^{-1}, S_{\text{vib}}^0 = 0.623 \text{ cal mole}^{-1} \text{ K}^{-1},$$

$$-\left(\frac{G^0 - E_0^0}{T} \right)_{\text{vib}} = 0.111 \text{ cal mole}^{-1} \text{ K}^{-1}$$

and

$$\left(\frac{H^0 - E_0^0}{T} \right)_{\text{vib}} = 0.512 \text{ cal mole}^{-1} \text{ K}^{-1}.$$

Based on expressions (3.232) to (3.247), a computer programme in C⁺⁺ for the computation of thermodynamic functions is given in Appendix 3.6A. The vibrational and other relevant data pertinent to determine the thermodynamic functions manually and with the aid of computer programme are reported in Table 3.17. This data will be beneficial to students for generating and solving the problems.

For more accurate results, the contribution due to other degrees of freedom, viz., internal rotation, nuclear spin and electronspin must be added to the corresponding thermodynamic property whenever the situation demands.

Table 3.17 Symmetry numbers, moments of Inertia and vibrational frequencies for some selected gases.

Gas	σ	$I \times 10^{40} (\text{g cm}^2)$	Frequency (cm^{-1})
Br ₂	2	342.5	325
Cl ₂	2	113.9	560
F ₂	2	27.8	918
H ₂	2	0.463	4400
I ₂	2	741.5	214.55
N ₂	2	13.84	2358
O ₂	2	19.23	1580
CO	1	14.43	2170
HBr	1	3.26	2649
HCl	1	2.65	2991
HF	1	1.35	4139
HI	1	4.31	2309
NO	1	16.51	1904
OH	1	1.50	3738
CO ₂	2	70.2	1337, 2349, 667 (doubly degenerate)
CS ₂	2	24.7	657, 1523, 397 (doubly degenerate)
HCN	1	18.7	2089, 3312, 712 (doubly degenerate)
H ₂ O	2	1.784	3652, 1595, 3756
H ₂ S	2	3.63	2611, 1290, 2684
N ₂ O	1	66.1	589, 1285, 2224
SO ₂	2	42.5	1151, 524, 1361
C ₂ H ₂	2	23.51	3374, 1974, 3287, 612 (doubly degenerate) 729 (doubly degenerate)
NH ₃	3	3.22	3337, 950, 3414, (doubly degenerate), 1628 (doubly degenerate)
CH ₄	12	5.30	2914, 1526 (doubly degenerate), 3020 (triply degenerate), 1306 (triply degenerate)

• **Partition Function for Internal Rotation** In complex molecules, the rotation of one group of atoms relative to another (for example of the group CH_3 about the bond $\text{C}-\text{C}$ in ethane) must be taken into consideration. In case of large barrier height, U , for instance for CH_3-CH_3 , it is 3150, and for CH_3OH , it is 2700 cal mole^{-1} , the internal rotational motion is treated as torsional vibration and its contribution is added to the thermodynamic functions. On the other hand, if U is small, the torsional frequency is dropped out and the rotational partition function equals the product of $Z_{\text{rot}} \cdot Z_{\text{introt}}$. Z_{introt} is known as the partition function for free rotation and is expressed as

$$Z_{\text{introt}} = \frac{(8\pi^3 I_{\text{red}} kT)^{1/2}}{h\sigma_{\text{introt}}} = \frac{2.7935 \times 10^{19} (I_{\text{red}} T)^{1/2}}{\sigma_{\text{introt}}} \quad (3.248)$$

$$\ln Z_{\text{introt}} = 1.1513 \log I_{\text{red}} - 2.3026 \log \sigma_{\text{introt}} + 1.1513 \log T + 52.8356$$

Here I_{red} = reduced moment of inertia about the axis of internal rotation. σ_{introt} = symmetry number of internal rotation. It is equal to the number of positions of maximum attraction between the atoms and rotating groups in rotation through 360° , i.e. the number of potential maxima occurring in one revolution of the rotating group. For C_2H_6 , for example $\sigma_{\text{introt}} = 3$, i.e. during one revolution the hydrogen atoms of one CH_3 group occupy position corresponding to the minimum distance from a hydrogen atom of the other CH_3 group three times.

For two groups rotating relative to one of the axes of the molecules, I is formed by the equation

$$I_{\text{red}} = \frac{I_A I_B}{I_A + I_B} \quad (3.249)$$

where I_A and I_B are the moments of inertia of the groups rotating about this axis. If a molecule contains several groups performing internal rotation, the calculation should be performed for each of them, and then the results are summated.

If there is free internal rotation, the contribution owing to internal rotation to $(H_0 - E_0)$ and C_p^0 at not too low temperatures is given by

$$(H_0 - E_0)_{\text{introt}} = \frac{1}{2} RT \quad (3.250)$$

$$(C_p^0)_{\text{introt}} = \frac{1}{2} R \quad (3.251)$$

If there are several free internal rotations, a corresponding number of terms as in Eqs (3.250) and (3.251) have to be added.

For torsional oscillation of 800 cm^{-1} , the contribution to C_p^0 at $T = 200 \text{ K}$ as worked out from Eq. (3.244) for vibrational contribution to C_p^0 has been found to be $0.21 \text{ cal mole}^{-1} \text{ K}^{-1}$ as compared to $0.99 \text{ cal mole}^{-1} \text{ K}^{-1}$ from Eq. (3.251) for one free rotation.

The contribution to entropy and Gibbs free energy is given by

$$S_{\text{introt}}^0 = \frac{R}{2} \left[\ln T + \ln I_{\text{red}} - 2 \ln \sigma_{\text{introt}} + \ln \left(\frac{8\pi^3 k}{h^2} \right) + 1 \right] \quad (3.252)$$

$$= 2.2868 (\log T + \log I_{\text{red}} - 2 \log \sigma_{\text{introt}}) + 89.932$$

$$-\left(\frac{G^0 - E_0^0}{T} \right)_{\text{introt}} = S_{\text{introt}}^0 - \frac{R}{2} \quad (3.253)$$

$$= S_{\text{introt}}^0 - 0.993$$

For molecules like C_2H_6 or $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$, $\sigma_{\text{introt}} = 3$, and $I_{\text{red}} = I_A/4 = 2.759 \times 10^{-40} \text{ g cm}^2$, we get from Eq. (3.252)

$$S_{\text{introt}}^0 = 2.2868 \log T - 2.714 \quad (3.254)$$

• **Partition Function for Nuclear Spin** Owing to the very high energies of the excited nuclear states, the nuclear partition function of any molecule or atom is the degeneracy of the ground state nuclear energy level. The nuclear partition function is expressed as

$$Z_{\text{nuc}} = g_{0(\text{nuc})} \exp\left(\frac{-E_{0(\text{nuc})}}{\kappa T}\right) + g_{1(\text{nuc})} \exp\left(\frac{-E_{1(\text{nuc})}}{\kappa T}\right) + g_{2(\text{nuc})} \exp\left(\frac{-E_{2(\text{nuc})}}{\kappa T}\right) + \dots \quad (3.255)$$

Since higher states are rarely populated, Eq. (3.255) becomes

$$Z_{\text{nuc}} = g_{0(\text{nuc})} \exp\left(\frac{-E_{0(\text{nuc})}}{\kappa T}\right) \quad (3.256)$$

If $E_{0(\text{nuc})} = 0$, Eq. (3.256) reduces to

$$Z_{0(\text{nuc})} = g_{0(\text{nuc})} \quad (3.257)$$

Further, the degeneracy of ortho state is given by

$$g_{0(\text{nuc})}^{\text{ortho}} = (I + 1)(2I + 1) \quad (3.258)$$

where I is the spin quantum number of the nucleus.

For hydrogen atom, $I = \frac{1}{2}$,

$$Z_{0(\text{nuc})}^{\text{ortho}} = g_{0(\text{nuc})}^{\text{ortho}} = 3$$

For deuterium atom, $I = 1$

$$Z_{0(\text{nuc})}^{\text{ortho}} = g_{0(\text{nuc})}^{\text{ortho}} = 6$$

When nuclear spin occurs, a factor taking into account its influence on the rotational level must be introduced into the expression for rotational partition function. Assuming that Z_{rot} and the nuclear partition function Z_{nuc} to be independent of each other, we get

$$\begin{aligned} Z_{\text{rotnuc}} &\approx Z_{\text{rot}} Z_{\text{nuc}} \\ &= Z_{\text{rot}} \prod_i (2I_i + 1) \\ &= Z_{\text{rot}} (2I_1 + 1) (2I_2 + 1) (2I_3 + 1) \dots \end{aligned} \quad (3.259)$$

where I_i is the nuclear spin quantum number.

The number of multipliers of the form $(2I_i + 1)$ in Eq. (3.259) equals the number of atoms in the molecule.

The spin of a nucleus equals the sum of the spins of the particles which form it. Therefore, if the sum of the protons and neutrons is an even number, the spin equals an integer or zero, otherwise the spin is a half integer. The values of spin quantum number for selected elements are given below.

<i>Element</i>	C, He, O	F, H, P	D, N	Cl
<i>Spin</i>	0	1/2	1	5/2

Spin does not influence $(H^0 - E_0^0)/T$ and C_p^0 , but it does change the entropy and Gibbs energy. In this connection, complete (absolute or spectroscopic) and practical (thermochemical) entropies/Gibbs energy are distinguished. The latter equals the total entropy/Gibbs energy less the spin entropy, i.e.

$$S_{\text{pract}}^0 = S_{\text{abs}}^0 - R \sum \ln(2I + 1) \quad (3.260)$$

Similarly

$$\left(\frac{G^0 - E_0^0}{T}\right)_{\text{pract}} = -\left(\frac{G^0 - E_0^0}{T}\right)_{\text{abs}} - R \sum \ln(2I + 1) \quad (3.261)$$

We may consider that every atom has an identical spin regardless of whether it is in the isolated state or is a part of a compound. Therefore, in calculating ΔS^0 and ΔG^0 and, consequently, in calculating equilibrium, the spin components mutually eliminate each other. Nuclear spin must be taken into account only for very low temperatures (for hydrogen below 0°C , for deuterium below 70°C , and for other substances at still lower temperatures). The standard entropy of ethene with account taken of nuclear spin effect is $57.98 \text{ cal mole}^{-1} \text{ K}^{-1}$. We know that

$$S_{298}^0 = S_{\text{trans}} + S_{\text{rot}}^0 + S_{\text{vib}}^0$$

For ethene, $S_{298}^0 = 36.02 + 15.80 + 0.65 = 52.47 \text{ cal mole}^{-1} \text{ K}^{-1}$

If the hydrogen spin nuclear effect is considered, we get from Eq. (3.260)

$$S_{298}^0 = 52.47 + 4R \ln \left(2 \times \frac{1}{2} + 1 \right) = 57.98 \text{ cal mole}^{-1} \text{ K}^{-1}$$

In case of molecules, consisting of same atoms, the rotational terms are divided into two intercombining groups, having different statistical weights. The terms with greater statistical weight are called *ortho terms* while with less statistical weight are called *para terms*. When nuclear spin is 0, the para terms are absent. The Z_{rot} in this case contains members either with even or odd J . In case of nuclear spin, however, we have

$$\begin{aligned} Z_{\text{rot}} Z_{\text{nuc}} &= g_{\text{ortho}} \sum_{\text{ortho}} (2J+1) \exp[-BhcJ(J+1)/\kappa T] \\ &+ g_{\text{para}} \sum_{\text{para}} (2J+1) \exp[-BhcJ(J+1)/\kappa T] \end{aligned} \quad (3.262)$$

In case of H_2 , the ortho term ($I = 1/2$) have statistical weights, $g_{\text{ortho}} = 3$ (for odd values of J) and the para terms ($I = 0$) $g_{\text{para}} = 1$ (for even values of J). Consequently, the partition function, Eq. (3.262), in such a case is expressed as

$$\begin{aligned} Z_{\text{rot}} Z_{\text{nuc}} &= 3 \sum_{J=1,3,5} (2J+1) \exp[-BhcJ(J+1)/\kappa T] \\ &+ \sum_{J=0,2,4} (2J+1) \exp[-BhcJ(J+1)/\kappa T] \end{aligned} \quad (3.263)$$

For sufficiently high temperatures, ($T > 100 \text{ K}$, $Bhc \ll \kappa T$) each term of the sums of Eq. (3.263) can be approximated to $\kappa T/2Bhc$. Heat capacity, $C_{v,r}$, of both the modifications of hydrogen is equal to $5R/2$. However, at low temperatures, the heat capacities of both the modifications of hydrogen are different due to different dependence of each of the two sums of Eq. (3.263) upon temperature. Since ordinary hydrogen is a mixture of three parts of ortho and one part of para modifications, its total heat capacity, the rotational components of which are defined by the formula

$$C_{\text{rot}} = \frac{3C_{v,\text{rot,ortho}} + C_{v,\text{rot,para}}}{4} \quad (3.264)$$

exhibits a peculiar temperature variation that differs from ordinary trend. This anomaly in the heat capacity of hydrogen was the first experimental fact that led to the discovery of its ortho- and para-modifications.

• **Partition Function for Electronic Excitation** The degeneracy of each electronic level $g_{\text{elec}} = 2j + 1$. Therefore, the expression for electronic partition function may be expressed as

$$\begin{aligned} Z_{\text{elec}} &= \sum_{i=0}^{i=1,2,3} (2j_i + 1) \exp\left(\frac{-E_{i(\text{elec})}}{\kappa T}\right) \\ &= (2j_0 + 1) + (2j_1 + 1) \exp\left(\frac{-E_{1(\text{elec})}}{\kappa T}\right) + \dots \end{aligned} \quad (3.265)$$

where j_i is the quantum number of the electronic energy levels and equals the orbital quantum number plus the total spin of the electrons in the molecule.

The electronic levels correspond to a very high energy, i.e. only a negligible fraction of the molecules is in an excited state. The influence of second term is noticeable only when $T > h\nu / 4\kappa$. Other levels have to be taken into account in addition to the ground level only at very high temperatures, when optical excitation of the molecules takes place. Even in this case, however, we may limit ourselves to two or three terms of Z_{elec} . Consequently, because of the absence of multiplet electronic levels in the majority of polyatomic gases except Cl_2 , O_2 , NO and certain other gases at $T > 2000$ K, we can conclude that $j = 0$, $g_{\text{elec}} = 1$ and $Z_{\text{elec}} = 1$.

$$S_{\text{elec}}^0 = R \ln g_0(\text{elec}) \quad (3.266)$$

$$\left(\frac{G^0 - E_0^0}{T} \right)_{\text{elec}} = -R \ln g_0(\text{elec}) \quad (3.267)$$

The electronic partition function of chlorine atom in the ground state ($^2P_{3/2}$) as computed from Eq. (3.265) is

$$Z_{\text{elec}} = g_{0(\text{elec})} = (2j_0 + 1) = \left(2 \times \frac{3}{2} + 1 \right) = 4$$

provided the energies of the higher excited states are very large. If the energy of the first excited state of chlorine atom ($^2P_{1/2}$) is 1.8×10^{-20} J, the electronic partition function at 1800 K as determined from Eq (3.265) is

$$\begin{aligned} Z_{\text{elec}} &= (2j_0 + 1) + (2j_1 + 1) \exp\left(\frac{-E_1(\text{elec})}{\kappa T}\right) \\ &= 4 + 2 \exp\left[\frac{-1.8 \times 10^{-20} \text{ J}}{(1.381 \times 10^{-23} \text{ JK}^{-1})(1800 \text{ K})}\right] = 4 + 2 \exp(-0.724) = 4.969 \end{aligned}$$

(v) Frequency of Inactive Vibration Alternatively, the thermodynamic data, especially C_p^0 , can also be employed to determine the frequency of an inactive vibration provided the frequencies of all its active modes are determined spectroscopically. For this purpose C_p^0 of the chemical species is calculated by omitting the unknown frequency, comparison of this value with the observed C_p^0 yields ΔC_p . This is the contribution of the missing frequency, ν , to the calculated C_p^0 .

The inactive frequency ν is then calculated from the relation

$$\Delta C_p = \frac{g_i R x^2 e^x}{(e^x - 1)^2} \quad (3.268)$$

where

$$x = \frac{h\nu}{\kappa T} = \frac{1.4388\nu}{T}$$

Problem 3.41: The symmetry number of methane is 12. If its vibrational spectra contain the frequencies 2914.2, 1526.0, 1526.0, 3020.3, 3020.3 and 3020.3 cm^{-1} , calculate the missing frequency (assuming that it exists as a triplet) if its C_p^0 is $8.57 \text{ cal mole}^{-1} \text{ deg}^{-1}$.

Solution The IR spectra of methane should have $3n-6$ ($n=5$) = 9 normal modes of vibration and consequently according to the Eq. (3.223). the observed

$$C_p^0 = \left[4 + \sum_{i=1}^9 \frac{g_i x_i^2 \exp x_i}{(\exp x_i - 1)^2} \right] = 8.57 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

But the calculated C_p^0 for methane with the above frequencies would be

$$\begin{aligned} C_p^0(\text{calculated}) &= R \left[4 + \sum_{i=1}^9 \frac{g_i x_i^2 \exp x_i}{(\exp x_i - 1)^2} \right] \\ &= 8.08 \text{ cal deg}^{-1} \text{ mole}^{-1} \end{aligned}$$

The difference between the observed and calculated C_p^0 for methane is contribution ΔC_p of the missing frequency to the calculated C_p^0 . Consequently,

$$\Delta C_p = 8.57 - 8.08 = 0.49 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

But
$$\Delta C_p = \frac{Rg_i x^2 e^x}{(e^x - 1)^2}$$

Therefore
$$\frac{0.49}{1.987} = \frac{3(x^2 e^x)}{(e^x - 1)^2}$$

or
$$\frac{x^2 e^x}{(e^x - 1)^2} = 0.082$$

This equation is solved graphically for various values of x and it yields $x = 6.2$.

But
$$x = 1.4388 \frac{\nu}{T} = \frac{1.4388\nu}{298.15}$$

Therefore,
$$\nu = 1286.3 \text{ cm}^{-1}$$

This calculated missing frequency compares reasonably well with the observed frequency of 1306.2 cm^{-1} .

(vi) Equilibrium Constants from Frequency Data According to the well-known thermodynamic relation for Gibbs' free energy of a gaseous substance

$$\begin{aligned} G &= F + pV \\ &= -N_A \kappa T \left[\ln Z - V \left(\frac{\partial \ln Z}{\partial V} \right)_T \right] + E_0^0 \end{aligned} \quad (3.269)$$

Thus, the standard free energy change of the gaseous, chemical reaction can be determined from molecular parameters and spectroscopic data of the reactants and products. Hence, from the equation

$$\Delta G^0 = -RT \ln K \quad (3.270)$$

we can get the equilibrium constants K . Assuming the gas to be ideal, Eq. (3.269) modifies to

$$G = -N_A \kappa T (\ln Z - 1) + E_0^0 \quad (3.271)$$

since
$$\left[\frac{\partial \ln Z_{\text{rot}}}{\partial V} \right]_T = \left[\frac{\partial \ln Z_{\text{vib}}}{\partial V} \right]_T = 0$$

and
$$\left[\frac{\partial \ln Z_{\text{trans}}}{\partial V} \right]_T = \frac{1}{V} \quad (3.272)$$

For one mole, Eq. (3.271) reduces to

$$G^0 = -RT \ln Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} + E_0^0 + RT \quad (3.273)$$

Let us consider a reaction, $A + B \rightarrow C$.

Since the partition function of each species of the chemical reaction is evaluated relative to a different reference point, thus while calculating ΔG^0 , a common zero must be selected. This is achieved by carrying out the reaction at 0 K, since at this temperature molecules will have only zero point energy as the translational and rotational energy of the molecules will be zero. However, the potential energy curves of molecules may lie at different levels on the absolute energy scale. The potential energy diagrams for three diatomic molecules is shown in Fig. 3.47, Selecting the arbitrary zero as shown in Fig. 3.47, we may write

$$\begin{aligned}
 G_A^0 &= -RT \ln Z_{\text{trans}}^A Z_{\text{rot}}^A Z_{\text{vib}}^A + a + RT \\
 G_B^0 &= -RT \ln Z_{\text{trans}}^B Z_{\text{rot}}^B Z_{\text{vib}}^B + b + RT \\
 G_C^0 &= -RT \ln Z_{\text{trans}}^C Z_{\text{rot}}^C Z_{\text{vib}}^C + c + RT
 \end{aligned}
 \quad (3.274)$$

But $(c - a - b)$ is the total heat of reaction at absolute zero including the zero point energies. Let us call this quantity ΔE_0^0 . Hence, from Eq. (3.274)

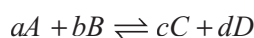
$$\Delta G^0 = -RT \ln \frac{Z_{\text{trans}}^C Z_{\text{rot}}^C Z_{\text{vib}}^C}{Z_{\text{trans}}^A Z_{\text{rot}}^A Z_{\text{vib}}^A Z_{\text{trans}}^B Z_{\text{rot}}^B Z_{\text{vib}}^B} + \Delta E_0^0 - RT \quad (3.275)$$

Comparing Eqs (3.270) and (3.275), we get

$$K = \frac{Z_{\text{trans}}^C Z_{\text{rot}}^C Z_{\text{vib}}^C}{Z_{\text{trans}}^A Z_{\text{rot}}^A Z_{\text{vib}}^A Z_{\text{trans}}^B Z_{\text{rot}}^B Z_{\text{vib}}^B} \frac{e^{-\Delta E_0^0 / RT}}{e^{+\Delta n}} \quad (3.276)$$

where Δn is the difference between the number of product and reactant molecules, i.e. $(n_c - n_b - n_a)$. E_0^0 can be determined for some reactions from spectroscopic data while for other reactions thermal data are required to get E_0^0 . This method of evaluating equilibrium constants is especially useful in gathering information on the efficiency of isotopic substitution reactions.

Further, the equilibrium constant for the most general reaction,



is expressed as

$$K_p = \frac{(Z_C)^c (Z_D)^d}{(Z_A)^a (Z_B)^b} \left(\frac{1}{N_A} \right)^{\Delta n} \exp \left(\frac{-\Delta E_0^0}{RT} \right) \quad (3.277)$$

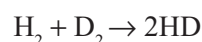
where $Z = Z_{\text{trans}}^0 Z_{\text{rot}} Z_{\text{vib}} Z_{\text{elec}} Z_{\text{nuc}}$ and Z_{trans}^0 is the translational partition function at 1 atm. ΔE_0^0 is the difference in zero point energies of products and reactants, i.e.

$$\Delta E_0^0 = cE_{(C)}^0 + dE_{(D)}^0 - aE_{(A)}^0 - bE_{(B)}^0$$

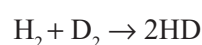
and

$$\Delta n = (c + d) - (a + b)$$

Problem 3.42: The vibrational frequencies (in cm^{-1}) for HD, H_2 and D_2 are 3817, 4395 and 3118 respectively. Calculate the equilibrium constant for the exchange reaction



Solution The exchange reaction is



The total energy change for this reaction at 0 K is the algebraic sum of the zero point energies

$$\begin{aligned}
 \Delta E_0^0 &= 2E_0^0(\text{HD}) - E_0^0(\text{H}_2) - E_0^0(\text{D}_2) \\
 &= \frac{hc}{2} (2\bar{\nu}_{\text{HD}} - \bar{\nu}_{\text{H}_2} - \bar{\nu}_{\text{D}_2}) \quad (\because E = hc\bar{\nu})
 \end{aligned}$$

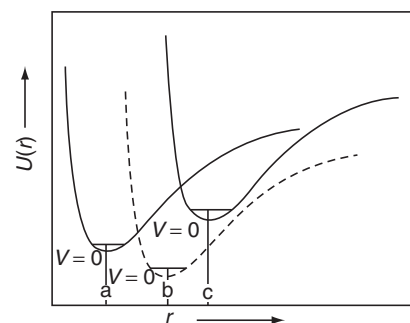


Fig. 3.47 Schematic potential energy curves for species A, B and C.

Thus,

$$K = \frac{Z_{HD}^2}{Z_{H_2} Z_{D_2}} e^{-hc(2\bar{\nu}_{HD} - \bar{\nu}_{H_2} - \bar{\nu}_{D_2})/2\kappa T}$$

$$= \frac{\left[V \left(\frac{2\pi M_{HD} \kappa T}{h^2} \right)^{\frac{3}{2}} \left(\frac{8\pi^2 I_{HD} \kappa T}{\sigma_{HD} h} \right) (1 - e^{-hc\bar{\nu}_{HD}/\kappa T})^{-1} \right]^2 \times e^{-hc(2\bar{\nu}_{HD} - \bar{\nu}_{H_2} - \bar{\nu}_{D_2})/2\kappa T}}{V \left(\frac{2\pi M_{H_2} \kappa T}{h^2} \right)^{\frac{3}{2}} \left(\frac{8\pi^2 I_{H_2} \kappa T}{\sigma_{H_2} h} \right) (1 - e^{-hc\bar{\nu}_{H_2}/\kappa T})^{-1} \times V \left(\frac{2\pi M_{D_2} \kappa T}{h^2} \right)^{\frac{3}{2}} \left(\frac{8\pi^2 I_{D_2} \kappa T}{\sigma_{D_2} h} \right) (1 - e^{-hc\bar{\nu}_{D_2}/\kappa T})^{-1}}$$

For each vibrational partition function $h\nu \gg T$ at room temperature and hence $Z_{\text{vib}} \sim 1$.

Also

$$\sigma_{H_2} = \sigma_{D_2} = 2; \sigma_{HD} = 1$$

Thus,

$$K = \left(\frac{M_{HD}^2}{M_{H_2} M_{D_2}} \right)^{3/2} \cdot \frac{4I_{HD}^2}{I_{H_2} I_{D_2}} e^{-hc(2\bar{\nu}_{HD} - \bar{\nu}_{H_2} - \bar{\nu}_{D_2})/2\kappa T}$$

We know that

$$M_{HD} = 3, M_{H_2} = 2, M_{D_2} = 4; \bar{\nu}_{HD} = 3817 \text{ cm}^{-1}; \bar{\nu}_{H_2} = 4395 \text{ cm}^{-1};$$

$$\bar{\nu}_{D_2} = 3118 \text{ cm}^{-1}; \text{ and } I_{HD} = \frac{2}{3} I_{D_2}; I_{H_2} = \frac{1}{2} I_{D_2},$$

Hence

$$K = \left(\frac{9}{8} \right)^{3/2} \times \frac{4 \times 8}{9} e^{-hc(121)/2\kappa T}$$

$$= 3.17 \text{ at } T = 300 \text{ K}$$

This value will not be accurate since we have used the integrated form of the rotational partition function, which is not a good approximation for H_2 at room temperature.

(vii) Specific Heat of Adsorption from Group Frequency Shift The physical adsorption of adsorbate on the surface of silica causes a frequency shift of the surface silica OH groups. This frequency shift has been found to vary linearly with the specific heat of adsorption, ΔQ_{ad} and can be utilised to calculate the heat of adsorption of adsorbate on a dehydroxylated silica surface ΔH_{ad} , when the corresponding heat of adsorption on the hydroxylated silica surface ΔH_h is known, since

$$\Delta Q_{ad} = \Delta H_{ad} - \Delta H_h \quad (3.278)$$

Problem 3.43: During the physical adsorption of benzene, *n*-hexane, diethylether, etc., on the surface of hydroxylated silica surface, it is observed that the frequency shift of the OH vibration for one half surface coverage and ΔQ_{ad} can be expressed by

$$\Delta \nu_{OH} (\text{cm}^{-1}) = 62.5 (\text{cm}^{-1} \text{ kcal}^{-1} \text{ mole}) \Delta Q_{ad} + 25 \text{ cm}^{-1} \quad (3.279)$$

If the frequency shift for adsorption on hydroxylated silica surface is 200 cm^{-1} , calculate the specific heat of adsorption of water on this silica surface

Solution Since

$$\Delta\nu_{OH} = 62.5 \Delta Q_{ad} + 25$$

Therefore, for $\Delta\nu_{OH} = 200 \text{ cm}^{-1}$

$$\Delta Q_{ad} = \frac{175}{62.5} = 2.80 \text{ kcal mole}^{-1}$$

(viii) Intermedions from Vibrational Frequency of Some Adsorbed Chemical Species The adsorption of an adsorbate on metal or metal oxide adsorbent surfaces gives rise to IR absorption bands higher or lower than that of the free adsorbate molecule. This may be due to the difference in the electronic structure of the free adsorbate and adsorbed molecules. The various species formed due to adsorption of single adsorbate, differ from each other by an integral number of electrons, i.e.

$$X = X_{ad}^{n\pm1} \quad X_{ad}^{n\pm2} \quad X_{ad}^{n\pm3}, \text{ etc.}$$

where n is a fraction less than 1.

The vibrational frequencies of some adsorbed CO species on surface of metals or metal oxides is of two types. In the first type, the number of electrons contained in the adsorbed CO species varies by an integral number whereas in the other no such relationship exists. The species of the first group are called *intermedions* and are assumed to be responsible for chemical reactivity. The second type is known as *carbonyls*. They are more stable whereas the intermedions are easily formed and removed. The position of a band due to intermedion is independent of the nature of the substrate but dependent only on the cation involved. The fractional part of the non-integral number of valence electrons associated with the intermedions is termed as polarisation fraction and is dependent upon ionic charge.

The empirical relationship between the number of valence electrons E and the vibrational frequency $\bar{\nu}$ of the adsorbed CO species on metal surfaces is

$$[2269.96 \pm \bar{\nu}(\text{CO})] [12.1182 - E(\text{CO})] = 268.31 \text{ cm}^{-1} \quad (3.280)$$

Problem 3.44: The adsorption of CO on copper (II) oxide and cobalt surfaces gives rise to vibrational bands at 2173, 2121, 2127 and 2000 cm^{-1} in case of copper (II) oxide while at 2160, 2091 and 2179 cm^{-1} in case of cobalt (Co). Calculate the number of valence electrons in different chemical species of CO which result due to adsorption and based on these observation classify the species as intermedions and carbonyls.

Solution We know that, $[2269.96 \pm \bar{\nu}(\text{CO})] [12.1182 - E(\text{CO})] = 268.31 \text{ cm}^{-1}$. Thus, for $\bar{\nu} = 2173 \text{ cm}^{-1}$, $[2269.96 \pm 2173] [12.1182 - E(\text{CO})] = 268.31$ or $E(\text{CO}) = 12.1182 - 2.7672 = 9.35$.

Similar calculations for other frequencies yield.

$$E(2121) = 10.32; E(2127) = 10.24; E(2000) = 11.12; E(2160) = 9.68;$$

$$E(2091) = 10.62; E(2179) = 9.17$$

Applying the criteria for intermedions and carbonyls, the classification is given below.

Adsorbent	Intermedions		Carbonyls	
	Band Position (cm^{-1})	Number of Electrons	Band Position (cm^{-1})	Number of Electrons
Copper (II) oxide	2173	9.35	2127	10.24
	2121	10.32	2000	11.12
Cobalt	2160	9.68	—	—
	2091	10.62	2179	9.17
			—	—

(ix) Barrier to Internal Rotation from Bandwidth The bandwidth Γ_T in the spectra of liquids and solids can be split into temperature dependent ($\Gamma_T - \Gamma_0$) and temperature independent (Γ_0) components respectively. The temperature dependent component ($\Gamma_T - \Gamma_0$) is directly proportional to $e^{-U/RT}$, where U is the energy barrier to reorientation by Brownian motion of the molecules of the type XH_3 where $X = \text{C}, \text{N}, \text{P}$. Therefore, we can write

$$\Gamma_T = \Gamma_0 + A_0 e^{-U/RT} \quad (3.281)$$

where A_0 is the constant.

This expression holds good for molecules having $U > 1$ kcal where rotational modulation of the vibration is not likely to contribute appreciably to bandwidth. It follows from Eq. (3.281) that

$$\ln(\Gamma_T - \Gamma_0) = -\frac{U}{RT} + \ln A_0 \quad (3.282)$$

Therefore, simply by measuring the bandwidth at low temperature to get Γ_0 where there is no rotation and also at some higher temperature to get Γ_T one can get U from a plot of $\ln(\Gamma_T - \Gamma_0)$ against $1/T$. The plot will be a straight line with

$$\text{slope } (m) = -\frac{U}{R} \text{ and intercept } (b) = \ln A_0.$$

The accuracy of this method depends upon the separation of the bands into rotational and non-rotational components from Coriolis constants.

Problem 3.45: The spectra of solid $\text{Au}_2\text{I}_2(\text{CH}_3)_4$ as CSI disk in the temperature range 90–298 K have been recorded. The bandwidths of the asymmetric deformation band at 1460 cm^{-1} are 15 cm^{-1} at 90 K, 27 cm^{-1} at 180 K, and 40 cm^{-1} at 298 K. If, at 90 K, there is no effective rotation of methyl group, calculate the barrier height of the methyl group in the molecule.

Solution Since there is no rotation of methyl groups at 90 K, $\Gamma_0 = 15 \text{ cm}^{-1}$. Then the values $\Gamma_T - \Gamma_0$ at different temperature are

$\Gamma_T - \Gamma_0 (\text{cm}^{-1})$	$\frac{1}{T} \times 10^3$
12	5.55
25	3.35

The values of U and A_0 are evaluated by plotting $\ln(\Gamma_T - \Gamma_0)$ against $\frac{1}{T}$. The plot is shown in Fig. 3.48. The slope and intercept of this line are

$$\text{slope } (m) = -0.33 \times 10^3$$

$$\text{intercept } (b) = 4.35$$

According to Eq. (3.282), the slope $= -U/R$ and intercept $= \ln A_0$. Therefore $U = 0.33 \times 1.987 \times 10^3 = 0.662 \text{ kcal mole}^{-1} = 232 \text{ cm}^{-1}$ and $A_0 = 77.47 \text{ cm}^{-1}$.

(x) Enthalpy of H-bonded Adducts from Bandwidth The broadening of the natural bandwidth may not only be due to Doppler effect and molecular collisions but also due to weak interactions of the type charge transfer and hydrogen bonding. Width of band, when affected due to these types of interactions, can be correlated with the energetics of adducts formed. Thus, if width of XH band where $X = \text{O}, \text{N}, \text{S}$, etc., in some molecular systems with electron-loving and hating groups, changes as a result of formation of some adducts with other molecular systems, then based on the experimental data on bandwidth of the

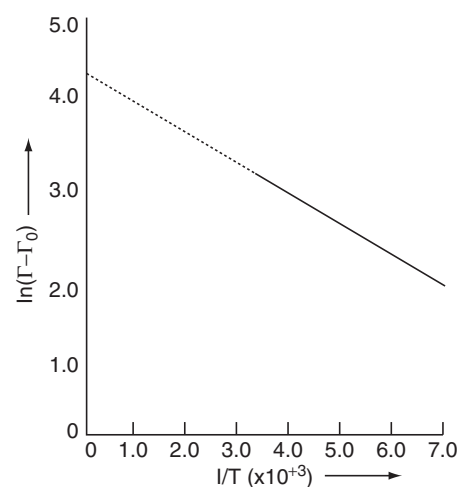


Fig. 3.48 The variation of bandwidth with temperature.

complex formed and enthalpy of complexation, empirical relations between these two quantities could be framed by a least square treatment.

Problem 3.46: On the basis of infrared study of H-bonded complexes formed between phenol derivatives having electron attracting and repelling groups and poly-functional bases, the following equations have been established by a least square treatment.

$$(a) -\Delta H = 3.66 + 0.070 \Delta \nu_{\text{OH}} (r = 0.985) \text{ for 1-methyl-2-pyrimidone} \quad (3.283a)$$

$$(b) -\Delta H = 9.61 + 0.055 \Delta \nu_{\text{OH}} (r = 0.984) \text{ for 3-methyl-4-pyrimidone} \quad (3.283b)$$

$$(c) -\Delta H = 9.83 + 0.058 \Delta \nu_{\text{OH}} (r = 0.994) \text{ for 1,3-dimethyluracil} \quad (3.283c)$$

and

$$(d) -\Delta H = -13.78 + 0.091 \Delta \nu_{\text{OH}} (r = 0.989) \text{ for pyrimidine, where units of } \Delta H \text{ are } \text{kJ mole}^{-1} \text{ and of } \Delta \nu_{\text{OH}} \text{ are } \text{cm}^{-1} \quad (3.283d)$$

By making use of these relations, calculate the enthalpy of H-bonded adducts formed between the following systems, given the values of $\Delta \nu_{\text{OH}}$.

- (i) Pyrimidine + 4-methoxyphenol ($\Delta \nu_{\text{OH}} = 373$)
- (ii) 1,3-dimethyluracil + 3-fluorophenol ($\Delta \nu_{\text{OH}} = 253$)
- (iii) 1-methyl-2-pyrimidone + 4-chlorophenol ($\Delta \nu_{\text{OH}} = 33$)
- (iv) 3-methyl-4-pyrimidone + 3-nitrophenol ($\Delta \nu_{\text{OH}} = 316$)

Solution By substituting the values of $\Delta \nu_{\text{OH}}$ (cm^{-1}) of the adducts formed between the phenol derivatives and the poly functional bases, in the respective equations, the following values of enthalpy of complexation are obtained.

Systems	$-\Delta H (\text{kcal mole}^{-1})$
Pyrimidine + 4-methoxyphenol	4.82
1,3-dimethyluracil + 3-fluorophenol	5.86
1-methyl-2-pyrimidone + 4-chlorophenol	6.40
3-methyl-4-pyrimidone + 3-nitrophenol	6.45

(xi) Mean Velocity of S-adatom from Bandwidth Chemisorption of hydrogen on metal surfaces is believed to involve r and S-type adsorption. An S-type adatom may dissipate energy as a result of transfer from the excited vibrational state to the ground state through collisions with the metal ions. The mean velocity v_m of an S-adatom is given by

$$v_m = \left(\frac{2\kappa T}{\pi m_H} \right)^{\frac{1}{2}} \quad (3.284)$$

and if the mean free path of this adatom is $Y \text{ \AA}$, then the frequency f of its collision with the metal ion is

$$f = \frac{\left(\frac{2\kappa T}{\pi m_H} \right)^{\frac{1}{2}}}{Y} \quad (3.285)$$

where m_H = mass of hydrogen atom. The decay constant would then be

$$\tau = \frac{f}{c} \quad (3.286)$$

where c is the velocity of light.

The bandwidth $\Delta \nu_{1/2}$ of the adsorption band which is a measure of its dissipation energy is then given by

$$\Delta \nu_{1/2} = \frac{\tau}{2} \quad (3.287)$$

Thus, from observed value of $\Delta \nu_{1/2}$, one can calculate mean velocity of an S-adatom.

Problem 3.47: During the chemisorption of hydrogen on Pt it is observed that there are two types r and S of adatoms. If the mean free path of a S -adatom is $3 \text{ \AA}$, calculate the temperature for $\Delta\nu_{1/2} = 100 \text{ cm}^{-1}$, $\kappa = 1.380 \times 10^{-16} \text{ erg deg}^{-1}$ and $m_H = 1.673 \times 10^{-24} \text{ g}$.

Solution Since $\Delta\nu_{1/2} = \frac{\tau}{2}$

Therefore, $\tau = \Delta\nu_{1/2} \times 2 = 100 \times 2 = 200 \text{ cm}^{-1}$,

$$f = c \times \tau = 200 \times 3 \times 10^{10} = 6 \times 10^{12} \text{ s}^{-1}$$

and $v_m = f \times Y = 6 \times 10^{12} \times 3 \times 10^{-8} = 18 \times 10^4 \text{ cm s}^{-1}$.

Since
$$v_m = \left(\frac{2\kappa T}{\pi m_H} \right)^{\frac{1}{2}}$$

Therefore,
$$T = \frac{v_m^2 \pi m_H}{2\kappa} = \frac{(18 \times 10^4)^2 \times 3.142 \times 1.673 \times 10^{-24}}{2 \times 1.380 \times 10^{-16}} \text{ K} = 617 \text{ K}$$

or $T = (617 - 273) = 344^\circ \text{C}$

3.16.3 Biological Applications

Infrared absorption spectroscopy in spite of its limitations due to absorption of water has been proved to be a potential tool in conformational analysis of model polypeptides and proteins and of biopolymers, i.e. α -helical and/or unordered conformations can be discriminated from β -structures. This technique also imparts information about the interaction of lipid and protein components in cellular membranes. The technique of infrared dichroism has also played a chief role in the conformational analysis of polypeptides and proteins, especially when ordinary IR spectroscopy fails to distinguish between the various conformations. Before discussing the applications in detail, the various factors affecting the conformation of model polypeptides and proteins demand attention. The IR absorption bands of polypeptides and proteins are not only delocalised but are sensitive to the folding of the peptide backbone and to H-bonding with other peptide linkages, i.e. conformation or 2° structure. Since peptide backbone of polypeptides and proteins often includes arrays which can be described by symmetry space groups, one can differentiate between the various conformations. Depending upon the nature of the media, pH, temperature, segment length, ionic strength, etc., polypeptides and proteins may exist in one particular/specific conformation or mixture of conformations, e.g. at low ionic strength, and near neutral pH, poly L-lysine exists in an unordered state but above pH 11, the α -helical form becomes predominant, since above pH 11, the electrostatic repulsion between the side chains is small. At 55°C and pH 11.3, the polymer has β -pleated sheet structure. At neutral pH and low ionic strength, poly L-aspartate and poly L-glutamate have unordered structure but exhibit α -helical conformation at acid pH. It is to be noted that it is not always possible to shift all polymers from one conformation to another by change of environment.

Plane polarised IR radiation is absorbed preferentially by chromophores whose transition dipole moments are parallel to the polarisation plane. The absorption intensity of an infrared band depends upon the orientation of the dipole moment of the chromophore relative to the incident beam of IR radiation. In the case of $\text{C}=\text{O}$ stretching vibration of esters, the dipole lies along the $\text{C}=\text{O}$ axis. Hence the orientation of $\text{C}=\text{O}$ group can be determined by infrared dichroism.

Many polymers including polypeptides exhibit infrared dichroism. Consequently, the infrared absorption band of a given vibration splits into two components of different frequency, preferentially absorbing radiation polarised parallel and perpendicular respectively to the molecular axis. The selection rules for infrared dichroism as worked out from group theory are valid for ordered polymers, helices in particular. Globular molecules do not exhibit infrared dichroism since the molecules cannot be oriented properly with respect to the plane of polarisation of the incident radiation.

In an infinite, single-stranded α -helix, coupling along the backbone and through hydrogen bond splits the intensity of the normal vibration into two components parallel and perpendicular to the helical axis. In oriented strongly coupled systems, it is found that

$$\frac{I_{\parallel}}{I_{\perp}} \approx \cot^2 \delta \quad (3.288)$$

where $I_{\parallel}$ and $I_{\perp}$ are the intensity decrements for parallel and perpendicularly polarised radiation, to the screw axis of the polymer and δ is the angle between the transition dipole moment of the vibration and screw axis of the helix.

For a most general peptide chain where both inter- and intra-molecular hydrogen bonds exist, the vibration frequency is given by

$$\nu(\delta, \delta') = \nu_0 + \sum_s D_s \cos(s\delta) + \sum_{s'} D_{s'} \cos(s'\delta') \quad (3.289)$$

where ν_0 is the unperturbed frequency and is found in randomly coiled H-bonded forms. Primed and unprimed terms arise from inter- and intra-molecular interactions.

When $D_{s'} = 0$, then the frequency ν of a mode involving the coupled vicinal vibrators is given by

$$\nu(\delta) = \nu_0 + \sum_s D_s \cos(s\delta) \quad (3.290)$$

Here δ is the phase angle between vicinal vibrators and $D_s = (B_s - A_s) \nu_0$; B_s and A_s are the potential and kinetic interaction factors between s neighbours.

For an infinite helical chain, δ can take on any value but only two yield infrared absorption: $\delta = 0$, and $\delta = \chi$, where χ is the angle between two consecutive groups relative to helix axis ($2\pi/3.6$ in the case α -helices). Since hydrogen bonds here are formed between every third residue, D_1 and D_3 are dominant, but D_2 is also significant. Two frequencies can be observed:

$$\begin{aligned} \nu(0) = \nu(\parallel) &= \nu_0 + D_1 + D_2 + D_3 \\ \nu(\chi) = \nu(\perp) &= \nu_0 + D_1 \cos \chi + D_2 \cos(2\chi) + D_3 \cos(3\chi) \end{aligned} \quad (3.291)$$

Here, $\nu(\parallel)$ and $\nu(\perp)$ are polarised parallel and perpendicular to the helix axis respectively.

(a) Parallel β -conformation In this conformation, the two adjacent peptide linkages in a chain can move either in phase ($\delta = 0$) or out of phase ($\delta = \pi$). When groups in adjacent chains, coupled by H bonds, move in phase, the vibration is infrared active. Two modes of vibration result with frequencies

$$\begin{aligned} \nu(0, 0) &= \nu_0 + D_1 + D_1'(\parallel) \\ \nu(\pi, 0) &= \nu_0 - D_1 + D_1'(\perp) \end{aligned} \quad (3.292)$$

Primed and unprimed terms arise from the inter- and intra-molecular interaction of groups in adjacent chains, and the polarisation is relative to the backbone axis.

(b) Antiparallel β -conformation The spectrum arises from four peptide linkages, involving portions of two arms of an antiparallel loop or two antiparallel chains. The frequencies of the resulting modes of vibration are

$$\begin{aligned} \nu(0, \pi) &= \nu_0 + D_1 - D_1'(\parallel) \\ \nu(\pi, 0) &= \nu_0 - D_1 + D_1'(\perp, \text{ in plane}) \\ \nu(\pi, \pi) &= \nu_0 - D_1 - D_1'(\perp, \text{ out of plane}) \\ \nu(0, 0) &= \text{inactive} \end{aligned} \quad (3.293)$$

(c) Unordered State For an unordered state, the vibrational interactions between peptide groups average to zero and only ν_0 is observed.

IR absorption band characteristic of a particular conformation of polypeptides and proteins are the amide bands. In other words, amide bands can be fixed as the criteria to distinguish between the various

Table 3.18 IR bands associated with the peptide linkage.

Frequencies (cm^{-1})	Assignment
3300 } 3100 }	NH str, $2 \times$ amide II in Fermi resonance
1650	Amide I (C = O str, 80%, C—N str, 10%, NH bend 10%)
1560	Amide II (C—N str, 40%, NH bend 60%)
1300	Amide III (C = O str, 10%, C—N str, 30%, NH bend 30%, O = C—N bend 10%, other 20%)
625	Amide IV (O = C—N bend 40%, other 60%)
725	Amide V (NH bend, O/P)
600	Amide VI (C = O bend, O/P)
200	Amide VII (C—N twist, O/P)

str—stretch, O/P—out of plane

Table 3.19 Amide bands (in cm^{-1}) in polyglycine-I and polyglycine-II.

Assignment	Polyglycine-I	Polyglycine-II
Amide I (C = O str)	1685 and 1630	1641
Amide II (NH bend)	1524	1558
Amide III (C—N str)	1297	1309
Amide IV (O = C—N bend)	589	740
Amide V (NH out-of-plane bend)	710	
Amide VI (C = O out-of-plane bend)	628 and 614	701 and 573
Amide VII (C—N twist, out-of-plane)	217	365

conformations. IR bands associated with a peptide linkage as well as in polyglycine-I and polyglycine-II are listed in Tables 3.18 and 3.19 respectively.

In addition, the assignment of the amide bands corresponding to the different conformations in the model systems needs to be described here for use to discriminate between the conformations in the biomembranes. In case of α -helical poly-benzyl-L-glutamate, the amide I and II bands appear at 1656 and 1550 cm^{-1} respectively while at 1630 and 1525 cm^{-1} in the β -structured polymer. α - and β -helical polymer-L-lysine exhibit amide-I bands at 1652 and 1636 cm^{-1} respectively. The energy of the amide-I band may also be used to differentiate between α -helical or unordered conformations of a given polypeptide under certain conditions, e.g. solid film IR spectra of poly-L-lysine in the α -helical and unordered structures have amide-I bands at 1652 and 1657 cm^{-1} respectively. The IR frequencies of the amide-I and II bands corresponding to different conformations of poly-L-lysine have been summarised in Table 3.20.

Further, since the energy of the amide-I bands in the α -helical and unordered structures may be very close, the position of band varies from one peptide to another and band broadening due to side chains may occur, the amide-I band cannot always be used to distinguish between α -helical and unordered conformations until the polypeptide exhibits infrared dichroism, e.g. the amide-I band in the solid film spectra of α -helical-poly-L-glutamic acid and poly- γ -benzyl-L-glutamate appears at 1652 and 1656 cm^{-1} respectively. The latter in chloroform exhibits

Table 3.20 IR frequencies (cm^{-1}) of amide-I and II bands of poly-L-lysine.

Helix	Antiparallel- β	Unordered
1516 _w } 1535 _s }, II	1530 _s , II	1535, II
1650 _{vs} } 1652 _m }, I	1636 _s } 1685 _m }, I	1656, I

amide-I band between 1651–1656 cm^{-1} .

The amide-II band is not very helpful to differentiate between the various conformations since α -helical and β -structures both give bands near 1510 and 1540 cm^{-1} . The vibrational modes of COO^- -group in proteins may also interfere since their energy lies in the 1550–1560 cm^{-1} range. Nevertheless, the amide-II band may be used for conformational analysis in cases where polypeptides and proteins exhibit infrared dichroism in the said region. In case of poly-L-glutamide at pH 7.0, COO^- absorption even broadens the amide-I band.

Amide-V band proved to be very successful in differentiating between α -helical and unordered structures, e.g. poly- γ -methyl-L-glutamate in the α -helical, unordered and β -structures exhibit three bands at 600, 650 and 690 cm^{-1} in the amide-V region. The infrared spectra of lysozyme also give three amide bands at 600, 650 and 690 cm^{-1} . Hence, simply by comparing the spectra of lysozyme with that of poly- γ -methyl-L-glutamate in the amide-V region, it can safely be concluded that lysozyme is a mixture of α -helical, β and unordered structures.

Conformationally dependent bands also fall in the far infrared region of the spectra of the polypeptides and proteins, hence this region may also be exploited for conformational analysis, e.g. α -helical-poly-L-alanine exhibits four bands at 190, 167, 120 and 90 cm^{-1} while its β -form shows only two bands at 442 and 247 cm^{-1} . The bands are due to H-bond stretching and bending and the torsional oscillations about $\text{C}_\alpha\text{—C}$ and $\text{C}_\alpha\text{—N}$ axes whereas the band at 247 cm^{-1} of β -structure may be due to CO—NH torsional oscillation.

Poly- β -benzyl-L-aspartate (insoluble in aqueous buffers) unlike most of the model polypeptides consists of L-amino acids and forms left- rather than right-handed helices. However, when the polymer spread at an air–water interface and is studied by infrared dichroism, it exhibits bands; at 1740 cm^{-1} (ester $\text{C}=\text{O}$), 1658 cm^{-1} (amide-I), 1552 cm^{-1} (amide-II) which are not characteristic of the left-handed α -helical form but conforms to the right-handed helices. These observations can be supplemented by the parallel polarisation of the C—O band at 1168 cm^{-1} since the left-handed form shows perpendicular dichroism at this frequency. The IR dichroism results also find support from the electron diffraction studies of the polymer spreaded at the air–water interface.

The information gathered from model systems can now be utilised for the conformational analysis of biomembranes. IR spectra of erythrocyte membrane dried from phosphate buffer of pH = 7.4 exhibit band at 1652 cm^{-1} but no absorption has been observed in the 1630–1640 cm^{-1} range. From this it can safely be inferred that the protein in the membrane exists in the α -helical and/or unordered conformation since the band observed at 1652 cm^{-1} is characteristic of these conformations. IR spectra of some of the biomembranes of animals and plants exhibit strong absorption due to α -helical and/or unordered polypeptide but also a shoulder near 1630–1640 cm^{-1} . The appearance of band near 1635 cm^{-1} reveals that these membranes contain a significant amount of their peptide linkages in a β -conformation also. The appearance of an additional band near 1690 cm^{-1} in the mitochondrial membranes indicates the presence of antiparallel β -conformation in this membrane.

The structure of membrane proteins depends upon their interactions with membrane lipids. Thus, the IR bands characteristic of membrane lipids may be utilised for the understanding of lipid-protein interactions. However, all the IR bands of membrane lipids are hard to be characterised due to lipid polymorphism. Nevertheless, the assignment of some of the major bands of fatty acid chains and phosphatides are listed in Table 3.21. The model data can be exploited to study the lipid-protein interactions as is evident from the following examples. The aqueous dispersions of membrane lipids show a band due to CH_2 rocking mode at 720 cm^{-1} . However, this band does not appear in the film spectra of plasma membranes of human erythrocytes indicating that in these membranes, the planar, all *trans* configuration of hydrocarbon chains is not favoured. This may be due to apolar association between membrane lipids and proteins that makes other configurations energetically more probable.

In some of the biomembranes, the intensity ratio of CH_2 asymmetric stretching (2930 cm^{-1}) and symmetric stretching (2855 cm^{-1}) modes of vibration respectively have been found to be 0.3 in case of whole membrane, 0.1 in case of lipid extract and 1.4 in the extracted residue, at liquid nitrogen temperature. The band at 720 cm^{-1} due to CH_2 rock has been observed only in the lipid extracts. These results can be fixed as criteria for the close range, nonpolar interactions between apolar protein side chains and phospholipid hydrocarbon chains.

Table 3.21 Assignment of some major infrared bands (cm^{-1}) of the fatty acid chains of phospholipids.

Expected	Assignment	Observed	Remarks
1460	CH_2 bend and str	1640	Double near 1640 cm^{-1} in condensed lipids, due to interaction between fatty acid chains
1380–1180	CH_2 wag		
1300–1170	CH_2 twist	1200	Ill defined
1150–870	C—C str and CH rock	1150–870	Not precisely localised
~3000	C = C—H str		
1580–1650	C = C str		
690–980	C = C—H O/P bend		
970	CH bend(ethylenic)		
2926	CH_2 asym str. (O/P)		
2853	CH_2 sym str. (I/P)		
720	CH_2 – rock	720	*
	P = O str	1350–1250	H-bonding shifts the P = O str to lower frequencies, e.g. P = O, 1227 in phosphatidyl-ethanolamine; In phosphatidyl-serine P = O, 1220–1180
	P—O—C str	980–1050	
	NH_3^+	2100	Weak band in dimyristoyl cephalin
	N—H str (lipid associated)	3330	In some lipoproteins
	OH str	3600	Free cholesterol
	OH str	3330	Cholesterol ester

O/P—out of plane, I/P— in plane, str—stretch, sym—symmetric, asym—asymmetric.

*This band reflects interaction between adjacent hydrocarbon chains. This band arises only when at least 4 successive carbon atoms in a hydrocarbon chain are arranged in a planar all *trans* configuration. When interactions between chains are strong as in solids, this vibration yields a doublet separated by 6 cm^{-1} . In liquid state, the $700\text{--}1350\text{ cm}^{-1}$ region of long chain hydrocarbons becomes less distinctive.

The shoulder at 1711 cm^{-1} due to lipid carbonyl in the IR spectra of erythrocyte membranes does not appear in the lipid extracts. This may be due to lipid protein interaction.

The IR spectra of red blood cells membrane and its lipid extract exhibit band due to P = O stretching mode of vibration at 1225 cm^{-1} . This low value as compared to the expected value of $1250\text{--}1350\text{ cm}^{-1}$ may be due to H-bonding. From these results, it is suggested that in these types of membranes, the phosphatide head groups lie in water and are not ionically bonded to membrane proteins.

The IR absorption spectra of lipid free erythrocyte membranes exhibit a major band at 1652 cm^{-1} and a shoulder at 1628 cm^{-1} . This may be taken as evidence for the transformation of some structures to β -conformation upon lipid removal.

Infrared spectroscopy can also be used as an effective tool to observe ligands such as CO, NO, O_2 , CN^- , N_3^- and N_2O directly in metalloproteins in vivo (intact tissue) or in vitro (isolated tissue) to obtain useful information about the metal, the ligand and their environments. This is being elaborated here with the following examples: The absorption band of free CO in the gaseous phase is observed at 2237 cm^{-1} ($\Delta\nu_{1/2} = 100\text{ cm}^{-1}$) while in the region $1905\text{--}1980\text{ cm}^{-1}$ ($\Delta\nu_{1/2} = 4\text{--}30\text{ cm}^{-1}$) in hemeoproteins. C—O stretch in carbonyl (HbA $^{12}\text{C}^{16}\text{O}$) appears at 1951 cm^{-1} whereas at 1907 cm^{-1} in case of HbA $^{13}\text{C}^{16}\text{O}$ and HbA $^{12}\text{C}^{18}\text{O}$. The magnitude of the observed isotopic

shift in each case is 44 cm^{-1} and conforms to the shift expected for a simple diatomic molecule as computed from the relationship

$$\bar{\nu} = 1303.16 \sqrt{\frac{k}{\mu_m}}$$

Similarly, the frequency shifts observed between $^{14}\text{N}^{16}\text{O}$ (1615 cm^{-1})/and $^{15}\text{N}^{16}\text{O}$ (1587 cm^{-1}); $^{16}\text{O}_2$ ($1155, 1107\text{ cm}^{-1}$) and $^{18}\text{O}_2$ ($1096, 1064\text{ cm}^{-1}$) in hemoglobin, and $^{-14}\text{N}^{14}\text{N}^{14}\text{N}^-$ (2046 cm^{-1}), $^{-15}\text{N}^{14}\text{N}^{14}\text{N}^-$ (2040 cm^{-1}), $^{-14}\text{N}^{14}\text{N}^{15}\text{N}^-$ (2028 cm^{-1}) in high-spin myoglobin provide evidence for the assignment of bands due to bound NO, O_2 and N_3^- in nitrosyl, oxygenyl and azide hemeproteins respectively. In case of low-spin myoglobin, the respective azide bands are observed at $2030, 2021$ and 2004 cm^{-1} . The two bands at 2046 and 2040 cm^{-1} due to azides are of equal intensity because there is an equal probability of either the ^{-14}N end or ^{-15}N end bounding to Fe(III). However, there is no evidence to suggest that N_2O is serving as a ligand bound to different or any metal site since when N_2O is administered to brain tissue, the two bands appearing at 2230 and 2217 cm^{-1} fall in the infrared band frequency region for N_2O in different solvents with varying polarity.

The ligand infrared band frequency is affected by oxidation state of metal also. Cyanide bound to Fe(II) of reduced cytochrome C oxidase is observed at 2060 cm^{-1} while at 2152 cm^{-1} when bound to Fe(III) of the oxidised form of cytochrome C oxidase. The difference between the CN stretching frequencies in the reduced and oxidised form of the protein may be because of greater back π -donation from Fe(II) than from Fe(III). Similarly, $^{15}\text{N}^{16}\text{O}$ when bound to Fe(II) and Fe(III) of hemeproteins exhibits N—O bands at 1587 and 1865 cm^{-1} , respectively. Thus, it is quite evident that IR spectra can safely be employed to differentiate between low and high oxidation states of metals in proteins.

Infrared spectra have also revealed multiple species of hemoglobin carbonyls and myoglobin carbonyls and azides that have not been detected crystallographically. These multiple carbonyls could also not be differentiated by ^{13}C -NMR spectra because the interconversion between the species is too fast for the NMR time-scale.

Problem 3.48: Calculate the B species (only Raman active) for amide-I and II bands in cyclictetraglycine (CTG) if the A and E species (both are Raman and IR active) of amide-I band are observed at 1685 and 1640 cm^{-1} , and of amide-II band at 1575 and 1538 cm^{-1} respectively.

In CTG, there are four residues and therefore, $\delta = 0, \pi/2$ or π . Take D_s' to be zero in CTG.

Solution For $A(\delta = 0)$, $B(\delta = \pi)$ and $E(\delta = \pi/2)$, species we may write from Eq. (3.290) the following equations respectively

$$\nu(0) = \nu_0 + 2D_1 + D_2 \quad (3.294)$$

$$\nu(\pi) = \nu_0 - 2D_1 + D_2 \quad (3.295)$$

$$\nu(\pi/2) = \nu_0 - D_2 \quad (3.296)$$

The unperturbed frequency ν_0 can be taken from nylon-66 because here the amide groups are separated from each other through methylene groups. The amide-I and II bands in nylon-66 have been observed at 1640 and 1540 cm^{-1} respectively. Using these frequencies together with the unperturbed frequencies for amide-I and II bands from nylon-66, Eqs (3.294) and (3.296) give

$$D_1 = 22.5\text{ cm}^{-1} \quad \text{amide I}$$

$$D_2 = 0.0\text{ cm}^{-1}$$

$$D_1 = 16.5\text{ cm}^{-1} \quad \text{amide II}$$

$$D_2 = 2.0\text{ cm}^{-1}$$

Using these values of D_1 and D_2 for amide-I and II bands, the B species for amide-I and amide-II bands are calculated at 1595 and 1509 cm^{-1} from Eq. (3.295). The corresponding values obtained from normal coordinate analysis are 1713 cm^{-1} and 1534 cm^{-1} , respectively.

3.17 FAR IR ABSORPTION SPECTROSCOPY

Molecules made up of only light atoms absorb in the far IR region. Pure rotational absorption of gases having permanent dipole moment such as H_2O , O_3 , HCl and AsH_3 is observed in this region and can be used for the identification of such molecules. Moreover, as mentioned earlier, this technique can be used for the identification of both inorganic and metallo-organic compounds since their vibrational frequencies fall below 670 cm^{-1} .

3.18 NEAR IR ABSORPTION SPECTROSCOPY

Sources of radiation in near IR spectroscopy are tungsten-halogen lamps with quartz windows. Quartz or fused silica cells with path lengths between 0.1–10 cm and are transparent up to 300 nm are used for absorption measurements in this region. PbS photoconductors are used as detectors. Commercial spectro-photometers are available to record the near IR spectra in the 180–2500 nm wavelength range. It is to be noted that in near IR spectroscopy, the wavelength on the horizontal axis is reported in nanometers or micrometers in contrast to mid-IR spectroscopy in which the abscissa is wave number in units of cm^{-1} . Commonly used solvents in this region are, CCl_4 , CS_2 , CHCl_3 , dioxane, heptane, C_6H_6 , CH_3CN and DMSO. However, out of these solvents only CCl_4 and CS_2 are transparent in the entire near IR region.

Further, in addition to the conventional IR absorption spectroscopy, the other infrared techniques that deserve proper place in IR spectroscopy and are capable of solving numerous qualitative and quantitative problems which are difficult to handle or not at all soluble by other spectroscopic methods are explained below.

3.19 MID IR REFLECTANCE SPECTROSCOPY (MIRS)

Reflectance Spectroscopy (RS) deals with the study of the spectral composition of surface reflected radiation with respect to its angularly dependent intensity and the composition of the incident radiation. MIRS reflection spectroscopy is useful especially for solid samples that are difficult to handle such as polymer films and fibers, foods, rubbers, agriculture products, etc. Mid-IR reflection spectra are similar in general appearance but not identical to the corresponding absorption spectra. It provides the same information as do the absorption spectra. Four types of reflection, viz., (a) regular (specular), (b) diffuse, (c) internal, and (d) attenuated total reflection, are dealt in RS.

(a) Specular Reflectance Spectroscopy (SRS) Specular reflection occurs from a smooth surface. Here the angle of incidence equals the angle of reflection. In case of infrared absorbing surfaces, the relative intensity of reflection is less for absorbed wavelengths than for unabsorbed wavelengths. Thus, the specular reflectance spectrum consists of a plot of reflectance, R , i.e. the fraction of the energy of incident radiation that is reflected, on the vertical axis against the wave number on the horizontal axis. SRS is used to examine and characterise surfaces, virgin and coated solids. However, scope of SRS is limited as compared to diffuse and total reflection spectroscopy.

(b) Diffuse Reflectance Spectroscopy (DRS) Diffuse reflection takes place from matte surfaces, i.e. randomly oriented plane surfaces of a finely divided powder. Here, it is assumed that specular reflection occurs at each of these plane surfaces and the intensity of the radiation reflected in all directions is isotropic, i.e. it is assumed to be independent of the viewing angle. The relative reflectance intensity for a powder sample is given by Kubelka–Munk function which is written as

$$F(R'_\infty) = \frac{(1 - R'_\infty)}{2R'_\infty} = \frac{K}{S} \quad (3.297)$$

where R'_∞ is the ratio of the intensity of the reflected radiation by the sample to that of a non-absorbing standard such as finely ground potassium chloride. The quantity, K is the molar absorption coefficient of the analyte and S is the scattering coefficient. For a dilute sample, K is related to the molar decadic coefficient ϵ and the molar concentration of the analyte by the expression

$$K = 2.303 \epsilon C$$

Diffuse Reflection Spectra (DRS), thus, consists of a curve obtained by plotting $F(R'_\infty)$ versus wave number. Diffuse Reflectance IR Fourier Transform Spectroscopy (DRIFTS) is particularly useful to obtain directly the spectra of powdered samples with a minimum of sample preparation.

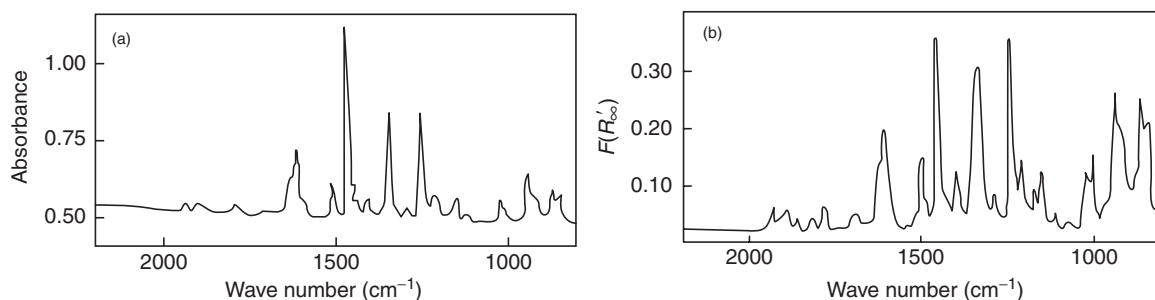


Fig. 3.49 Comparison of the conventional infrared absorption spectrum (a) for carbazole with its diffuse reflectance spectrum (b).

Unlike in transmittance spectroscopy, the DRIFT spectrum is independent of the thickness of the layer, provided it exceeds 5μ . DRIFT spectrum of 5 per cent finely ground mixture of carbazole in KCl is compared with the conventional IR absorption spectrum of carbazole in KBr pellet in Fig. 3.49.

The relative intensity of the bands are different but the position of the bands are the same. Water soluble and water containing substances that are difficult to examine by IR transmittance measurements can also easily be investigated by DRIFTS, e.g. two phase systems such as suspensions, emulsions or colloids, etc. Thus the biochemical problems, i.e. spectra of polypeptides, amino acids, etc., can also be studied by this technique.

(c) Internal Reflection or Attenuated Total Reflectance Spectroscopy (IRS/ATRS) Refractive index of material depends upon the wavelength of incident radiation. In the absence of strong absorption bands, the refractive index decreases as the wavelength increases. In the region of strong absorptions, very sharp changes in refractive index take place as shown in Fig. 3.50. This phenomenon is of importance in the practical application of internal reflection spectroscopy.

When a beam of radiation passes from high-refractive-index phase to low-refractive-index phase, reflection occurs. If the sample absorbs radiation and the angle of incidence exceeds a certain definite or critical value (θ_c), total reflection takes place. Even when the angle of incidence exceeds the critical value, some radiation penetrates the second phase, i.e. the less dense medium before the reflection occurs and the penetrating radiation is called the evanescent radiation. The depth of penetration is of the order of a wavelength of radiation and depends upon the refractive indices of both the phases, angle of incidence and wavelength of incident radiation, λ . Mathematically, the depth of penetration, also called sampling depth, is described as follows.

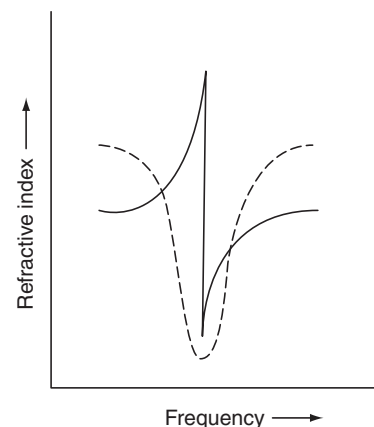


Fig. 3.50 The change in refractive index of a material in the neighbourhood of an absorption band. The solid line represents the refractive index, the dashed line the absorption.

$$\text{Depth of penetration} = \frac{\lambda_1}{2\pi(\sin^2\theta - n_{21}^2)^{1/2}} \quad (3.298)$$

Here $\lambda_1 = \lambda/n_1$ (cm), θ is the angle of incidence with respect to the surface normal, and n_{21} is the ratio of the refractive indices of the sample (n_2) and the Internal Reflection Element (IRE) (n_1). From the expression (3.298), it is clear that (i) penetration is greater at longer wavelengths for the mid-IR region ($2.5\text{--}25\mu\text{m}$), that means a factor of 10 difference in sampling depth across the spectrum affects its photometry as compared to transmission; (ii) as θ gets larger, the sampling depth is smaller, and to the limit of grazing incidence, the sampling depth approaches 0.1λ ; and (iii) for a fixed θ , penetration is greater as n_{21} approaches unity, i.e. where the refractive indices are matched. The behaviour of depth of penetration which is of the order of few micrometers with angle of incidence is shown in Fig. 3.51. From the behaviour it is inferred that incident angles of 30° , 45° and 60° can be chosen for practical purposes. When the low refractive index material absorbs the evanescent radiation, a fraction of radiation energy

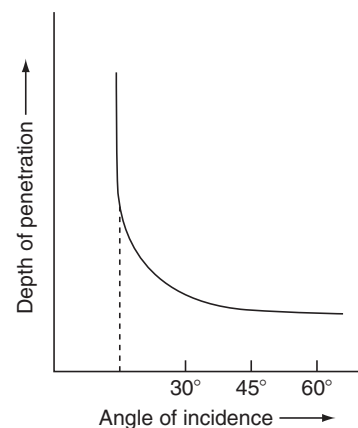


Fig. 3.51 The behaviour of depth of penetration with the angle of incidence.

transferred is lost and the total reflection is attenuated at wavelength of absorption bands. This phenomenon is called attenuated total reflectance (ATR). Mostly, the ATR technique is restricted to plotting or directly recording the apparent extinctions and/or transmittances of the sample under investigation as a function of wavelength. Attenuated total reflectance spectrum is similar but not identical to ordinary absorption or transmission spectrum. Though same bands are obtained, their relative intensities are different. Thus, the method of ATR provides a valuable tool for examining materials that are too opaque for transmission methods. A series of reflection is obtained by placing two samples on opposite sides of an internal reflection transparent element with high refractive index as shown in Fig. 3.52. Mixed crystal of thallium bromide/ thallium iodide is frequently used as an internal reflection element. Plates of germanium and zinc selenide are also used as elements. When the refractive index of reflector material is lower than the refractive index recorded at the peak maximum (Fig. 3.50) then anomalous band shapes and band broadening are observed. The preparation of samples is not difficult in internal reflection spectroscopy. For liquid samples, ATR crystal can be dipped into a liquid. Water solutions can also be studied if the crystal is insoluble in water. Cells for liquid samples are also available. With plastic materials such as many resins or rubber and also threads, yarns, fabrics, solids of limited solubility, films, pastes, powders, etc., the optical contact between sample and reflecting surface is made simply by pressing the sample and the reflecting surface together. In case of hard materials, the optical contact can be improved with a few drops of a liquid of high refractive index such as CS_2 . Even if CS_2 evaporates, optical contact is still maintained. The transmission spectrum of solid epoxy resin in KBr is compared with the ATR spectrum of the said resin in Fig. 3.53.

The method of internal reflection IR spectroscopy is more suitable than DRIFTS for studying adsorption of a particularly oriented crystal surface. Even in case of mono molecular layers or only partially covered surfaces, multiple reflection provides large extinctions because of which qualitative analysis of surface layers can be carried out, e.g. surface spectrum of a polished silicon plate that is exposed to atmosphere exhibits two bands at 3448 and 2135 cm^{-1} for angle of incidence = 45° and 165-fold reflection (Fig. 3.54). They are assigned to —OH and —CH stretching vibrations of the adsorbed molecules respectively. Broad band centred at 2060 cm^{-1} is observed during the chemisorption of hydrogen on a single crystal of silicon. This is assigned to Si—H stretching vibration since SiH_4 exhibits a Si—H stretching vibration at 2188 cm^{-1} also.

The surface reactions such as oxidation, reduction, the formation of intermediates (catalysis), electrode surface reactions, etc., can also be investigated by this method. Since semiconductors have high refractive indices and are also transparent to IR radiation, they can be studied by IRS. Moreover, the free electrons in the semiconductor barriers can absorb IR radiation. Thus, it is possible to measure the number of free carriers and its change by irradiation as a function of wavelength. Gas chromatographic fractions can also be studied by this method. The hot gas conducted directly through a capillary cell cooled from the side by means of the Peltier effect so that the fraction concerned deposits on the reflector. Similarly the decomposition products of pyrolysis can be trapped for analysis by IRS.

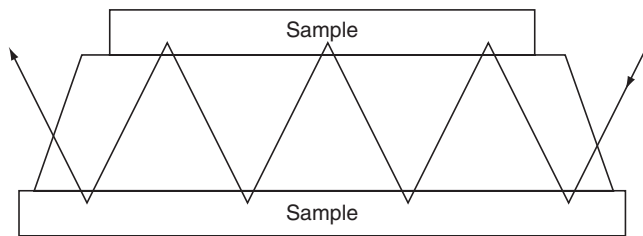


Fig. 3.52 Multiple Internal reflection effect.

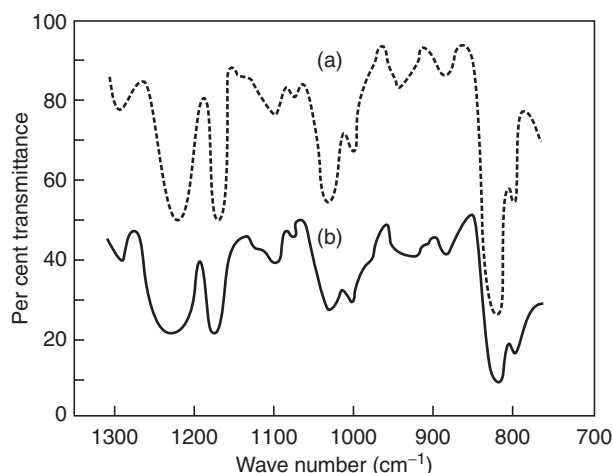


Fig. 3.53 Comparison of transmission spectrum of a solid epoxide resin according to the KBr method (a) with the attenuated total reflection spectrum of a solid epoxide resin (b).

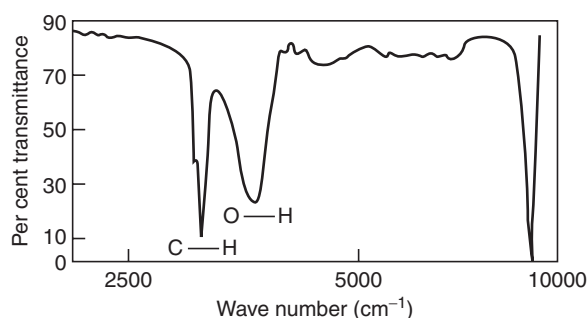


Fig. 3.54 Surface spectrum of a polished silicon plate by means of internal reflection.

3.20 NEAR IR REFLECTANCE SPECTROSCOPY (NIRS)

The first overtone of O—H and carbonyl stretching vibrational band absorbs near 7100 and in the region 3300–3600 cm^{-1} respectively. So the absorption band near 7100 cm^{-1} can be used for the quantitative analysis of compounds containing O—H groups, i.e. phenols, alcohols, organic acids, and hydrogen peroxides while the region in the 3300–3600 cm^{-1} range can be used for the determination of esters, ketones and carboxylic acids. Water in glycerol, organic films, hydrazine and fuming nitric acid can also be determined by NIRS. NIRS can also be used for the characterisation and determination of primary and secondary amines in the presence of tertiary amines in the mixtures since the former amines have overlapping absorption bands in the 3300–10,000 cm^{-1} region because of various N—H stretching vibrations and their overtones. Tertiary amines have no such bands in this region. Primary amines absorb in the region of combination band of N—H stretching vibration at about 5000 cm^{-1} . So primary amines can be directly determined at this wave number.

Near IR reflectance spectroscopy is also used for the quantitative estimation of components of a finely ground solids, e.g. determination of protein, moisture, starch, oil, lipids and cellulose in agricultural products such as grains and oilseeds. NIR spectrum is obtained by plotting $\log(I/R)$ where R is the ratio of intensity of reflected radiation from the sample to the reflectance from a standard reflector as a function of wavelength in nm. Finely ground solid sample is irradiated with one or more narrow bands of radiation having wavelengths in the range 4000–10,000 cm^{-1} . The diffuse reflectance spectrum of a sample of wheat that depends on the composition of analyte is shown in Fig. 3.55. MgO or BaSO₄ is used as a standard reflector in this case. The reflectance band at about 1940 nm is due to water and can be used for the determination of moisture in the sample. The other signal at about 2100 nm is due to the overlapping of signals of starch and protein. Thus, by making the measurements at two wavelengths in this region, the amount of each of these components can be determined. Less time and sample preparation are the major advantages of near IR spectroscopy.

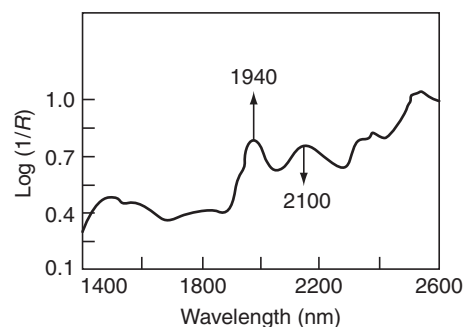


Fig. 3.55 Diffuse-reflectance spectrum of a sample of wheat.

3.21 PHOTOACOUSTIC OR OPTOACOUSTIC IR SPECTROSCOPY (PAIS/OAIS)

The technique of PhotoAcoustic Spectroscopy (PAS) utilises the transformation of radiation energy by gases, liquids and solids into acoustic energy. So, when there is absorption by the sample at a particular wavelength or wave number, a sound is produced, called acoustic signal. PAS is not a new technique. The first person to observe the photoacoustic effect (PA) was J Tyndall who, in 1881, made a detailed study of the sound produced by gases when chopped light was made to fall on them. He attributed the effect to the periodic heating of the gas by absorption of IR radiation. Alexander Graham Bell, in 1881, showed that sonorousness under the influence of intermittent light is property common to all matter and even visible light could produce PA effect. He observed that loudest sounds are produced from substances in a loose, porous, spongy condition and from those that have darkest or most absorbent colours. Lamp black and soot, or coloured gases such as NO₂ gave sounds which were at times painful to the ear and could even be heard across the room. The apparatus used by him called Bell's spectrophone is shown in Fig. 3.56.

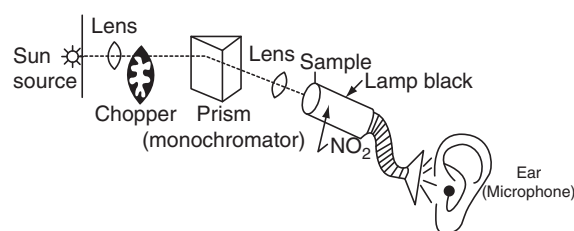


Fig. 3.56 Bell's 'spectrophone'.

It consists of a light source (the sun), a chopper (a wheel with holes driven by a motor, generally a man), a monochromator (the prism) and a sensitive pressure transducer (the ear). The sample to be studied is placed on the front of the eye-piece of the spectroscope. The walls on the inside of the spectroscope are lined with lamp black and NO₂ is used as the gas to fill the inside of the spectroscope. This is to ensure maximum noise of photoacoustic signal. Only the transmitted light produces a sound so that when there is absorption at a particular wavelength there will not be any acoustic signal. One is thus able to hear bands of 'sound and silence' compared to the bands of 'light and darkness' in the conventional spectroscopic methods. Thus, the acoustic signal is useful noise unlike the usual noise which is generally wasteful such as the noise produced by creaking wheels of a bullock-cart or the squeaking of a door.

According to modern analysis of PA effect, in case of a gas, the energy absorbed is converted entirely or partially into kinetic energy of the gas molecules, thereby giving rise to pressure fluctuations that are detected as audible sound. In case of solids, the radiation absorbed is converted in part or in whole into heat by non-radiative de-excitation processes in time less than 10^{-6} s. This resultant periodic heat flows from the solid absorber to the surrounding photoacoustic material, i.e. gas creates pressure fluctuations. Thus, PA effect is based on the detection of acoustic waves generated by a modulated radiation source. In order to obtain photoacoustic signal, the intermittent or chopped radiation from the source assembly is directed towards photoacoustic cell that contains a photoacoustic material such as air or any suitable gas, i.e. N_2 , C_3H_6 , Ar, He, H_2 . A simple cell for photoacoustic detection is an acoustically sealed chamber that contains a window, the sample and microphone. The periodic heat flows from the sample creates in the cell pressure fluctuations that are detected by the microphone. Thus, the photoacoustic spectrum consists of a curve that results from a plot between relative acoustic signal on the vertical axis and wave number or wavelength on the horizontal axis.

There are several factors that affect the signal intensity. The most important factor is the internal cell volume. Signal intensity is inversely proportional to the cell volume, so it is desirable to have the smallest possible volume. Another important factor is the distance between the window and the solid sample. If this distance is less than the thermal diffusion length of the gas, heat generated at the sample will be lost to the window, decreasing the signal intensity. Signal intensity can also be lost due to acoustic damping that results from viscous friction in the gas and heat losses to the walls during sound transmission. This is usually only a problem when the microphone is at the end of a small diameter tube.

The background signal and noise should be minimised since they also affect the signal intensity. The two factors that are important for minimising the background signal are (i) scattered radiation should not strike the microphone diaphragm since microphone is sensitive to signals generated by modulated radiation absorbed by diaphragm; and (ii) radiation absorption by interior surfaces of the cell must be minimised. This is achieved by using cells made of either polished metal or optical grade glass. The two important sources of noise in a PA cell are mechanical vibrations and acoustic leaks. The microphone diaphragm is partially sensitive to vibrations. This effect is minimised by mounting the entire cell assembly on a base plate that is vibrationally isolated from the table. The acoustic leaks in the cell not only increase the background noise but also decrease the signal intensity. A back seal in a back-vented microphone increases the damping of this noise source. Even front-vented microphones have acoustic leaks and must have the damping increased.

As with UV/V spectral studies, PAS has been used to obtain spectra in the mid-infrared region for qualitative studies. This holds for the investigation of solid substances, as well as, chemically modified solid surfaces normally inaccessible to IR conventional methods because of their tendency to scatter radiation. Such substances include physically thick samples such as commercial catalyst pellets or opaque, such as chars and carbons. Mid-IR PAS of CO on alumina supported platinum in the $1700\text{--}2200\text{ cm}^{-1}$ region is shown in Fig. 3.57. A strong band at 2060 cm^{-1} and weaker, broad band at about 1820 cm^{-1} correspond to the CO stretching vibrations of the adsorbed CO molecules. PAIS of degassed alumina is compared with that of alumina exposed to acetic acid vapour in Fig. 3.58.

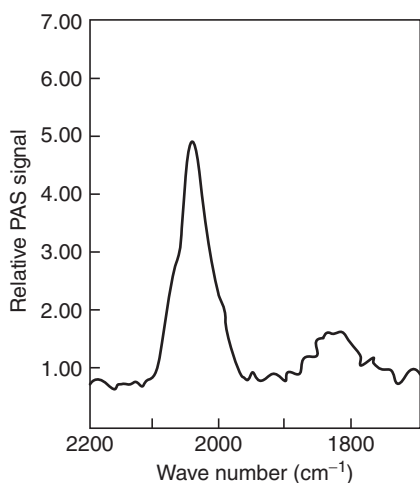


Fig. 3.57 Photoacoustic mid-infrared spectrum of CO on alumina supported 5 per cent Pt.

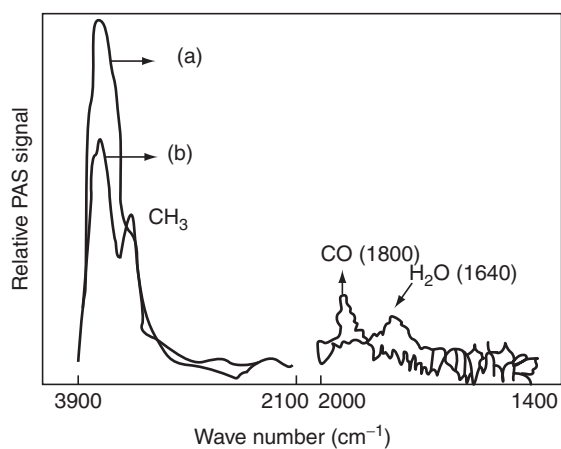


Fig. 3.58 Photoacoustic infrared spectrum of (a) degassed alumina, and (b) alumina exposed to acetic acid vapours.

Alumina shows the broad absorption characteristic of surface Al—OH groups and of bound water and the deformation band of the latter. After esterification, decline in the intensity of O—H and H₂O bands has been observed and a band in the C—H region as well as a CO stretching band near 1800 cm⁻¹ appeared. These two new bands are attributed to the formation of a surface ester, Al—OCOCH₃. In addition, the method has been used for detecting the components of mixtures separated by thin layer and high performance liquid chromatography. Most of these studies are done with FT-IR instruments because of their better signal-to-noise ratio, characteristics and increased signal intensity. PAIS has been primarily used for the analysis of gases and for the study of vibrational relaxation times. The concentrations of gaseous pollutants in the atmosphere are also monitored by this technique. Here a tunable CO₂ laser source is used in conjunction with photoacoustic cell filled with some photoacoustic material that provides maximum noise. A system of this kind can analyse a mixture often gases with a sensitivity of 1 ppb and a cycle time of 5 minutes. The vibrational relaxation process may be best understood as follows: The exchange of energy between vibrational degrees of freedom and translational degrees of freedom can be characterised by relaxation time, If the frequency of intermittent radiation is much less than the relaxation time, then the transfer of energy from the vibrational to the translational modes would be very small. Since in photoacoustic effect, it is the translational energy that contributes to the sound signal, a study of the change in the phase and amplitude of the pressure signal with modulation frequency enables one to understand the vibrational-translation process better. For such investigations, pulsed lasers are used.

PAS particularly in the near IR (PANIS) has the potential for providing quantitative information about the surface coverage on chemically modified surfaces. Absorption bands arising from second overtone of the aliphatic C—H stretch vibrational mode in octadecyl-, decyl- and hexyl-modified silica gel are observed at 1188 nm as shown in Fig. 3.59. The second overtone of the aliphatic C—H stretch vibrational mode is observed at 1710 nm. It is found that the magnitude of the signal amplitude of both overtones when measured during modification as a function of time has a linear relationship with carbon coverage, i.e. carbon content of modified silica gel. Similar behaviour has also been observed in β -phenethyl modified silica gel at the first (1664 nm) and second (1130 nm) overtones of the aromatic C—H stretch vibrational mode. The amplitude of the second overtone of the aliphatic C—H stretch vibrational mode in alkyl-modified silica gel, i.e. hexyl, octyl, decyl, dodecyl and octadecyl, varies linearly with chain length and carbon content of modified silica. The signal amplitude for the first overtone of the N—H stretch vibrational mode for primary aliphatic amines at 1520 nm when recorded as a function of time in case of aminopropyl-modified silica gel bears linear relationship with amine as well as silica contents of modified silica.

The advantages of PAS over the conventional methods may be summarised as follows: (i) there is no problem about scattered radiation. This is taken as advantage in studying the spectra directly in TLC plate, (ii) small amount of the sample can easily be studied, (iii) difference spectrum can easily be obtained, and (iv) the photoacoustic spectrum is a power spectrum and hence depends not only on photo flux but also on the frequency (energy). Thus the signal due to overtone would be twice as strong as that of the fundamental vibrational mode.

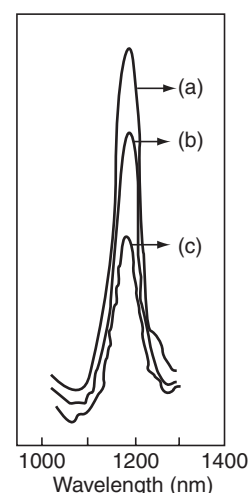


Fig. 3.59 Photoacoustic near infrared spectrum of (a) octadecyl-, (b) decyl-, and (c) hexyl modified silica gel.

3.22 IR EMISSION SPECTROSCOPY(IMS)

Molecules that absorb IR radiation can also emit characteristic IR frequencies on heating. The lack of applications of IMS is because of poor signal-to-noise ratio, characteristics of the IR emission signal particularly when the analyte is at a temperature only slightly higher than its surroundings. This problem has been solved with the aid of interferometric technique. Microgram quantities (1–10 μ g) of pesticides such as DDT, malathion and dieldrin can be identified by the interferometer of a FT spectrometer. Solutions of the samples are prepared in a suitable solvent. The solution is then evaporated on a NaCl or KBr plate. Plate is heated electrically near the spectrometer entrance. The components, i.e. SO₂, CO₂, etc., emitted from industrial stacks can be identified with the aid of interferometric technique. The emitted radiations from a distant industrial plumes are collected with a reflecting telescope and directed into the interferometer of FT infrared spectrometer for detection.

PROBLEMS

1. Deduce the structure of a compound, C_3H_8O which has an infrared band at 2941 cm^{-1} but none near 3333 cm^{-1} and 1724 cm^{-1} .

[Ans: Methylethylether]

2. Deduce the structure of a compound, C_2H_5ON , which has infrared bands at 3333 , 3173 and 1678 cm^{-1}

[Ans: Acetamide]

3. Deduce the structure of a compound, $C_4H_6O_3$ which has infrared bands at 1750 and 1820 cm^{-1} .

[Ans: Aceticanhydride]

4. Deduce the structure of a compound C_8H_8O which has an infrared band at 1689 cm^{-1} but no broad band near 3333 cm^{-1} .

[Ans: Acetophenone]

5. Find out to what functional groups vibrations with the wave numbers 3100 , 2260 , 1600 , 1570 , 750 and 686 cm^{-1} belong in the infrared spectrum of phenylisocyanate?

[Ans: 686 , 750 and 3100 cm^{-1} correspond to the group $\equiv C-H$, 2260 cm^{-1} to $-N=C=O$ and 1600 cm^{-1} to



6. (a) Complete the vacant spaces in the following table.

Molecule	$w_e\text{ (cm}^{-1}\text{)}$
$^1H^{35}Cl$	2990.95
$^2H^{35}Cl$	—
$^3H^{35}Cl$	—
$^1H^{37}Cl$	—
$^2H^{37}Cl$	—
$^3H^{37}Cl$	—

(b) Write all the possible isotopes of ^{12}C ^{14}N and determine their frequencies if the vibration frequency of ^{12}C ^{14}N is observed at 2028.62 cm^{-1} .

7. The three fundamental modes of vibration of MgF_2 are observed at 240 , 447 and 870 cm^{-1} . The intensities of the bands follow the order: $I(870) > I(240) > I(447)$. Identify the types of vibration associated with the said absorption bands.

[Ans: $\nu_{\text{asym}} = 870\text{ cm}^{-1}$, $\nu_{\text{sym}} = 447\text{ cm}^{-1}$, $\delta = 240\text{ cm}^{-1}$]

8. Three bands have been observed at 140 (weak), 129 (medium) and 403 (strong) in the infrared absorption spectra of $SnCl_4$. Identify the types of vibrations associated with the bands.

[Ans: $\nu_{\text{asym}} = 403\text{ cm}^{-1}$, $\nu_{\text{sym}} = 129\text{ cm}^{-1}$, $\delta = 104\text{ cm}^{-1}$]

9. Determine (a) the maximal vibration quantum number, (b) the vibrational energy on the zeroth level, (c) maximal vibrational energy, and (d) the bond energy for mole of the following systems.

Molecule	DI	FO	H_2	K_2	N_2	OH	HF
$w_e\text{ (cm}^{-1}\text{)}$	1639.6	1060	4400.4	92.96	2358.03	3737.9	4138.7
$x_e \times 10^3$	12.1	14.6	27.4	3.82	6.00	29.7	21.7

[Ans: For HF, (a) 22 (b) $4.0677 \times 10^{-25}\text{ kJ}$ (c) $94.154 \times 10^{-25}\text{ kJ}$ (d) $542.54\text{ kJ mole}^{-1}$]

10. Calculate the amplitude of vibrations in $V = 0$ level of the following systems from their force constant data.

Molecule	H_2	NO	CO	N_2	O_2
$k\text{ (millidynes/\AA)}$	5.2	15.5	18.7	22.6	11.4

- **Hint:** For maximum displacement, potential energy = zero point vibrational energy, i.e.

$$U = \frac{1}{2}kA_0^2 = \frac{1}{2}h\nu_v, \quad E_v = h\nu_v \left(V + \frac{1}{2} \right), \text{ For } V = 0, \quad E_0 = \frac{1}{2}h\nu_0$$

[Ans: For CO, $A_0 = 4.78 \times 10^6\text{ cm}$]

11. Compute the maximal displacement above equilibrium distance as a percentage of r_e for the following systems from their vibrational frequencies.

Molecule	Br_2	CO	FO	K_2	O_2	N_2
$w_e\text{ (cm}^{-1}\text{)}$	325.3	2169.81	1060	92.96	1580.19	2358.03
$r_e\text{ (\AA)}$	2.28	1.128	1.32	3.92	1.207	1.098

- **Hint:** Total potential energy = Zero point vibrational energy, i.e. $\frac{1}{2}k(r - r_e)^2 = \frac{1}{2}h\nu_v$

[Ans: 24 per cent for O_2]

12. The prominent maxima for different rotational levels in the R-branch of the rotation-vibration band in the absorption spectrum of HCl vapour are given below. Determine the number of molecules on each rotational quantum level if their extinction coefficients are independent of the rotational energy.

J	0	1	5	8	10	12
$w_e\text{ (cm}^{-1}\text{)}$	2906.3	2925.8	2997.8	3044.9	3072.8	3098.4
D	0.155	0.418	0.362	0.065	0.011	0.001

[Ans: $J = 0$, 3.07×10^{22} molecules; $J = 12$, 18.06×10^{19} molecules]

13. Compute the wave numbers of the first five lines in the P-branch and R-branch of the rotation-vibration absorption spectrum of HF using the needed data from the book.

[Ans: P-branch, wave number of first line = 3915.93 cm^{-1} for R-branch, wave number of third line = 4084.81 cm^{-1}]

14. Compute the wave numbers of thirteen absorption bands in the R-branch of rotation-vibration spectrum of HCl, taking into consideration that the rotational constant B_v varies. Given $w_e = 2990.95\text{ cm}^{-1}$, $x_e = 17.65 \times 10^{-3}$, $B_e = 10.59\text{ cm}^{-1}$, $r_e = 1.274\text{ \AA}$. Find the value of α from that of $\bar{\nu}$ of the line $J = 12$ (see parameters of problem 3.12).

[Ans: $J = 0$, $\bar{\nu} = 2906.01\text{ cm}^{-1}$, $J = 4$, $\bar{\nu} = 2981.65\text{ cm}^{-1}$, $J = 10$, $\bar{\nu} = 3075.51\text{ cm}^{-1}$]

15. The force constant for N_2 molecule is 22.6 millidynes/ $\text{\AA}$. How much energy is needed to increase the nuclear separation by $0.5\text{ \AA}$?

- **Hint:** $U = \frac{1}{2}kA^2$, $A = 0.5\text{ \AA}$, $1eV = 8068\text{ cm}^{-1}$

16. The values of w_e and x_e for some diatomics are listed below in the tabular form. Compute their zero point energies.

Molecule	Br ₂	Cl ₂	F ₂	I ₂	P ₂
w_e	325.3	559.75	917.55	214.55	780.69
$x_e \times 10^3$	3.31	4.81	12.9	2.87	3.61

17. The force constant for NO molecule is 15.5 millidynes/Å. Determine the frequency of vibration of the molecule and the spacing between its vibrational levels in eV.
18. Find the temperature at which the number of NO molecules in the $V = 1$ level be $\frac{1}{4}$ th of that of $V = 0$ level. $w_e = 1904.4 \text{ cm}^{-1}$, $x_e = 7.45 \times 10^{-3}$.

• **Hint:** $\frac{N_{V=1}}{N_{V=0}} = e^{-\Delta E / kT} = \frac{1}{4}$

19. (a) Compare the relative populations of the first six states of P_2 molecules at 300 and 500 K. Use the data from the book.
- (b) Find the temperature at which the number of P_2 molecules in the $V = 1$ state equals $1/e$ of number of molecules in the ground state ($V = 0$)
- (c) Draw a curve between population and vibrational quantum number.
- (d) Check whether the results are affected significantly if $w_e x_e$ is ignored.

• **Hint:** $\frac{N_{V=1}}{N_{V=0}} = e^{-(w_e - w_e x_e)hc / kT}$

20. Explain why the infrared absorption spectrum of α -chloroketone shows two bands around 1720 and 1740 cm^{-1} ? Assign these bands also.
21. Determine the vibrational component of the partition function for the following molecules at 500 K from their vibration frequencies:

Molecule	K ₂	BrCl	ClF	DI	DF
$w_e(\text{cm}^{-1})$	92.96	444.27	786.15	1639.6	2998.19

22. Determine total number of molecules on the vibrational quantum levels $V = 1$ and on the zeroth rotational quantum state at 1000 K for the following systems.

Molecule	$w_e(\text{cm}^{-1})$	$w_e x_e(\text{cm}^{-1})$
³⁵ C ¹⁹ F	787.50	7.00
³⁷ C ¹⁹ F	777.99	6.83
³⁵ Cl ⁷⁹ Br	443.10	1.80
³⁵ Cl ⁸¹ Br	441.42	1.79
¹ H ¹²⁷ I	2308.09	38.98
² H ¹²⁷ I	1640.14	20.16
³ H ¹²⁷ I	1345.50	13.57

23. For the molecule HD, $r_e = 0.7413 \text{ Å}$, $w_e = 3817.1 \text{ cm}^{-1}$ and $w_e x_e = 94.96 \text{ cm}^{-1}$. Compute the vibrational energies on the 0th, 7th, 12th, 16th and maximal vibrational quantum levels. Calculate $(r - r_e)$ and plot the Morse curve.
- [Ans: $V = 0$, $E = 3.744 \times 10^{-23} \text{ kJ}$, $r - r_e = 0.6380 \text{ Å}$, 0.8706 Å , $V = 20$, $E = 76.098 \times 10^{-23} \text{ kJ}$, $r - r_e = 0.3839 \text{ Å}$, 0.5689 Å]

24. The fundamental band of HCl is observed at 2886 cm^{-1} and it fits into the empirical equation $\nu = 2885.90 + 20.577 m - 0.3034 m^2$ where $m = +1, +2, +3, \dots$ for R-branch $m = -1, -2, -3, \dots$ for P-branch.

Determine the values of B_e , B_0 , B_1 Given $\alpha_e = 0.3312 \text{ cm}^{-1}$.

- **Hint:** Compare the empirical relation with the general expression for the rotational lines of a band i.e.

$$\nu = \nu_0 + (B_{V''} + B_{V'})m + (B_{V''} - B_{V'})m^2$$

- **Hint:** For fundamental band, $V'' = 1$ and $V' = 0$, $B_V =$

$$B_e - \alpha_e \left(V + \frac{1}{2} \right) \quad [\text{Ans: } B_e = 10.5911 \text{ cm}^{-1}]$$

25. Using the spectral data from the book, determine the thermodynamic functions at 298.15 K for the following diatomics: K₂, P₂, DI, Cl₂, Br₂, BrCl, F₂, ClF, OH, HF, DF.
26. Determine the thermodynamic functions for the following systems at 298.15 K.

Molecule	H ₂ S	SO ₂	HCN	CS ₂	N ₂ O	PH ₃
Frequencies	2611	1151, 524,	712, 2089	397, 657	589, 1285	2327, 991,
(cm^{-1})	1290	1361	3312	1523	2224	2421,
	2684					1121

Search other relevant data required in the calculations from the book. Compare the results thus determined with the one's obtained by computer programs given in the book.

[Ans: Thermodynamic function (cal/mole.K)]

	SO ₂	CS ₂
Free energy	-50.95	-41.174
Enthalpy	2.53	2.386]

27. The fine structure of the fundamental vibrational band of HCl shows the following lines:

2998.04	2981.00	2963.29	2944.90	2925.90	2906.24
2863.02	2841.58	2819.56	2796.97	2773.82	2750.13

Determine r_0 , r_1 and r_e .

28. (a) Calculate the equilibrium constant K_p , of the reaction $\frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2 = \text{HCl}$ at 900 K and 1 atmospheric pressure from the following rotational moments of inertia and vibrational frequencies.

Substance	HCl	Cl ₂	H ₂
$I \times 10^{40}(\text{g cm}^2)$	2.612	116.3	0.459
$w_e(\text{cm}^{-1})$	2989.4	564.9	4396.6

The heat of reaction in the ideal gaseous state at absolute zero is $-92.140 \text{ kJ mol}^{-1}$

[Ans: $K_p = 8.357 \times 10^5$]

- (b) Calculate the equilibrium constant, K_p of the reaction of thermal dissociation of iodine $I_2 = 2I$, at 1274 K and $1.0133 \times 10^5 \text{ Pa}$ if $\Delta H_0^0 = 148.766 \text{ kJ mole}^{-1}$, the vibrational frequency of I_2 molecule is $w_e = 214.25 \text{ cm}^{-1}$, and the moment

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of inertia is $750.1 \times 10^{-40} \text{ g cm}^2$. The statistical weight of the zeroth electronic level of iodine atom is 4, and that of the zeroth electronic level of the I_2 molecule is unity.

[Ans: $K_p = 0.173$]

- (c) Calculate equilibrium constant, K_p of the reaction $\text{NO} = \frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2$ at 1000 K and 1 atmospheric pressure if the rotational moments of inertia of the molecules, vibrational frequencies, and statistical weights of the zeroth electronic levels are as follow.

Substance	NO	N ₂	O ₂
$I \times 10^{40} (\text{g cm}^2)$	16.43	14.01	19.34
$\omega_e (\text{cm}^{-1})$	1916.5	2359.4	1579.8
$g_{0, \text{elec}}$	4	1	3

The heat of reaction which proceeds in the ideal gaseous state at absolute zero is $-90.761 \text{ kJ mole}^{-1}$.

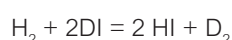
[Ans: $K_p = 2.532 \times 10^5$]

- (d) Determine the equilibrium constant of the reaction $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$ at 300 and 1000 K and $1.0133 \times 10^5 \text{ Pa}$ ($= 1 \text{ atm}$) if the moments of inertia of the molecules, vibrational frequencies and heats of their formation in the ideal gaseous state at absolute zero are as follows.

Substance	$I \times 10^{40} (\text{g cm}^2)$	$\omega_e (\text{cm}^{-1})$	$\Delta H_f^0 (\text{kJ mole}^{-1})$
CO ₂	67.8336	1351.2, 2396.4, 672.2 (doubly degenerate)	-393.229
H ₂	0.459	4396.6	0
H ₂ O	1.0296 1.9674, 2.9970	3835.4 3938.7, 1647.6	-238.906
CO	14.49	2170.0	-113.88

[Ans: $K_p (1000 \text{ K}) = 1.2787$]

- (e) Determine the equilibrium constant of the gaseous isotopic exchange reaction between hydrogen and deuterium iodide, viz.,



at 298 K. From spectroscopic measurements, $\Delta H_f^0 = 83 \text{ cal}$, and the moments of inertia are as follows: H₂ (45.9×10^{-42}), DI (855×10^{-42}), HI (431×10^{-42}), D₂ (92.0×10^{-42}), g cm^2 , σ for H₂ and D₂ are each 2 and for HI and DI they are 1.

[Ans: $K_p = 1.22$]

- Hint:** At room temperature, the four vibrational factors are not very different from unity. Thus, for metathetic or double decomposition reactions, a very simple expression can be derived for equilibrium constant, particularly if diatomic molecules only participate in the process, e.g. in the case of the gas reaction



1 2 3 4

$$\ln K = -\frac{\Delta H_f^0}{RT} + \frac{3}{2} \ln \frac{M_3 M_4}{M_1 M_2} + \ln \frac{I_3 I_4}{I_1 I_2} + \ln \frac{\sigma_1 \sigma_2}{\sigma_3 \sigma_4}$$

29. Which of the following vibrations of acetylene are infra-red active.

- (a) $\vec{\text{H}}-\vec{\text{C}} \equiv \vec{\text{C}}-\vec{\text{H}}$ (C-H-stretch)
 (b) $\vec{\text{H}}-\vec{\text{C}} \equiv \vec{\text{C}}-\vec{\text{H}}$ (C-H-stretch), 3287 cm^{-1}
 (c) $\vec{\text{H}}-\vec{\text{C}} \equiv \vec{\text{C}}-\vec{\text{H}}$ (C≡C-stretch)
 (d) $\begin{array}{c} \uparrow \\ \text{H}-\text{C} \equiv \text{C}-\text{H} \\ \downarrow \end{array}$ (C≡C-H bend)
 (e) $\begin{array}{c} \uparrow \\ \text{H}-\text{C} \equiv \text{C}-\text{H} \\ \downarrow \end{array}$ (C≡C-H bend) 729 cm^{-1}

[Ans: (b), (e)]

30. The frequencies for three fundamental modes of vibration of CS₂ have been observed at 396.7 (IR), 656.5 (R) and 1523 (IR). Calculate the frequencies of the bands for the following arbitrary transitions: (i) $V(0, 0, 0) \rightarrow V(2, 0, 0)$; (ii) $V(0, 0, 0) \rightarrow V(0, 1, 2)$; (iii) $V(0, 0, 2) \rightarrow V(2, 2, 0)$ and (iv) $V(0, 1, 0) \rightarrow V(0, 0, 1)$.

31. The vapour phase spectrum of methyl-thioformate shows resolved rotational contours. The PR separations as determined from the CH₃ asymmetric stretching (3043 R, 3036 Q, 3023 P, in cm^{-1}) and CH₃ symmetric stretching (2966 R, 2955 Q, 2946 P, in cm^{-1}) bands both of type A have been found to be 20 and 20 cm^{-1} respectively. Determine (a) moments of inertia of the molecule, (b) the values of the parameters I and κ_a and (c) the configuration of the molecule if the rotational constants of the cis and trans configurations are

Rotational constant (in MHz)	cis	trans
A	17941.60	17510.18
B	4131.91	11401.15
C	3440.69	7252.33

32. Using the value of $B = 58000 \text{ MHz}$ and $\bar{\nu} = 2160.0 \text{ cm}^{-1}$ for CO, calculate the frequencies of the first few lines of the R and P-branches in the vibration-rotation spectrum of CO.

$$\left[\begin{array}{l} \text{Ans: } \bar{\nu}_R = 2160.0 + 3.87(J+1); \text{cm}^{-1} \\ \bar{\nu}_P = 2160.0 - 3.87J; \text{cm}^{-1} \end{array} \right]$$

33. The frequencies of the first few vibronic transitions to an excited state ${}^7\text{Li}_2$ are given below:

Vibronic transitions	$\bar{\nu}_{\text{obs}} (\text{cm}^{-1})$
$0 \rightarrow 0$	14020
$0 \rightarrow 1$	14279
$0 \rightarrow 2$	14541
$0 \rightarrow 3$	14805
$0 \rightarrow 4$	15074
$0 \rightarrow 5$	15345

From these data calculate the values of ω_e and $\omega_e x_e$ for the excited state of ${}^7\text{Li}_2$.

$$[\text{Ans: } \omega_e'' = 267.76 \text{ cm}^{-1}; \omega_e'' x_e'' = 0.04 \text{ cm}^{-1}]$$

APPENDIX 3.1 A: HARMONIC VIBRATOR

The vibrational energies of molecule is obtained from the solution of the Schrödinger wave equation. The potential of a linear vibrator is given by

$$U(x) = 2\pi^2 m \nu_0^2 x^2 \quad (3.1 A-1)$$

where x is the displacement of the particle of mass m from its equilibrium position $x = 0$. The one-dimensional time independent Schrödinger wave equation is expressed by

$$\hat{H}\Psi(x) = E\Psi(x) \quad (3.1 A-2)$$

where $\hat{H}$ is the operator corresponding to the Hamiltonian of the system and the eigen value E is simply a number. Thus the wave equation for a harmonic vibrator can be expressed as

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m}{h^2} [E_v - U(x)]\Psi = 0 \quad (3.1 A-3)$$

where $U(x) = 2\pi^2 m \nu_0^2 x^2$

The wave function should be continuous, single-valued and finite throughout the region of values $-\infty$ to $+\infty$ for x . In order to solve the differential equation we introduce two quantities,

$$\lambda = \frac{8\pi^2 m E}{h^2} \text{ and } \alpha = [4\pi^2 m \nu_0 h]$$

Accordingly, Eq. (3.1 A-3) becomes

$$\frac{d^2\Psi}{dx^2} + [\lambda - \alpha^2 x^2]\Psi = 0 \quad (3.1 A-4)$$

Let us now find the asymptotic solution of the wave function for large value of $|x|$. For any value of energy constant E , a value of $|x|$ can be found such that for it and all larger values of $|x|$, λ is negligibly small relative to $\alpha^2 x^2$, the asymptotic form of the equation then becomes:

$$\frac{d^2\Psi}{dx^2} = \alpha^2 x^2 \Psi \quad (3.1 A-5)$$

This equation is satisfied asymptotically by the exponential function

$$\Psi = e^{\pm \frac{\alpha}{2} x^2} \quad (3.1 A-6)$$

i.e.,

$$\frac{d\Psi}{dx} = \pm \alpha x e^{\pm \frac{\alpha}{2} x^2}$$

and

$$\frac{d^2\Psi}{dx^2} = \alpha^2 x^2 e^{\pm \frac{\alpha}{2} x^2} \pm \alpha e^{\pm \frac{\alpha}{2} x^2}$$

The second term is negligible in the region considered. The asymptotic solution $e^{+\frac{\alpha}{2} x^2}$ is unsatisfactory since it rapidly tends to infinity with the increasing value of $|x|$. The satisfactory asymptotic solution of the equation throughout the configuration space ($-\infty < x < +\infty$) is now obtained by the power series method as follows:

Let

$$\Psi = e^{-\frac{\alpha}{2} x^2} f(x) \quad (3.1 A-7)$$

$$\therefore \frac{d^2\Psi}{dx^2} = e^{-\frac{\alpha}{2} x^2} [\alpha^2 x^2 f - \alpha f - 2\alpha x f' + f''] \quad (3.1 A-8)$$

where

$$f' = \frac{df}{dx} \text{ and } f'' = \frac{d^2f}{dx^2}$$

Dividing Eq. (3.1 A-4) by $e^{-\frac{\alpha}{2} x^2}$ and comparing the resultant equation with Eq. (3.1 A-8) we get

$$f'' - 2\alpha x f' + (\lambda - \alpha) f = 0 \quad (3.1 A-9)$$

Let us now introduce a new variable ξ related to x by the expression:

$$\xi = \sqrt{\alpha} x \quad (3.1 A-10)$$

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and to replace the function $f(x)$ by $H(\xi)$ to which it is equal. Consequently Eq. (3.1 A-9) becomes

$$\frac{d^2 H}{d\xi^2} - 2\xi \frac{dH}{d\xi} + \left(\frac{\lambda}{\alpha} - 1\right)H = 0 \quad (3.1 A-11)$$

Let us now represent $H(\xi)$ as a power series, i.e.

$$H(\xi) = \sum_{v=0,1,2}^{\infty} a_v \xi^v = a_0 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \dots \quad (3.1 A-12a)$$

The first and second derivatives of the series are

$$\frac{dH}{d\xi} = \sum_v v a_v \xi^{v-1} = a_1 + 2 a_2 \xi + 3 a_3 \xi^2 + \dots \quad (3.1 A-12b)$$

$$\frac{d^2 H}{d\xi^2} = \sum_v v(v-1) a_v \xi^{v-2} = 1.2 a_2 + 2.3 a_3 \xi + \dots \quad (3.1 A-12c)$$

Substituting the set of Eqs. (3.1 A-12 a-c) into Eq. (3.1 A-11), we get

$$\begin{aligned} & 1.2 a_2 + 2.3 a_3 \xi + 3.4 a_4 \xi^2 + 4.5 a_5 \xi^3 + \dots \\ & - 2 a_1 \xi - 2.2 a_2 \xi^2 - 3.2 a_3 \xi^3 + \dots \\ & + \left(\frac{\lambda}{\alpha} - 1\right) a_0 + \left(\frac{\lambda}{\alpha} - 1\right) a_1 \xi + \left(\frac{\lambda}{\alpha} - 1\right) a_2 \xi^2 + \left(\frac{\lambda}{\alpha} - 1\right) a_3 \xi^3 = 0 \end{aligned} \quad (3.1 A-13)$$

For $H(\xi)$ to be the solution of Eq. (3.1 A-11), the seires will vanish for all values of ξ provided the coefficients of individual power of ξ also vanishes, i.e.

$$\begin{aligned} \xi^0 \quad & 1.2 a_2 + \left(\frac{\lambda}{\alpha} - 1\right) a_0 = 0 \\ \xi^1 \quad & 2.3 a_3 + \left(\frac{\lambda}{\alpha} - 1 - 2\right) a_1 = 0 \\ \xi^2 \quad & 3.4 a_4 + \left(\frac{\lambda}{\alpha} - 1 - 2.2\right) a_2 = 0 \\ \xi^3 \quad & 4.5 a_5 + \left(\frac{\lambda}{\alpha} - 1 - 2.3\right) a_3 = 0 \end{aligned}$$

Accordingly we write the general expression for the coefficient of ξ^v ,

$$(v+1)(v+2) a_{v+2} + \left(\frac{\lambda}{\alpha} - 1 - 2v\right) a_v = 0 \quad (3.1 A-14)$$

or

$$a_{v+2} = -\frac{\frac{\lambda}{\alpha} - 2v - 1}{(v+1)(v+2)} a_v \quad (3.1 A-15)$$

From this recursion formula, one can determine the coefficients $a_2, a_3, a_4, a_5, \dots$ successively in terms of a_0 and a_1 which are arbitrary.

For $a_0 = 0$, the odd powers will appear.

For $a_1 = 0$ only the even powers will appear, i.e.

$a_0 = 0$	$a_1 = 0$
$a_2 = \frac{-\left(\frac{\lambda}{\alpha} - 1\right)}{2} a_0$	$a_3 = \frac{-\left(\frac{\lambda}{\alpha} - 3\right)}{2.3} a_1$
$a_4 = \frac{-\left(\frac{\lambda}{\alpha} - 5\right)\left(\frac{\lambda}{\alpha} - 1\right)}{3.4.2} a_0$	$a_5 = \frac{-\left(\frac{\lambda}{\alpha} - 7\right)\left(\frac{\lambda}{\alpha} - 3\right)}{4.5.2.3} a_1$

or we can write

$$a_2 = \frac{-\left(\frac{\lambda}{\alpha} - 1\right)}{2} a_0, \quad a_3 = \frac{-\left(\frac{\lambda}{\alpha} - 3\right)}{3} a_1$$

$$a_4 = \frac{-\left(\frac{\lambda}{\alpha} - 5\right)\left(\frac{\lambda}{\alpha} - 1\right)}{4} a_0, \quad a_5 = \frac{-\left(\frac{\lambda}{\alpha} - 7\right)\left(\frac{\lambda}{\alpha} - 3\right)}{5} a_1 \quad (3.1 A-16)$$

Since $a_2, a_4, \dots$ are related to a_0 and $a_3, a_5, \dots$ are related to a_1 , we can split the solution in even and odd series. Accordingly, we can write

$$H(\xi) = [a_0 + a_2 \xi^2 + a_4 \xi^4 + \dots] + [a_1 \xi + a_3 \xi^3 + a_5 \xi^5 + \dots]$$

or

$$H(\xi) = a_0 \left[1 + \frac{1+\gamma}{2} \xi^2 + \frac{(1-\gamma)(5-\gamma)}{4} \xi^4 + \dots \right] + a_1 \left[\xi + \frac{3-\gamma}{3} \xi^3 + \frac{(3-\gamma)(7-\gamma)}{5} \xi^5 + \dots \right] \quad (3.1 A-17)$$

Here $\gamma = \frac{\lambda}{\alpha}$. Since the values of a_0 and a_1 are arbitrary, we have obtained two independent solutions of Eq. (3.1 A-11) and

therefore Eq. (3.1 A-17) represents the most general solution of Eq. (3.1 A-11). It can easily be seen that when $\gamma = 1, 5, 9, \dots$ the even series becomes a polynomial and the odd series remains an infinite series.

Similarly, for $\gamma = 3, 7, 11, \dots$ the odd series becomes a polynomial and the even series remains an infinite series.

Thus when $\gamma = 2n + 1$; $n = 0, 1, 2, 3, \dots$ one of the solutions becomes a polynomial. Returning to eq. (3.1 A-15) we have

$$\frac{a_{v+2}}{a_v} = \frac{\left(2v+1-\frac{\lambda}{\alpha}\right)}{(v+1)(v+2)} = \frac{2}{v} \text{ for large values of } v.$$

Thus $\lim_{v \rightarrow \infty} \frac{a_{v+2}}{a_v} = 0$, i.e. the series always converges which shows that both the infinite series in Eq. (3.1 A-17) will converge for all values of ξ .

Let us now compare the series for H and that for e^{ξ^2} .

$$H(\xi) = \sum_{v=0,2,4,\dots}^{\infty} a_v \xi^v$$

$$\frac{a_{v+2}}{a_v} = \frac{\left(2v+1-\frac{\lambda}{\alpha}\right)}{(v+1)(v+2)}$$

$$e^{\xi^2} = 1 + \xi^2 + \frac{\xi^4}{2} + \frac{\xi^6}{3} + \dots + \frac{\xi^v}{\frac{v}{2}} + \frac{\xi^{v+2}}{\frac{v}{2}+1} \quad (3.1 A-18)$$

For large values of ξ , the first few term of these series is unimportant. Let the ratio of the coefficients of v th terms in the expansion of $H(\xi)$ and e^{ξ^2} equals c , which may be small or large, i.e. $\frac{a_v}{b_v} = c$, if b_v is the coefficient of ξ^v in the expansion of e^{ξ^2} . For large value of v , the asymptotic relations will be:

$$a_{v+2} = \frac{2}{v} a_v \text{ and } b_{v+2} = \frac{2}{v} b_v$$

Thus

$$\frac{a_{v+2}}{b_{v+2}} = \frac{a_v}{b_v} = c,$$

if v is large. Therefore the higher terms of the series for $H(\xi)$ differ from those of e^{ξ^2} only by a multiplication constant. But the ratio of $\frac{a_{v+2}}{b_{v+2}}$ (in the limit of large v) is the same as that of the coefficients of ξ^{v+2} and ξ^v in the expansion of e^{ξ^2} . Consequently if the series in Eq. (3.1 A-17) is not terminated, $H(\xi)$ will behave as e^{ξ^2} for large value of ξ , therefore $\Psi(\xi)$ and the product $e^{-\xi^2/2} \cdot H(\xi)$ will behave as $e^{\xi^2/2}$ in this region, thus making it unacceptable as wave function, i.e. the boundary condition

$$\Psi(\xi) \rightarrow 0 \text{ as } \xi \rightarrow \pm \infty \quad (3.1 \text{ A-19})$$

will not be satisfied. The boundary conditions will only be satisfied by the wave function if the infinite series terminates to a polynomial as mentioned earlier and this can happen only when γ is an odd integer, i.e.

$$\gamma = 2n + 1; \quad n = 0, 1, 2, \dots$$

$$\text{or} \quad \lambda = (2n + 1) \alpha \quad (3.1 \text{ A-20})$$

The condition expressed in Eq. (3.1 A-20) for the existence of the n th wave function becomes:

$$E = E_n = (n + 1/2) h\nu_0, \quad n = 0, 1, 2, 3, \dots \quad (3.1 \text{ A-21})$$

where $\alpha = \frac{h\nu_0}{2}$, the zero point energy of the molecule. Equation (3.1 A-21) represents the discrete energy eigen values of the operator H .

APPENDIX 3.2 A ANHARMONIC VIBRATOR

The wave equation for anharmonic vibrator can be expressed as

$$\frac{d^2\Psi(\rho)}{d\rho^2} + \frac{8\pi^2 I_e}{h^2} [E_v - U(\rho)] \Psi(\rho) = 0$$

$$\text{where} \quad \rho = \frac{r - r_e}{r_e} \quad (3.2 \text{ A-1})$$

To solve this equation advantage can be taken of the Morse potential of the type:

$$U(\rho) = D(1 - e^{-a\rho})^2 \quad (3.2 \text{ A-2})$$

For small ρ (small vibrations), the Morse function reduces to $U(\rho) = Da^2\rho^2$ or $f = \frac{-2Da^2\rho}{r_e} = -kr_e\rho$, where $k = \frac{2Da^2}{r_e^2}$. In this

case the molecule is an harmonic oscillator. Thus substituting $U(\rho) = Da^2\rho^2 = \frac{kr_e^2\rho^2}{2}$ into Eq. (3.2 A-1) we get the equation of a harmonic oscillator.

By means of the Morse function, Eq (3.2 A-1) transforms as ($y = e^{-a\rho}$)

$$\begin{aligned} \left[\frac{d^2\Psi}{d\rho^2} = \frac{d}{d\rho} \left(\frac{d\Psi}{d\rho} \right) = \frac{d}{d\rho} \left(\frac{d\Psi}{dy} \frac{dy}{d\rho} \right) = \frac{d\Psi}{dy} \frac{d^2y}{d\rho^2} + \frac{dy}{d\rho} \cdot \frac{d}{d\rho} \frac{dy}{d\rho} \frac{d}{dy} \left(\frac{d\Psi}{dy} \right) \right. \\ \left. = \frac{d\Psi}{dy} \frac{d^2y}{d\rho^2} + \left(\frac{dy}{d\rho} \right)^2 \frac{d^2\Psi}{dy^2} = a^2 y \frac{d\Psi}{dy} + a^2 y^2 \frac{d^2\Psi}{dy^2} \right] \\ \frac{d^2\Psi}{dy^2} + \frac{1}{y} \frac{d\Psi}{dy} + \frac{8\pi^2 I_e}{a^2 h^2} \left(\frac{(E_v - D)}{y^2} + \frac{2D}{y} - D \right) \Psi = 0 \end{aligned} \quad (3.2 \text{ A-3})$$

Now using the function ψ of the type

$$\Psi = \frac{f(y)}{\sqrt{y}} \quad (3.2 \text{ A-4})$$

and computing $\frac{d\Psi}{dy}$ and $\frac{d^2\Psi}{dy^2}$ from (3.2 A-4) and substituting the respective values into Eq. (3.2 A-3), we get

$$f'' + \lambda^2 \left(\frac{Q}{y^2} + \frac{2D}{a^2 y} - \frac{D}{a^2} \right) f = 0 \quad (3.2 \text{ A-5})$$

where $\lambda^2 = \frac{8\pi^2 I_e}{h^2}$ and $Q = \frac{E_v - D}{a^2} + \frac{1}{4\lambda^2}$

The sought for asymptotic solution of Eq. (3.2 A-5) holds for any high value of y . Since we can ignore terms containing y in the denominator, the sought for solution should satisfy the differential equation

$$f'' - D \frac{\lambda^2}{a^2} f = 0 \quad (3.2 A-6)$$

The solution to this equation has the form, $f_{as} = e^{\pm \beta y}$, where $\beta^2 = \frac{\lambda^2}{a^2} D$. The asymptotic solution $e^{+\beta y}$ is unsatisfactory since it tends rapidly to infinity with increasing value of y . But solution $e^{-\beta y}$ is satisfactory ($f \rightarrow 0$ when $y \rightarrow \infty$) throughout the range of variation of the variable y .

The general solution of the equation throughout the configuration space is obtained by the function

$$f = C(y)e^{-\beta y} \quad (3.2 A-7)$$

Compute $f'' (= C''e^{-\beta y} - 2\beta C'e^{-\beta y} + \beta^2 C e^{-\beta y})$ from Eq. (3.2 A-7) and substitute the values of f' and f'' into Eq. (3.2 A-5) to obtain a differential equation for $C(y)$.

$$C'' - 2\beta C' + \lambda^2 \left(\frac{Q}{y^2} + \frac{2D}{a^2 y} \right) C = 0 \quad (3.2 A-8)$$

The solution of this equation has the form:

$$C = \sum_k b_k y^{v+k} \quad (3.2 A-9)$$

Substituting the polynomial into Eq. (3.2 A-8), we get

$$\begin{aligned} \sum b_k (v+k)(v+k-1) y^{v+k-2} - 2\beta \sum b_k (v+k) y^{v+k-1} + 2\beta^2 \sum b_k y^{v+k-1} \\ + \lambda^2 Q \sum b_k y^{v+k-2} = 0 \end{aligned} \quad (3.2 A-10)$$

Equating the coefficients of y^{v+k-1} we get

$$[(v+k+1)(v+k) + \lambda^2 Q] = [2\beta(v+k) - 2\beta^2] b_k \quad (3.2 A-11)$$

Imposing the condition $b_0 = 0$ and $b_{v+2} = 0$, we obtain from the recurrent equation

$$v(v+1) = -\lambda^2 Q \text{ (for } b_0 = 0, \text{ i.e. } k=0)$$

and $v+v+1 = \beta$ (for $b_{v+2} = 0$, i.e. $V+2 = k+1$ or $k = V+1$)

Eliminating v we get

$$-\lambda^2 Q = (\beta - V)(\beta - V - 1) = \beta^2 - 2\beta(V + 1/2) + V(V + 1) \quad (3.2 A-12)$$

Substituting the value of Q from Eq (3.2 A 5) and also noting that $\beta^2 = \left(\frac{\lambda^2}{a^2} \right) D$, we get

$$E_v = 2\beta \frac{a^2}{\lambda^2} (V + 1/2) - \frac{a^2}{\lambda^2} (V + 1/2)^2 \quad (3.2 A-13)$$

Also we know that

$$x_e = \frac{hc\omega_e}{4D} \quad \text{and} \quad \omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \frac{a}{2\pi c} \sqrt{\frac{2D}{I_e}}$$

So Eq. (3.2 A-13) reduces to

$$E_v = h c \omega_e (V + 1/2) - h c \omega_e x_e (V + 1/2)^2$$

or the vibrational term is

$$G_v (\text{in } cm^{-1}) = \frac{E_v}{hc} = \omega_e (V + 1/2) - \omega_e x_e (V + 1/2)^2 \quad (3.2 A-14)$$

From spectroscopic data it follows that the best approximation is the formula

$$E_v = h c \omega_e (V + 1/2) - h c \omega_e x_e (V + 1/2)^2 + h c \omega_e y_e (V + 1/2)^3 + \dots \quad (3.2.A-15)$$

APPENDIX 3.3 A ENERGY LEVELS FOR THE DIATOMIC ROTATOR–VIBRATOR OR ENERGY LEVELS OF DIATOMIC NONRIGID ROTATOR-ANHARMONIC VIBRATOR

The radial part of the Schrödinger wave equation for the diatomic nonrigid rotator-anharmonic oscillator can be written as

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[-\frac{J(J+1)}{r^2} + \frac{8\pi^2\mu}{h^2} \{E - U(r)\} \right] R = 0 \quad (3.3 A-1)$$

Here for simplicity the subscripts are omitted, i.e. $E = E_{J,V}$ or $E_{\text{rot-vib}}$ and $\psi_{J,V} = \psi_{\text{rot-vib}} = \psi$, sub-scripts are omitted. The equation is further simplified by putting

$$R(r) = \frac{1}{r} \Psi(r) \quad (3.3 A-2)$$

so that

$$\begin{aligned} \frac{1}{r^2} \frac{d}{dr} \left[r^2 \frac{d}{dr} \left(\frac{1}{r} \Psi \right) \right] &= \frac{1}{r^2} \frac{d}{dr} \left[r^2 \left(-\frac{\Psi}{r^2} + \frac{1}{r} \frac{d\Psi}{dr} \right) \right] \\ &= \frac{1}{r^2} \frac{d}{dr} \left[-\Psi + r \frac{d\Psi}{dr} \right] = \frac{1}{r^2} \left[-\frac{d\Psi}{dr} + \frac{d\Psi}{dr} + r \frac{d^2\Psi}{dr^2} \right] = \frac{1}{r} \frac{d^2\Psi}{dr^2} \end{aligned}$$

Thus Eq. (3.3. A-1) in terms of function ψ becomes

$$\frac{d^2\Psi}{dr^2} + \left[-\frac{J(J+1)}{r^2} + \frac{8\pi^2\mu}{h^2} \{E - U(r)\} \right] \Psi = 0 \quad (3.3 A-3)$$

The simple Hooke's law potential energy function $U(r) = \frac{1}{2}k(r-r_e)^2$, fails to agree with experiment in that it yields equally spaced levels, whereas the observed vibrational levels show a convergence for increasing values of V . On the other hand, as has always been discussed, the Morse function,

$$U(r) = D[1 - e^{-a(r-r_e)}]^2 \quad (3.3 A-4)$$

leads to very accurate values for the energy level of nearly all the molecules and only for a few molecules it is necessary to consider further improvements. This function has a minimum value of zero at $r = r_e$ and approaches a finite value for a large value of r . At $r = 0$, $U(r)$ is infinite, whereas Morse function is finite at all other values of r . The very large value of Morse function at $r = 0$ does not create any serious problem.

Lumping together Eqs.(3.3 A-3) and (3.3 A-4) we get

$$\frac{d^2\Psi}{dr^2} + \left[-\frac{J(J+1)}{r^2} + \frac{8\pi^2\mu}{h^2} \{E - D - De^{-2a(r-r_e)} + 2De^{-a(r-r_e)}\} \right] \Psi = 0 \quad (3.3 A-5)$$

Substituting $z = e^{-a(r-r_e)}$ and $\lambda = \frac{h^2}{8\pi^2\mu r_e^2} J(J+1)$ into Eq. (3.3 A-5), we obtain

$$\frac{d^2\Psi}{dz^2} + \frac{1}{z} \frac{d\Psi}{dz} + \frac{8\pi^2\mu}{a^2 h^2} \left[\frac{E-D}{z^2} + \frac{2D}{z} - D - \frac{\lambda r_e^2}{z^2 r^2} \right] \Psi = 0 \quad (3.3 A-6)$$

Now the quantity $\frac{r_e^2}{r^2}$ can be expressed in terms of z as

$$z = e^{-a(r-r_e)}$$

$$\ln z = -ar + ar_e$$

or

$$\frac{\ln z}{+ar_e} = -\frac{r}{r_e} + 1$$

or

$$\frac{r}{r_e} = \left(1 - \frac{\ln z}{ar_e} \right)$$

or

$$\frac{r_e^2}{r^2} = \frac{1}{\left(1 - \frac{\ln z}{ar_e} \right)^2}$$

or

$$\frac{r_e^2}{r^2} = 1 + \frac{2}{ar_e} (z-1) + \left(-\frac{1}{ar_e} + \frac{3}{a^2 r_e^2} \right) (z-1)^2 + \dots \quad (3.3 A-7)$$

Substituting the first three terms of the Taylor expansion into Eq. (3.3.A-6) we obtain

$$\frac{d^2\Psi}{dz^2} + \frac{1}{z} \frac{d\Psi}{dz} + \frac{8\pi^2\mu}{a^2h^2} \left(\frac{E-D-C_0}{z^2} + \frac{2D-C_1}{z} - D-C_2 \right) \Psi = 0 \quad (3.3 A-8)$$

Here

$$C_0 = \lambda \left(1 - \frac{3}{ar_e} + \frac{3}{a^2r_e^2} \right)$$

$$C_1 = \lambda \left(\frac{4}{ar_e} - \frac{6}{a^2r_e^2} \right) \quad (3.3 A-9)$$

$$C_2 = \lambda \left(-\frac{1}{ar_e} + \frac{3}{a^2r_e^2} \right)$$

Making the further substitutions:

$$\Psi(z) = e^{-y/2} y^{b/2} L(y)$$

where

$$y = 2 dz$$

$$d^2 = \frac{8\pi^2\mu}{a^2h^2} (D + C_2) \quad (3.3 A-10)$$

$$b^2 = -\frac{32\pi^2\mu}{a^2h^2} (E - D - C_0)$$

and proceeding as follows:

$$\Psi(z) = e^{-dz} (2d)^{b/2} z^{b/2} L(z)$$

$$\begin{aligned} \frac{d\Psi}{dz} &= \left[e^{-dz} \frac{d}{dz} \{ (2d)^{b/2} z^{b/2} L(z) \} \right] + \left[(2d)^{b/2} y^{b/2} L(z) \right] \frac{d}{dz} e^{-dz} \\ &= (e^{-dz} (2d)^{b/2} z^{b/2}) \left[\frac{dL}{dz} + \frac{b}{2} z^{-1} L(z) - dL(z) \right] \end{aligned}$$

or

$$\frac{d\Psi}{dz} = \{ (2d)^{b/2} e^{-dz} z^{b/2} \} \left[\frac{dL}{dz} + \left(\frac{b}{2} z^{-1} - d \right) L(z) \right] \quad (3.3 A-11)$$

$$\frac{d^2\Psi}{dz^2} = (2d)^{b/2} [\{ e^{-dz} z^{b/2} \} \frac{d}{dz} \left[\frac{dL}{dz} + \left(\frac{b}{2} z^{-1} - d \right) L(z) \right] + \left[\frac{dL}{dz} + \left(\frac{b}{2} z^{-1} - d \right) L(z) \right] \cdot \frac{d}{dz} (e^{-dz} z^{b/2})]$$

or finally

$$\frac{d^2\Psi}{dz^2} = [(2d)^{b/2} e^{-dz} z^{b/2}] \left[\frac{d^2L}{dz^2} + (bz^{-1} - 2d) \frac{dL}{dz} + \left[\frac{b}{2} \left(\frac{b}{2} - 1 \right) z^{-2} - b dz^{-1} + d^2 \right] L(z) \right] \quad (3.3 A-12)$$

The first term of Eq. (3.3 A-8), i.e.

$$\begin{aligned} \frac{d^2\Psi}{dz^2} + \frac{1}{z} \frac{d\Psi}{dz} &= [(2d)^{b/2} e^{-dz} z^{b/2}] \left[\frac{d^2L}{dz^2} + (b+1)z^{-1} - 2d \right] \frac{dL}{dz} \\ &\quad + \left[\frac{b^2}{4} z^{-2} - (b+1)dz^{-1} + d^2 \right] L(z) \end{aligned} \quad (3.3 A-13)$$

and the second term of Eq. (3.3 A-8), i.e.

$$\begin{aligned} \frac{8\pi^2\mu}{a^2h^2} \left[\frac{E-D-C_0}{z^2} + \frac{2D-C_1}{z} - (D+C_2) \right] e^{-z/2} z^{b/2} L(z) \\ &= \frac{8\pi^2\mu}{a^2h^2} [e^{-dz} (2d)^{b/2} z^{b/2}] \left[-\frac{b^2 a^2 h^2}{32\pi^2\mu} \frac{1}{z^2} + \frac{2D-C_1}{z} - \frac{d^2 a^2 h^2}{8\pi^2\mu} \right] L(z) \\ &= [e^{-dz} (2d)^{b/2} z^{b/2}] \left[-\frac{b^2}{4z^2} + \frac{8\pi^2\mu(2D-C_1)}{a^2h^2z} - d^2 \right] L(z) \end{aligned} \quad (3.3 A-14)$$

Finally the sum of the Eqs. (3.3 A-13) and (3.3 A-14) yields

$$\frac{d^2L}{dz^2} + [(b+1)z^{-1} - 2d] \frac{dL}{dz} + \left[-(b+1)dz^{-1} + \frac{8\pi^2\mu(2D-C_1)}{a^2h^2z} \right] L(z) = 0$$

or

$$\frac{d^2L}{dz^2} + [(b+1)z^{-1} - 2d] \frac{dL}{dz} + \left[\frac{8\pi^2\mu(2D-C_1)}{a^2h^2z} - (b+1)dz^{-1} \right] L(z) = 0 \quad (3.3 A-15)$$

Now

$$y = 2dz \text{ or } z^{-1} = 2d/y,$$

$$dy = 2d \, dz \text{ or } dz = dy/2d; \quad \frac{dL}{dz} = \frac{1}{2d} \cdot \frac{dL}{dy}$$

and

$$dz^2 = \frac{dy^2}{4d^2}$$

So Eq. (3.3 A-15) becomes

$$4d^2 \frac{d^2L}{dy^2} = \left[\frac{(b+1)2d}{y} - 2d \right] 2d \cdot \frac{dL}{dy} + \left[\frac{8\pi^2\mu(2D-C_1)2d}{a^2h^2y} - (b+1)d \cdot \frac{2d}{y} \right] L(y) = 0$$

or

$$\frac{d^2L}{dy^2} + \left[\frac{(b+1)}{y} - 1 \right] \frac{dL}{dy} + \frac{1}{y} \left[\frac{4\pi^2\mu(2D-C_1)}{a^2h^2d} - \frac{1}{2}(b+1) \right] L(y) = 0$$

or finally

$$\frac{d^2L}{dy^2} + \left[\frac{(b+1)}{y} - 1 \right] \frac{dL}{dy} + \frac{V}{y} L(y) = 0 \quad (3.3 A-15a)$$

in which

$$V = \frac{4\pi^2\mu}{a^2h^2d} (2D-C_1) - \frac{1}{2}(b+1) \quad (3.3 A-16)$$

We now try a power series solution of the form

$$L(y) = \sum_{v=0}^{\infty} a_v y^v = a_0 y^0 + a_1 y^1 + a_2 y^2 + a_3 y^3 + \dots$$

$$L'(y) = a_1 + 2a_2 y + 3a_3 y^2 + \dots$$

and

$$L''(y) = 2a_2 + 3 \cdot 2a_3 y + \dots$$

Substituting these values of $L(y)$, $L'(y)$ and $L''(y)$ into Eq.(3.3 A-15a) and arranging the coefficients of y in the ascending order we get

$$[(b+1) a_1 + V a_0] y^{-1} + [2a_2 + 2(b+1) a_2 + V a_1 - a_1] y^0 + [3 \cdot 2 a_3 + 3(b+1) a_3 + V a_2 - 2a_2] y^1 = 0$$

For $L(y)$ to be the solution of Eq (3.3 A-15a) the series will vanish for all values of y provided the coefficients of individual powers of y also vanish separately, i.e.

$$\begin{aligned} y^{-1}: & \quad 1 a_1 (b+1) + a_0 V = 0 \\ y^0: & \quad 2 a_2 (b+1+1) + a_1 (V-1) = 0 \\ y^1: & \quad 3 a_3 (b+1+2) + a_2 (V-2) = 0 \end{aligned}$$

$$(v+1) a_{v+1} (b+1+v) + a_v (V-v) = 0$$

or

$$\frac{a_{v+1}}{a_v} = \frac{v-V}{(v+1)(v+1+b)} \quad (3.3 A-17)$$

Further, $L(y)$ to be a polynomial, the series $L(y)$ must terminate after a finite number of terms which is possible only if

$$v-V=0 \text{ or } v=V, \text{ i.e } V=0, 1, 2, 3, \dots$$

The solutions for V integral satisfy the boundary conditions when $L \rightarrow 0$ as $r \rightarrow -\infty$ instead of as $r \rightarrow 0$. Further in order to obtain E from Eq (3.3 A-16), we proceed as follows:

$$b = \frac{8\pi^2\mu}{a^2h^2d}(2D - C_1) - 2V - 1 = \frac{16\pi^2\mu}{a^2h^2d}\left(D - \frac{C_1}{2}\right) - 2\left(V + \frac{1}{2}\right)$$

or

$$b^2 = \left(\frac{16\pi^2\mu}{a^2h^2d}\right)^2\left(D - \frac{C_1}{2}\right)^2 + 4\left(V + \frac{1}{2}\right)^2 - \frac{64\pi^2\mu}{a^2h^2d}\left(D - \frac{C_1}{2}\right)\left(V + \frac{1}{2}\right) \quad (3.3 A-18)$$

Substituting the value of b^2 into Eq.(3.3 A-16) and simplifying the resultant equation, we get

$$-\frac{32\pi^2\mu}{a^2h^2}(E - D - C_0) = \left(\frac{16\pi^2\mu}{a^2h^2d}\right)^2\left(D - \frac{C_1}{2}\right)^2 + 4\left(V + \frac{1}{2}\right)^2 - \frac{64\pi^2\mu}{a^2h^2d}\left(D - \frac{C_1}{2}\right)\left(V + \frac{1}{2}\right)$$

or

$$E = D + C_0 - \frac{8\pi^2\mu}{a^2h^2d^2}\left(D - \frac{C_1}{2}\right)^2 - \frac{a^2h^2}{8\pi^2\mu}\left(V + \frac{1}{2}\right)^2 + \frac{2}{d}\left(D - \frac{C_1}{2}\right)\left(V + \frac{1}{2}\right) \quad (3.3 A-19)$$

Further substituting the values of d , we obtain:

$$E = D + C_0 - \frac{8\pi^2\mu}{a^2h^2}\left(\frac{a^2h^2}{8\pi^2\mu}\right)\left(\frac{D - \frac{C_1}{2}}{(D + C_2)}\right)^2 - \frac{a^2h^2}{8\pi^2\mu}\left(V + \frac{1}{2}\right)^2 + \left(\frac{ah}{\pi}\right)\frac{1}{\sqrt{2\mu}}\frac{\left(D - \frac{C_1}{2}\right)\left(V + \frac{1}{2}\right)}{\sqrt{D + C_2}}$$

or

$$E = D + C_0 - \frac{\left(D - \frac{C_1}{2}\right)^2}{(D + C_2)} + \left(\frac{ah}{\pi}\right)\frac{1}{\sqrt{2\mu}}\frac{\left(D - \frac{C_1}{2}\right)\left(V + \frac{1}{2}\right)}{\sqrt{D + C_2}} - \frac{a^2h^2}{8\pi^2\mu}\left(V + \frac{1}{2}\right)^2 \quad (3.3 A-20)$$

Further simplification is carried out by expanding in terms of power series of $\frac{C_1}{D}$ and $\frac{C_2}{D}$ and substituting the values of the parameters C_0 , C_1 and C_2 in the resultant equation, i.e.

$$\begin{aligned} \frac{\left(D - \frac{C_1}{2}\right)^2}{(D + C_2)} &= D \left[1 - \frac{C_1}{2D}\right]^2 \left[1 + \frac{C_2}{D}\right]^{-1} \\ &= D \left[1 + \frac{C_1^2}{4D^2} - \frac{C_1}{D}\right] \left[1 - \frac{C_2}{D} + \frac{C_2^2}{D^2} - \dots\right] \\ &= D \left[1 - \frac{C_2}{D} + \frac{C_2^2}{D^2} + \frac{C_1^2}{4D^2} + \frac{C_1C_2}{D^2} - \frac{C_1}{D} + \dots\right] \end{aligned}$$

Neglecting the higher terms in C_1 and C_2 ,

$$\begin{aligned} &= D \left[1 - \frac{1}{D}(C_1 + C_2)\right] + \frac{1}{D^2} \left[\frac{C_1^2}{4} + C_2^2 + C_1C_2 + \dots\right] \\ &= D - (C_1 + C_2) + \frac{1}{D} \left[\frac{C_1^2}{4} + C_2^2 + C_1C_2 + \dots\right] \\ &= D - \lambda \left(\frac{4}{ar_e} - \frac{6}{a^2r_e^2} - \frac{1}{ar_e} + \frac{3}{a^2r_e^2}\right) + \frac{\lambda^2}{D} \left(\frac{4}{a^2r_e^2} + \frac{1}{a^2r_e^2} - \frac{4}{a^2r_e^2}\right), \end{aligned}$$

the cube and higher terms in ar_e are ignored,

$$= D - \lambda \left(\frac{3}{ar_e} - \frac{3}{a^2r_e^2}\right) + \frac{\lambda^2}{D} \frac{1}{a^2r_e^2}$$

and

$$C_0 = \lambda \left(1 - \frac{3}{ar_e} + \frac{3}{a^2r_e^2}\right)$$

So the sum of the first three terms of the Eq. (3.3 A-20) is

$$D + C_0 - \frac{\left(D - \frac{C_1}{2}\right)^2}{(D + C_2)} = D + \lambda \left(1 - \frac{3}{ar_e} + \frac{3}{a^2r_e^2}\right) - D + \lambda \left(\frac{3}{ar_e} - \frac{3}{a^2r_e^2}\right) - \frac{\lambda^2}{Da^2r_e^2}$$

$$\begin{aligned}
&= \lambda - \frac{\lambda^2}{Da^2r_e^2} = J(J+1) \frac{h^2}{8\pi^2\mu r_e^2} - \frac{J^2(J+1)^2}{Da^2r_e^2} \left(\frac{h^2}{8\pi^2\mu r_e^2} \right)^2 \\
&= J(J+1)B_e h c - \frac{J^2(J+1)^2}{Dr_e^2} \left(\frac{h^2}{8\pi^2\mu r_e^2} \right)^2 \left(\frac{2D}{4\pi^2c^2\mu\omega_e^2} \right) \\
&= J(J+1)B_e h c - J^2(J+1)^2 h c \left(\frac{h^3}{128\pi^6\mu^3c^3\omega_e^2r_e^6} \right) \\
&= hcB_eJ(J+1) - hcD_eJ^2(J+1)^2
\end{aligned} \tag{3.3 A-21}$$

where $B_e = \frac{h}{8\pi^2I(=\mu r_e^2)_C}$ and $D_e = \frac{h^3}{128\pi^6\mu^3\omega_e^2c^3r_e^6}$

$$\frac{\left(D - \frac{C_1}{2}\right)}{(D+C_2)^{\frac{1}{2}}} = \frac{D\left(1 - \frac{C_1}{2D}\right)}{\sqrt{D}\left(1 + \frac{C_2}{D}\right)^{\frac{1}{2}}} = \sqrt{D} \left(1 - \frac{C_1}{2D}\right) \left(1 - \frac{C_2}{2D}\right) = \sqrt{D} \left[1 - \frac{1}{2D}(C_1+C_2) + \dots\right]$$

[Squares and higher terms in C_1 and C_2 are ignored.]

$$\begin{aligned}
\frac{\left(D - \frac{C_1}{2}\right)}{(D+C_2)^{\frac{1}{2}}} &= \sqrt{D} \left[1 - \frac{\lambda}{2D} \left(\frac{4}{ar_e} - \frac{6}{a^2r_e^2} - \frac{1}{ar_e} + \frac{3}{a^2r_e^2} \right) \right] = \sqrt{D} \left[1 - \frac{\lambda}{2D} \left(\frac{3}{ar_e} - \frac{3}{a^2r_e^2} \right) \right] \\
&= \sqrt{D} - \frac{3\lambda}{2\sqrt{D}} \left(\frac{1}{ar_e} - \frac{1}{a^2r_e^2} \right) = \sqrt{D} - \frac{3J(J+1)}{2\sqrt{D}} \left(\frac{h^2}{8\pi^2\mu r_e^2} \right) \left(\frac{1}{ar_e} - \frac{1}{a^2r_e^2} \right)
\end{aligned}$$

Accordingly the fourth term of Eq. (3.3 A-20) yields

$$\begin{aligned}
\frac{ah}{\pi\sqrt{2\mu}} \frac{\left(D - \frac{C_1}{2}\right)}{\sqrt{D+C_2}} \left(V + \frac{1}{2}\right) &= \frac{ah}{\pi\sqrt{2\mu}} \left(V + \frac{1}{2}\right) \left[\sqrt{D} - \frac{3J(J+1)}{2\sqrt{D}} \left(\frac{h^2}{8\pi^2\mu r_e^2} \right) \left(\frac{1}{ar_e} - \frac{1}{a^2r_e^2} \right) \right] \\
&= \frac{ah\sqrt{D}}{\pi\sqrt{2\mu}} \left(V + \frac{1}{2}\right) - \frac{3J(J+1)}{2\sqrt{D}} \left(\frac{ah^3}{8\pi^3\mu r_e^2} \right) \frac{1}{\sqrt{2\mu}} \left(\frac{1}{ar_e} - \frac{1}{a^2r_e^2} \right) \left(V + \frac{1}{2}\right) \\
&= \left(\frac{ah}{\pi\sqrt{2\mu}} \right) \left(\frac{2\pi c\omega_e\sqrt{\mu}}{a\sqrt{2}} \right) \left(V + \frac{1}{2}\right) - \frac{3h^3J(J+1)}{16\pi^3\mu r_e^2\sqrt{D}} \left(\frac{2\pi c\omega_e\sqrt{2\mu}}{\sqrt{2D}} \right) \frac{1}{\sqrt{2\mu}} \left(\frac{1}{ar_e} - \frac{1}{a^2r_e^2} \right) \left(V + \frac{1}{2}\right) \\
&= hc\omega_e(V+1/2) - \alpha_e hcJ(J+1)(V+1/2)
\end{aligned} \tag{3.3 A-22}$$

where

$$\omega_e = \frac{a}{2\pi c} \sqrt{\frac{2D}{\mu}} \quad \text{and} \quad \alpha_e = \frac{3h^2\omega_e}{16\pi^2\mu r_e^2 D} \left(\frac{1}{ar_e} - \frac{1}{a^2r_e^2} \right)$$

The fifth term of Eq.(3.3 A-20) yields

$$\begin{aligned}
-\frac{a^2h^2}{8\pi^2\mu} \left(V + \frac{1}{2}\right)^2 &= - \left(\frac{4\pi^2c^2\omega_e^2\mu}{2D} \right) \left(\frac{h^2}{8\pi^2\mu} \right) \left(V + \frac{1}{2}\right)^2 \\
&= - \left(\frac{4\pi^2c^2\omega_e^2\mu}{2} \right) \left(\frac{h^2}{8\pi^2\mu} \right) \left(\frac{4x_e}{h\omega_e c} \right) \left(V + \frac{1}{2}\right)^2 \\
&= -hc\omega_e x_e (V+1/2)^2
\end{aligned} \tag{3.3 A-23}$$

Lumping together Eqs' (3.3 A-20), (3.3 A-21), (3.3 A-22) and (3.3 A-23) we obtain

$$E_{v,J} = hc\omega_e \left(V + \frac{1}{2}\right) - hc\omega_e x_e (V+1/2)^2 + hcJ(J+1)B_e - hcD_eJ^2(J+1)^2 - hc\alpha_e (V+1/2)J(J+1) \tag{3.3 A-24a}$$

or rotational–vibrational term will be

$$T_{V,J} = \frac{E_{V,J}}{hc} = \omega_e \left(V + \frac{1}{2} \right) - \omega_e x_e (V + 1/2)^2 + J(J+1)B_e - D_e J^2 (J+1)^2 - \alpha_e (V + 1/2)J(J+1) \quad (3.3 \text{ A-24b})$$

which is the equation for the rotational-vibration energy levels of a diatomic molecule.

Thus from Eq. (3.3 A-24b) we can also write the expression for the rotational terms for the nonrigid rotator as

$$F_J(\text{cm}^{-1}) = \frac{E_J}{hc} = B_e J(J+1) - D_e J^2 (J+1)^2 - \alpha_e (V + 1/2)J(J+1) \quad (3.3 \text{ A-25})$$

APPENDIX 3.4 A: MOLECULAR CONSTANTS OF DIATOMIC MOLECULES

Molecule	ω_e , (cm ⁻¹)	$x_e \times 10^3$	B_e , (cm ⁻¹)	r_e , Å	D_{298} , kJ mole ⁻¹
Br ₂	325.3	3.31	0.0821	2.28	192.9
BrCl	444.27	4.15	0.152	2.13	215.0
Cl ₂	559.75	4.81	0.244	1.987	242.3
ClF	786.15	7.84	0.516	1.63	252.5
CO	2169.81	6.11	1.931	1.128	1075.0
DF	2998.19	15.3	11.00	0.818	273.2
DI	1639.6	12.1	32.84	1.61	298.5
F ₂	917.55	12.9	0.89	1.41	159.0
FO	1060	14.6	1.104	1.32	215.7
H ₂	4400.4	27.4	60.86	0.741	435.9
HBr	2648.97	17.1	8.465	1.414	366.5
HCl	2990.9	17.65	10.59	1.274	431.4
HF	4138.7	21.7	20.95	0.917	566.1
HI	2309.01	17.2	65.11	1.61	298.4
I ₂	214.55	2.87	0.037	2.66	151.0
IO	681.47	6.3	0.340	1.868	222.0
K ₂	92.96	3.82	0.056	3.92	53.14
N ₂	2358.03	6.00	1.998	1.098	945.6
NO	1904.4	7.45	1.704	1.151	631.0
O ₂	1580.19	0.76	1.445	1.207	498.7
OH	3737.9	29.7	18.895	0.969	428.0
P ₂	780.69	3.61	0.303	1.893	489.1

ω_e = Intrinsic wave number; x_e = anharmonic constant; B_e = rotational constants; r_e = equilibrium internuclear distance; D_{298} = dissociation energy.

APPENDIX 3.5 A: RECIPROCAL TABLE FOR THE CONVERSION OF MICRONS (μ) TO WAVE NUMBERS (CM⁻¹)

λ , μ	$\bar{\nu}$, cm ⁻¹	λ , μ	$\bar{\nu}$, cm ⁻¹	λ , μ	$\bar{\nu}$, cm ⁻¹	λ , μ	$\bar{\nu}$, cm ⁻¹
2.50	4000	2.74	3649	2.98	3355	3.44	2906
2.51	3984	2.75	3636	2.99	3344	3.46	2890
2.52	3968	2.76	3623	3.00	3333	3.48	2873
2.53	3952	2.77	3610	3.02	3311	3.50	2857

(Continued)

Reciprocal table for the conversion of microns (m) to wave numbers (cm^{-1})—Cont'd.

2.54	3937	2.78	3597	3.04	3289	3.52	2841
2.55	3921	2.79	3584	3.06	3267	3.54	2824
2.56	3906	2.80	3571	3.08	3246	3.56	2809
2.57	3891	2.81	3558	3.10	3225	3.58	2793
2.58	3875	2.82	3546	3.12	3205	3.60	2778
2.59	3861	2.83	3533	3.14	3184	3.62	2762
2.60	3846	2.84	3521	3.16	3164	3.64	2747
2.61	3831	2.85	3508	3.18	3144	3.66	2732
2.62	3816	2.86	3496	3.20	3135	3.68	2717
2.63	3802	2.87	3484	3.22	3105	3.70	2703
2.64	3788	2.88	3472	3.24	3086	3.72	2688
2.65	3773	2.89	3460	3.26	3067	3.74	2674
2.66	3759	2.90	3448	3.28	3048	3.76	2660
2.67	3745	2.91	3436	3.30	3030	3.78	2646
2.68	3731	2.92	3424	3.32	3012	3.80	2632
2.69	3717	2.93	3412	3.34	2994	3.82	2618
2.70	3703	2.94	3401	3.36	2976	3.84	2604
2.71	3690	2.95	3389	3.38	2958	3.86	2591
2.72	3676	2.96	3378	3.40	2941	3.88	2577
2.73	3663	2.97	3367	3.42	2923	3.90	2564
3.92	2551	4.84	2066	6.00	1667	8.40	1190
3.94	2538	4.88	2049	6.10	1639	8.50	1176
3.96	2525	4.92	2033	6.20	1613	8.60	1162
3.98	2513	4.96	2016	6.30	1587	8.70	1149
4.00	2500	5.00	2000	6.40	1563	8.80	1136
4.04	2475	5.05	1980	6.50	1538	8.90	1124
4.08	2451	5.10	1960	6.60	1515	9.00	1111
4.12	2427	5.15	1942	6.70	1492	9.10	1099
4.16	2404	5.20	1923	6.80	1471	9.20	1087
4.20	2381	5.25	1905	6.90	1449	9.30	1075
4.24	2358	5.30	1887	7.00	1429	9.40	1064
4.28	2336	5.35	1869	7.10	1408	9.50	1052
4.32	2314	5.40	1851	7.20	1389	9.60	1042
4.36	2293	5.45	1835	7.30	1370	9.70	1031
4.40	2273	5.50	1818	7.40	1351	9.80	1020
4.44	2252	5.55	1802	7.50	1333	9.90	1010
4.48	2232	5.60	1876	7.60	1316	10.00	1000
4.52	2212	5.65	1770	7.70	1299	10.20	980
4.56	2193	5.70	1754	7.80	1282	10.40	962
4.60	2174	5.75	1739	7.90	1266	10.60	943
4.64	2155	5.80	1724	8.00	1250	10.80	926
4.68	2137	5.85	1709	8.10	1235	11.0	909
4.72	2119	5.90	1695	8.20	1220	11.20	893
4.76	2101	5.95	1681	8.30	1205	11.40	877

λ, μ	$\bar{\nu}, \text{cm}^{-1}$	λ, μ	$\bar{\nu}, \text{cm}^{-1}$	λ, μ	$\bar{\nu}, \text{cm}^{-1}$	λ, μ	$\bar{\nu}, \text{cm}^{-1}$
11.60	862	13.40	746	16.60	602	21.00	476
11.80	847	13.80	725	17.00	588	22.00	455
12.00	833	14.20	704	17.50	571	23.00	435
12.20	820	14.60	685	18.00	556	24.00	417
12.40	806	15.00	666	18.50	541	25.00	400
12.60	794	15.40	649	19.00	526	26.00	385
12.80	781	15.80	633	19.50	513	27.00	370
13.00	769	16.20	617	20.00	500	28.00	357

APPENDIX 3.6 A: PROGRAM IN C++ FOR THE COMPUTATION OF STATISTICAL THERMODYNAMIC FUNCTIONS FROM SPECTROSCOPIC DATA

Developed by Hardeep Kaur Randhawa, Department of Computer Science and Applications KMV, Jalandhar

program name : Randhawa.cpp
purpose : program to compute statistical thermodynamic functions from spectroscopic data.

```
//Define directives
#include <iostream.h>
#include <iomanip.h>
#include <string.h>
#include <process.h>
#include <math.h>
#include <conio.h>
#include <stdio.h>
#include <dos.h>
#define H 6.625600E-27
#define VL 2.997925E+10
#define R 1.987170
#define AK 1.380540E-16
#define CTR 7.2810
#define CTS 2.313
#define CROL 175.683
#define CROLS 177.67
#define CRONL 264.559
#define CRONLS 267.54
int i,j;
istream &bottom(istream &stream);
void eins(int m,float cons,int i,double *,double *,double *,double
*,double *,double *);
void fun(int i);

//output manipulator which specify float(fixed) format.
ostream &for2(ostream &stream)
{
    stream.setf(ios::fixed);
    stream.width(11);
    stream.precision(6);
    stream.setf(ios::showpoint);
    return stream;
}
```

```

//output manipulator which specify integer format.
ostream &for3(ostream &stream)
{
    stream.width(4);
    stream.setf(ios::left);
    return stream;
}

//Manipulator to press any key to continue.
istream &bottom(istream &stream)
{
    cout<<"\nPress any key to continue :\n\n";
    getch();
    return (stream);
}

//Manipulator to produce a sound and wait.
ostream &beep(ostream &stream)
{
    cout<<'\\a';           //produces a sound
    delay(500);           //waits for 500 milliseconds
    cout<<'\\a';
    return (stream);
}

//Manipulator to clear the screen.
ostream &clear(ostream &stream)
{
    clrscr();
    return (stream);
}

//This creates the class out1
class out1
{
    int x1,y1;
public:
    out1(int i,int j){x1=i;y1=j;}    //Constructing out1
    ~out1(){ }                       //Destructing out1
    friend ostream &operator<<(ostream &stream,out1 ol);
};

//This creates the class out2
class out2
{
    int x2,x3;
public:
    out2(int k2,int k3) {x2=k2;x3=k3;}    //Constructing out2
    ~out2(){ }                           //Destructing out2
    friend ostream &operator<<(ostream &stream,out2 o2);
};

//This creates the class init
class init
{
    double x;
public:
    init(){x=0.0;}                    //Constructing init
    ~init(){ }                        //Destructing init
    double getx(){return x;}
};

//This creates the class ln1
class ln1
{

```

```

int nta,q,noa;
char nom[20];
double mi,xyz[6];
protected:
    int na[10],m,1,11,p,atom;
    float am[10];
    double ai;
public:
    void setdatal();
    void displayl();
    void lin_nlin();
    void ainer();
};
//Defines a derived class data from lnl.
class data:public lnl
{
int n;
float cons, htv[30], gtv[30], cpv[30], sv[30], htro[30], cpro[30],
gtro[30], sro[30], httr[30], cptr[30], gttr[30], str[30], ht[30],
cp[30], gt[30], s[30], optr[30], op[30];
double wm, sigma, t[30], w[30], eh[30], ecp[30], eg[30], es[30];
public:
    data(){};
    friend ostream &operator<<(ostream &stream,data o);
    friend istream &operator>>(istream &stream,data &o);
    void cal();
    void output();
};
//Display *-----*-----*----- and so on.
ostream &operator<<(ostream &stream,outl ol)
{
    register i,j;
    stream<<"\n";
    for(j=1;j<=ol.yl;j++)
    {
        stream<<"*";
        for(i=0;i<ol.xl;i++)
            stream<<"-";
    }
    stream<<"*"<<"\n";
    return stream;
}
//Display some spaces,one * and again some spaces i.e. " * ".
ostream &operator<<(ostream &stream,out2 o2)
{
    register k2,k3;
    for(k2=1;k2<=o2.x2;k2++)
        stream<<" ";
    stream<<"*";
    for(k3=1;k3<=o2.x3;k3++)
        stream<<" ";
    return stream;
}
/*Input name of the molecule, nature of the molecule, type of atoms,
no. of atoms of the same kind, the atomic mass of the respective atoms,
and moment of inertia. */
void lnl:: setdatal()
{
    cout<<"Enter name of the molecule(nom) : ";
    cin>>nom;
    cout<<"\nEnter the nature of the molecule(1) (linear-1, non_

```



```

linear-2): ";
cin>>l;
cout<<"\nEnter the type of atoms in the molecule(atom): ";
cin>>atom;
cout<<"\nEnter the number of atoms of the same kind and their \n"
<<" respective atomic mass (na[],am[])\n";
for(p=1;p<=atom;p++)
{
    cout<<"na["<<p<<" ] = ";
    cin>>na[p];
    cout<<"am["<<p<<" ] = ";
    cin>>am[p];
}
cout<<"\nEnter the value of moment of inertia (mi) (scientific):";
cin>>mi;
if(mi==0)
{
    cout<<"\nEnter the number of axis (noa) : ";
    cin>>noa;
    cout<<"\nEnter the values of the moments of inertia along";
    <<noa<<" axis(xyz[])(scientific) :\n";
    for(q=1; q<=noa; q++)
    {
        cout<<"xyz["<<q<<" ] = ";
        cin>>xyz[q];
    }
}
}
//Function to check whether the molecule is linear or non_linear.

void lnl::lin_nlin()
{
    nta=0;
    for(p=1; p<=atom; p++)
        nta=nta+ *(na+p);
    l1=1-1;
    if(l1==0)
    { m=3*nta-5;
      cout<<"\nThe molecule is linear and has "<<m
        <<" vibrational frequency points.\n";
    }
    else
    { if(l1 < 0)
      {
        cout<<"\nThere is some error in the program.\n";
        cout<<"\nPress any key to exit.";
        getche();
        exit(0);
      }
      else
      {
        m=3*nta-6;
        cout<<"\nThe molecule is non-linear and has "<<m
          <<" vibrational frequency points.\n";
      }
    }
    cin>>bottom;
}
//Function to calculate log(moment of inertia).
void lnl :: ainer()
{

```

```

if(mi==0)
{
    ai=0.0;
    for(q=1; q<=noa; q++)
        ai=ai+log(*(xyz+q));
}
else
    ai=log(mi);
}
/*Function to display name of the molecule, number of atoms of
the same type, atomic mass of the respective atoms and moment of
inertia. */
void lnl :: displayl()
{
    cout<<"\nThe name of the molecule is : "<<nom;
    cout<<"\n\nThe number of atoms and the atomic mass of the
    respective"
    << "atoms are : "<<"\n\n";
    for(p=1; p<=atom; p++)
        cout<<for3<<na[p]<<for2<<am[p]<<"\n";
    cout.setf(ios::scientific);
    cout<<"\nMoment of inertia = "<<mi;
    if(mi==0)
    {
        cout<<"\n\nMoments of inertia along "<<noa<<" axis are :\n";
        for(q=1; q<=noa; q++)
            cout<<xyz[q]<<"\n";
    }
    cout<<"\n\nlog(moment of interia) = "<<for2<<ai<<"\n";
}

//Input symmetry number, fundamental vibrational frequencies,
total //no. of temperatures and the values of the five initial
temperatures.
istream &operator>>(istream &stream,data &o)
{
    cout<<"\nEnter the symmetry number (sigma) : ";
    stream>>o.sigma;
    <prog>cout<<"\nEnter the values of the fundamental vibrational
    frequencies"
    <<"(w[]) : "<<"\n" ;
    for(j=1;j<=o.m;j++)
    {
        cout<<"w["<<j<<"] = " ;
        stream>>o.w[j];
    }
    cout<<"\nEnter the total number of temperatures(n:5 - 27): ";
    stream>>o.n;
    cout<<"\n\nEnter the values of the five initial temperatures {t [
    ]} : \n";
    for(i=1;i<=5;i++)
    {
        cout<<"t["<<i<<"] = ";
        stream>>o.t[i];
    }
    cout<<beep;
    return stream;
}
/*Display the symmetry no.,no. of vibrational frequencies and the
values of the fundamental vibrational frequencies, total no. of
temperatures and the values of the five initial temperatures.

```

```

ostream &operator<<(ostream &stream,data o)
{
    stream<<clear;
    stream<<"\n\nThe value of sigma is : "<<for2<<o .sigma<<"\n\n";
    stream<<"The no. of vibrational frequencies is : "<<for3<<o.m<<"\n\n";
    stream<<"The fundamental vibrational frequencies are : "<<"\n\n";
    for(j=1;j<=o.m;j++)
    stream<<setw(11)<<setprecision(4)<<setiosflags(ios::fixed)
        <<setiosflags(ios::left)<<setiosflags(ios::showpoint)<<o.w[j];
    stream<<"\n\nTotal no. of temperatures is : "<<for3<<o.n<<"\n\n";
    stream<<"Five initial temperatures are : "<<"\n\n";
    for(i=1;i<=5;i++)
    stream<<for2<<o.t[i];
    stream<<"\n";
    return stream;
}
//Function to calculate contributions of various degrees of freedom to
//the thermodynamic functions and the total thermodynamic functions.
void data::cal()
{
    double x,x1,x2,he,cpe,ge,se;int k;
    wm=0.0;
    for(p=1; p<=atom; p++)
    wm=wm+ *(na+p)* *(am+p);
    cons=H*VL/AK;
    for(i=1;i<=n;i++)
    {
        if(i-5 >0)
        *(t+i) = *(t+i-1)+100;
        *(httr+i) = 2.5*R;
        *(cptr+i) = 2.5*R;
        *(gttr+i) = -1.5*R*log(wm)-2.5*R*log(*(t+i))+CTR;
        *(str+i) = 1.5*R*log(wm)+2.5*R*log(*(t+i))-CTS;
        if(11==0)
        {
            *(htro+i) = R;
            *(cpro+i) = R;
            *(gtro+i) = -R*ai-R*log(*(t+i))+R*log(sigma)-CROL;
            *(sro+i) = R*ai+R*log(*(t+i))-R*log(sigma)+CR0LS;
        }
    }
    else
    {
        if (11>0)
        {
            *(htro+i) = 1.5*R;
            *(cpro+i) = 1.5*R;
            *(gtro+i) = R*log(sigma)-0.5*R*ai-1.5*R*log(*(t+i))-CRONL;
            *(sro+i) = -R*log(sigma)+0.5*R*ai+1.5*R*log(*(t+i))+CRONLS;
        }
    }
    else
    { cout<<"error\n"; exit(0); }
}
eins(m,cons,i,t,w,eh,ecp,eg,es);
*(htv+i)=R* *(eh+i);
*(gtv+i)=R* *(eg+i);
*(cpv+i)=R* *(ecp+i);
*(sv+i) =R* *(es+i);
*(ht+i) = *(httr+i)+ *(htro+i) + *(htv+i);
*(cp+i) = *(cptr+i)+ *(cpro+i) + *(cpv+i);
*(gt+i) = *(gttr+i)+ *(gtro+i) + *(gtv+i);

```

```

    *(s+i) = * (str+i)+ * (sro+i) + * (sv +i);
  } //END OF FOR LOOP
}
/*Function to display Einstein functions, contributions from various
degrees of freedom to enthalpy, heat capacity, Gibb's energy,
entropy functions and thermodynamic functions of the molecule in the
gaseous state. */
void data::output()
{
  out1 a(13,5),*pa;
  out2 b03(0,3),b24(2,4),b43(4,3),b44(4,4),b40(4,0),b01(0,1), b
    11(1,1),b10(1,0),b21(2,1),b12(1,2),b22(2,2),b23(2,3),
    b20(2,0),b00(0,0),b30(3,0);
  out2 *pb03,*pb24,*pb43,*pb44,*pb40,*pb01,*pb11,*pb10,*pb21, *pb12,
    *pb22,*pb23,*pb20,*pb00,*pb30;
  pa = &a; pb03=&b03; pb24=&b24; pb43=&b43; pb44=&b44;
  pb40=&b40; pb01=&b01; pb11=&b11; pb10=&b10; pb21=&b21;
  pb12=&b12; pb22=&b22; pb23=&b23; pb20=&b20; pb00=&b00;
  pb30=&b30;
  cin>>bottom;
  cout<<clear;
  cout<<"The following are the values of the various Einstein
  functions\n"
    <<"at different temperatures..... \n" ;
  cout<<*pa;
  cout<<*pb03<<"TEMP. [K]"<<*pb24<<"EH[I]"<<*pb43<<"ECP[I]"<<*pb44
    <<"EG[I]"<<*pb44<<"ES[I]"<<*pb40;
  cout<<*pa;
  for(i=1;i<=n;i++)
  {
    cout<<*pb01<<for2<<t[i]<<*pb11<<for2<<eh[i]<<*pb11<<for2<<ecp[i]
      <<*pb11<<for2<<eg[i]<<*pb11<<for2<<es[i]<<*pb10; cout<<*pa;
    fun(i);
  }
  cin>>bottom;
  cout<<clear;
  cout<<"\nThe following are the values of the Thermo functions for\n"
    <<"each of the various statistical contributions and also
    their\n"
    <<"total values\n";
  cout<<"\nEnthalpy function(cal/mole.K)..... \n";
  cout<<*pa;
  cout<<*pb03<<"TEMP. [K]"<<*pb21<<"TRANS.CONT."<<*pb12<<"ROT.CONT."
    <<*pb22<<"VIB.CONT."<<*pb23<<"ENTHALPY"<<*pb20;
  cout<<*pa;
  for(i=1;i<=n;i++)
  {
    cout<<*pb01<<for2<<tt[i]<<*pb11<<for2<<httr[i]<<*pb11<<for2<<htr
      o[i]
      <<*pb11<<for2<<htv[i]<<*pb11<<for2<<ht[i]<<*pb10;
    cout<<*pa;
    fun(i);
  }
  cin>>bottom;
  cout<<clear;
  cout<<"\nHeat capacity(cal/mole.K)..... \n";
  cout<<*pa;
  cout<<*pb03<<"TEMP. [K]"<<*pb21<<"TRANS.CONT."<<*pb12<<"ROT.CONT."
    <<*pb22<<"VIB.CONT."<<*pb20<<"HEAT CAPACITY"<<*pb00; cout<<*pa;
  for(i=1;i<=n;i++)

```

```

{
    cout<<*pb01<<for2<<t[i]<<*pb11<<for2<<cptr[i]<<*pb11<<for2<<cpro[
    i]
        <<*pb11<<for2<<cpv[i]<<*pb11<<for2<<cp[i]<<*pb10;
    cout<<*pa;
    fun(i);
}
cin>>bottom;
cout<<clear;
cout<<"\nGibbs energy function(cal/mole.K)..... \n";
cout<<*pa;
cout<<*pb03<<"TEMP. [K]"<<*pb21<<"TRANS.CONT."<<*pb12<<"ROT.CONT."
    <<*pb22<<"VIB.CONT."<<*pb20<<"GIBB'S ENERGY"<<*pb00; cout<<*pa;
for(i=1;i<=n;i++)
{
    cout<<*pb01<<for2<<t[i]<<*pb11<<for2<<gttr[i]<<*pb11<<for2<<gtro[i]
        <<*pb11<<for2<<gtv[i]<<*pb11<<for2<<gt[i]<<*pb10;
    cout<<*pa;
    fun(i);
}
cin>>bottom;
cout<<clear;
cout<<"\nEntropy(cal/mole.K)..... \n";
cout<<*pa;
cout<<*pb03<<"TEMP. [K]"<<*pb21<<"TRANS.CONT."<<*pb12<<"ROT.CONT."
    <<*pb22<<"VIB.CONT."<<*pb23<<"ENTROPY"<<*pb30;
cout<<*pa;
for(i=1;i<=n;i++)
{
    cout<<*pb01<<for2<<t[i]<<*pb11<<for2<<str[i]<<*pb11<<for2<<sro[i]
        <<*pb11<<for2<<sv[i]<<*pb11<<for2<<s[i]<<*pb10; cout<<*pa;
    fun(i);
}
cin>>bottom;
cout<<clear;
cout<<"\nIdeal gas thermodynamic functions..... \n";
cout<<*pa;
cout<<*pb03<<"TEMP. [K]"<<*pb20<<"HEAT CAPACITY"<<*pb00<<"GIBB•S
ENERGY"
    <<*pb03<<"ENTHALPY"<<*pb23<<"ENTROPY"<<*pb30;
cout<<*pa;
for(i=1;i<=n;i++)
{
    cout<<*pb01<<for2<<t[i]<<*pb11<<for2<<cp[i]<<*pb11<<for2<<gt[i]<<*pb
    11
        <<for2<<ht[i]<<*pb11<<for2<<s[i]<<*pb10;
    cout<<*pa;
    fun(i);
}
}

//Function to compute Einstein functions.
void eins(int m, float cons,int i, double *pt, double *pw, double *peh,
    double *pecp, double *peg, double *pes)
{
    double x, x1, x2, he, cpe, ge, se;
    int k;
    float d;
    init q;
    *(peh+i)=q.getx();      *(pecp+i)=q.getx();
    *(peg+i)=q.getx();      *(pes+i)=q.getx();

```

```

for(k=1;k<=m;k++)
{
    x=cons* *(pw+k)/ *(pt+i);
    x1=exp(x);
    x2=x1-1.0;
    he=x/x2;
    cpe=x*x*x1/(x2*x2);
    ge=log(1.0-exp(-x));
    se=x/x2-ge;
    *(peh+i)= *(peh+i)+he;
    *(pecp+i)=*(pecp+i)+cpe;
    *(peg+i)=*(peg+i)+ge;
    *(pes+i)=*(pes+i)+se;
}
}
//Function to pause the output.
void fun(int i)
{
    outl ob(13,5);
    if(i==7 || i==14 || i==21)
    {
        cin>>bottom;
        cout<<ob;
    }
}
//Function main()
main()
{
    char ch;
    data x;
    void (data::*psetdatal)();
    void (data::*pdisplayl)();
    void (data::*plin_nlin)();
    void (data::*painer)();
    void (data::*pcal)();
    void (data::*poutput)();
    data *px;
    psetdatal=&data::setdatal;
    pdisplayl=&data::displayl;
    plin_nlin=&data::lin_nlin;
    painer=&data::ainer;
    pcal=&data::cal;
    poutput=&data::output;
    px=&x;
    cout<<beep<<clear;
    do
    {
        cout<<clear;
        (px->*psetdatal)();
        (px->*painer)();
        (px->*pdisplayl)();
        (px->*plin_nlin)();
        cin>>*px;
        cout<<*px;
        (px->*pcal)();
        (px->*poutput)();
        cout<<clear;
        gotoxy(1,10);
        cout<<"\nDo you want to process for some other molecule?\n"
            <<"\nEnter 'y or Y' for yes, anyother key for no.: ";
        ch=getch();
    }
}

```

```

} while(ch=='y' || ch=='Y');
return 0;
}

```

```

/*      END OF THE PROGRAM      */

```

Description Of The Input Variables.

```

1.nom      Name of the molecule
2.1        Nature of the molecule
3.atom     Type of atoms
4.na[]     No. of atoms of the same type
5.am[]     Atomic mass
6.mi       Moment of inertia  ( gm.cm 2 )
7.noa      No. of axis
8.xyz[]    Moments of inertia along different axis (gm.cm2)
9.sigma    Symmetry number
10.w[]     Fundamental vibrational frequencies (cm-1)
11.n       Total no. of temperatures
12.t[]     Temperatures

```

Testing data

1. For carbondioxide(CO₂)

```

nom - carbondioxide or CO2
1      -1
atom  -2
na[1] -1
am[1] -12.0
na[2] -2
am[2] -16.0
mi     -71.1 e-40
noa    -3
sigma  -2.0
w[1]   -667.03
w[2]   -667.03
w[3]   -2349.03
w[4]   -1330.00
n      -any value from (5 - 27)
t[1]   -100.00
t[2]   -200.00
t[3]   -273.15
t[4]   -298.15
t[5]   -300.00

```

2. For water (H₂O)

```

nom      -water or H2O
1        -2
atom     -2
na[1]    -2
am[1]    -1.008
na[2]    -1
am[2]    -16.0
mi       -0.0
noa      -3
xyz[1]   -1 929e-40
xyz[2]   -1 007e-40
xyz[3]   -3.013e-40
sigma    -2.00
w[1]     -3651.07
w[2]     -1595.00
w[3]     -3755.08
n        -any value from (5 - 27)

```


Temperatures (i.e. $t[1]$ $t[5]$) are same as for carbondioxide

Output at 298.15K (in units cal / molc.k)

Molecule	Heat capacity	Gibb's energy	Enthalpy	Entropy
CO ₂	8.879392	-43.545517	7.509235	51.054661
H ₂ O	8.002221	-37.025913	7.955631	44.981861

CHAPTER 4 RAMAN SPECTROSCOPY

The secret of those who make discoveries is to look upon nothing as impossible.

—Humboldt

4.1 INTRODUCTION

Raman effect is an optical analog of the Compton effect which arises due to the scattering of x -ray photons by electrons. It was discovered by Sir CV Raman of India in 1928 and Raman was awarded the Nobel Prize in 1932 for this discovery, which led to a period of intense experimental activity for the elucidation of molecular structure, for locating the various functional groups or chemical bonds in molecules, and for the quantitative analysis of complex mixtures.

Recall from Chapter 1 that when electromagnetic radiation outside the x -ray region, i.e. visible region, interacts with pure chemical substance in any of its forms, i.e. solid, liquid, or gas, it may undergo scattering in addition to absorption and transmission. If I_0 is the intensity of incident radiation and I_s , I_t and I_a are the intensities of the scattered, transmitted and absorbed radiations respectively then mathematically we can write

$$I_0 = I_a + I_s + I_t \quad (4.1)$$

Raman spectroscopy deals with the measurement of intensity of radiation, scattered by the molecules of chemical substances as a function of wavelength, and the Raman spectrum is thus a graph on which the intensity is plotted on the vertical and wavelength on the horizontal axes. The spectrum of scattered radiation not only consists of a central line (also called *Rayleigh line*), the frequency of which belongs to the frequency of source (ν_0), but also a series of displaced lines with frequency, say ν_R on both sides of the central line. This phenomenon of scattering with modified frequency due to the Kramer–Heisenberg process is known as the Raman effect, combination scattering or Raman scattering.

Raman scattering is generally weak and is ≈ 1 per cent of the incident radiation or ≈ 0.01 – 0.001 per cent of the Rayleigh scattering for many simple molecules. The Raman scattering process, unlike fluorescence, does not involve absorption of radiation. Scattering occurs in 10^{-12} second after excitation whereas fluorescence emission occurs in $\approx 10^{-6}$ – 10^{-8} second after excitation. It also differs from Tyndall scattering (which is due to colloids and emulsions) and Rayleigh scattering (which is due to ordinary liquids, gases, crystals and glasses) in the sense that there is no change of frequency or colour of the scattered beam from that of the incident beam. Rayleigh scattering is valid for particles whose size is not more than 0.1 of the light wavelength of 40–70 nm, while Tyndall scattering is valid for particles of the size between 1–100 nm. When white light is used in Rayleigh scattering, there is enhancement of different colours already present in the incident beam. The blue colour of the sky is due to Rayleigh scattering of the sunlight by the particles of the air with dimensions less than one tenth of the wavelength of light. The scattering intensity is proportional to ν_0^4 law. The lines in the Raman scattering are frequently arranged symmetrically on both sides of the Rayleigh line. The lines with frequency greater than that of the Rayleigh line are called *anti-Stokes lines* while those with lower frequency are called *Stokes lines*. The difference between the frequencies of Raman (ν_R) and Rayleigh (ν_0) lines matches with the fundamental vibrational (ν_{vib}) or the rotational (ν_{rot}) frequency of the molecule of the scattering material. In other words, we can say that the frequency shift, also called the Raman shift, which is the difference between the frequencies of

Rayleigh line and a particular Raman line, i.e. $\Delta\nu_R = \nu_0 - \nu_R = \frac{\lambda_R - \lambda_0}{\lambda_R \lambda_0}$, corresponds to one of the vibrational or rotational frequencies of a particular bond within the molecule that gives rise to that Raman scattering line. If ν^s and ν^a are the frequencies of the Stokes and anti-Stokes Raman lines respectively then we may write

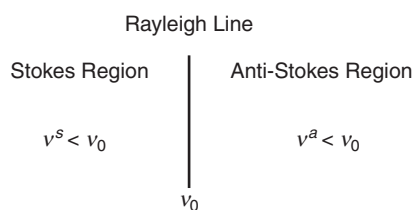


Fig. 4.1 A sketch showing Raman effect.

$$\nu^s = \nu_0 - \nu_{vib} \quad (4.2)$$

$$\nu^a = \nu_0 + \nu_{vib}$$

$$\nu^s = \nu_0 - \nu_{rot}^* \quad (4.3)$$

$$\nu^a = \nu_0 + \nu_{rot}^*$$

and the pictorial view of Raman scattering is shown in Fig. 4.1.

4.2 CLASSICAL THEORY OF RAMAN SCATTERING

The origin of Raman scattering can best be understood by considering the behaviour of a molecule under the influence of an electric field of electromagnetic radiation.

When a molecule is under the influence of a static electric field E , a dipole moment induced into it is given by

$$M = \alpha E \quad (4.4)$$

where α , the polarisability of the molecule, occurs because of the distortion of the electron cloud of the molecule under the impact of E .

Thus, a molecule under the influence of an electric field of the electromagnetic radiation will also have induced fluctuating dipole moment M , such that

$$M = \alpha E \sin(2\pi\nu_0 t) \quad (4.5)$$

where ν_0 is the frequency of incident radiation. This induced moment oscillates with the frequency of the incident radiation. These forced vibrations of the molecular dipole are the cause of ordinary Rayleigh scattering of radiation. However, by virtue of specific dynamic conditions, a change can occur in the polarisability of the molecule, this change being due to certain participation also of nuclei in the vibrations of the dipole. These dynamic conditions are due to a forced coupling of electrons and nuclei, as a result of which the forced vibrations of the electrons (with frequency ν_0) cause vibrations of the nuclei. The vibrations of the latter which are much slower than those of the electrons (because of the great difference in the electron and nuclear masses) are what lead to a change in the polarisability of the molecule. This latter factor alters the frequency of radiation, i.e. light being scattered. Consequently, displaced lines on both sides of the Rayleigh line appear in the Raman spectrum of molecules. The polarisability of a molecule (given vibrations of frequency ν) is designated by $\alpha = \alpha_0 + \alpha_A \sin 2\pi\nu t$, where α_0 is the polarisability of a nonvibrating molecule and α_A is the amplitude of change in polarisability during vibrations. Thus, Raman effect in a molecule is due to changes in size, shape or orientation of the polarisability due to internal motions, i.e. rotation or vibration of the molecule. The molecular polarisability of most of the molecules is anisotropic and its variation as a function of distance from the centre of mass of the molecule in any direction is governed by the hypothetical law:

$$r \propto \frac{1}{\sqrt{\alpha_0}} \quad (4.6)$$

where α_0 is the polarisability in each direction.

The origin of rotational Raman scattering lies in the anisotropy of the polarisability of a diatomic molecule.

The component of polarisability α with respect to the incident radiation along the internuclear axis (say X -direction) α_x , is larger than the components α_y and α_z along the Y - and Z -directions respectively, i.e. $\alpha_x > \alpha_y = \alpha_z$. Now if ν_{rot} is the rotational frequency of the diatomic molecule then

$$\alpha = \alpha_y + (\alpha_x - \alpha_y) \sin(2\pi\nu_{rot}^* t) \quad (4.7)$$

Combining Eqs (4.5) and (4.7), we get

$$M = [\alpha_y + (\alpha_x - \alpha_y) \sin 2\pi \nu_{rot}^* t] E \sin(2\pi \nu_0 t) \\ = \alpha_y E \sin(2\pi \nu_0 t) + \frac{1}{2} (\alpha_x - \alpha_y) E [\cos 2\pi (\nu_0 - \nu_{rot}^*) t] - \cos 2\pi (\nu_0 + \nu_{rot}^*) t] \quad (4.8)^*$$

$$*2 \sin A \sin B = \cos (A - B) - \cos (A + B)$$

The lines in the rotational spectrum of a diatomic molecule will, thus, be positioned at frequencies ν_0 , $\nu_0 - \nu_{rot}^*$, and $\nu_0 + \nu_{rot}^*$. Here, ν_{rot}^* is the frequency of rotational motion, the frequency with which the polarisability changes twice that of rotational frequency. The polarisability of the molecule returns to its initial value after a rotation of 180° as shown in Fig. 4.2 (i.e. returns to its initial values twice on every revolution). Consequently ν_{rot}^* in Eq. (4.7) is $2 \nu_{rot}$. But this is not so in case of vibrational motion of molecules.

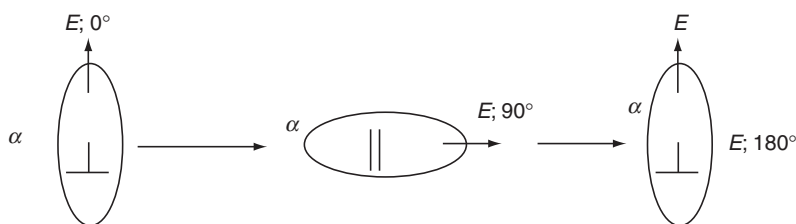


Fig. 4.2 Changes observed in the polarisability during the complete rotation.

The vibrational Raman scattering of diatomic molecules is because of the change in the molecular polarisability α , along the internuclear axis during vibration. The variation of α with Q , the normal coordinate of vibration with frequency ν , is expressed by the relation,

$$\alpha = \alpha_0 + \left(\frac{d\alpha}{dQ} \right)_0 Q \quad (4.9)$$

where α_0 is the polarisability when the nuclei are in their equilibrium position and $(d\alpha/dQ)_0$ is the rate of change of α_0 with Q for infinitesimal nuclear displacements. The hypothetical variation of α with internuclear bond distance, r is shown in Fig. 4.3.

Now if the change $(\alpha - \alpha_0)$ is denoted by $\Delta\alpha$ and ν_{vib} is the vibrational frequency of a diatomic molecule, then from Eq. (4.7) we write

$$\alpha = \alpha_0 + \Delta\alpha \sin (2\pi \nu_{vib} t) \quad (4.10)$$

Combining Eqs (4.5) and (4.10), we get

$$M = [\alpha_0 + \Delta\alpha \sin (2\pi \nu_{vib} t)] E \sin (2\pi \nu_0 t) \\ = \alpha_0 E \sin (2\pi \nu_0 t) + \frac{\Delta\alpha E}{2} [\cos 2\pi (\nu_0 - \nu_{vib}) t - \cos 2\pi (\nu_0 + \nu_{vib}) t] \quad (4.11)$$

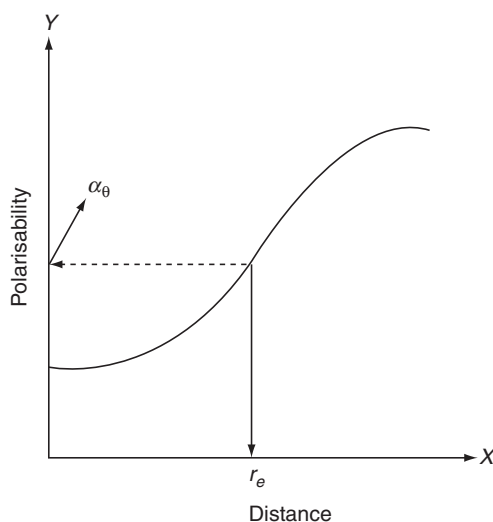


Fig. 4.3 Hypothetical variation of polarisability of diatomic molecule as a function of internuclear distance.

Thus, the scattered radiation will appear at frequencies ν_0 , $\nu_0 + \nu_{\text{vib}}$ and $\nu_0 - \nu_{\text{vib}}$ in the Raman vibrational spectrum of a diatomic molecule.

The classical theory though explains the origin of Raman effect in relation to the position of the Raman lines in the spectrum, yet it fails to solve the problem of the intensity of the Raman lines as well as the discrete nature of the spectrum. According to this theory, the intensity of both the lines, i.e. Stokes and anti-Stokes, should be the same which, of course, is contrary to the experimental facts. Secondly, the Raman spectrum should be continuous according to the classical theory since the molecular dipole rotates to the electric field of radiation wave, but in reality Raman spectrum has a discrete linear structure.

The answers to these problems came from the quantum mechanical treatment of Raman scattering.

4.3 QUANTUM MECHANICAL PICTURE OF RAMAN SCATTERING

This model is based upon the Kramer–Heisenberg theory of light dispersion. Accordingly, when a photon of frequency ν_0 interacts with the molecule of the scattering substance, it may jump from any of its initial vibrational or rotational level $E'_{V'/J'}$, where $V'/J' = 0, 1, 2, 3, \dots$ to any higher vibrational or rotational level $E''_{V''/J''}$. The higher level is an unstable level of both the photon and the molecule and its lifetime is of the order of 10^{-17} second. The molecule in the virtual level subsequently returns to any one of the initial vibrational or rotational levels $E'_{V'/J'}$ with the emission of a photon. This process of release of photon from the virtual level to the initial level may be divided into the following three stages (Fig. 4.4).

(a) Stage I The molecule may return from the virtual state to any of the initial states such that the frequency of the released photon is equal to that of the incident photon, i.e. $E''_{V''/J''} - E'_{V'/J'} = h\nu_0$. This will be true for $0 \rightarrow 0$, $1 \rightarrow 1$, $2 \rightarrow 2$, etc., transitions. This phenomenon of emission of photon is called *Rayleigh scattering* and is due to the interaction of photon with the nucleus. The energy level diagram for Rayleigh scattering is given in Fig. 4.4 (a).

(b) Stage II The molecule in state $V'/J' = 0$ absorbs the incident photon and jumps to the virtual level with the subsequent return to any one of the initial states with the release of photon with lower frequency (ν^s) than that of the incidence photon, i.e. $E''_{V''/J''} - E'_{V'/J'} = h\nu^s$. This will be true for $0 \rightarrow 1$, $0 \rightarrow 2$, $0 \rightarrow 3$, etc., transitions. This is known as *Stokes–Raman scattering*. The schematic diagram for Stokes–Raman scattering or effect is presented in Fig. 4.4 (b).

(c) Stage III The molecule in any of the higher initial levels, say $V'/J' = 1$ gains energy from the incident photon and jumps to any one of the virtual levels. The molecule subsequently returns to any of the initial levels with the release of the photon with frequency (ν^a) higher than that of the incident photon, i.e. $E''_{V''/J''} - E'_{V'/J'} = h\nu^a$. This is true for $1 \rightarrow 0$, $2 \rightarrow 0$, etc., transitions. This process of release of photon is called anti-Stokes Raman effect, and with lower frequency (ν^s) by the mechanism of Stage II. This will be true for $1 \rightarrow 2$, $1 \rightarrow 3$, etc., transitions. The schematic diagram for the mechanism of release of a photon in Stage III is given in Fig. 4.4 (c).

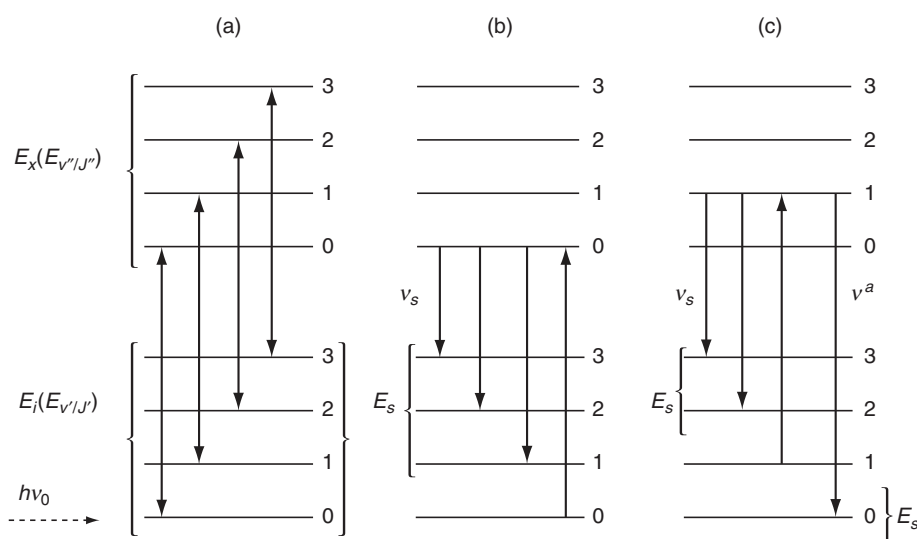


Fig. 4.4 Energy level diagram of Raman effect: (a) Rayleigh scattering, (b) Stokes–Raman scattering, and (c) Anti-Stokes and Stokes Raman scattering.

The three-stage process may also be discussed from the general expression deduced below. We know that (Fig. 4.4)

$$h\nu_0 = E_x - E_i \quad (4.12)$$

$$h\nu_R = E_x - E_s \text{ (or } E_s - E_x) \quad (4.13)$$

Combining Eqs (4.12) and (4.13), we get

$$\nu_0 \pm \nu_R = \frac{E_s - E_i}{h} \quad (4.14)$$

For Stage I, $E_s = E_i$; for Stage II, $E_s < E_i$; and for Stage III, $E_s > E_i$.

The use of Eq. (4.14) will be made later on while discussing the vibrational and rotational Raman spectra of diatomic molecules.

4.4 CHARACTERISTIC PARAMETERS OF RAMAN LINES

Normal Raman scattering, also called spontaneous or first-order Raman scattering, occurs when the intensity of the incident radiation corresponds to that of the source. Normal Raman scattering is linear since the induced dipole moment varies linearly with the electric field of the incident radiation, i.e. $M \propto E$. The important parameters of Raman lines in the normal Raman scattering are the frequency shift, the degree of polarisation, the intensity, the width and the shape of the Raman lines.

(a) Intensity of Raman Lines According to Placzek's theory, the intensity of Raman line I_R varies directly as $(\nu_0 - \nu_{\text{vib}})^4$ except in the vicinity of Raman resonance scattering, i.e. the intensity of Raman lines depends upon the frequency of incident radiation. Stokes lines are invariably stronger than their counterparts, i.e. anti-Stokes lines, since at room temperature the higher levels are thinly populated than the lower levels. The intensity of a fundamental Raman band is given by

$$I_R = I_{nm} = \frac{\text{const.} N (\nu_0 - \nu_{nm})^4 (45\alpha'^2 + 13\beta'^2)}{1 - \exp(-h\nu_{nm}/\kappa T)} \cdot \frac{h}{8\pi^2 \nu_{nm}} \quad (4.15)$$

where N is the number of molecules in the initial energy state m , and n is the higher energy state α' represents the average of the derivatives of the three principal polarisabilities and β' is the magnitude of the derivative of the anisotropy part of the polarisability of the molecules. The constants 45 and 13 arise in the averaging over all configurations in the experimental arrangement when the scattered light is observed per unit solid angle at right angles to the incident direction.

It is found that the ratio of intensities of anti-Stokes and Stokes lines is governed by the Maxwell-Boltzmann law and is expressed as

$$\frac{I^a}{I^s} = e^{\frac{-h\nu_{\text{rot/vib}}}{\kappa T}} \quad (4.15a)$$

where κ is the Boltzmann constant and I^a and I^s are the intensities of anti-Stokes and Stokes lines, respectively. However, for accurate determination of I^a/I^s , the frequency factor, which is $(\nu_0 - \nu_{\text{vib}})^4$ for the Stokes and $(\nu_0 + \nu_{\text{vib}})^4$ for the anti-Stokes lines should be taken into account.

The intensity of anti-Stokes lines grows with the growth of temperature since at higher temperature, the density of population of higher level increases. Thus, by raising the temperature, we observe anti-Stokes lines which are missing at low temperatures. The small quanta of radiation favour Stokes as well as anti-Stokes lines while large quanta favour only Stokes lines.

(b) Width and Shape of Raman Lines Raman lines are generally narrow in gases, liquids and crystals while in amorphous substances, the lines are broad and diffuse. The width of Raman lines increases with the increase of temperature and roughly varies directly to the square root of absolute temperature. This increase is because of the increase in the anharmonicity of vibrations. The shape of Raman lines is independent of the frequency of incident radiation. An unsymmetrical continuum called *Raman wing*, adjacent to and on both sides of the Rayleigh line with continuously decreasing intensity, appears in the case of liquids. The Raman wing arises because in case of liquids, the rotational motion is hindered. The intensity and width of a Raman wing varies from liquid to liquid and depends upon the anisotropy of the molecules of the liquid.

(c) Frequency Shifts of Raman Lines Frequency shifts of Raman lines from the Rayleigh line vary from 4,000 to a few wave numbers (cm^{-1}) and are independent of the frequency of the incident radiation. Frequency shifts grow with the growth of temperature. The frequency-shifts-versus-temperature plot runs parallel to the width-versus-temperature plot.

(d) Polarisation of Scattered Radiation Raman scattered radiation is at least partially polarised irrespective of the polarisation of the incident radiation. The extent of polarisation of the scattered radiation depends upon the structure of the molecule as well as on the symmetry of vibrational motion. It also helps in the determination of phase changes in liquid crystals and solids when these substances are heated. When a beam of radiation is incident on a molecule with isotropic polarisability, it scatters. The induced dipole moment is supposed to be perpendicular to the direction of incident radiation. The scattered radiation may be polarised in a plane parallel and perpendicular to the plane of polarisation of the incident radiation as shown in Fig. 4.5. The plane of vibration or displacement is always perpendicular to the plane of polarisation of radiation. Here we are now going to define a very important quantity called the *degree of depolarisation of scattered light* ρ . It is the ratio of the intensity of scattered light polarised in a plane perpendicular to the plane of polarisation of the incident light to the intensity of scattered light that is polarised in the parallel plane. Mathematically, it is expressed as

$$\rho_p' = \frac{I_{\perp}}{I_{\parallel}} \quad (4.16)$$

Here, the direction of observation of scattered light with an analyser is perpendicular to the Z -axis in the XY plane. $I_{\perp}$ is the intensity of scattered light parallel to the ZX plane and $I_{\parallel}$ is that parallel to the XY plane (Fig. 4.5). On the other hand, if the incident light is travelling in the $-Y$ direction and the scattered light is observed in the X -direction, and if the incident light is polarised in the Z -direction, the degree of depolarization is defined by the equation

$$\rho_p' = \frac{I(Y)}{I(Z)} \quad (4.16a)$$

where $I(Y)$ and $I(Z)$ are the observed intensities of light polarized in the Y - and Z -directions respectively. If the incident light is unpolarised then the degree of depolarisation of the scattered light is given by

$$\rho = \frac{2\rho_p'}{1 + \rho_p'} \quad (4.16b)$$

When the polarisability of the molecule remains isotropic during vibration, i.e. $\Delta\alpha = 0$ then $\rho_p' = 0$. However, when the polarisability of the molecule is anisotropic during vibrational motion then $\rho_p' \neq 0$ and the scattered

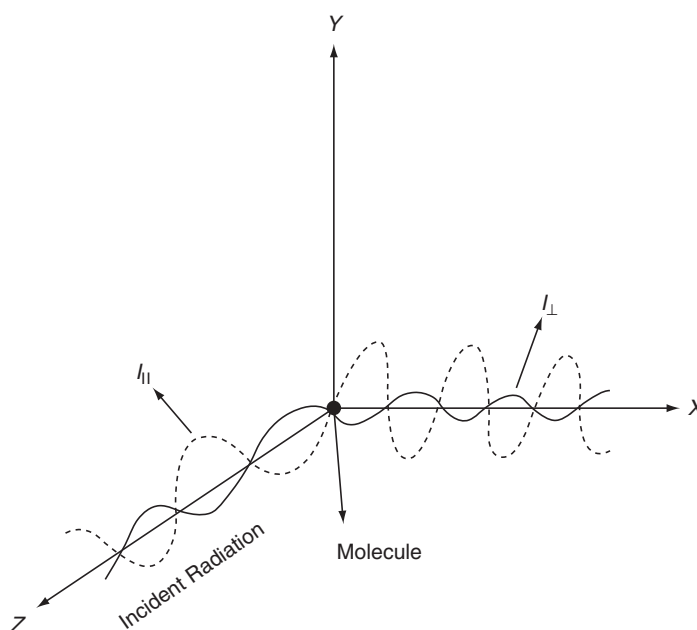


Fig. 4.5 The parallel and perpendicular components of the scattered radiation. The incident beam is along the Z -axis and the molecule is positioned at the origin.

radiation will be polarised in the parallel and perpendicular planes. For $I_{\perp} = I_{\parallel}$, $\rho_p' = 1$, the Raman lines will be completely depolarised. Thus the value of ρ_p' lies between 0 and 1. The symmetrical breathing vibrations of molecules such as CO_2 , CH_4 and C_6H_6 have completely polarised Raman lines, i.e. $\rho_p' = 0$. In particular, Raman lines of totally symmetric fundamentals are polarised and those of other fundamentals are depolarised.

Depolarisation ratio plays a major role in ascertaining the symmetry of a vibrational mode participating in the scattering event and the form of the molecules, i.e. more precisely, the form of the polarisability ellipsoid of the molecule. In other words, investigations of the depolarisation of Raman lines are important in the assignment of vibrations and in the final analysis of molecular structure. Let us now frame the rules for the polarisation of Raman lines. *The degree of polarisation depends on the anisotropic character of the molecules.* Experimentally, it has been established that normally the plane polarised Raman lines are sharp and intense, whereas depolarised lines are diffuse and of weak intensity.

The state of polarisation of the Raman lines is studied by measuring the depolarisation ratio ρ which is defined as

$$\rho = \frac{6\beta'^2}{45\alpha'^2 + 7\beta'^2} \quad (4.16c)$$

for unpolarised incident radiation, and for the polarised incident radiation, the depolarisation ρ_p' is defined as

$$\rho_p' = \frac{3\beta'^2}{45\alpha'^2 + 4\beta'^2} \quad (4.16d)$$

For totally asymmetric vibration $\alpha' = 0$, the scattered light is totally unpolarised and $\rho = \frac{6}{7}$ and $\rho_p' = \frac{3}{4}$. However, the symmetric vibrations are polarised and the depolarisation ratio lies between 0 and $\frac{6}{7}$ for unpolarised incident radiation and between 0 and $\frac{3}{4}$ for polarised incident radiation. Often the former criterion is employed for practical purposes. $\rho = 0 - \frac{6}{7}$ polarised $\geq \frac{6}{7}$ depolarised.

Further, it is observed that symmetric vibrations give rise to intense Raman lines and asymmetric vibrations appear as weak lines and sometimes are unobservable.

In certain cases, polarisation is inverted and $\rho \rightarrow \infty$. The inverted polarisation does not occur in normal Raman scattering but occurs in *resonance Raman scattering*. This arises when the polarisation plane of radiation scattered at right angles to the incident beam lies perpendicular to that of the incident radiation, when this is perpendicular to the direction of scattering, e.g. some of the bands in the resonance Raman spectra of cytochrome C and haemoglobin exhibit inverse polarisation.

4.5 EQUIVALENCE OF BEER–LAMBERT LAW OF ABSORPTION IN RAMAN SCATTERING

Let us suppose that a single molecular species is irradiated with radiation of intensity I_0 (W cm^{-2}). The intensity of the scattered radiation I_s at a single Raman frequency will be given by

$$I_s = \sigma I_0(w) \quad (4.17)$$

where σ has the dimensions of cm^2 .

For N molecules, the total intensity of the scattered radiation is

$$\bar{I}_s = N\sigma I_0(w) \quad (4.18)$$

If ΔN = the number of molecules/ml, A = cross-sectional area illuminated in cm^2 , Δx = path length of the illuminated volume in cm then

$$N = \Delta N A \Delta x \quad (4.19)$$

Combining Eqs (4.17), (4.18) and (4.19), we get

$$\bar{I}_s = (\sigma \Delta N)(A I_0)(\Delta x) = k \bar{I} \Delta x \quad (4.20)$$

where $\bar{I} = A I_0$ and $k = \sigma \Delta N$ is the loss factor in cm^{-1} .

Equation (4.20) is equivalent to the Beer law for the loss of energy from the exciting beam due to Raman scattering into a given Raman band.

Raman cross-sections are not easily determinable, and a few data are available. The value of σ is 10^{-28} cm^2 . Systems with large polarisable atoms or biologically important groups such as I— , $\text{—C}=\text{C—}$ are likely to be strong scatterers. Ionic bonds tend to scatter poorly.

4.6 SECOND-ORDER RAMAN SPECTRUM

The Raman spectrum due to overtones and combinational tones is called second-order Raman spectrum. Raman frequency of the first overtone is not exactly equal to twice the Raman frequency of the fundamental. Similarly, a combination tone is not equal to the sum or difference of the two fundamental frequencies. This is due to the fact that the vibrational levels are not spaced uniformly as in the case of a harmonic vibrator. The order of intensity of overtones and combination bands predicted by theory is vanishingly small as compared to the intensity of fundamental vibrations. Consequently, it is very difficult to observe second-order Raman spectra using a conventional source of radiation, i.e. Hg arc. However, with the advent of lasers it is now possible to record second-order Raman spectra also.

4.7 GENERAL SELECTION RULE FOR RAMAN SCATTERING

The general selection rule is worked out from the transition probability $|M|^{nm}$ for Raman effect, i.e.

$$|M|^{nm} = |E| \int \psi_n \alpha \psi_m d\tau \quad (4.21)$$

If α is constant, the integral vanishes due to orthogonality of wave functions. Therefore, in order that a particular vibration or rotation be Raman active, α must change during vibration or rotation, i.e. $\Delta\alpha \neq 0$.

4.8 RAMAN SPECTRA OF DIATOMIC MOLECULES

Raman effect is employed to find the vibrational, rotational, rotational–vibrational spectra as well as the rotational and vibrational constants not only of homonuclear, say H_2 , N_2 , O_2 , etc., but also of heteronuclear, say HCl , NO , CO , etc., diatomic molecules. Thus, we can say that Raman spectroscopy complements infrared spectroscopy.

4.8.1 Pure Rotational Raman Spectra of Diatomic Molecules— Selection Rules for Pure Rotational Spectra

- (i) The first selection rule, as worked out from the transition probability for Raman effect, is $\Delta\alpha \neq 0$.
- (ii) The second selection rule is established by means of a three-stage scheme of the scattering process (Fig. 4.4). Considering the transition from $E_i \rightarrow E_x$ and the selection rule $\Delta J = \pm 1$, we get two possible values of J_x for the rotational quantum number of the transition state, i.e.

$$J_x = J_i \pm 1 \quad (4.22)$$

Here J_i refers to the initial state. Upon transition to the final state, i.e. for the transition $E_x \rightarrow E_s$ the rotational quantum number of E_s , must be equal to J_s given by

$$J_s = J_x \pm 1 = (J_i \pm 1) \pm 1 = J_i \pm 2 \quad (4.23)$$

Hence, the second selection rule for pure rotational Raman spectrum is $\Delta J = 0, \pm 2$ but not $\Delta J = \pm 1$ as in the case of far infrared and microwave spectra. The second factor (i.e. ± 2) appears since during a complete rotation, the polarisability ellipsoid rotates twice as fast as the molecule. It is to be noted that any linear molecule belonging either to the $C_{\infty h}$ or $D_{\infty h}$ point group has a rotational Raman spectrum.

Transition between Two Levels We know from Eq. (4.14) that

$$\nu_0 \pm \nu_R = \frac{E_s - E_i}{h}$$

and it is also known that $E_J = BhcJ(J+1)$ for rigid rotator diatomic molecule and $E_J = BhcJ(J+1) - DhcJ^2(J+1)^2$ for nonrigid rotator diatomic molecule.

Let $E_{J'}$, and $E_{J''}$, be the energy of initial and final states and J' and J'' be the corresponding quantum numbers; then

$$E_{J''} = B h c J''(J'' + 1) \quad (4.24)$$

$$E_{J'} = B h c J'(J' + 1) \quad (4.25)$$

From Eqs (4.14), (4.24) and (4.25), we get the energy difference ΔE between the two states, i.e.

$$\begin{aligned} \Delta E &= E_{J''} - E_{J'} \\ \Delta E &= B h c (J'' - J')(J' + J'' + 1) \end{aligned} \quad (4.26)$$

or
$$\Delta E = \frac{E_{J''} - E_{J'}}{h} = B c (J'' - J')(J' + J'' + 1) \quad (4.27)$$

$$= \nu_0 \pm \nu_R$$

Now applying the selection rule $\Delta J = 0$, we get $\nu_0 = \pm \nu_R$ which is the case of Rayleigh scattering, i.e. the frequency of incident radiation is equal to the frequency of the scattered radiation. When

$$\Delta J = +2, J'' = J' + 2, \text{ then, } \nu_R = \nu_0 - 2Bc (2J' + 3)$$

or
$$\nu^s = \nu_0 - 2Bc (2J' + 3) \quad (4.28)$$

This represents the S-branch of the rotational band. Similarly, when $\Delta J = -2$, we get

$$\nu^a = \nu_0 + 2Bc (2J' - 1) \quad (4.29)$$

and it corresponds to the O-branch of the rotational band.

The position of the rotational lines in the O- and S-branches of the Raman band as worked out from Eqs (4.28) and (4.29) are compared with the experimental observations as under.

J'	<i>Theory</i>	<i>Experimental</i>
	S	O
0	$\nu_0 - 6Bc$	$\nu_0 - 2Bc$
1	$\nu_0 - 10Bc$	$\nu_0 + 2Bc$
2	$\nu_0 - 14Bc$	$\nu_0 + 6Bc$
3	$\nu_0 - 18Bc$	$\nu_0 + 10Bc$

It is evident from the above data that the position of the first line (S-branch) on the left-hand side of the exciting line is spaced $6Bc$ from it, while the first line of the anti-Stokes region of the spectrum is positioned at $2Bc$ (O-branch) on the left-hand side of the Rayleigh line which seems to be unusual. However, it is observed that in the anti-Stokes region of the spectrum or the O-branch of the Raman spectrum, $J' \neq 0, 1, 2, 3, \dots$ but $J' = 2, 3, 4, \dots$ Accordingly, the first line in the O-region will also be at $6Bc$ from the Rayleigh line. The spacing between the rotational lines in the Stokes and anti-Stokes region of the spectrum is $4Bc$ but not $2Bc$ as is observed in the infrared and microwave regions of the spectra of diatomic molecules. The schematic diagram for the theoretical rotational spectrum of diatomic molecule is presented in Fig. 4.6.

Similarly, we can show that for a non-rigid rotator diatomic molecule, $\nu_0 = \pm \nu_R$ for $\Delta J = 0$

and for $\Delta J = +2$

$$\nu^s = \nu_0 - (4B - 6D)c \left(J' + \frac{3}{2} \right) - 8Dc \left(J' + \frac{3}{2} \right)^2 \quad (4.30)$$

and for $\Delta J = -2$

$$\nu^a = \nu_0 + (4B - 6D)c \left(J' + \frac{3}{2} \right) - 8Dc \left(J' + \frac{3}{2} \right)^2 \quad (4.31)$$

Equations (4.30) and (4.31) may also be expressed as

$$\bar{\nu}_{\text{rot}} = \mp (4B - 6D) \left(J' + \frac{3}{2} \right) - 8D \left(J' + \frac{3}{2} \right)^2 \quad (4.32)$$

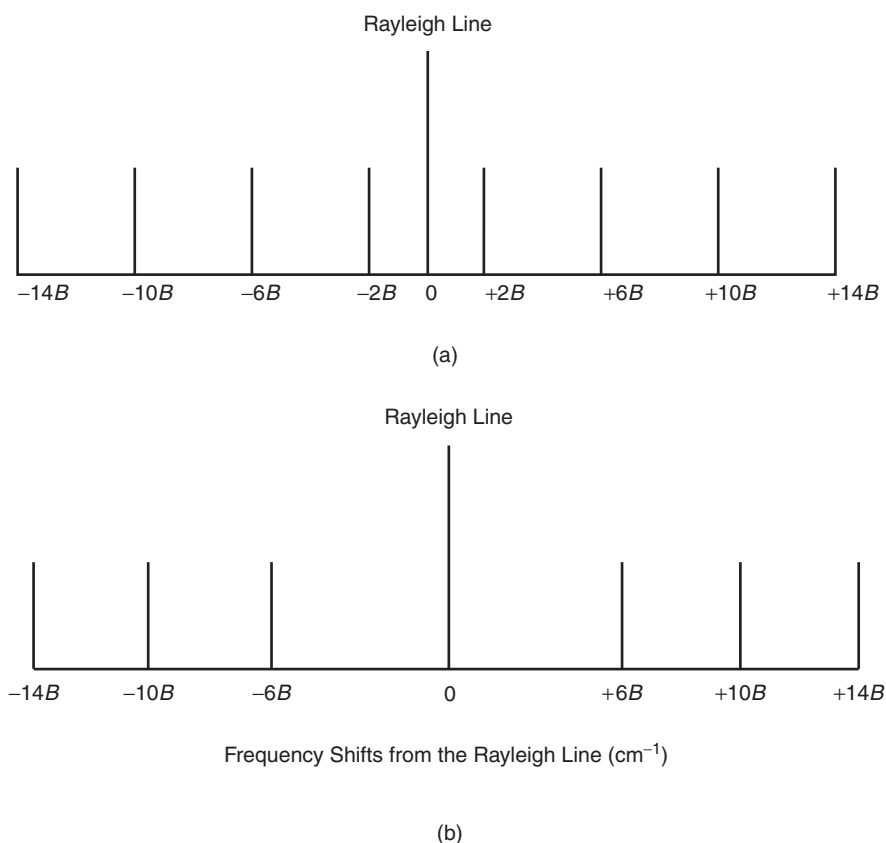


Fig. 4.6 Theoretical rotational spectra of diatomic molecule (a) for $J' = 0, 1, 2, 3, \dots$ and (b) for $J' = 2, 3, 4, \dots$

Rearranging Eq. (4.32), we get

$$\frac{\bar{\nu}_{\text{rot}}}{\left(J' + \frac{3}{2}\right)} = \mp (4B - 6D) - 8D \left(J' + \frac{3}{2}\right) \quad (4.33)$$

Thus, a plot of $\bar{\nu}_{\text{rot}} / (J' + 3/2)$ against $(J' + 3/2)$ will give a straight line with slope of $-8D$ and intercept $= \mp (4B - 6D)$. From the slope and intercept, the rotational constants, i.e. B and D , can be determined. The precision of the measurement does not normally warrant the retention of the term D in Raman spectroscopy.

For molecules $\Lambda > 0$ and also for symmetric-top molecules, the selection rules are $\Delta J = 0, \pm 1$ in the infrared region of the spectrum. The second selection rule for the rotational Raman spectrum for these types of molecules have been worked out by the three-stage scheme of scattering process (as done earlier for diatomics, Fig. 4.4) and is

$$\Delta J = 0, \pm 1, \pm 2$$

This rule also holds good for asymmetric-top molecules.

Thus, the rotational Raman spectrum of these type of molecules has in addition to S- and O-branches ($\Delta J = 0, \pm 2$), the usual R- and P-branches ($\Delta J = \pm 1$). By employing these selection rules, we get from Eq. (4.27), the frequencies of the S- and O-branches, i.e.

$$S(\Delta J = +2) \rightarrow \nu^s = \nu_0 - 2Bc(2J' + 3) \quad (4.34)$$

$$O(\Delta J = -2) \rightarrow \nu^o = \nu_0 + 2Bc(2J' - 1) \quad (4.35)$$

and as well as of P- and R-branches, i.e.

$$P(\Delta J = -1) \rightarrow \nu^s = \nu_0 - 2Bc(J' + 1) \quad (4.36)$$

$$R(\Delta J = +1) \rightarrow \nu^a = \nu_0 + 2BcJ' \quad (4.37)$$

The positions of lines in S- and O-branches [from Eqs (4.34) and (4.35)] and in P- and R-branches [from Eqs (4.36) and (4.37)] are

J'	S	O	P	R
0	$\nu_0 - 6Bc$	$\nu_0 - 2Bc$	$\nu_0 - 2Bc$	ν_0
1	$\nu_0 - 10Bc$	$\nu_0 + 2Bc$	$\nu_0 - 4Bc$	$\nu_0 + 2Bc$
2	$\nu_0 - 14Bc$	$\nu_0 + 6Bc$	$\nu_0 - 6Bc$	$\nu_0 + 4Bc$
3	$\nu_0 - 18Bc$	$\nu_0 + 10Bc$	$\nu_0 - 8Bc$	$\nu_0 + 6Bc$

In order that O- and R-branches of the spectrum should coincide with the experimental spectrum then $J' = 2, 3, 4, \dots$ for O-region and $J' = 1, 2, 3, \dots$ for R-branch of the spectrum. The spacing between the rotational lines in S- and O- regions is $4Bc$ while it is $2Bc$ in the P- and R- branches of the spectrum as expected. The schematic diagram for the rotational-vibrational spectrum of these types of molecules is presented in Fig. 4.7.

Thus, knowing B from the rotational spectrum of diatomic molecules, we can determine the intensities of Raman lines and the bond length of diatomic molecules, e.g. in case of HCl, $B = 10 \text{ cm}^{-1}$, and we know that

$$B = \frac{h}{8\pi^2 Ic}$$

where the terms and symbols have their usual meanings, since $I = \mu_m r^2$.

Therefore,

$$r^2 = \frac{6.6 \times 10^{-27} (\text{erg s})}{8 \times 22/7 \times 22/7 \times 3 \times 10^{10} (\text{cm s}^{-1}) \times 35/36 \times 1.66 \times 10^{-24} (\text{g}) 10 (\text{cm}^{-1})}$$

$$= (1.27 \times 10^{-8})^2 (\text{cm}^2)$$

or

$$r = 1.27 \times 10^{-8} \text{ cm} = 1.27 \text{ \AA} = 0.127 \text{ nm}$$

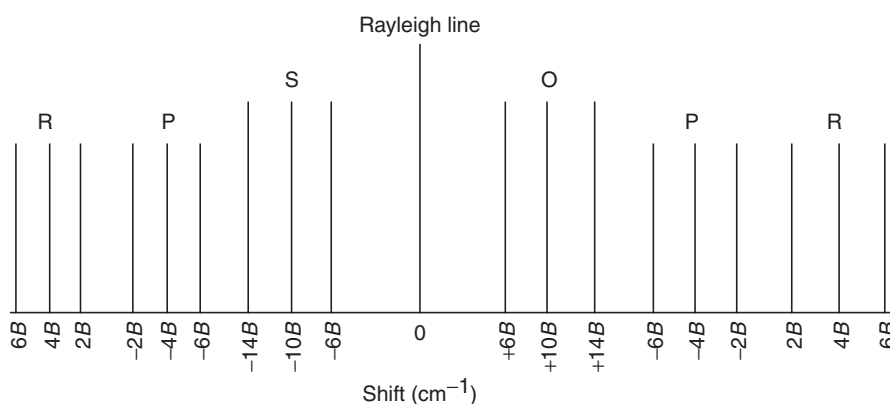


Fig. 4.7 Schematic diagram of rotation-vibration spectra of symmetric top molecules and for molecules $A > 0$.

Using Eq. (4.34), i.e.

$$\nu^s = \nu_0 - 2Bc(2J' + 3)$$

we get

$$\bar{\nu}_{\text{rot}} = 2B(2J' + 3)$$

Since

$$J' = 0, 1, 2, 3, \dots$$

Therefore, for

$$J = 0 \rightarrow 2, \bar{\nu}_{\text{rot}} = 6B = 60 \text{ cm}^{-1}$$

$$1 \rightarrow 3, \bar{\nu}_{\text{rot}} = 10B = 100 \text{ cm}^{-1}$$

$$2 \rightarrow 4, \bar{\nu}_{\text{rot}} = 14B = 140 \text{ cm}^{-1}$$

Further from Eq. (4.15), we write

$$\frac{I^a}{I^s} = e^{\frac{-hc\bar{\nu}_{\text{rot}}}{\kappa T}}$$

$$\frac{I^a}{I^s} = e^{\frac{-6.6 \times 10^{-17} (\text{erg s}) \times 3 \times 10^{10} (\text{cm s}^{-1}) \times \bar{\nu}_{\text{rot}}}{1.38054 \times 10^{-16} (\text{erg K}^{-1}) T}}$$

$$= e^{-1.434 (\text{cm K}) \frac{\bar{\nu}_{\text{rot}}}{T}}$$

The intensity ratios for these transitions at room temperature, i.e. 298 K, are

$$J = 0 \rightarrow 2; \frac{I^a}{I^s} = 7.49 \times 10^{-3}$$

$$1 \rightarrow 3; \frac{I^a}{I^s} = 6.18 \times 10^{-3}$$

$$2 \rightarrow 4; \frac{I^a}{I^s} = 5.09 \times 10^{-3}$$

It is clear from the data that the intensities of anti-Stokes lines decrease as the rotational quantum number increases as expected. Similarly, we can also depict the effect of temperature on the intensities of Raman lines for fixed quanta of radiation. Let us calculate the intensity ratio at three different temperatures, say 300, 310 and 320 K, on the $0 \rightarrow 2$ transition, i.e. $\bar{\nu}_{\text{rot}} = 60 \text{ cm}^{-1}$. The ratios at these temperatures are

$$\left(\frac{I^a}{I^s} \right)_{300} = e^{\frac{-1.434 \times 60}{300}} = 7.50 \times 10^{-3}$$

$$\left(\frac{I^a}{I^s} \right)_{310} = e^{\frac{-1.434 \times 60}{310}} = 7.57 \times 10^{-3}$$

$$\left(\frac{I^a}{I^s} \right)_{320} = e^{\frac{-1.434 \times 60}{320}} = 7.64 \times 10^{-3}$$

From the above data it is clear that as the temperature grows, the intensities of anti-Stokes lines increase while those of Stokes lines decrease as expected.

The effects of nuclear spin have also been observed as in the infrared spectrum in the case of linear molecules with centre of symmetry, e.g. O_2 , H_2 and CO_2 . In case of O_2 and CO_2 , every alternate rotational level is absent since spin of oxygen is zero, e.g. in O_2 , every level with even values of J will be missing. In case of H_2 and other molecules with nonzero spin, the spectral lines show an alternation of intensity. Further, in case of linear molecules with more than three heavy atoms, the rotational fine structure is often unresolved in the Raman spectrum due to large moment of inertia. Consequently, in such cases direct structural information cannot be obtained from the rotational Raman spectrum.

The pure rotations of spherical-top molecules ($I_x = I_y = I_z$), viz. CH_4 , SiH_4 , are inactive in the Raman spectrum, since $\Delta\alpha = 0$, i.e. no change in polarisability takes place due to rotation of such type of molecules. However, in the case of asymmetric-top molecules ($I_x \neq I_y \neq I_z$), all the rotations will be Raman active. The Raman spectrum of such molecules is complex and is often analysed by assuming the molecule as intermediate between the oblate ($I_x < I_y = I_z$) and prolate ($I_x > I_y = I_z$) types of symmetric-top molecules. For symmetric-top molecules, e.g. CH_3F , CH_3Cl , etc., ($I_x = I_y \neq I_z$), the rotation about the top axis produces no change in the polarisability but end-over-end rotations will produce a change in the polarisability. The selection rules are

$$\Delta K = 0, \Delta J = 0, \pm 1, \pm 2 \text{ (except for } K = 0 \text{ levels when } \Delta J = \pm 2 \text{ only)}$$

where $J = 0, 1, 2, \dots$; $K = \pm J, \pm (J-1), \dots, 0$ and K will have total $(2J+1)$ values. K is the rotational quantum number for the axial rotation. Therefore, the selection rule $\Delta K = 0$ reveals that rotation about the top axis will be Raman inactive. The restriction, $K = 0$ when $\Delta J = \pm 2$ imposed on the selection rule means that $\Delta J = \pm 1$ for transitions involving $J = 0$ since $K = \pm J, \pm (J-1), \dots, 0$. Thus, for $J \neq 0$, $K \neq 0$, the transition according to selection rule $\Delta J = \pm 1$, is not forbidden.

4.8.2 Pure Vibrational Raman Spectra of Diatomic Molecules

The selection rules for pure vibration of Raman spectrum are the following:

- $\Delta\alpha \neq 0$, i.e. the spectrum is due to a change in the polarisability along the internuclear axis.
- The second selection rule is identical to that of infrared vibrational spectra, i.e. $\Delta V = \pm 1, \pm 2, \pm 3, \dots$

Transition between Two Vibrational States The energy of a vibrational level is given by the expression

$$E_V = hcw_e \left(V + \frac{1}{2} \right) - hcw_e x_e \left(V + \frac{1}{2} \right)^2$$

If V' and V'' are the vibrational quantum numbers for lower and upper states respectively then we may write

$$E_{V'} = hcw_e \left(V' + \frac{1}{2} \right) - hcw_e x_e \left(V' + \frac{1}{2} \right)^2 \quad (4.38)$$

$$E_{V''} = hcw_e \left(V'' + \frac{1}{2} \right) - hcw_e x_e \left(V'' + \frac{1}{2} \right)^2 \quad (4.39)$$

From Eqs. (4.14), (4.38) and (4.39), we get

$$\frac{\Delta E}{hc} = w_e (V'' - V') - w_e x_e (V'' - V') (V' + V'' + 1) = \nu_0 - \nu_R \quad (4.40)$$

where $\Delta E = E_{V''} - E_{V'}$

or
$$\nu_R = \nu_0 - [w_e (V'' - V') - w_e x_e (V'' - V') (V' + V'' + 1)] \quad (4.41)$$

Applying the selection rules, we get

(i) For $\Delta V = +1$

$$\nu_R = \nu_0 - [w_e - 2w_e x_e (V' + 1)] \quad (4.42)$$

or
$$\nu^s = \nu_0 - [w_e - 2w_e x_e (V' + 1)]$$

Since
$$\nu_0 - \nu^s = \bar{\nu}_{\text{vib}}$$

Therefore,
$$\bar{\nu}_{\text{vib}} = w_e - 2w_e x_e (V' + 1) \quad (4.43)$$

Since for the $0 \rightarrow 1$ transition, $V' = 0$, consequently,

$$\bar{\nu}_{\text{vib}} = w_e (1 - 2x_e) \quad (4.44)$$

For the $1 \rightarrow 2$ transition

$$\bar{\nu}_{\text{vib}} = w_e (1 - 4x_e). \text{ This is called the } \textit{first hot band}.$$

Similarly, for $\Delta V = -1$,

$$\bar{\nu}_{\text{vib}} = -w_e (1 - 2x_e) \quad (4.45)$$

Thus, the frequency of the first line in the vibrational Raman spectrum of diatomic molecules observed at

$$\bar{\nu}_{\text{vib}} = \pm w_e (1 - 2x_e) \quad (4.46)$$

shows that the fundamental vibrational line lies on both sides of the excitation line at a space of $w_e (1 - 2x_e)$.

This is true for solids and liquids which have no rotational fine structure.

(ii) For $\Delta V = \pm 2$,

$$\bar{\nu}_{\text{vib}} = \pm 2w_e (1 - 3x_e) \quad (4.47)$$

and

(iii) For $\Delta V = \pm 3$,

$$\bar{\nu}_{\text{vib}} = \pm 3w_e (1 - 4x_e) \quad (4.48)$$

It follows that the fundamental, its first, second ... overtones are positioned at $w_e (1 - 2x_e)$, $2w_e (1 - 3x_e)$ and $3w_e (1 - 4x_e)$ respectively on both sides of the central line as expected. The Raman frequency shifts conform to the fundamental and its overtones in the infrared spectrum of diatomic molecules. The spacing between two consecutive lines is not constant, but decreases as ΔV increases. This is due to the anharmonic nature of the diatomic vibrator. However, if the diatomic vibrator behaves as a harmonic oscillator, the vibrational lines are observed at frequencies, w_e , $2w_e$ and $3w_e$ and the spacing between the consecutive lines is w_e as expected. The intensity of these lines decreases sharply and follows the order $I_{\Delta V (\pm 1)} \gg I_{\Delta V (\pm 2)} \gg I_{\Delta V (\pm 3)}$. Consequently, overtones are observed with great difficulties. At room temperature, $I^s \gg I^a$ since at this temperature, the population

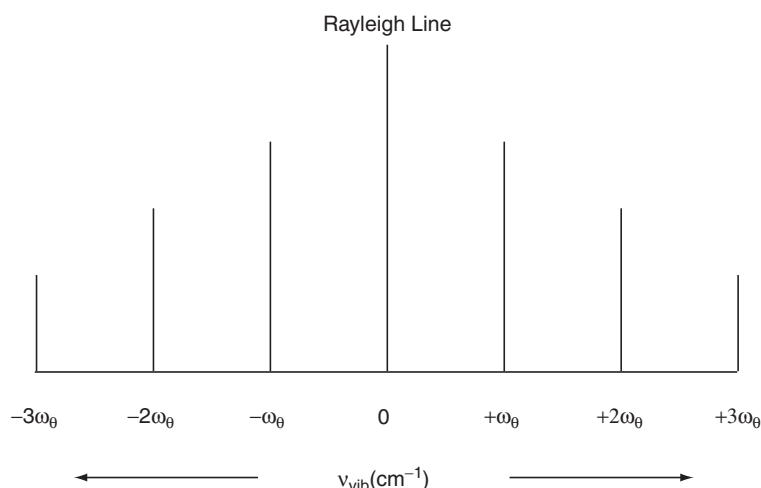


Fig. 4.8 Schematic vibrational Raman spectrum of diatomic harmonic vibrator.

of $V = 0$ level is higher than $V = 1$ level. The schematic diagram of a pure vibrational Raman spectrum of diatomic harmonic oscillator is presented in Fig. 4.8.

Thus, from the position of Stokes or anti-Stokes lines and the Rayleigh line, we can predict the vibrational frequency and force constant of diatomic molecule, e.g. when H^{35}Cl is irradiated with $4358 \text{ \AA}$ Hg line, the Stokes line has been observed at 20057 cm^{-1} . The vibrational frequency of HCl^{35} will be

$$\bar{\nu}_{\text{vib}} = \nu_0 - \nu^s = \frac{1}{(4358 \times 10^{-8})} (\text{cm}^{-1}) - 20057 (\text{cm}^{-1}) = (22946 - 20057) \text{ cm}^{-1} = 2889 \text{ cm}^{-1}$$

We know that

$$\bar{\nu}_{\text{vib}} (\text{cm}^{-1}) = 1303.16 \sqrt{\frac{k (\text{millidynes/\AA})}{\mu_m (\text{amu})}}$$

Therefore,

$$k = \frac{2889 \times 2889 \times 35}{1303.16 \times 1303.16 \times 36} = 4.77 \text{ millidynes/\AA}$$

4.8.3 Rotational-Vibrational Raman Spectra of Diatomic Molecules

The rotational fine structure appears in the vibrational spectra of a sample in the gaseous phase. The selection rules of vibrational ($\Delta V = \pm 1, \pm 2, \pm 3, \dots$) and rotational ($\Delta J = 0, \pm 2$) are valid in this case also. Because of the rule $\Delta J = 0$, a central line (Q-branch) appears in the fine structure which, of course, is missing in the vibrational structure of the infrared vibrational band since in the infrared spectra, $\Delta J = 0$ is not allowed. Further due to the rule $\Delta J = \pm 2$, the analog of P- and R-branches with a spacing of $2B$ in infrared spectra appears as O and S with spacing of the order of $4B$ in the Raman rotational-vibrational spectra. The Stokes lines for $V = 0 \rightarrow 1$ transition are

$\Delta J = 0$	$\bar{\nu}_{\text{rot-vib}} = \nu_0 - w_e (1 - 2x_e)$	for all J	Q-branch
$\Delta J = +2$	$\bar{\nu}_{\text{rot-vib}} = \nu_0 - w_e (1 - 2x_e) + B(4J + 6)$	$J = 0, 1, 2, \dots$	S-branch
$\Delta J = -2$	$\bar{\nu}_{\text{rot-vib}} = \nu_0 - w_e (1 - 2x_e) + B(4J - 2)$	$J = 2, 3, 4, \dots$	O-branch

The scheme diagram of the theoretical rotational-vibrational spectrum of a diatomic molecule is presented in Fig. 4.9. The theoretical structure pattern of Fig. 4.9 corresponds to the experimentally observed spectra of O_2 and HCl as shown in Fig. 4.10.

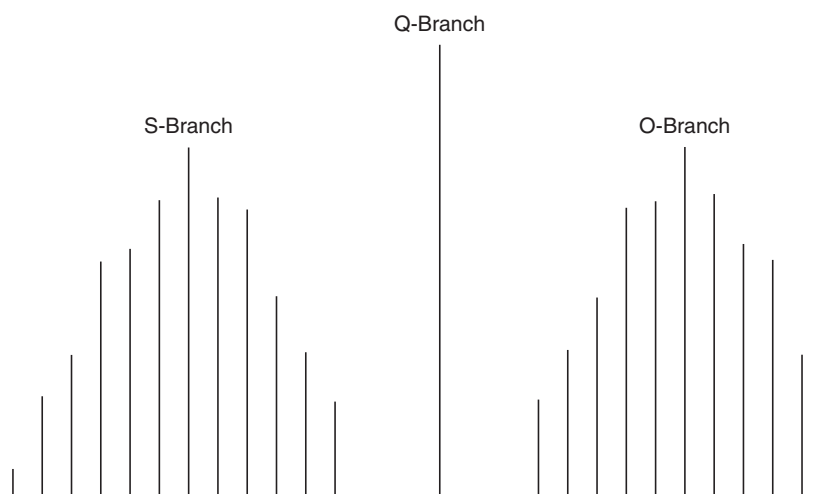
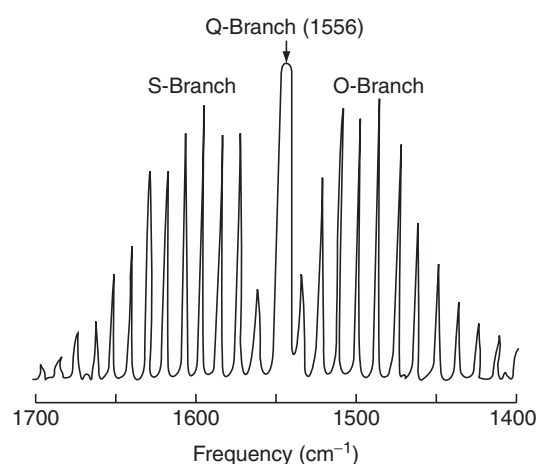
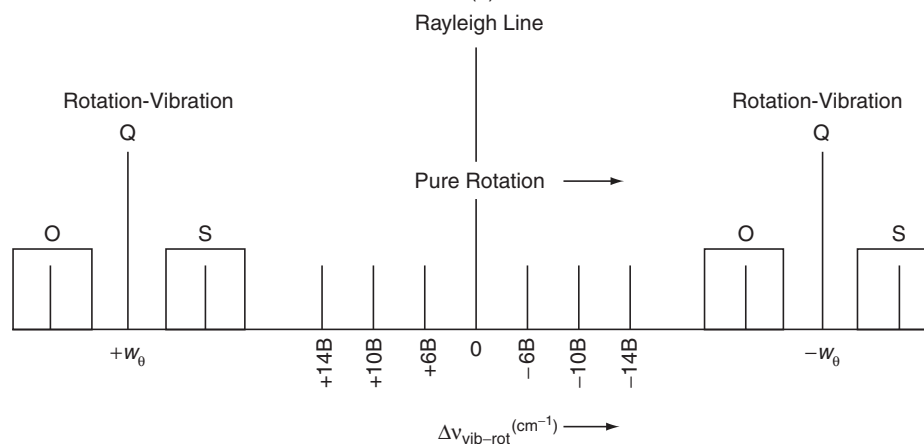


Fig. 4.9 Theoretical Raman rotational-vibrational spectrum of a diatomic molecule. Stokes lines for $V=0 \rightarrow 1$ transition.



(a)



(b)

Fig. 4.10 (a) Vibration-rotation band of oxygen, and (b) Schematic diagram for rotation-vibration Raman spectrum of HCl vapour; $B=10 \text{ cm}^{-1}$; $w_e = 2860 \text{ cm}^{-1}$.

4.9 VIBRATIONAL RAMAN SPECTRA OF POLYATOMIC MOLECULES

The vibrational Raman spectra are generally simpler as compared to infrared since fewer combination and overtone bands appear. Just like vibrational infrared spectra, the vibrational Raman spectra of polyatomic molecules are more complex than diatomic molecules. However, the basic features of the spectra can be understood by extending the treatment of the Raman vibrational spectra of diatomic molecules to polyatomic molecules.

For polyatomic molecules, as in the infrared spectra, we need to know the number of fundamental modes of vibrations and their symmetry in order to ascertain the Raman activity of each vibration. All molecules having centre of symmetry, say CO_2 , exhibit the principle of mutual exclusion according to which *all vibrations of a molecule, with centre of symmetry, which are Raman active are infrared inactive and vice versa*. In other words, if a molecule has centre of symmetry, no fundamental frequency can appear in both the Raman and infrared spectra. The asymmetric stretching (2349 cm^{-1}) and bending (667 cm^{-1}) vibrations of CO_2 are infrared active, while symmetric stretching (1330 cm^{-1}) is Raman active only. In general, symmetrical vibrations give rise to Raman scattering while antisymmetrical vibrations usually yield strong infrared absorption. Just like infrared spectra, the different symmetry properties of normal modes are important when considering the rotational fine structure of the vibrational bands.

4.10 VARIOUS FORMS OF RAMAN SCATTERING

4.10.1 Electronic Raman Effect/Scattering (ERE/ERS)

Normal Raman scattering is associated with the excitation and de-excitation of rotational and vibrational quanta and is a two-photon process. The two-photon process is feasible provided the transitional levels have the same parity. This is possible only if the energy gap between the transitional levels is small as in the case of rotational and vibrational energy levels. Due to this reason, the Raman scattering is suited for low-lying energy levels with the same parity as the ground state. Since these conditions are not met easily by electronic levels, the electronic Raman scattering was observed at a much later stage than vibrational and rotational Raman scattering. However, the electronic energy levels of paramagnetic ions particularly those of rare earths qualify the parity rule, therefore, these types of ions exhibit electronic Raman scattering. Electronic Raman scattering has been observed in Ce, Yb, Eu, Nd, Pr, etc., ions. The NO molecule also exhibits electronic Raman scattering in the ultraviolet and visible region. To summarise, electronic Raman scattering occurs when the differences ($\nu_0 - \nu_R$) corresponds to the energy of electronic excitation of the molecules or ions. In NO, besides the lines $\nu_R = \nu_0 \pm \nu_{\text{vib/rot}}$, we also find the lines,

$$\nu_R = \nu_0 \pm ({}^2\Pi_{3/2} - {}^2\Pi_{1/2}) \quad (4.49)$$

where ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$ are the components of the ground state of the NO molecule, i.e. ${}^2\Pi$. The direct combination of these terms is not allowed by the selection rule $\Delta\Sigma = 0$. However, the general selection rule for the rotational and vibrational terms of symmetric molecules according to which *two terms that combine with the third do not ordinarily intercombine*, holds good in this case.

4.10.2 Resonance Raman Scattering/Effect (RRS/RRE)

Electronic absorption spectrum of a molecule arises because of the transition between two electronic states of a molecule. The energy separation between two electronic states is very large. Each electronic state has vibrational and rotational energy levels associated with it so that electronic transition is spread over a wide range of frequencies and hence the spectrum is called *band spectrum*.

When the frequency of the exciting radiation in Raman scattering falls in the electronic absorption band spectrum of the molecule, there is a dramatic gain in the scattering efficiency ($\sim 10^2$ – 10^6). The intensity of Raman scattering increases as the frequency of the exciting radiation is continuously varied and becomes maximum at the frequency of maximum electronic absorption. This is known as resonance Raman effect or scattering. When the exciting frequency is close to or coincides with an absorption transition between discrete energy levels, e.g. rotational–vibrational level in a molecule of the gas phase, then Resonance Raman Effect (RRE) is called Discrete Resonance Raman Effect (DRRE). Due to high intensity of scattered radiation observed in RRE, very low concentration of analyte, i.e. as low as 10^{-8} mole lit^{-1} , has been observed in contrast to the concentration limit of normal or spontaneous Raman effect which is greater than 0.1 mole lit^{-1} . Since resonance enhancement is restricted to the Raman lines associated with a chromophore, Raman resonance spectra consist of a few lines.

The schematic diagram for resonance Raman scattering process is compared with fluorescent, phosphorescent and absorption emission processes in Fig. 4.11. The RRE differs from normal Raman effect in that the electron is promoted to an excited electronic state E_x^e followed by an immediate relaxation to a vibronic or vibrational level, E_s^v of the electronic ground state, E_i^e . Fluorescence arises from the radiative transitions from the lowest vibrational level of the higher electronic state to the various vibrational levels (E_s^v) of the ground electronic state (E_i^e). Thus, RRE differs from fluorescence in that the relaxation to the ground state is now preceded by

prior relaxation to the lowest vibrational level of the excited state. Fluorescence is due to the transition between the states of the same multiplicity, i.e. singlet ($S_1 \rightarrow S_0$), while phosphorescence is due to transition between electronic states of different multiplicity, i.e. singlet (S_1) $\rightarrow$ triplet (T_1) $\rightarrow$ singlet (S_0). However, in certain cases, triplet–triplet transitions are also possible, e.g. in the phosphorescence spectra of fluorescein, two absorption bands corresponding to $T_1 \leftarrow T_0$ and $T_2 \leftarrow T_0$ transitions have been observed. Vibrational analyses of triplet–triplet absorptions have imparted information about the geometry of the triplet molecules and their interaction with the environment. The energy released in the nonradiative transitions occurring in fluorescence and phosphorescence goes into the vibrational energy of the molecules. The spacing between the bands in the fluorescence spectrum is equal to the difference in energy between the vibrational levels of the ground state while the spacing between the bands in the absorption spectrum is equal to the difference in energy between the vibrational levels of the excited state. If the spacing of the vibrational levels in the excited state are similar to those in the ground state, there will be an approximate ‘mirror image’ relationship between the absorption and fluorescence spectra (Fig. 4.11). The time scale for these processes is quite different. The time for Raman relaxation is less than 10^{-14} second, for fluorescent emission is of the order of 10^{-6} – 10^{-8} second, for phosphorescence is 10^{-3} – 10^2 second, for vibrational transition is $\sim 10^{-13}$ second, for rotational transition is 10^{-12} second and for electronic transition is $\sim 10^{-15}$ second.

The intensity rule of normal Raman effect does not hold good in RRS. The intensity of 1088 and 288 cm^{-1} Raman lines of calcite increases manifold in the ultraviolet region than given by $(\nu_0 - \nu_{is})^4$. This effect may be explained on the assumptions: (i) all the molecules are in nondegenerate electronic levels, and (ii) all are oriented identically in space. Now, if a single excited electronic level x is effective, the intensity of Raman line of displacement ν_{is} depends upon the frequency of the exciting radiation ν_0 by the relation

$$I_{is} = C(\nu_0 \pm \nu_{is})^4 \left[\frac{\nu_{xi}^2 + \nu_0^2}{(\nu_{xi}^2 - \nu_0^2)^2} \right] \quad (4.50)$$

where the term C is independent of ν_0 .

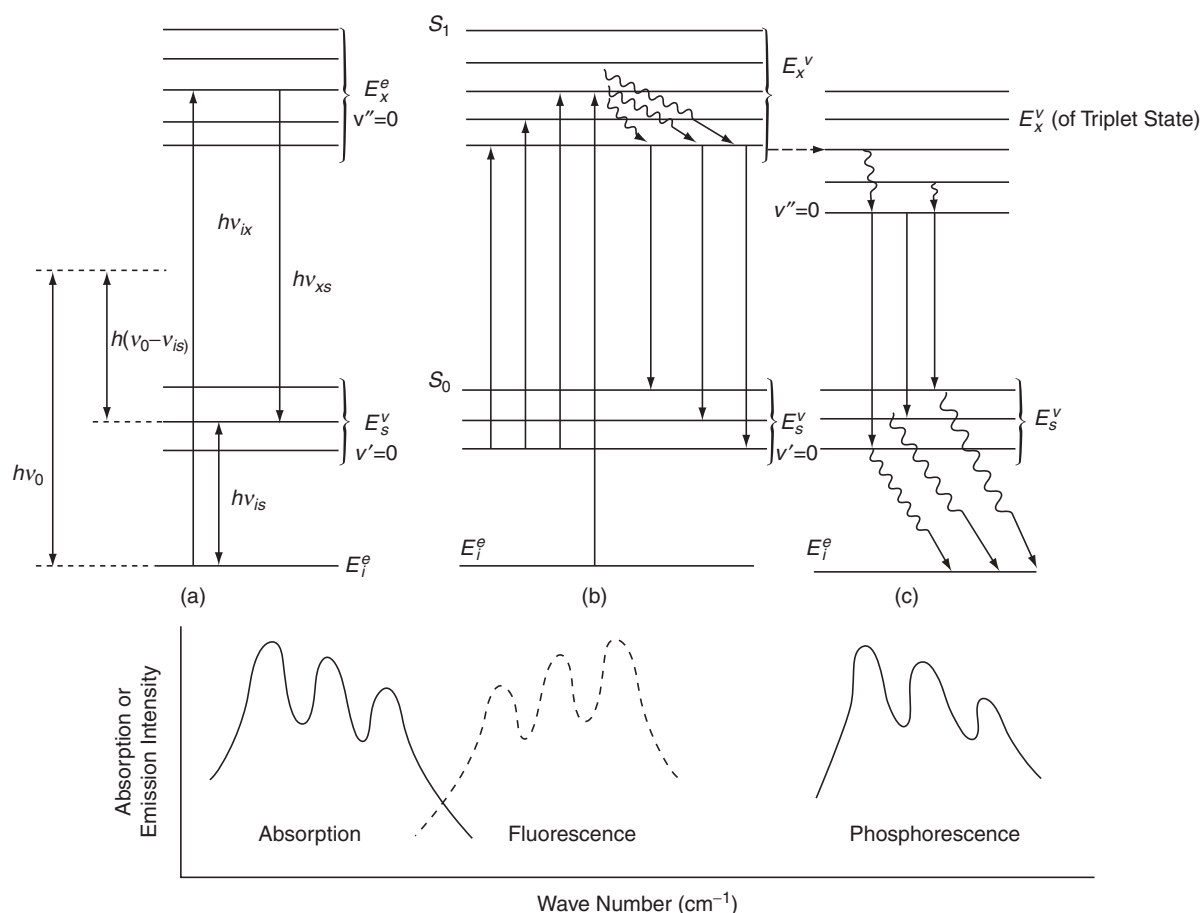


Fig. 4.11 Schematic energy level diagram of (a) resonance Raman scattering, (b) fluorescence emission and absorption processes, and (c) phosphorescence process. The wavy arrows stand for radiationless relaxation.

This effect is used to supplement absorption and fluorescent studies and for investigating the structural changes in molecules and excited electronic states. This process has been used to study biological molecules, viz., haemoglobin, oxyhaemoglobin, de-oxyhaemoglobin, cytochrome-C, rubridoxin, carotenoid pigments, vitamin A type molecules and bacteriorhodospin, etc., under physiologically significant conditions. Oxidation state and spin of iron atoms in haemoglobin and cytochrome-C have been determined. The resonance Raman bands are due solely to vibrational modes of the tetrapyrrole chromophore group of these molecules. A major limitation of RRE-like normal Raman effect is the interference by the fluorescence either by the analyte or by the other species present in the sample.

4.10.3 Stimulated Raman Scattering/Effect (SRS/SRE)

This is a nonlinear Raman scattering involving a four-photon process, i.e. two with the frequency of incident radiation and one each with the frequency of Stokes and anti-Stokes Raman lines. SRS is coherent and can be used as a source of laser radiation. This process occurs when one or more high-intensity lasers are used as exciters. The intensity of the exciters should be greater than the threshold intensity for normal Raman scattering, i.e. >1 mW. The intensities of the stimulated Raman lines grow dramatically under these conditions and is greater than that of the normal Raman lines by a factor of e^{10} to e^{20} . When the intensity of incident radiation is very high, higher order Stokes lines with progressively diminishing intensities are observed with frequency shifts corresponding to $2\nu_{\text{vib}}$, $4\nu_{\text{vib}}$, etc. Anti-Stokes lines may also be observed. The Stokes and anti-Stokes lines are highly directional. The fundamentals and octaves are not equally spaced in SRS. Since a limited number of Raman lines are observed in SRS, it is not good for study of structure of molecules and chemical processes.

The first such effect was observed in nitrobenzene excited with a ruby laser at $6943 \text{ \AA}$ which gives rise to Stokes radiation at $7650 \text{ \AA}$ with an intensity of over 25 per cent of ruby laser. The direction of scattered radiation was almost collinear with the incident laser radiation.

The vibrational bands obtained in some of the molecules by SRS are CCl_4 —460, CS_2 —655, C_6H_6 —990, 3064, styrene—999, 1631, 3056, benzonitrile—1002, 2229 and acetone—2921 cm^{-1} .

4.10.4 Spin-Flip Raman Scattering/Effect (SFRS/SFRE)

In this process, Raman scattering is because of the flipping of the spin of the electronic state between two opposite directions under the action of a photon. The shift in this process is twice the cyclotron frequency of the electron.

4.10.5 Continuous Wave Stimulated Raman Gain Spectroscopy (CWSRGS)

The gain in the Raman scattering is achieved via the polarisability term β , using two laser sources of high intensities. The intensity of one of the laser beams (probe) is enhanced by the other (pump). High resolution is attained with two continuous single-frequency lasers. This process of achieving Raman gain is called continuous-wave stimulated Raman gain spectroscopy.

4.10.6 Inverse Raman Effect/Scattering (IRE/IRS)

When a sample is excited simultaneously by a monochromatic radiation of high intensity and a continuous radiation beam with a well-defined absorption band (continuum), a sharp absorption spectrum corresponding to the Raman transitions is observed on the anti-Stokes side. This is called inverse Raman scattering. The absorption spectrum is due to the absorption of vibrational quanta from the continuum. Since no threshold is found in IRE, the complete Raman spectrum may be obtained in principle. IRE may be employed to study gases, liquids, solids and even free radicals provided a suitable broad continuum and pulse lasers are available.

4.10.7 Hyper Raman Scattering/Effect (HRS/HRE)

The dipole moment induced in a molecule by high electric field of incident laser radiation of high intensity is given by the expression

$$M = \alpha E + \frac{1}{2}\beta E^2 + \frac{1}{6}\gamma E^3 + \dots \quad (4.51)$$

The molecular distortions caused by the weak electric field of radiation are insufficient to change the bond energies in the molecule. Consequently, the induced dipole moment varies directly as E and the first term α is the cause of normal Raman effect. However, under high electric field it is not so and the higher terms, viz., β , γ , etc.,

i.e. second- and third-order hyperpolarisability tensors, etc., which perturbs the linear behaviour appears. The higher terms become significant only when E is very high. The second term β is the cause of hyper Raman effect and the intensity of Raman lines in hyper scattering depends upon this quantity.

This is a very weak nonlinear incoherent scattering process and is observed along with stimulated Raman effect. This is due to high electric field of incident laser radiation with frequency ν_0 (Ruby laser) and occurs in the neighbourhood of frequency $2\nu_0$ as exciting radiation with frequency shifts corresponding to vibrational, rotational or phonon frequencies, i.e. the Raman lines in this effect appear as $2\nu_0 \pm \nu_{\text{vib}}$ rather than in the normal Raman form $\nu_0 \pm \nu_{\text{vib}}$, or in other words, hyperfine scattering occurs when non-linear inelastic scattering takes place with higher harmonics of the incident radiations as exciter. The scattering rules of normal Raman scattering are not valid in the case of hyper Raman scattering. Consequently, the normal modes of vibration which are infrared and normal Raman inactive may be hyper Raman active. H_2O , CCl_4 , CH_3CN , etc., exhibit hyper Raman effect. Soft mode of SrTiO_3 ($T_c = 110\text{ K}$) is inactive in normal Raman scattering but is active in hyper Raman scattering (*a strongly anharmonic vibration with the frequency tending to zero for $T \rightarrow T_c$ is called a soft vibration*), e.g. the soft mode of Hg_2Cl_2 appears at 12.5 cm^{-1} at room temperature (T) and tends to zero for $T \rightarrow T_c$ (185 K), T_c being the phase transition temperature.

4.10.8 Coherent Anti-Stokes Raman Scattering/Effect (CARS/CARE)

CARS is a nonlinear Raman scattering process which arises due to the coherent polarisability term γ of the molecule. A molecule is simultaneously excited with laser exciters with frequencies ν_0 and ν'_0 such that $\nu_0 > \nu'_0$ coherent scattered radiation will be produced at frequency $2\nu_0 - \nu'_0$ only if $(\nu_0 - \nu'_0)$ corresponds to one of the Raman frequencies ν_R^a of the molecule, i.e. $\nu_0 - \nu'_0 = \nu_R^a$. CARS is very intense, coherent and directional. Therefore, due to its coherency and directionality, it can be isolated from incoherent fluorescence if any in the medium by spatial filtering. Further, CARS will be free from fluorescence since the frequencies of anti-Stokes lines are on the higher side of the excitation frequencies. Coherent anti-Stokes Raman spectrum is recorded by keeping the frequency ν_0 (pump) constant and varying ν'_0 (probe) to cover the entire range of the Raman spectrum. CARS is used to determine the vibrational and rotational constants of molecules very accurately. It is used for measurement of air pollutants in the environment and study of transient molecules, i.e. short-lived species produced in various chemical and physical processes. Temperatures in combustion and jet engines, industrial furnaces and their exhausts can be measured from the temperature dependence of intensity of scattered radiation.

4.10.9 Coherent Stokes Raman Scattering/Effect (CSRS/CSRE)

This is similar to CARS except that CSRS is produced at frequency $2\nu'_0 - \nu_0$ provided $\nu'_0 - \nu_0$ coincides with a Raman frequency ν_R^s of the medium, i.e. $\nu'_0 - \nu_0 = \nu_R^s$.

4.10.10 Higher-Order Raman Spectral Excitation Scattering/Effect (HORSES/HORSEE)

This is higher-order mixing process, e.g. six photons or second-order four photons mixing, which occurs when the intensities of the coherent anti-Stokes Raman frequencies, i.e. $2\nu_0 - \nu'_0$ and Stokes Raman frequencies, i.e. $2\nu'_0 - \nu_0$ are very large. These frequencies may further interact with the frequencies of incident beams to produce scattered radiations at still higher frequencies, e.g. $3\nu_0 - 2\nu'_0$. This higher-order scattering process is known as higher-order Raman spectral excitation scattering. The second-order Raman spectra may be observed by HORSES.

4.10.11 Surface-Enhanced Raman Scattering/Effect (SERS/SERE)

The intensity of Raman scattered radiation grows by a factor of 10^3 – 10^6 when the molecules adsorbed on metal surfaces are involved in scattering. This is known as surface enhanced Raman scattering. Consequently, detection limits in the range 10^{-9} – 10^{-12} mole lit^{-1} have been observed. When pyridine is adsorbed on a silver surface, the intensity increases by a factor of 6. The enhancement depends upon (i) type of adsorbent and adsorbate, (ii) nature of metal surface whether it is a film or colloidal particle, and (iii) on the nature of adsorption, i.e. chemical adsorption or physical adsorption. This effect arises because of the interaction between the conduction electrons in metals and adsorbate, i.e. the adsorbed molecule on the metal surface. The coupling occurs through an electric field (called image electric field) generated in the metal by the adsorbate. The induced dipole moment is then expressed as

$$M = \alpha(E + E_{ad}) \quad (4.52)$$

The higher polarisability terms are negligible. E_{ad} becomes very large when the frequency of incident radiation is in resonance with the normal mode of the conduction electrons in the metal. Now since $M \propto (E + E_{ad})$ rather than E , the intensity increases manifold. This effect is used for studying corrosion of metal surfaces, vibrational structure of chemical entities and biomolecules available in small quantities since the cross-section increases on adsorption. Surface microstructure of industrial materials may also be determined by this process.

4.10.12 Time-Resolved Raman Spectroscopy (TRRS)

When the normal Raman scattering is recorded instantaneously using picosecond pulses from high-intensity lasers, the spectroscopy is called Time-Resolved Raman Spectroscopy (TRRS or TR²S) while when the time-resolved resonance Raman scattering is observed using picosecond pulses, the spectroscopy is known as Time-Resolved Resonance Raman Spectroscopy (TR³S). Time-resolved Raman spectroscopy is used for the study of mechanism involved in a number of photochemical, photophysical and photobiological processes. Transient species with lifetimes of the order of 0.1 picoseconds have been studied.

4.10.13 Raman Optical Activity (ROA)

The small differences between the intensity of Raman scattered radiation from left and right circularly polarised radiation is known as Raman Optical Activity (ROA) and is shown by optically active substances. ROA is expressed in terms of a parameter called Circular Intensity Differential (CID) and is defined as

$$\delta = \frac{I_R - I_L}{I_R + I_L} \quad (4.53)$$

where I_R and I_L are the intensities of scattered radiation from right and left circularly polarised incident radiation.

4.10.14 Raman-Induced Kerr Effect Spectroscopy (RIKES)

When a medium is irradiated simultaneously with a weak linearly polarised beam of radiation with frequency ν_0 (probe) and a circularly polarised beam of frequency ν'_0 (pump) from a high-power laser, a new beam with frequency ν results. The new beam is because of the nonlinear interaction between the frequencies ν_0 and ν'_0 and is perpendicularly polarised with respect to probe. The new beam exhibits resonance only when $\nu'_0 - \nu_0$ is near the frequency of the Raman active vibration of the medium, i.e. $\nu'_0 - \nu_0 = \nu_{\text{vib}}$. This process of induction of Kerr effect, only at Raman shifted frequencies of a medium by a laser beam is known as Raman induced Kerr effect spectroscopy. Some organic liquids exhibit this effect.

4.11 BASIC PRINCIPLES OF A RAMAN SPECTROMETER

To obtain a good Raman spectrum, the intensity of incident radiation should be very strong since the Raman scattering is generally weak and secondly the irradiating beam should be highly monochromatic as Raman lines appear on both sides of the Rayleigh line. The flowsheet diagram of a basic laser Raman spectrometer is shown in Fig. 4.12.

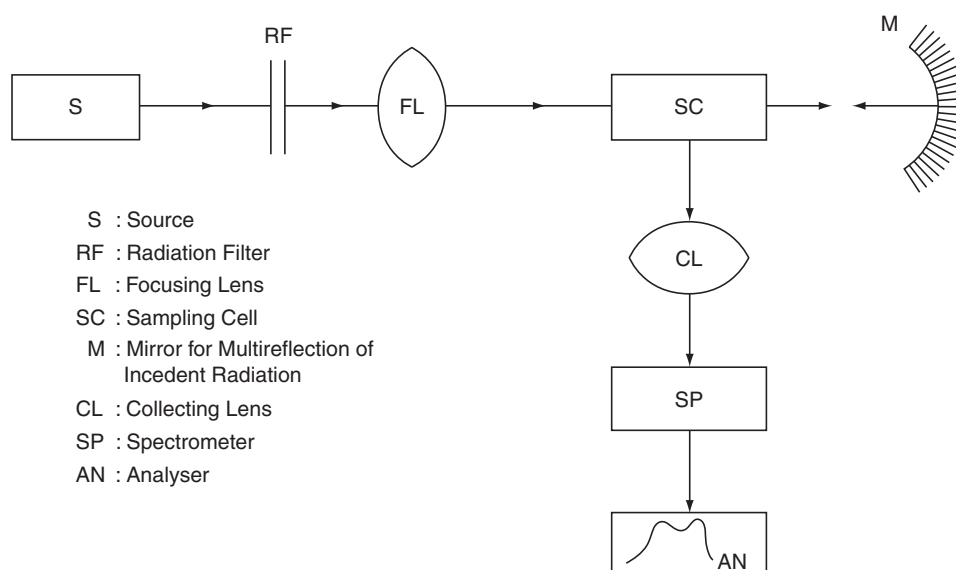


Fig. 4.12 Flowsheet diagram of a simple Raman spectrometer.

It consists of (i) a suitable stable gas laser source (S), and (ii) an optical system comprising RF , FL and M to focus the beam on or into the sample as well as CL to feed the scattered radiation to SP for counting the scattered photons as a function of frequencies. This analysis is then displayed as a plot of scattering intensity versus frequency by the recorder. Typical hypothetical and experimental Raman spectra are presented in Figs 4.13 to 4.15.

Before the advent of a lasers, mercury arcs were used as a source of radiation, i.e. light- and most of the work was carried out at 4358 ($2s \rightarrow 2p_2$) and 5461 ($2s \rightarrow 2p_1$) Å lines of mercury. An aqueous solution of sodium nitrite or quinine sulphate filters out the undesirable 4047 Å ($2s \rightarrow 2p_3$) line of mercury. Saturated solution of iodine in carbon tetrachloride filters out 4358 Å line of mercury. These days, the commonly used lasers for Raman excitation are (i) continuously operating He-Ne (6328 Å), Ar⁺ ion (4880, 5145 Å) and Hg-Cd (4415, 3250 Å) gas lasers; (ii) pulsed and the continuously operating forms of Ruby (6943 Å) and the Nd-YAG (1.06 micron) solid state lasers; (iii) tunable dye lasers, e.g. rhodamine 6G laser, with continuously variable wavelength in the visible region (0.43–0.65 μm); and (iv) UV lasers (184–260 nm) have been developed by the principle of repeated stimulated anti-Stokes Raman scattering in hydrogen under pressure and thus shifting the harmonics of Q-switched Nd-YAG laser. The power of lasers used for linear Raman spectroscopy, i.e. $M \propto E$, is of the order of 50 mW–2 W.

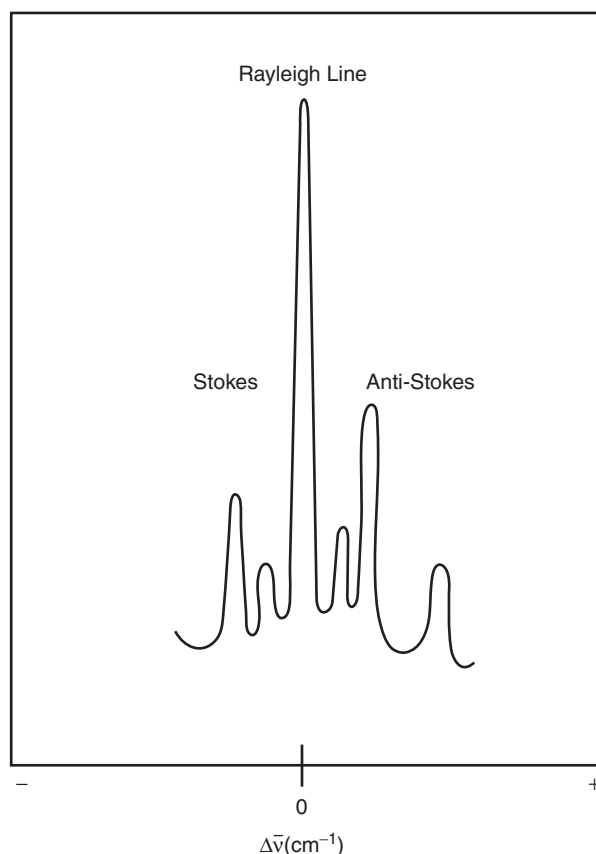


Fig. 4.13 Hypothetical laser Raman spectrum.

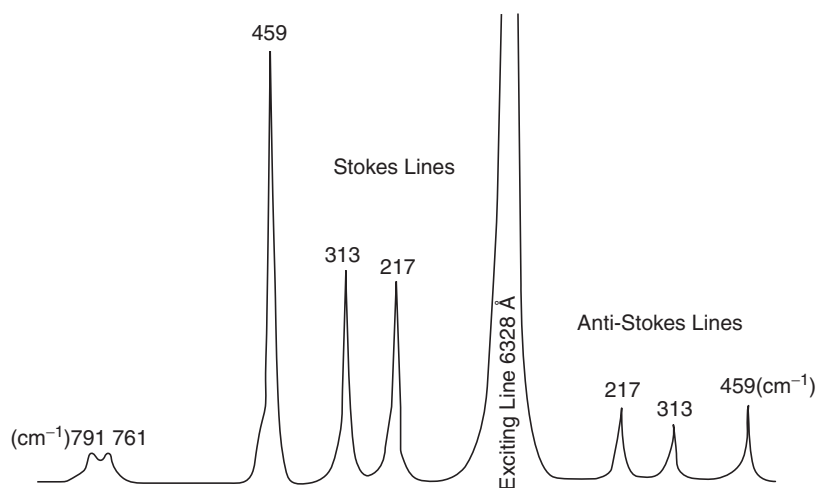


Fig. 4.14 Laser Raman spectrum of carbon tetrachloride.

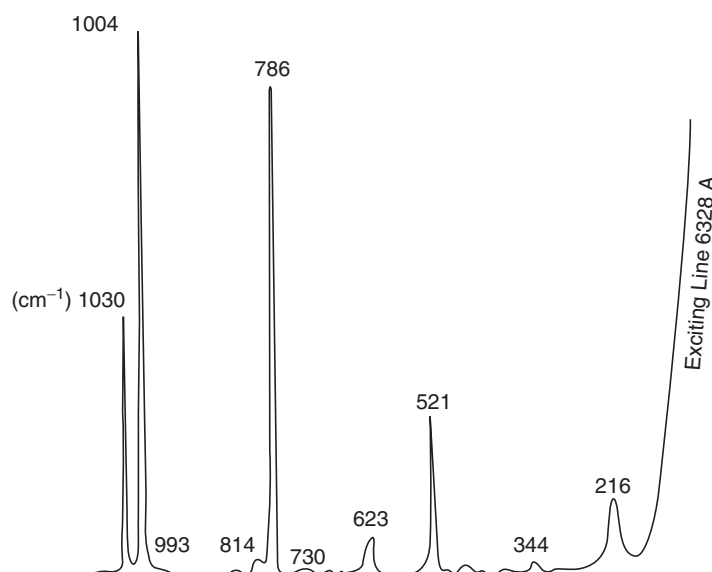


Fig. 4.15 Laser Raman spectrum of toluene in the region of up to 1100 cm^{-1} .

The choice of lasers which, of course, are interchangeable for specific type of studies are most important because of their high cost. The He-Ne (100 mW, 6328 Å) laser is frequently used due to its narrow wavelength. With this laser source we need not (i) cool the sample, and (ii) use filters to get monochromatic beam of radiation as is done in case of Hg-arc source. Further, Raman spectra can be recorded using 0.03 ml or less of the analyte whereas 10 ml of liquid or several litres of gaseous sample are required when Hg arc is used as a source of radiation. Fluorescence emission in the sample which could be excited by 4358 Å line of Hg complicates Raman spectroscopy and may be completely eliminated by careful sample and reagent purification and using 6328 Å line of He-Ne laser as a source of excitation. The other main advantages of laser sources are (i) the second-order Raman spectra can be recorded; (ii) the polarisation of laser beam is well-defined and may be controlled within 0.1 per cent; (iii) the broadening due to Doppler effect can be minimised; and (iv) the width of the laser line is of the order of 0.005 cm^{-1} or less; therefore, precise information could be obtained on the width and fine structure of Raman bands.

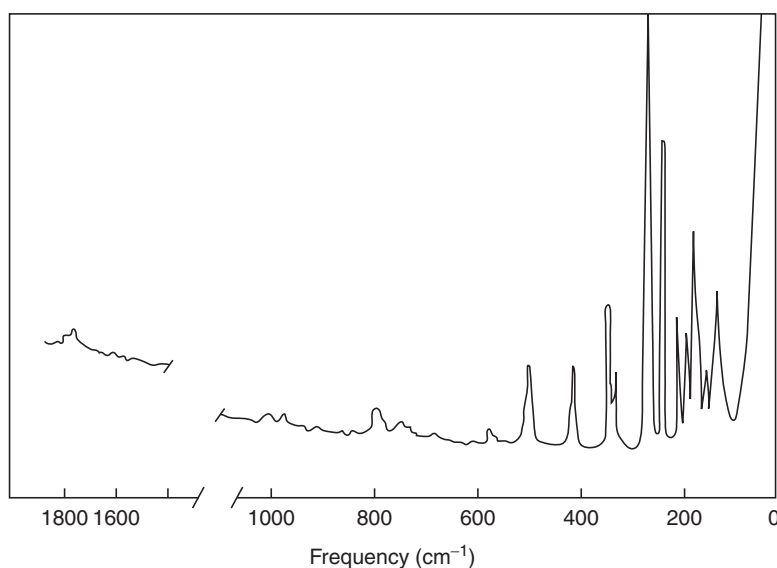
The Krypton-ion laser with lines at 5682 and 6471 Å is useful for the samples absorbing at 5000 Å except for resonance Raman spectral work. Generally, the best choice is an argon laser with lines at 5145 or 4880 Å with high output power. The additional advantage of argon-ion laser is that the detector efficiency and Raman scattering cross-section is great near 5000 Å. These factors and high power levels are a must for work with dilute solutions. When the background fluorescence is low, the signal-to-noise ratio of Raman band approximates to the square root of the product of analyte concentration, time of measurement and laser power. Fluorescence declines most rapidly at higher laser power and low irradiating wavelength. The presence of fluorescence indicates absorption of radiation, some of which is dissipated as heat and causes localised heating and hence analyte damage, especially when the analyte is a biological sample.

The sample cells used in Raman spectroscopy are made up of nonfluorescent fused quartz and have well-polished flat bottoms. The top of the cell is sealed with a transparent cap to avoid dust and is designed to permit deoxygenation of the sample. The cell is completely filled to avoid reflections from the curved air-liquid interface. The spectra of clear coloured or colourless liquids, suspensions or moderately turbid solutions are recorded by focusing the beam vertically through the bottom window into the sample and then collecting the scattered radiation in a direction perpendicular to the incident beam. The spectra of solids are recorded in capillaries, but solids give too much Rayleigh background.

The samples which are sensitive to laser wavelengths, e.g. CBr_3COCl , CCl_3COCl , etc., are likely to be degraded and hence the spectra of such samples are recorded by the rotating cell technique. The Raman spectrum of CBr_3COCl recorded by this technique is shown in Fig. 4.16.

The irradiation of biological substances absorbing at laser wavelength leads to local heating which may degrade some biological molecules. In these type of biological systems, e.g. cytochrome-C, haemoglobin, etc., the resonance Raman scattering of laser radiations from vibrational modes of biological molecules can be recorded because of the high detection efficiency ($10^{-8}\text{ mole lit}^{-1}$) of RRS.

The characteristic Raman wave numbers for certain univalent and multivalent bonds which are averages of a large number found for the homologous series are listed in Table 4.1.

Fig. 4.16 Laser Raman spectrum of CBr_3COCl .Table 4.1 Raman vibrational frequencies (in cm^{-1}) of some univalent and multivalent bonds.

Bond	Bond Frequency
H—H	4158
C—H (aromatic)	3050
C—H (aliphatic)	2924
N—H	3370
O—H	3650
S—H	2572
S—D	1865
C—C	993
C = C	1620
C $\equiv$ C	2120
C—N	1033
C = N	1650
C $\equiv$ N	2150
C—O	1030
C = O	1700
C $\equiv$ O	2146
S—S	509
C—S	650
C = S	1225
C—Cl	710
C—Br	597
C—I	526

4.12 APPLICATIONS OF RAMAN SPECTROSCOPY

Due to simplicity of this technique, studies of Raman spectra have many advantages over infrared spectra. The possibility of detecting directly the frequencies of infrared inactive vibrations makes the method of Raman scattering particularly valuable. This method is likewise very important for studying the structure of molecules, the structural changes occurring in molecules due to association, dissociation, solvation, etc., in studies of chemical

equilibria, for analysing complex mixtures, for identifying compounds, and to find the energy difference between rotamers, etc. Raman technique is also useful for studying the kinetics of fast reactions.

Laser Raman spectroscopy enjoys a significant biological advantage over infrared spectroscopy since water interferes to a far less extent. Consequently, the scattering from water can largely be ignored, e.g. the scattering from the water OH bending vibration in the amide 1 region (1650 cm^{-1}), although significant in intensity, is relatively weak compared to its infrared absorption. The water background in Raman spectroscopy can be overcome either by using high concentration of biological samples, e.g. polypeptides like poly-L-alanine, poly-L-proline and polyglycine or protein, or by using computer-assisted difference techniques. With the latter technique, it is possible to analyse even very low concentrations of the analyte in solution or suspensions. The Raman vibrational bands of H_2O and D_2O are recorded in Table 4.2.

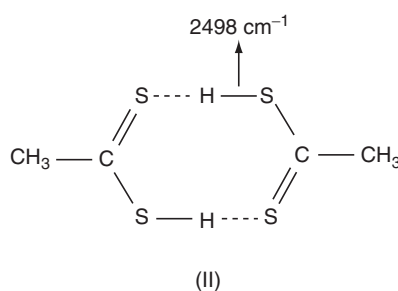
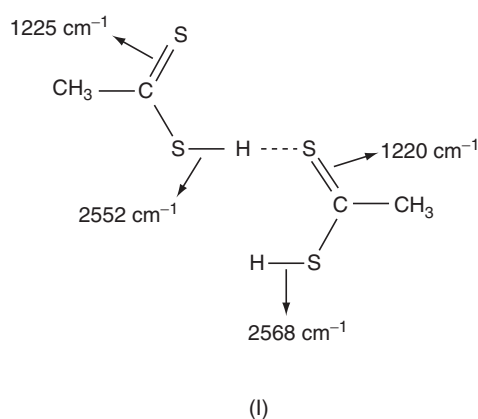
Table 4.2 Raman vibrational bands (in cm^{-1}) of H_2O and D_2O .

Vibration	H_2O	D_2O
O—X stretching	3493 (vs, vb), 3300 (s), 3600, 3500 (mc)	2532 (vs, vb), 2400 (s), 2600 (rnc)
Association	vw, b	—
X—O—X' bending	1640 (m)	1280 (m)
Libration (three bands)	~450–780 (w)	375–550 (w)
Hindered translation	~152–175 (w), 60 (w)	~152–175 (w)

b—broad, vb—very broad, s—strong, vs—very strong, m—medium, mc—minor components, w—weak, vw—very weak, X = H or D.

4.12.1 Study of Environmental Effects on Molecular Systems

The molecules are generally affected by their environments. The shift in the Raman lines of the molecule with change of environment may, therefore, provide valuable information about the environmental effects since Raman lines are sensitive to inter as well as intra-molecular interactions, e.g. the appearance of two SH bands at $2568/1863$ and $2552/1853$ and two C=S bands $1225/1212$ and $1220/1198\text{ cm}^{-1}$ in the Raman spectra of $\text{CH}_3\text{CSSH}/\text{CH}_3\text{CSSD}$ in CH_2Cl_2 and a single band at 2498 cm^{-1} in the Raman spectra of neat acid is an evidence that dithioacids exist as an open-chain dimer (I) in the solution phase while cyclic dimer (II) in the virgin liquid phase as shown below.



A comparison of laser Raman spectra of NbOCl_3 in the gas (at 300 °C) and solid phase reveals that a shift occurs in the $\text{Nb}=\text{O}$ stretching frequency from 997 cm^{-1} in the gas phase, characteristic of $\text{Nb}=\text{O}$ double bond, to 770 cm^{-1} in the solid phase characteristic of a bridged oxygen. Thus, it appears that in gas phase, the NbOCl_3 molecule is a simple tetrahedron, although it has polymeric structure in the solid state as shown by x-ray crystallography.

4.12.2 Mechanism of Tautomerism and Polymerisation

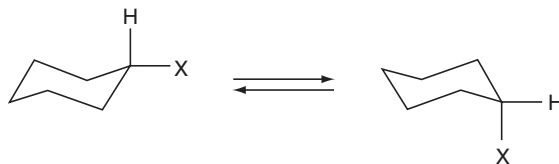
The tautomerism and polymerisation established by other methods may be confirmed by Raman spectroscopy. The two Raman lines at 1632 and 1725 cm^{-1} which are characteristic of ethylenic bond have been observed in the Raman spectrum of ethylacetoacetate ($\text{CH}_3\text{COCH}_2\text{COOCH}_2\text{CH}_3$) but are absent in the spectrum of ethyldimethylacetoacetate [$(\text{CH}_3)_2\text{HCCOCH}_2\text{COOCH}_2\text{CH}_3$] which shows two bands characteristic of the carboxyl group at 1707 and 1738 cm^{-1} . From this we infer that ethylacetoacetate exhibits keto-enol tautomerism. The intensity of the Raman band due to the double bond of methyl-methacrylate decreases gradually during polymerisation and the band almost disappears in the final polymers. This leads us to infer that polymerisation occurs because of the opening of the double bond. Further, by monitoring the intensity of double bond during the course of polymerisation, we can study the kinetics of polymerisation also.

4.12.3 Conformational Equilibria

The results on conformational equilibria may be supplemented by Raman spectroscopy as well. Let us consider the conformational equilibria.

where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OH}$, etc.

The frequencies of the Raman bands due to $\text{C}-\text{X}$ link in the two conformers say axial (a), and equatorial (e) are different due to the steric interactions with the adjacent protons, i.e. $\nu_{\text{C}-\text{X}}(e) > \nu_{\text{C}-\text{X}}(a)$. The intensity is directly proportional to the amount of the scattering species, i.e.



$$I_e \propto C_e$$

$$I_a \propto C_a$$

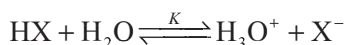
Thus,

$$K = \frac{I_e}{I_a} = \frac{C_e}{C_a} \cdot \frac{\alpha_e}{\alpha_a} \left[\text{assume } \frac{\alpha_e}{\alpha_a} \approx 1 \right] \quad (4.54)$$

Here, I_e and I_a are the intensities of the bands at $\nu_{\text{C}-\text{X}}(e)$ and $\nu_{\text{C}-\text{X}}(a)$ respectively, C_e and C_a stands for the concentrations of the respective conformers. Thus, by simply monitoring the intensities of the $\nu_{\text{C}-\text{X}}$ bands corresponding to the two conformers, we can determine K , the conformational equilibrium constant. The free energy difference for the two conformers in most of the compounds lies below 1 kcal mole^{-1} .

4.12.4 Study of Ionic Equilibria

Let us consider the dissociation of a mineral acid (HX) in water,



where K is the dissociation constant of the acid. The scattering intensity is directly proportional to the concentration of the scattering species, i.e.

$$I_{\text{X}^-} \propto [\text{X}^-]$$

$$I_{\text{HX}} \propto [\text{HX}]$$

$$K_{\text{HX}} = \frac{I_{\text{X}^-}}{I_{\text{HX}}} = \frac{\alpha[\text{X}^-]}{\alpha'[\text{HX}]} \left[\text{assume } \frac{\alpha}{\alpha'} \approx 1 \right] \quad (4.55)$$

Thus, by simply monitoring the scattering intensities of the vibrational bands of X^- and HX respectively, we can determine the value of K from Eq. (4.55).

Similarly, we can study the following equilibria.



$$K_{\text{H}_2\text{X}} = \frac{I_{\text{HX}^-}}{I_{\text{H}_2\text{X}}} = \frac{\beta [\text{HX}^-]}{\beta' [\text{H}_2\text{X}]} \left[\text{assume } \frac{\beta}{\beta'} \approx 1 \right] \quad (4.56a)$$

and

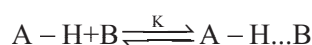


$$K_{\text{HX}^-} = \frac{I_{\text{X}^{2-}}}{I_{\text{HX}^-}} = \frac{\gamma [\text{X}^{2-}]}{\gamma' [\text{HX}^-]} \left[\text{assume } \frac{\gamma}{\gamma'} \approx 1 \right] \quad (4.56b)$$

Raman spectra of aqueous solutions of nitric and sulphuric acids of moderate concentrations give definite proof of the existence of unionised molecules. It is observed that sulphate ions are formed in very dilute solutions of sulphuric acid.

4.12.5 Study of Hydrogen-bonded Equilibria

Let us consider the following hydrogen-bonded equilibria.



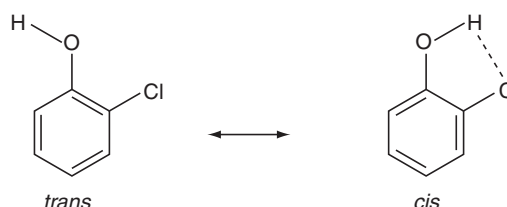
where A or B = O, N, S, F, etc.

The A—H stretching frequency will be modified as a result of H-bond formation. Thus, by measuring the scattered intensity of the free A—H and H-bonded A—H bands as function of concentration of B, the value of equilibrium constant K can be determined by the expression

$$K = \frac{[\text{A} - \text{H} \cdots \text{B}]}{[\text{A} - \text{H}][\text{B}]} \quad (4.57)$$

o-chlorophenol has two non-equivalent configurations in solution of carbontetrachloride, i.e.

The *cis* form is stabilised by the influence of OH $\cdots$ Cl interactions. Consequently, two bands corresponding to free OH (*trans*) and H-bonded OH, i.e. O—H $\cdots$ Cl (*cis*) should appear in the Raman spectrum of *o*-chlorophenol. The hydrogen bond equilibrium constant K can then be determined from the expression



$$K = \frac{I_{\text{cis}}}{I_{\text{trans}}} \quad (4.58)$$

where $I_{\text{cis}}/I_{\text{trans}}$ is intensity ratio of the OH stretching bands of the H-bonded and free OH groups. The intensity ratio of the first infrared overtones of the OH stretching band at 6910 cm^{-1} for the *cis* and at 7050 cm^{-1} for the *trans* isomer has been found to be of the order of 10.

4.12.6 Nature of Chemical Bond

The totally symmetric vibrations of the tetrahedral complex ML_4 (ZnCl_4^{2-} , 275 cm^{-1} ; CdCl_4^{2-} , 260 cm^{-1} ; PO_4^{3-} , 938 cm^{-1} ; SO_4^{2-} , 982 cm^{-1} ; ClO_4^- , 928 cm^{-1}) and octahedral complex ML_6 (SF_6 , 775 cm^{-1} ; UF_6 , 666 cm^{-1}) are Raman active only. The force constant for the M—L bond can be estimated from the frequency of the totally symmetric vibration employing the equation, $\nu_{\text{M-L}} = 1303.16 \sqrt{k/\mu_m}$ where k is the force constant in millidynes/Å and μ_m is the reduced mass in amu provided $\nu_{\text{M-L}}$ is in cm^{-1} . The high values of force constants for PO_4^{3-} (5.06), SO_4^{2-} (6.04); ClO_4^- (5.58) as compared to those of ZnCl_4^{2-} , (1.02); CdCl_4^{2-} , (1.07), SF_6 (4.21) and UF_6 (4.60) indicate the presence of $d\pi-p\pi$ bond between the central atom and oxygen atom in addition to the σ bond in the former systems.

4.12.7 Molecular Structure

The structure of molecules and complex ions can be deduced from the activity and depolarisation ratios of the Raman bands.

Let us first explore how depolarisation ratio could be helpful for structural determination of XYZ_2 type molecular systems. These systems can have either planar or pyramidal structure. All of its six fundamental modes of vibration are Raman as well as infrared active. For the planar structure, the three modes should be polarised and three should be depolarised while four should be polarised and two should be depolarised for the pyramidal structure. Accordingly, the number of polarised and depolarised Raman bands is structure specific. Therefore, simply on the basis of depolarisation selection criterion we can assign either planar or pyramidal structure to XYZ_2 systems, e.g. out of the six fundamental modes of vibrations of $SOCl_2$, the four bands at wave numbers 1230, 490, 344 and 192 cm^{-1} are polarised and two at 445 and 284 cm^{-1} are depolarised; consequently $SOCl_2$ has a pyramidal structure.

Structural elucidation by the activity selection criterion is also possible. Let us apply this criterion to XY_3 systems which can have either trigonal or pyramidal structure. Out of the six modes of vibrations, only four are observable, since the two fundamental modes are doubly degenerate. From the activity of Raman bands listed in Table 4.3, we can take decision regarding the structure of XY_3 systems.

Table 4.3 Activity of XY_3 systems.

Pyramidal XY_3		Trigonal XY_3	
No. of Modes	Activity	No. of Modes	Activity
2	R(p) ($\parallel$)	1	R(p)
		1	IR($\parallel$)
2	R(dp), IR($\perp$)	2	R(dp), IR($\perp$)

p = polarised; dp = depolarised

For example, the four observable normal modes of vibration of SO_3 are at wave numbers 1332, 1068, 530 and 653 cm^{-1} . The bands at 1332, 1068 and 530 are Raman active only. As a consequence thereof, SO_3 has a planar or trigonal structure. On the other hand, in case of NH_3 , out of its four Raman observable bands, viz., 3337, 950, 3414 and 1628 cm^{-1} , only two bands at 3337 (p) and 950 (p) cm^{-1} appear in the spectrum. The fact that the two doubly degenerate vibrations at 3414 and 1628 cm^{-1} have not been observed in the Raman spectrum is in agreement with the usual weakness of Raman lines corresponding to non-totally symmetric vibrations. Consequently, NH_3 has pyramidal structure.

The criterion of 'similarity', i.e., molecules having similar spectra will have similar structural pattern, can also be employed to establish the structure of molecular systems, e.g. the Raman spectrum of tetramethylammonium ion $[(CH_3)_4N]^+$ is similar to that of tertiary butane $(CH_3)_4C$ which has a regular tetrahedral structure. This lends support to the regular tetrahedral structure established by stereochemistry of $[CH_3)_4N]^+$ ion. Thallous ions may either exist as Tl^+ or Tl_2^{++} in aqueous solutions. Only a single Raman band appears in the Raman spectrum of this ion and is assigned to $Tl-Tl$ bond stretching vibration. From this it is inferred that thallous ions exist as Tl_2^{++} but not as Tl^+ in aqueous solutions. Mercurous (Hg_2^{++}) and argentous (Ag_2^{++}) ions also show similar behaviour.

4.12.8 Energy Difference Between Rotamers

The intensity of Stokes lines is directly proportional to

$$I^s \propto \left(1 - e^{\frac{-h\nu}{\kappa T}}\right)^{-1} \quad (4.59)$$

Let I_t and I_g be the scattered intensities, ν_t and ν_g the vibrational frequencies and N_t and N_g , the number of molecules of the *trans* and *gauche* forms respectively. Then

$$I_t = N_t \left(1 - e^{\frac{-h\nu_t}{\kappa T}}\right)^{-1} \quad (4.60)$$

$$I_g = N_g \left(1 - e^{\frac{-h\nu_g}{\kappa T}}\right)^{-1} \quad (4.61)$$

From Eq. (4.60) and (4.61), we get

$$\frac{I_t}{I_g} = \frac{N_t}{N_g} \left(\frac{1 - e^{-h\nu_g/\kappa T}}{1 - e^{-h\nu_t/\kappa T}} \right) \quad (4.62)$$

$$\frac{I_t}{I_g} = \frac{N_0 e^{-E_t/\kappa T}}{N_0 e^{-E_g/\kappa T}} \left(\frac{1 - e^{-h\nu_g/\kappa T}}{1 - e^{-h\nu_t/\kappa T}} \right)$$

Taking logarithm of both sides, we obtain

$$\ln \left(\frac{I_t}{I_g} \right) = \frac{\Delta E}{\kappa T} + \ln \frac{1 - e^{-\frac{h\nu_g}{\kappa T}}}{1 - e^{-\frac{h\nu_t}{\kappa T}}} \quad (4.63)$$

where $\Delta E = E_g - E_t$, $N_g = N_0 e^{-E_g/\kappa T}$, $N_t = N_0 e^{-E_t/\kappa T}$ and $N_0 = N_t + N_g$

Differentiating Eq. (4.63) with respect to $(1/T)$, we get

$$\frac{\partial}{\partial(1/T)} \left[\ln \left(\frac{I_t}{I_g} \right) \right] = \frac{\Delta E}{\kappa} + f(T) \quad (4.64)$$

where

$$f(T) = e^{-h\nu_g/\kappa T} \frac{(h\nu_g/\kappa)}{(1 - e^{-h\nu_g/\kappa T})} - e^{-h\nu_t/\kappa T} \frac{(h\nu_t/\kappa)}{(1 - e^{-h\nu_t/\kappa T})}$$

The plot of $\ln(I_t/I_g)$ versus $1/T$ will be a straight line with intercept $= \Delta E/\kappa$. From the intercept we can calculate ΔE . Thus, the energy difference between the rotational isomers can be determined simply by monitoring the intensities of the Raman bands corresponding to the two rotamers at different intervals of temperatures. I_t/I_g depends upon the choice of the baseline and also on the method of separation of two bands due to two rotamers overlapping each other. Consequently, the selection of vibrational frequencies corresponding to the two rotamers is vital for these types of studies. In addition to these two factors, ΔE also depends upon $f(T)$, e.g. the energy difference between the rotational isomers of 1,2-dibromoethane in the liquid state using 4880 Å line of Ar⁺ laser, as determined by monitoring the relative intensity of Raman bands at 660 (*trans* form) and to that at 551 cm⁻¹ (*gauche* form) in the temperature range 24.5–105.1°C is of the order of 955 ± 80 cal mole⁻¹ ignoring $f(T)$ factor. When $f(T)$ is taken into account, ΔE decreases by 38 cal mole⁻¹ at 24.5°C and 54 cal mole⁻¹ at 105.1°C. Consequently, $\Delta E = 910 \pm 80$ cal mole⁻¹. The value of ΔE determined by other methods lies in the range 650–1000 cal mole⁻¹.

4.12.9 Structure of Water

Water is the principal constituent of all living organisms and the most abundant compound on the surface of our planet. The human body is about 65 per cent water by mass, and some tissues such as the brain, lungs, and muscles contain close to 80 per cent water. The unique properties of water make it essential to the existence and continuation of life, and it is likely that water has played a major role in the formation of prebiological living systems. The thermodynamic properties of liquid water, its volume, density, heat capacity, compressibility, and so on, its static dielectric constant, x-ray diffraction pattern, refractive index and NMR chemical shift, can provide information only about structures with relatively long lifetimes. On the other hand, infrared and Raman spectroscopy, and inelastic neutron scattering tools where the radiation or particles interact with the liquid for very short times and hence provide information concerning molecular processes in the liquid with very short life spans (Fig. 4.17). The dielectric relaxation and ultrasonic absorption bridge the gap between groups of methods. The average lifetime of a given arrangement of molecules in a liquid must exceed by a factor often the vibrational period of the bonds which define 'the structure, in order to be considered structurally significant. The period of an O–H stretching vibration is approximately 10^{-14} second, while that of an intermolecular H bond [$\nu(\text{AH} \cdots \text{B})$ is 200 cm⁻¹] is about 2×10^{-13} second. Thus the lifetimes of the structural entities considered must be kept in mind in structural descriptions of liquid water.

The models of water structure can be divided roughly into two types: the uniformistic or continuum models, which assume the existence of only one type of molecule corresponding to the average of all the molecules need be considered; and mixture models, which require the existence of two or more different structural units. Evidence for a model of water structure is generally indirect. One or more of the physical properties of water are calculated, based on the assumptions of the given model, and compared to the experimentally known data. The best model

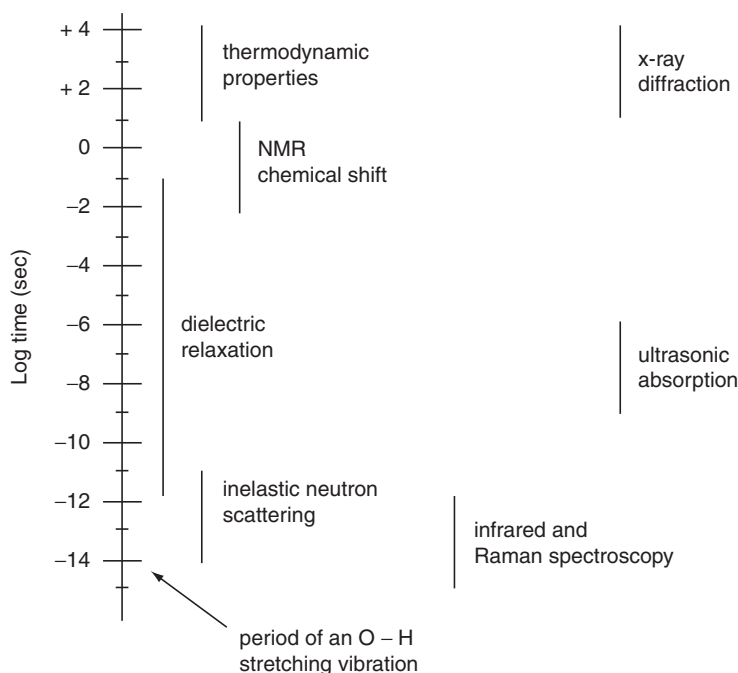


Fig. 4.17 Schematic diagram illustrating the time intervals for which various experimental methods provide information on molecular processes in ice and water.

would be the simplest model that is in agreement with known facts and that predicts the properties of liquid water with the use of the minimum number of adjustable parameters.

The infrared spectra of dilute solutions of D_2O in H_2O at -7.6 and $4^\circ C$ has shown that while the ν_{01} (O—D) band of ice is sharp ($\Delta\nu_{1/2} \sim 31\text{ cm}^{-1}$) and Lorentzian in shape, on melting the band broadens ($\Delta\nu_{1/2} \sim 150\text{ cm}^{-1}$) and becomes Gaussian in shape. Thus, the simplest band shape occurs in ice though there is maximum H-bonding and maximum physical coupling, while in water, the band broadness remains symmetrical even though there are fewer H-bonding interactions. Moreover, Gaussian distribution has been found to fit the broad ν_{01} (O—D) band of water as well as 10 to 15 narrow, Lorentzian components. This suggests that O—D band at $4^\circ C$ is due to continuous distribution of the perturbed O—D vibrators.

The Raman spectroscopic studies of solutions of D_2O in H_2O in contrast to infrared spectroscopic studies, provides strong support for a mixture model of liquid water. Photo-electric Raman spectra of D_2O in H_2O obtained with an argon ion laser source, exhibit a broadband at 2525 cm^{-1} with a pronounced shoulder at 2645 cm^{-1} . The former peak has been attributed to H-bonded, and the latter peak to non-H bonded, OD vibrators respectively. The enthalpy for the breakage of one H-bond obtained from the temperature variation of the ratio of the intensities of the 2525 and 2645 cm^{-1} bands and from the temperature dependence of the intermolecular Raman vibrations (H bond bending and stretching vibrations near 60 cm^{-1} and 160 cm^{-1} , respectively.) is $2.55\text{ kcal}/(\text{mole of O—H}\cdots\text{O})$. The corresponding entropy change is -8.5 cal/deg (mole of H bond). Thus, it is likely that a model able to correlate and account for all the known properties of water will include some of the salient characteristics of both the mixture and continuum type models.

4.13 BIOLOGICAL APPLICATIONS

Raman spectroscopic data on synthetic polypeptides, proteins and lipids not only supplemented the results of infrared spectral studies of biological systems but also came up with a number of new correlations for clarifying the conformational states of proteins and lipids in the biological membranes. This is important since structure of membrane proteins depends upon their interactions with membrane lipids. The assignment of some of typical Raman bands of poly-lysine and lipids are recorded in Tables 4.4 and 4.5 respectively. Some of the important correlations are (i) the low-frequency bands, i.e. $<50\text{ cm}^{-1}$ in certain proteins depend upon the protein configuration but not only on the state of the sample, i.e. film, solution or crystals. These low-frequency vibrations can be used for the detection of transitional motion of proteins in membrane since they reflect motions of all or very large portions of molecules in a system. (ii) Denaturation of insulin alters the amide I and III regions as well as scattering from S-S and C-S stretching and skeletal bending. The data suggest major conformational changes towards β -structure upon denaturation of insulin. (iii) Raman data on long chain fatty acids, fatty acid esters and phosphatides reveal

that bands between 1000 and 1200 cm^{-1} arise from skeletal vibrations where alternate carbons move in opposite directions in a hydrocarbon chain. The symmetric C—H stretching band from CH_3 group (2870 cm^{-1}) is intense as compared to that of CH_2 group (2850 cm^{-1}) in the crystalline state and vice versa in liquid state

Table 4.4 Raman and Infrared frequencies ($1500\text{--}1700 \text{ cm}^{-1}$) of poly-lysine in different conformations.

Helix		Antiparallel- β		Unordered	
Raman	IR	Raman	IR	Raman	IR
1517w	1516w 1535s } II	1511 w		1521 m	
1537m		1535w	1530s II		1535 II
				1547	
		1564 m		1565	
1600m					
1617m		1617m			
1639 s	1650vs 1652m } I	1631 vs	1636 s } I	1653 vs	1656 I
1647 vs				1665 vs	
		1672 vs	1685 m }	1683 vs	

s—strong; vs—very strong; m—medium; w—weak; I—amide I band; and II—amide II band

Table 4.5 Raman lines (cm^{-1}) of fatty acids and their esters.

Frequencies	Assignment
720	Head group deformation vibration
~845	CH_2 rock
967	$=\text{C—H}$ (out of plane) deformation
~1085	C—C stretching
1261	$=\text{C—H}$ (in-plane) deformation
1298	CH_2 twisting
1370	CH_2 wagging
1445	CH_2 deformation
1731	C=O (ester) stretching
~2100	C—D stretching
~2850	CH_2 symmetric stretching
~2870	CH_3 symmetric stretching
~2930	CH_2 asymmetric stretching
~2960	CH_3 asymmetric stretching

The weak band near 1080 cm^{-1} relative to the 1125 cm^{-1} band is indicative of *trans* structure in the crystalline state. This gets reversed upon melting due to the appearance of *gauche* isomer. Accordingly, the intensity of $1080/1125 \text{ cm}^{-1}$ bands may provide information about the structural changes in these types of systems in moving from crystalline to molten state or vice versa, e.g the intensity ratio of bands near 1066 and 1130 cm^{-1} in the spectra of aqueous suspensions of micellar dipalmitoyl lecithin corresponds to the all *trans* structures in the paraffin chain. The broad band at 1089 cm^{-1} appearing in the melted paraffin is assigned to the *gauche* rotations of the melt. Thus, from the ratios of the scattering intensity of bands at $1089/1130$ or $1089/1066 \text{ cm}^{-1}$, we can infer about the extent of ordering of paraffin chains in passing from micellar to molten state. Based on this criterion, the Raman lines near 1100 cm^{-1} and the intensity ratio of $1125/1085 \text{ cm}^{-1}$ bands in the spectra of lecithin and lecithin-cholesterol mixtures, the hydrocarbon chains of dipalmitoyl phosphatidyl ethanolamine are mainly

in *trans* configuration in the crystalline state while those of egg phosphatidyl choline are in the liquid state. The insertion of cholesterol into egg lecithin liposomers results in the decrease of contribution of *gauche* isomers while increase in that of the *trans* isomers. Cholesterol prohibits the formation of some but not all *gauche* isomers, thereby reducing the chain fluidity.

The Raman resonance spectrum due to the chromophore group of retinal cell is not affected by the primary photoreaction since the time scale of Raman resonance state of this system is smaller, i.e. 10^{-14} second than that of photoreaction which is of the order of 10^{-12} second. This time lag makes the technique of Raman resonance spectroscopy an ideal tool for investigating the transients formed in this biological process, e.g. the conjugated rhodospin protein of the retinal cell transports protons across the membrane on illumination of 11-*cis* retinal. The prosthetic group of this protein not only forms covalent bond with protein but also the carboxyl group reacts with amino group to form an imine. The rhodospin simply absorbs light, which then transforms the less stable 11-*cis* retinal into the more stable 11-*trans* retinal (Fig 4.18).

As a consequence, the conformational changes occur in the entire rhodospin molecule in order to accommodate the new guest, i.e. 11-*trans*-retinal in it. The energy from biological reactions changes the *trans* form back to the *cis* form. These conformational changes have been supplemented by Raman resonance scattering. The C=C stretching mode of the retinal moiety $\approx 1555\text{--}1529\text{ cm}^{-1}$ not only differs in wave number but also in band shape and width in the course of transformation of rhodospin to other transients in the photochemical processes. This

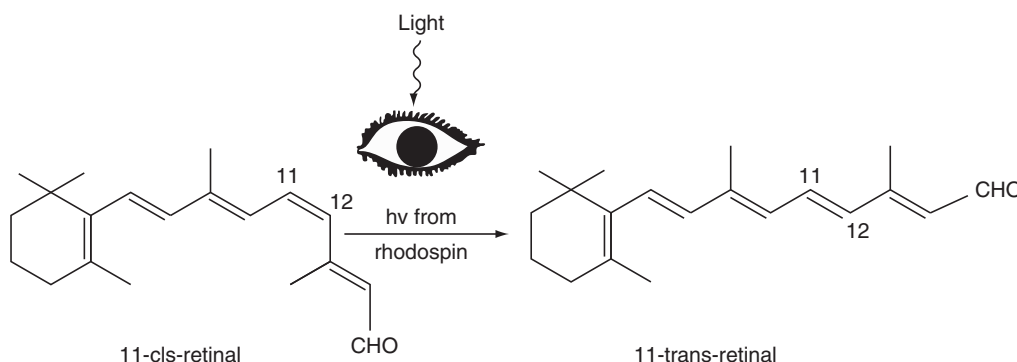


Fig. 4.18 Structural changes in 11-*cis* retinal on shining radiation.

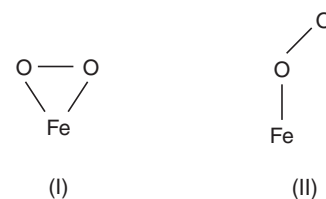
property of C = C stretching vibration has been exploited for kinetic studies of such transformations in biological processes. The C = C stretching mode of intact retinal is lower than that of free retinal or its basic Schiff base. This lends support to the hypothesis that chrome is bound as a protonated Schiff base, i.e. by a $\text{—C}=\text{N}^+\text{H}$ -bond. It is also observed that the purple colour of chrome of purple membrane is because of unprotonated Schiff base. The chromophore consists of a charge transfer complex formed between retinyllysine and a protein tryptophan.

This technique is used to probe the active site in a large number of metalloproteins including the haeme proteins, non-haeme oxygen carriers, transferrin, chlorophylls, vitamin B-12, iron-sulphurproteins and blue copper proteins and to investigate the reaction dynamics of chlorophyll, haeme group as well as of various helical forms of DNA and the transitions among them.

Resonance Raman studies of the Fe—O stretching region for haemoglobin provide structural information on the mode of dioxygen bonding. Two possible structures are the side on model I, and the end-on-model II.

ESR studies of oxycoboglobin and x-ray structure of a synthetic iron porphyrin provide evidence for structure (II). The Fe—O stretch (568 cm^{-1}) in the latter, i.e. dioxygen iron porphyrin, as determined by RRS is close to that of oxyhaemoglobin (567 cm^{-1}). This Raman data in conjunction with the x-ray structure of the dioxygenated synthetic iron porphyrin, suggest that dioxygen is end-on in haemoglobin. RRS of pure $^{16}\text{O}^{18}\text{O}$ haemoglobin exhibits two peaks separated by 20 cm^{-1} in the 550 cm^{-1} region. This observation corresponds to model (II) where two stretching frequencies separated by 20 cm^{-1} are expected for the $\text{Fe}^{18}\text{O}^{16}\text{O}$ and $\text{Fe}^{16}\text{O}^{18}\text{O}$ structures. The structure (I) is ruled out since only one iron-oxygen stretch is possible in the 550 cm^{-1} region because an end-for-end flip of $^{16}\text{O}^{18}\text{O}$ in (I) does not produce a second isotopic isomer.

O—O stretching frequencies in oxygen carriers may also be fixed criteria for the assignment of oxidation states. The range of O—O stretching frequencies in simple compounds and metal complexes is $1075\text{--}1164\text{ cm}^{-1}$ for O_2^{1-} and $738\text{--}879\text{ cm}^{-1}$ for O_2^{2-} . The value of $\nu(\text{O—O})$ in oxyhaemerythrin and haemocyanin has been observed at 844 and 742 cm^{-1} , respectively. These frequencies fall into the O_2^{2-} peroxide class suggesting thereby that these proteins have a peroxide type- O_2 .



PROBLEMS

- A compound is irradiated by 4358 Å line of mercury. Raman lines are observed at wavelengths of 4420, 4435, 4498 and 4620 Å. (a) Compute the value of the Raman shift for each line in terms of wave numbers. (b) What would be the wavelengths of the anti-Stokes lines corresponding to the Stokes lines at 4620 Å? (c) At what wave numbers will their Raman lines appear if the compound is irradiated with monochromatic light of 5460 Å?
(a) **Hint:** $\nu_0 - \nu_R = \Delta\nu_R$; $\nu_R < \nu_0$ for Stokes lines; $\nu_R > \nu_0$ for anti-Stokes lines; $\nu_0 = 22946 \text{ cm}^{-1}$.
[Ans: 322, 398, 714, 1301 cm^{-1} , 4124 Å]
(b) **Hint:** $\Delta\nu_R$ will remain the same; $\nu_R = 4620 \text{ Å} = 21645 \text{ cm}^{-1}$,
[Ans: 4124 Å]
(c) [Ans: 17993, 17917, 17601, 17014 cm^{-1}]
- The displacements from the Rayleigh line in the rotational Raman spectrum of HCl are expressed by $\Delta\nu_R = \pm (62.4 + 41.6 J) \text{ cm}^{-1}$. Compute the moment of inertia and bond length of HCl molecule.
• **Hint:** Compare the given expression with $\Delta\nu_R = 2B(2J + 3)$.
[Ans: $I = 1.626 \text{ amu Å}^2$, $r = 1.293 \text{ Å}$]
- The Raman spectrum of PCl_3 is excited by the mercury line 4358 Å. Spectrum shows Raman lines for $\Delta\nu_R = 184, 256, 482$ and 514 cm^{-1} . At what wavelengths will their Raman lines appear if PCl_3 is irradiated with monochromatic light of 5461 Å?
[Ans: 18128, 18056, 17830, 17798 cm^{-1}]
- A substance shows a Raman line at 4567 Å when an exciting line of 4358 Å is used. At what positions Stokes and anti-Stokes lines for the same substance will be observed when the position of Rayleigh line is at 4047 Å?
[Ans: 4227 Å (Stokes), 3882 Å (anti-Stokes)]
- The values of the w_0 and x_0 are 2358.03 cm^{-1} and 6.00×10^{-3} respectively for the ground state of N_2 . Compute the zero-point energy and the expected Raman displacement.
• **Hint:** For ground state $v = 0$ and the selection rule is $\Delta v = \pm 1$; $\Delta\nu_R = (E_{v=1} - E_{v=0})/hc$
[Ans: zero point energy = $8282.07 \times 10^{-16} \text{ erg}$; $\Delta\nu_R = 2329.74 \text{ cm}^{-1}$]
- The Rayleigh line in the Raman experiment is 4358 Å and the spectrum shows the Stokes line at 6433 Å. Find the wavelength of the anti-Stokes line. [Ans: 3295 Å]
- The bond lengths of N_2 and O_2 are 1.09 and 12.1 Å respectively. Their force constants are 22.6 and 11.4 millidynes/Å respectively. Draw schematic diagrams for the Raman spectra of N_2 and O_2 gases excited by 4358 Å line of mercury.
- The centre of vibrational band of O_2 lies at 1556 cm^{-1} while that of HCl vapour at 2886 cm^{-1} . Calculate the relative intensities of Stokes and anti-Stokes lines for both the cases at room temperature.
- When acetylene is irradiated with 4358 Å line of mercury, a Raman line attributed to symmetrical stretching vibration is observed at 4768 Å. Compute the fundamental frequency for the said vibration. [Ans: 1973 cm^{-1}]
- The Raman spectrum of CO_2 is recorded using a 4358 Å Hg line. The fundamental frequency for CO_2 symmetric stretch deduced from the Raman spectrum has been found to be 1330 cm^{-1} . Determine the position of Raman line corresponding to this fundamental mode of vibration.
[Ans: 4119 Å (anti-Stokes)]
- Compute in units of $\left(\frac{h}{8\pi^2 Ic}\right)$ the Stokes and anti-Stokes Raman frequencies which will result from rotational transitions into a final state of quantum number (a) $J = 4$, and (b) $J = 6$. [Ans: (a) Stokes: 22; anti-Stokes: 14]
- The fluorine molecules were excited by 4047 Å and 4358 Å Hg lines. The Stokes lines are observed at 4199 Å and 4534 Å respectively. Compute the ground state vibrational frequency of F_2 and its force constant also.
[Ans: 893 cm^{-1}]
- The Raman spectrum from liquid chloroform excited by the 4358.3 Å line of mercury consists of lines at 4289.9, 4309.1, 4358.3, 4408.7, 4429.0, 4489.1, 4507.9, 4602.2, 5018.7 Å. What are the six fundamental vibrational modes of chloroform?
[Ans: 262, 366, 668, 761, 1216 and 3019 cm^{-1}]
- The infrared and Raman spectra of sulphur dioxide are given below:

Frequency (cm^{-1})	IR	Raman
519	s, type band	p
1151	s, type band	p
1361	s, ⊥ type band	dp

Determine the structure of sulphur dioxide. Assign the bands on the basis of polarization and depolarization data.

- Hint:** All the three fundamental modes of vibration are IR and Raman active. So molecule has no centre of symmetry and hence has bent structure. The absence of complicated rotational structure and simple PR contour also indicates that the molecule is nonlinear.

[Ans: SO_2 , nonlinear]

- The infrared and Raman spectra of nitrous oxide are given in the tabular form as under.

Frequency (cm^{-1})	IR	Raman
589	s, PQR (⊥) contour	—
1285	vs, PR () contour	vs, p
2224	vs, PR () contour	s, dp

Determine the structure of the compound.

- Hint:** The presence of PR (||) and PQR (⊥) structures reveal that the molecule is linear. Since all the fundamental bands are IR active, the molecule does not possess centre of symmetry. Consequently the structure of the molecule is N—N—O but not N—O—N. Two bending (⊥) modes will be degenerate, which are weak and unobservable in Raman spectra. 1285 being vs and p is NO symmetric stretching band while 2224 being dp and s, is N—O asymmetric stretching band.

[Ans: N—N—O]

CHAPTER 5

ELECTRONIC
SPECTROSCOPY

Change and development is a never-ending process and so is man's cognition of truth through practice.

—Unknown

The beauty of a law of nature lies in the dimensions of physical quantities involved.

—H S Randhawa

5.1 INTRODUCTION

The electronic states of molecules originate from the levels of the atoms that constitute the molecule as a result of Stark splitting in the electric field of the molecule. Electronic spectroscopy deals with the study of absorption of visible (400–800 nm), the near ultraviolet (200–400 nm), the far, or, vacuum ultraviolet (200 nm or lower) and sometimes even in the far infrared (4000–12000 cm^{-1}) region of radiation by inorganic and organic molecules, namely CH_3NO_2 , C_6H_6 , C_2H_4 , CO , H_2 , AgCl , HgCl , HCl , N_2 , I_2 ; molecular ions, namely H_2^+ , N_2^+ , CH^+ ; stable and unstable (lifetime of the order of a few microseconds or less) molecular radicals, viz. OH , NH , CN , C_2 , etc., in the liquid/solution, solid and vapour phases. The absorption of radiation causes the electrons to cross over from a lower-energy electronic state, say Ψ'_{elec} , to a higher-energy electronic state, also called the excited electronic state, say Ψ''_{elec} . As a result of this transition, the electronic configuration of the molecule changes and hence the excited state becomes polarised. Accordingly, the electronic transition is accompanied by a change of dipole moment, also known as *instantaneous dipole moment*, and the corresponding signal will be intense.

Further, since each electronic state has vibrational and rotational energy states associated with it (Fig. 5.1), the electronic spectra of heteronuclear and homonuclear diatomics in the vapour phase will exhibit rotational fine and vibrational gross structures; but the rotational fine structure is not normally observed in the ultraviolet visible absorption spectrum because of small energy difference between the adjacent rotational energy states as compared to that of the vibrational energy states. The rotational fine structure is useful to gather information about the electronic states of molecules, rotational constants and hence the moments of inertia and bond lengths for both the lower and excited electronic states of the molecules. Further, since the rotational constants of isotopes are different, they can be detected and their per cent abundances can be measured by comparing the intensity of the respective bands. On the other hand, the vibrational parameters, viz. dissociation energy, the frequency of the fundamental vibrational mode, and hence the force constant, can be deduced for both the ground and excited electronic states from the vibrational coarse structure. Electronic spectroscopy is also used to study the kinetics of production and destruction of free radicals from the variation of band intensity with short period of time as in the technique of flash photolysis.

The technique of electronic spectroscopy applies equally to polyatomic molecules as well. In polyatomic molecules, the rotational energy levels are more closely spaced because of larger moments of inertia. Consequently, the rotational fine structure, in general, cannot be observed and the vibrational structures are usually present only as broad bands. In spite of this, electronic spectra of molecules are useful to gather information about the electronic structure of a large number of polyatomics.

Further, it is to be noted that the electron spectra of molecules are more complex as compared to rotational and vibrational spectra because a large number of transitions are simultaneously involved in it. This, and translational motion of molecules in the vapour and dilute solution, tends to blur out the absorption into a broad band. In pure liquids, molecular rotation is hindered because of molecular collisions and hence the rotational fine structure is blurred. The blurring out is enhanced in solution by the solvent interactions. The blurring of the rotational fine structure often masks the vibrational coarse structure in the spectrum. Due to this very reason, the rotational fine and vibrational coarse structures are generally missing in the low-resolution electronic spectra of molecules in the solution phase. Consequently, the electronic spectrum in the solution phase is usually broad and characterless, but still the intensity and frequency of the broad band in the electronic spectrum is a characteristic of a particular

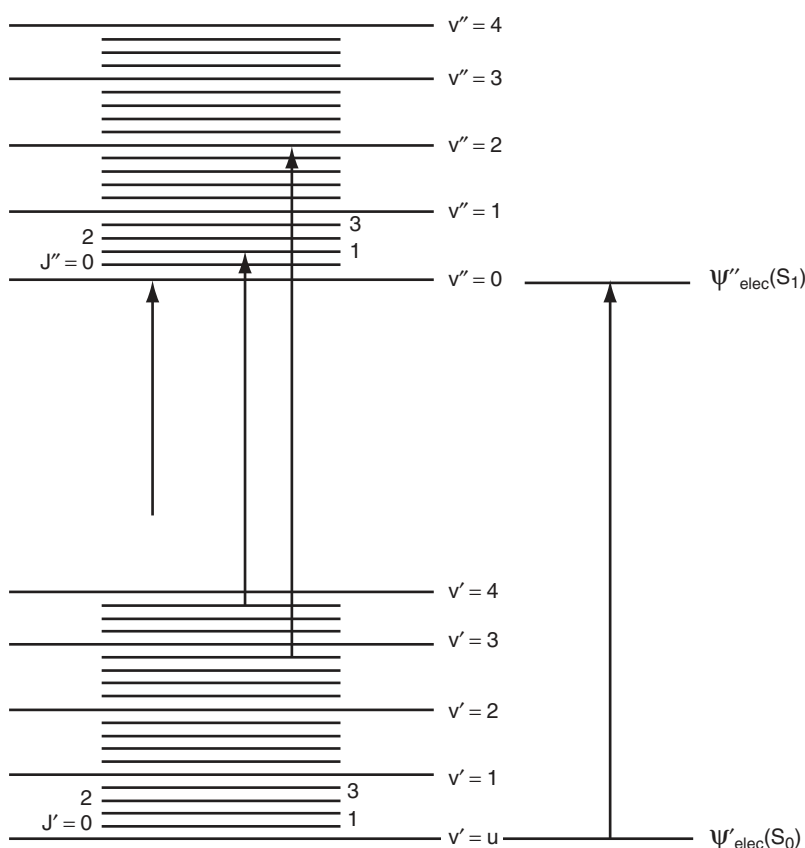


Fig. 5.1 Schematic diagram showing the vibrational and rotational energy levels of two electronic states, Ψ'_{elec} and Ψ''_{elec} , of a diatomic molecule.

functional group present in the molecule. Thus, the tool of electronic spectroscopy in the solution phase is extensively used for routine quantitative analysis of mixtures, identification of large organic molecules, structural diagnosis, determination of stability constants of molecular complexes, kinetics of formation of molecular complexes, etc.

The electronic spectra are not only studied in the absorption mode but can also be studied in the emission mode as well. The molecule with an electron in the upper energy electronic state loses the absorbed energy and returns back directly to the lower state. This results in the electronic absorption band spectrum. The molecule in the excited state may lose excess energy in order to return to the ground energy state via radiative and nonradiative intramolecular processes also. In the former, excess energy is lost by emission of radiation which results in electronic emission spectra, whereas in the latter the excess energy is lost without emission of radiation and is of little interest in the present context. The radiation emitted during a radiative transition is known as *fluorescence* (decay time $\sim 10^{-10}\text{s} - 10^{-4}\text{s}$) when the transition is between states of same multiplicity, i.e. singlet ($S_1 \rightarrow S_0$) transition, and *phosphorescence* (decay time seconds or even hours) when transition is between states of different multiplicity, i.e. triplet ($T_1 \rightarrow S_0$) transition. For most solutions and liquids at room temperature, the nonradiative processes are so rapid that fluorescence cannot be observed. However in some solutions, it can be seen even with the naked eye, e.g. in fluorescein. Since the nonradiative processes are temperature dependent, the fluorescence can be observed by cooling the solutions to supercooled liquids or glasses. Aromatic impurities in a crystal result in strong fluorescence. The phenomena of absorption and emission has been sketched in Fig. 5.2(a). The 0-0 band of fluorescence and absorption do not always occur at the same frequency because of solvent effects. Absorption takes place with the arrangement of solvent molecules suitable for the ground state and fluorescence with different arrangement of molecules appropriate for the excited state. Since absorption is at higher frequencies, ultraviolet lamps are required to excite the visible fluorescence.

When the molecule is in the gas phase, the emission may occur from an excited vibrational state. This is called *resonance fluorescence*. Resonance fluorescence also occurs if the molecule is in a solid state and is unable to rotate. The emission in such a case may be partially polarised and is distributed non-uniformly at different angles with respect to the direction and polarisation of the incident light. There is thus a close connection with Raman

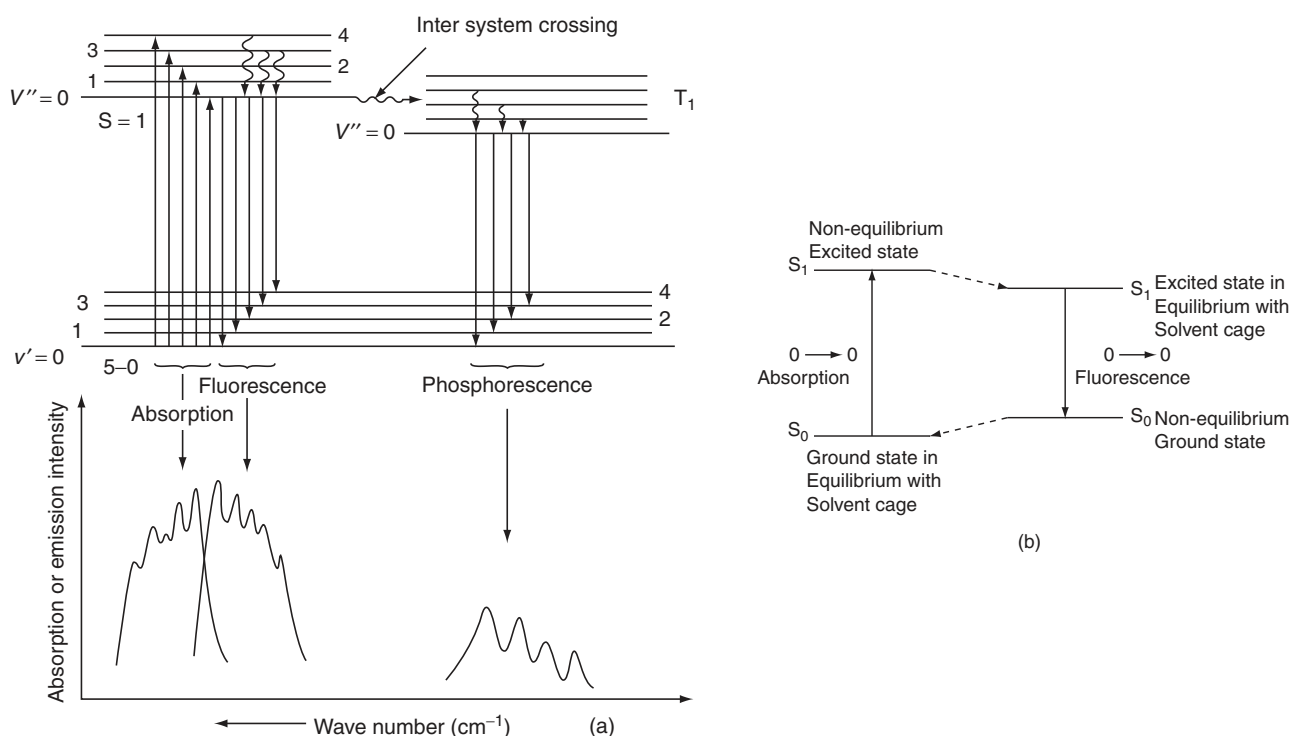


Fig. 5.2 Schematic energy-level diagram showing the (a) phenomena of absorption, fluorescence and phosphorescence, and (b) 0–0 bands of absorption and emission. The wavy arrows indicate radiationless vibrational relaxation. The diagrams for fluorescence and phosphorescence phenomena are called Jablonski diagrams.

spectra and this connection has been discussed in detail in Chapter 4, on Raman spectroscopy under the title resonance Raman effect/scattering.

The phenomena of phosphorescence and fluorescence will be described in detail later on under the title ‘fluorescence and phosphorescence’.

We have discussed here the subject of electronic spectroscopy in two parts, viz. high-resolution and low-resolution electronic spectroscopy of diatomic and polyatomics in the gas phase. The former deals with the high resolution (in gas phase) while the latter deals with the low-resolution electronic spectra of diatomics and polyatomics in the solution phase.

5.1.1 Multiplicity of Electronic States

It is defined by the expression $2S + 1$ where S is the algebraic sum of the spin quantum numbers of the electrons, i.e. $+\frac{1}{2}$ and $-\frac{1}{2}$ in the system. A molecule with two unpaired electrons ($\uparrow\uparrow$ or $\downarrow\downarrow$) is said to be in $(2 \times 1 + 1 = 3)$ a triplet state and is designated by the symbol T . Ground state of a triplet state is designated as T_0 . A molecule with two paired electrons ($\uparrow\downarrow$ or $\downarrow\uparrow$) is said to be in $(2 \times 0 + 1 = 0)$ a singlet state and is designated by the symbol S . Ground state is a singlet state and is denoted by S_0 . The higher-energy singlet and triplet states are designated as $S_1, S_2, S_3 \dots$ and $T_1, T_2, T_3 \dots$ respectively. Singlet states have invariably higher energy than the corresponding triplet states because of greater electron repulsion in the singlet state. In absorption molecular electronic spectroscopy, transition always occurs between electronic states of the same multiplicity, i.e. $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, are allowed but $S_0 \rightarrow T_0$ are forbidden transitions.

5.1.2 Electronic Transition Energy

Let E'_{elec} be the energy of the ground electronic state, say ψ'_{elec} , of the molecule before absorption of radiation; and E''_{elec} be that of the excited state, say ψ''_{elec} , of the molecule after absorption of radiation. The energy $E = \frac{hc}{\lambda}$ of radiation required to bring about the transition is given by

$$E = E''_{\text{elec}} - E'_{\text{elec}} = \Delta E = \frac{hc}{\lambda} \quad (5.1)$$

Here, the quantity ΔE is the energy difference between the electronic states ψ''_{elec} and ψ'_{elec} and equals E . Thus, the energy required to produce one excited-state molecule is given by

$$\Delta E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} (\text{J s}) \times 2.998 \times 10^8 (\text{m/s})}{\lambda \times 10^{-9} (\text{m})} = \frac{1.987 \times 10^{-16}}{\lambda} \text{ J/molecule} \quad (5.2)$$

Here λ is in nm.

The energy required to excite 6.023×10^{23} molecules is known as an *einstein* and the energy of an einstein of radiation of wavelength λ can be computed from the expression

$$\Delta E = \frac{1.196 \times 10^8}{\lambda (\text{in units of nm})} \text{ J mole}^{-1} \quad (5.3)$$

Problem 5.1: The band in the electronic spectrum of a molecule appears at 250 nm. Calculate (a) the energy required to produce one excited state molecule, and (b) the energy of an einstein of radiation.

Solution (a) In order to determine the energy required to produce one excited-state molecule we make use of the expression.

$$\Delta E = \frac{1.987 \times 10^{-16}}{\lambda (\text{nm})} \text{ J/molecule}$$

Substituting the given value of λ , we get

$$\Delta E = \frac{1.987 \times 10^{-16}}{250} = 7.958 \times 10^{-19} \text{ J/molecule}$$

(b) The energy of an einstein of radiation ($\lambda = 250$ nm) is given by

$$\begin{aligned} \Delta E &= \frac{1.196 \times 10^8}{\lambda (\text{in units of nm})} \text{ J mole}^{-1} \\ &= \frac{1.196 \times 10^8}{250} \text{ J mole}^{-1} \\ &= 4.784 \times 10^5 \text{ J mole}^{-1} \end{aligned}$$

5.2 HIGH-RESOLUTION ULTRAVIOLET/VISIBLE SPECTROSCOPY AND SELECTION RULES FOR ELECTRONIC TRANSITIONS IN LIGHT DIATOMICS

The high-resolution UV visible spectroscopy deals with the electronic spectra mainly of homo- and hetero-diatomics in the gas phase.

The selection rules for electronic transitions have been worked out quantum mechanically from the solution of the transition moment integral,

$$M_t (= e r_{12}) = \int \Psi_i^* \hat{M}_t \Psi_j d\tau \quad (\text{Eq. 2.37})$$

The square of the integral is a measure of transition probability which is proportional to integrated intensity of the absorption band, i.e.

$$I_a \propto \left| \int_{-\infty}^{+\infty} \Psi_i^* \hat{M}_t \Psi_j d\tau \right|^2$$

Here, $\hat{M}_t (= e r_{12})$ is the integral dipole moment operator and is related to the difference in the electronic dipole moments of the ground and excited states. The difference in the electronic dipole moments results because of

a different electron distribution in the two states, i.e. due to charge migration during transition. Thus when the transition moment integral becomes zero, the transition is forbidden. ψ_i and ψ_j are the wave functions of the energy states 'i' and 'j' respectively and are orthogonal to each other. $d\tau$ is the volume element. The components of M_i along the three axes are

$$M_i(x) = \int \Psi_i^* \hat{M}_i(x) \Psi_j d\tau \quad (\text{Eq. 2.38})$$

$$M_i(y) = \int \Psi_i^* \hat{M}_i(y) \Psi_j d\tau \quad (\text{Eq. 2.39})$$

$$M_i(z) = \int \Psi_i^* \hat{M}_i(z) \Psi_j d\tau \quad (\text{Eq. 2.40})$$

Further, note that the dipole moment operator operates only on the space part of the wave function. Accordingly, Eq. (2.37) is written as

$$M_i = \int \Psi''_{\text{space}} \hat{M}_i \Psi'_{\text{space}} d\tau_{\text{space}} \int \Psi''_{\text{spin}} \Psi'_{\text{spin}} d\tau_{\text{spin}} \quad (2.37^*)$$

Since the spin integral involves the dot product of the spin functions, the integral will be zero until the wave functions for the spin belong to the same state, i.e. $\Delta S = 0$. The components of M_i expressed by Eq. (2.37*) along the three axes can also be written in the same fashion as that for M_i expressed by Eq. (2.37). Thus, for an allowed transition, one of these integrals must be nonzero. This is possible only when the transition takes place between states of same symmetry, i.e. reversal of spin is not allowed. The transitions are observed even for $\Delta S \neq 0$. For example, the strongest transition in the Hg atom is observed at 253 nm. This is due to the fact that in heavy atoms and molecules, the interaction between spin and space (i.e. spin-orbital interaction) is infinite and hence the spin and space functions cannot be considered independent of each other. The mixed orbital wave function of the triplet state is given by

$$\Psi_T = \Psi_{T^0} + \lambda_{TS} \Psi_{S^0}$$

where λ_{TS} is the mixing coefficient; λ_{TS} is inversely proportional to the energy difference between the triplet and the singlet states. The smaller the value of $(E_S - E_T)$, greater is the mixing and stronger the singlet triplet transition.

- (i) Let us now prove that the transition between singlet and triplet states is forbidden. Let the wave functions for the spin part of the singlet and triplet states be

$$\psi_S = [\alpha(1) \beta(2) - \alpha(2) \beta(1)]$$

and

$$\psi_T = \alpha(1) \alpha(2)$$

$$= \beta(1) \beta(2)$$

or

$$= [\alpha(1) \beta(2) + \alpha(2) \beta(1)]$$

For simplicity, the normalisation constants are not considered. For one of the triplet wave functions, we write

$$\begin{aligned} \int \Psi''_{\text{spin}} \Psi'_{\text{spin}} d\tau_{\text{spin}} &= \int [\alpha(1) \beta(2) - \alpha(2) \beta(1)] \cdot [\alpha(1) \beta(2) + \alpha(2) \beta(1)] d\tau_{\text{spin}} \\ &= \int [\alpha(1) \alpha(1) d\tau_1 \int \beta(2) \beta(2) d\tau_2 + \alpha(1) \beta(1) d\tau_1 \int \beta(2) \alpha(2) d\tau_2 \\ &\quad - \int \alpha(2) \beta(2) d\tau_2 \int \alpha(1) \beta(1) d\tau_1 - \int \alpha(2) \alpha(2) d\tau_2 \int \beta(1) \beta(1) d\tau_1] \end{aligned}$$

Since the wave functions are normalised, the first and fourth integrals will be unity, whereas the second and third integrals will be zero.

Therefore, $\int \Psi''_{\text{spin}} \Psi'_{\text{spin}} d\tau_{\text{spin}} = 1 + 0 - 0 - 1 = 0$. Thus, this transition is forbidden. It can also be shown similarly that the integrals $\int [\alpha(1) \beta(2) - \alpha(2) \beta(1)] \alpha(1) \alpha(2) d\tau_{\text{spin}}$ and $\int [\alpha(1) \beta(2) - \alpha(2) \beta(1)] \beta(1) \beta(2) d\tau_{\text{spin}}$ are zero, indicating thereby that singlet-to-triplet transition is not allowed.

- (ii) Molecules having a centre of symmetry exhibit $g \rightarrow u$ and $u \rightarrow g$ transitions but not $g \leftrightarrow g$ and $u \leftrightarrow u$. In general, transitions which occur without change in the 'l' value of the orbital are forbidden, i.e. $\Delta l/\Delta L = \pm 1$. This is called *parity rule*.

Parity = $(-1)^l$, where l = orbital quantum number.

For parity = +1, the function has even parity.

For parity = -1, the function has odd parity.

Therefore, a state with even 'l' has even parity and odd 'l' has odd parity. Thus, for an allowed transition, the parity of a system should change. The parity of a closed system cannot change. For C, the electronic configuration is $1s^2 2s^2 2p^2$; Hence $L = \sum l_i = 2$. $\therefore$ Parity = $(-1)^2 = 1$, even parity. For N($1s^2 2s^2 2p^3$),

$$L = \sum l_i = 3$$

$\therefore$ parity = $(-1)^3 = -1$, odd parity.

For O($1s^2 2s^2 2p^4$), $L = \sum l_i = 4$, Parity = $(-1)^4$, even parity.

- (iii) Simultaneous excitation of more than one electron is not permissible.

The selection rules for various electronic transitions in light diatomics have been worked out in Chapter 2 on microwave spectroscopy. Some of the allowed electronic transitions for homonuclear- and heteronuclear-diatomics are listed here for ready reference.

Homonuclear	Heteronuclear
$\Sigma_g^+ \longleftrightarrow \Sigma_u^+$	$\Sigma^+ \longleftrightarrow \Sigma^+$
$\Sigma_g^+ \longleftrightarrow \Sigma_u^-$	$\Sigma^- \longleftrightarrow \Sigma^-$
$\Pi_g \longleftrightarrow \Sigma_u^+$, $\Pi_u \longleftrightarrow \Sigma_g^+$	$\Pi \longleftrightarrow \Sigma^+$, $\Pi \longleftrightarrow \Sigma^-$
$\Pi_g \longleftrightarrow \Sigma_u^-$, $\Pi_u \longleftrightarrow \Sigma_g^-$	$\Pi \longleftrightarrow \Pi$
$\Pi_g \longleftrightarrow \Pi_u$	$\Pi \longleftrightarrow \Delta$
$\Pi_g \longleftrightarrow \Delta_u$, $\Pi_u \longleftrightarrow \Delta_g$	$\Delta \longleftrightarrow \Delta$
$\Delta_g \longleftrightarrow \Delta_u$	$\Delta \longleftrightarrow \Phi$
.....	$\Phi \longleftrightarrow \Phi$

The symbols in the notations of an electronic state of a molecule are explained here by taking the example of $^2\Sigma_g^+$ (i.e. H_2^+ , N_2^+)

- Σ is the electronic state for which electronic angular momentum quantum number Λ is zero.
- 2 represents the multiplicity of the state, (i.e. $2S + 1 = 2$ for $S = +\frac{1}{2}$), the resultant electronic spin of the molecule in this state is $+\frac{1}{2}$.
- The superscript plus sign on the right-hand side indicates that the electronic eigen function corresponding to this state does not change sign on reflection at a plane through the internuclear axis.
- The subscript 'g' on the right-hand side represents the parity of the eigen function of the state which for the given state is even i.e. the wave function of a molecule does not change sign on reflection through the centre of symmetry.

5.2.1 Electronic Spectra of Diatomic Molecules

The electronic configuration of a molecule changes during the course of an electronic transition. Thus, each electronic transition is accompanied by an instantaneous dipole moment. Accordingly, the total electronic spectra, i.e. composite of electronic, vibrational and rotational, of homo- and hetero-diatomics will be active in the ultraviolet and visible region of radiation. Note that a number of electronically excited states are possible and in general, all electronic absorption transitions are permissible between states of same multiplicity, i.e. singlets, doublets, triplets, etc., and are weakly or strongly forbidden if multiplicity is different. Here, for convenience, we shall be treating the transition between ground electronic state as our lower electronic state and the lowest excited electronic state as the upper state of the molecule. The total wave function of the diatomic molecule may be written as

$$\Psi = \Psi_{\text{elec}} \Psi_{\text{vib}} \Psi_{\text{rot}} \quad (5.4)$$

and based on Born–Oppenheimer approximation, the total energy of a diatomic molecule is expressed as

$$E = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} \quad (5.5)$$

The energy levels of a rotating diatomic molecule are represented as

$$E_J = B hc J(J+1), J = 0, 1, 2, 3, \dots \quad (\text{Eq. 2.33})$$

while that of a vibrating molecule is represented by

$$E_v = h c w_e [V + 1/2] - h c w_e x_e [V + 1/2]^2 + \dots, V = 0, 1, 2, 3 \dots \quad (\text{Eq. 3.33})$$

The frequencies of separate lines in the electronic spectrum as worked out from Eqs. (2.33) and (3.33) are given by the formula

$$\begin{aligned} \bar{\nu} &= \frac{(E''_{\text{elec}} + E''_{\text{vib}} + E''_{\text{rot}}) - (E'_{\text{elec}} + E'_{\text{vib}} + E'_{\text{rot}})}{hc} \\ &= \frac{(E''_{\text{elec}} - E'_{\text{elec}})}{hc} + \frac{(E''_{\text{vib}} - E'_{\text{vib}})}{hc} + \frac{(E''_{\text{rot}} - E'_{\text{rot}})}{hc} \\ &= \frac{\Delta E_{\text{elec}}}{hc} + \frac{\Delta E_{\text{vib}}}{hc} + \frac{\Delta E_{\text{rot}}}{hc} \end{aligned}$$

or

$$\bar{\nu} = \bar{\nu}_{\text{elec}} + \bar{\nu}_{\text{vib}} + \bar{\nu}_{\text{rot}} \quad (5.6)$$

Here, single and double primes stand for the lower and upper states of the molecule.

The quantity $\bar{\nu}_{\text{vib}}$ characterises the vibrational gross or coarse structure of the band, and $\bar{\nu}_{\text{rot}}$, the rotational fine structure of the band in the electronic spectra of diatomics. The term $\bar{\nu}_{\text{elec}}$ determines the change in the electronic energy of the molecule when it crosses over from the lower-energy electronic state (Ψ'_{elec}) to the upper-energy electronic state (Ψ''_{elec}). The quantity $\bar{\nu}_{\text{elec}}$ exceeds $\bar{\nu}_{\text{rot}}$ and $\bar{\nu}_{\text{vib}}$ by a factor of 10^6 and 10^3 cm^{-1} respectively, i.e. $\bar{\nu}_{\text{elec}} \approx 10^3 \bar{\nu}_{\text{vib}} \approx 10^6 \bar{\nu}_{\text{rot}}$. This shows that (i) the electronic spectrum of molecule appears in the visible or ultraviolet regions of the spectrum, i.e. electronic spectrum is displaced with respect to its rotation–vibration spectrum towards short wavelengths, and (ii) the electronic spectra of molecules will exhibit a vibrational coarse- and rotational fine-structures as well.

The terms $\bar{\nu}_{\text{vib}}$ and $\bar{\nu}_{\text{rot}}$ as derived from Eqs (2.33) and (3.33) are expressed as

$$\bar{\nu}_{\text{vib}} = \left[w''_e \left(V'' + \frac{1}{2} \right) - w''_e x''_e \left(V'' + \frac{1}{2} \right)^2 \right] - \left[w'_e \left(V' + \frac{1}{2} \right) - w'_e x'_e \left(V' + \frac{1}{2} \right)^2 \right] \quad (5.7)$$

and

$$\bar{\nu}_{\text{rot}} = B_{v''} J''(J''+1) - B_{v'} J'(J'+1) \quad (5.8)$$

The two different frequencies, w'_e and w''_e and two different rotational constants $B_{v'}$ and $B_{v''}$ correspond to two different electronic states Ψ'_{elec} and Ψ''_{elec} respectively (contrary to infrared spectra where they belong to the same

electronic state, i.e. the ground electronic state Ψ'_{elec}). Each of these states are characterised by a definite frequency w_e and also anharmonicity constant x_e and definite equilibrium bond length ' r_e ', i.e. definite value of rotational constant B_e and, hence, moment of inertia I_e .

5.3 VIBRATIONAL COARSE STRUCTURE OF ELECTRONIC SPECTRA OF DIATOMICS

Disregarding the rotational fine structure, let us discuss the vibrational coarse structure of the electronic spectra of diatomic molecules. Under this condition, we write from Eqs (5.6) and (5.7)

$$\begin{aligned}\bar{\nu} &= \bar{\nu}_{\text{elec-vib}} = \bar{\nu}_{\text{elec}} + \bar{\nu}_{\text{vib}} \\ &= \bar{\nu}_{\text{elec}} + \left[w_e'' \left(V'' + \frac{1}{2} \right) - w_e'' x_e'' \left(V'' + \frac{1}{2} \right)^2 \right] - \left[w_e' \left(V' + \frac{1}{2} \right) - w_e' x_e' \left(V' + \frac{1}{2} \right)^2 \right] \quad (5.9)\end{aligned}$$

Here, the quantity $\bar{\nu}_{\text{elec-vib}}$ defines the centres or origins of a series of vibrational bands building the electronic spectrum.

5.3.1 Selection Rules

Energy transition $V' \rightarrow V''$ associated with an electronic transition $\Psi'_{\text{elec}} \rightarrow \Psi''_{\text{elec}}$ is permissible.

5.3.2 Sequence and Progression

According to the selection rule (5.3.1), a large number of vibrational lines are expected in the electronic vibrational spectra of the molecule due to which the analysis of the observed spectrum becomes cumbersome. This problem is solved to a large extent by considering the ground electronic state as the lower energy electronic state Ψ'_{elec} . Accordingly, the allowed transitions are

$$\Psi'_{\text{elec}} : V' (0, 1, 2, 3, \dots) \rightarrow \Psi''_{\text{elec}} : V'' (0, 1, 2, 3, \dots)$$

$$\begin{aligned}0 &\rightarrow 0, 0 \rightarrow 1, 0 \rightarrow 2, 0 \rightarrow 3, \dots; \\ 1 &\rightarrow 0, 1 \rightarrow 1, 1 \rightarrow 2, 1 \rightarrow 3, \dots; \\ 2 &\rightarrow 0, 2 \rightarrow 1, 2 \rightarrow 2, 2 \rightarrow 3, \dots; \\ 3 &\rightarrow 0, 3 \rightarrow 1, 3 \rightarrow 2, 3 \rightarrow 3, \dots; \text{ etc.}\end{aligned}$$

Such a set of transitions is termed as band and a series of bands having a constant value of $(V'' - V')$ is known as sequence, e.g. the following sets of transitions

$$\begin{aligned}(V'' - V') : V'' - V' = 0 : 0 \rightarrow 0, 1 \rightarrow 1, 2 \rightarrow 2, \dots \\ = +1 : 0 \rightarrow 1, 1 \rightarrow 2, 2 \rightarrow 3, \dots \\ = -1 : 1 \rightarrow 0, 2 \rightarrow 1, 3 \rightarrow 2, \dots \\ = +2 : 0 \rightarrow 2, 1 \rightarrow 3, 2 \rightarrow 4, \dots \\ = -2 : 2 \rightarrow 0, 3 \rightarrow 1, 4 \rightarrow 2, \dots\end{aligned}$$

constitute sequences. The transitions $1 \rightarrow 0, 2 \rightarrow 0, 3 \rightarrow 0$ do not form a sequence since $V'' - V' \neq \text{constant}$. On the other hand, a set of bands having a definite value of V' but varying values of V'' and vice versa is called a progression. For example, the following set of transitions in bands,

$$\begin{aligned}\text{i.e. } V' (0) &\rightarrow V'' (0, 1, 2, 3, \dots), \\ V' (=1) &\rightarrow V'' (0, 1, 2, 3, \dots), \\ V' (=2) &\rightarrow V'' (0, 1, 2, 3, \dots), \text{ etc,}\end{aligned}$$

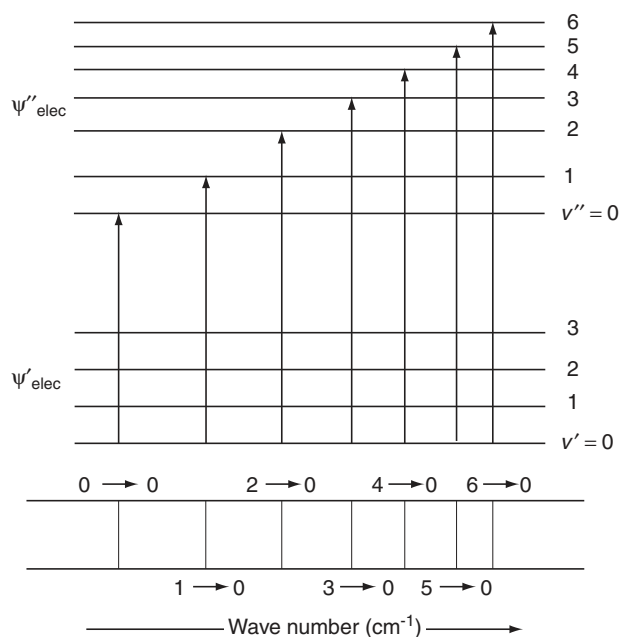


Fig. 5.3 Schematic energy-level diagram showing the vibrational coarse structure of the band in an electronic transition.

constitute V'' progressions while constitute V' progressions for a fixed value of V'' and varying values of V' . The vibrational coarse structure of a band $V' (= 0) \rightarrow V'' (= 1, 2, 3, 4, 5, 6, 7)$ is presented in Fig. 5.3. The coarse structure reveals that the spacing between the adjacent lines in a band decreases and is crowded together at higher frequencies. This is because of anharmonicity factor which increases as the vibrational quantum number increases.

5.3.3 Deslandres System of Bands of a Diatomic Molecule

An empirical formula corresponding to Eq. (5.9) derived by Deslandres is known as *Deslandres formula* and is expressed as

$$\bar{\nu} = \bar{\nu}_0 + [w''_0 V'' - w''_0 x''_0 V''^2] - [w'_0 V' - w'_0 x'_0 V'^2] \quad (5.10)$$

Compare Eqs (5.9) and (5.10) in order to obtain the relations between the constants involved in them, i.e.

$$\begin{aligned} \bar{\nu} = \bar{\nu}_{\text{elec-vib}} = & \left[\bar{\nu}_{\text{elec}} + \frac{w''}{2} \left(1 - \frac{x''}{2} \right) - \frac{w'}{2} \left(1 - \frac{x'}{2} \right) \right] \\ & + [w''(1-x'')V'' - w''x''V''^2] - [w'(1-x')V' - w'x'V'^2] \end{aligned} \quad (\text{Eq. 5.9})$$

Thus, the relations between the constants are

$$\begin{aligned} \bar{\nu}_0 &= \bar{\nu}_{\text{elec}} + \frac{w''}{2} \left(1 - \frac{x''}{2} \right) - \frac{w'}{2} \left(1 - \frac{x'}{2} \right) \\ w''_0 &= w''(1-x'') \\ w''_0 x''_0 &= w''x'' \\ w'_0 &= w'(1-x') \\ w'_0 x'_0 &= w'x' \end{aligned} \quad (5.11)$$

Further, if each frequency of the band is designated as $\bar{\nu}_{V',V''}$ then Eq. (5.10) can be rewritten as

$$\bar{\nu}_{V',V''} = \bar{\nu}_0 + (w''_0 V'' - w''_0 x''_0 V''^2) - (w'_0 V' - w'_0 x'_0 V'^2) \quad (5.12)$$

Table 5.1 Deslandres system of bands of diatomics.

$V \leq V'$	0	1	2	3	4	5	...
0	$\bar{\nu}_{00}$	$\bar{\nu}_{10}$	$\bar{\nu}_{20}$	$\bar{\nu}_{30}$	$\bar{\nu}_{40}$	$\bar{\nu}_{50}$	...
1	$\bar{\nu}_{01}$	$\bar{\nu}_{11}$	$\bar{\nu}_{21}$	$\bar{\nu}_{31}$	$\bar{\nu}_{41}$	$\bar{\nu}_{51}$	...
2	$\bar{\nu}_{02}$	$\bar{\nu}_{12}$	$\bar{\nu}_{22}$	$\bar{\nu}_{32}$	$\bar{\nu}_{42}$	$\bar{\nu}_{52}$	...
3	$\bar{\nu}_{03}$	$\bar{\nu}_{13}$	$\bar{\nu}_{23}$	$\bar{\nu}_{33}$	$\bar{\nu}_{43}$	$\bar{\nu}_{53}$	...
4	$\bar{\nu}_{04}$	$\bar{\nu}_{14}$	$\bar{\nu}_{24}$	$\bar{\nu}_{34}$	$\bar{\nu}_{44}$	$\bar{\nu}_{54}$	...
5	$\bar{\nu}_{05}$	$\bar{\nu}_{15}$	$\bar{\nu}_{25}$	$\bar{\nu}_{35}$	$\bar{\nu}_{45}$	$\bar{\nu}_{55}$	...
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	...
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	...

From this expression, the entire system of bands expressed by the Deslandres formula are deduced and are listed in Table 5.1.

The V'' progressions (correspond to $V' = \text{constant}$, i.e. 0, 1...) as deduced from Eq. (5.12) can be expressed as

$$\bar{\nu} = \bar{\nu}_{0V''} + w_0'' V'' - w_0'' x_0'' V''^2 \quad (5.13)$$

They are due to transitions from a definite vibrational state ($V'' = 0, 1, \dots$) of the ground electronic state Ψ'_{elec} to all possible vibrational levels ($V' = 0, 1, 2, 3, \dots$) of the upper electronic state Ψ''_{elec} (or vice versa). The V'' progressions are a group of bands that converge to a certain limit at high frequency because of anharmonicity parameters and are characteristic of the absorption spectra of molecules such as I_2 , Br_2 , N_2O_2 , NO , O_3 , SO_3 , H_2CO , C_6H_6 , etc. CO (in the Schumann region, $< 2000 \text{ \AA}$).

The V' progressions (correspond to $V'' = \text{constant}$, i.e. 0, 1, 2....) are expressed as

$$\bar{\nu} = \bar{\nu}_{0V'} - w_0' V' + w_0' x_0' V'^2 \quad (5.14)$$

The V' progressions are due to the transitions from a definite vibrational state ($V'' = 0, 1, \dots$) of an upper electronic state Ψ''_{elec} to all possible vibrational levels ($V' = 0, 1, 2, 3, 4, \dots$) in the ground electronic state Ψ'_{elec} of the molecule (or vice versa), i.e. $0 \leftrightarrow 0$, $0 \leftrightarrow 1$, $0 \leftrightarrow 2$, $0 \leftrightarrow 3, \dots$ and $1 \leftrightarrow 0$, $1 \leftrightarrow 1$, $1 \leftrightarrow 2$, $1 \leftrightarrow 3, \dots$. These progressions are characteristics of the emission spectrum particularly in the fluorescence spectrum, e.g. fluorescence spectra of I_2 (excited by green line of Hg $5461 \text{ \AA}$), O_2 , S_2 , NO , SO_2 , etc. The progressions observed in these systems correspond to $V'' = 26 \rightarrow V' = 1, 2, 3, 4, 5, \dots$

It is to be noted that emission spectra of a previously excited molecule by electric discharge, shock wave, temperature and also in chemical (chemiluminescence) excitation will consist of a large number of progressions because of all possible transitions from vibrational states ($V'' = 1, 2, 3, 4, 5, \dots$) in the upper electronic state Ψ''_{elec} to the vibrational states ($V' = 0, 1, 2, 3, \dots$) in the ground electronic state Ψ'_{elec} of Fig. 5.4. In such a situation, the various progressions will overlap and the result and pattern of the emission spectrum becomes very complicated. Many times, the overlapping of different progressions results in segregation of separate groups of bands in the spectrum. These correspond to the diagonal progressions of Deslandres Table, i.e. $\bar{\nu}'_{00}$, $\bar{\nu}'_{11}$, $\bar{\nu}'_{22}, \dots, \bar{\nu}'_{10}$, $\bar{\nu}'_{21}, \bar{\nu}'_{32}, \dots, \bar{\nu}'_{20}, \bar{\nu}'_{31}, \bar{\nu}'_{42}, \dots$ etc. Such progressions are observed in the emission spectra of C_2 , N_2 , CO , CN , etc.

The characteristic constant of each system of bands is the band $\bar{\nu}'_{00}$, i.e. the zero line of the band, which corresponds to the transition ($V'' = 0 \leftrightarrow V' = 0$) and is known as the *zero band*. The frequency of the zero line of the zero band does not coincide with the frequency ν_{elec} because of zero vibrational (or point) energy of the molecule, i.e. $\nu_0 \neq \nu_{\text{elec}}$. In other words, we can say that the pure electronic transition is strictly forbidden. This is often called the 0–0 band and is devoid of vibrational quanta, both in the ground and excited states. The band corresponding to a transition from a vibrationally excited state of a ground electronic state (V', Ψ'_{elec}) to the lower vibrational state of the upper electronic state ($V'', \Psi''_{\text{elec}}$) is called the *hot band*.

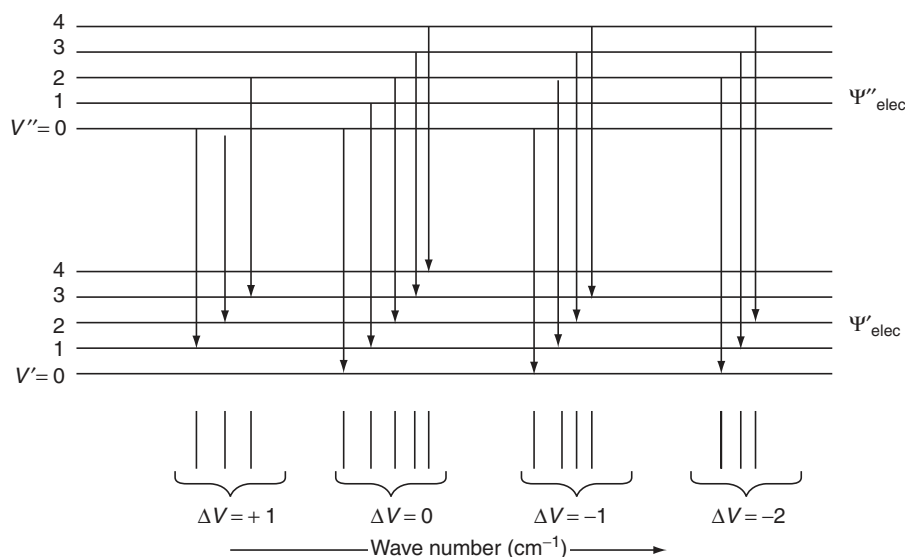


Fig. 5.4 Progressions in the emission spectrum of a pre-excited diatomic molecule.

Energy Difference Between Two Electronic States The ground (Ψ'_{elec}) and excited (Ψ''_{elec}) electronic states of a molecule are usually represented, by the different Morse potential curves. The energy difference, $\bar{\nu}_{\text{elec}}$, between two electronic states will thus correspond to the energy difference between the minima of two Morse curves. The energy difference between the two minima as deduced from Eq. (5.9) is given by

$$\bar{\nu}_{\text{elec-vib}}(V'=0 \rightarrow V''=0) = \bar{\nu}_{\text{elec}} + \left(\frac{w''_e}{2} - \frac{w''_e x''_e}{4} \right) - \left(\frac{w'_e}{2} - \frac{w'_e x'_e}{4} \right) \text{cm}^{-1}$$

$$\text{or } \bar{\nu}_{\text{elec}} = \bar{\nu}_{\text{elec-vib}}(V'=0 \rightarrow V''=0) - \left(\frac{w''_e}{2} - \frac{w''_e x''_e}{4} \right) + \left(\frac{w'_e}{2} - \frac{w'_e x'_e}{4} \right) \text{cm}^{-1}$$

$$\text{or } \bar{\nu}_{\text{elec}} = \bar{\nu}_{\text{elec-vib}}(V'=0 \rightarrow V''=0) - \text{zero point energy of the upper state} + \text{zero point energy of the ground state. (5.15)}$$

$$[1 \text{ cm}^{-1} \equiv 11.958 \text{ J mole}^{-1}]$$

Problem 5.2: The zero-point energy of the ground state of C_2 is 817.8 cm^{-1} and that of its lowest excited state is 890 cm^{-1} . The energy difference between the two minima of the electronic potential energy curves is $3.832 \times 10^{-19} \text{ J}$. Determine the energy of $V'=0 \rightarrow V''=0$ transition in cm^{-1} . What is the corresponding wavelength?

Solution

$$\bar{\nu}_{\text{elec}} = \frac{\Delta E}{hc} = \frac{3.832 \times 10^{-19} (\text{J})}{6.62 \times 10^{-34} (\text{J s}) \times 3 \times 10^{10} (\text{cm/s})} = 19295.8 \text{ cm}^{-1}$$

Substituting the values of zero-point energies of the ground and excited states together with the value of $\bar{\nu}_{\text{elec}}$ into Eq. (5.15), we get

$$\begin{aligned} \bar{\nu}_{\text{elec-vib}}(V'=0 \rightarrow V''=0) &= (19295.8 + 890 - 817.8) \text{ cm}^{-1} \\ &= 19368.0 \text{ cm}^{-1} \end{aligned}$$

The corresponding wavelength is $5163.1 \text{ \AA}$.

Problem 5.3: The analysis of the vibrational structure of a band in the ultraviolet spectrum of CO leads to the following data:

Ground state		Excited state	
$(1\Sigma^+)$			$(^1\Pi)$
$w_e' \text{ (cm}^{-1}\text{)}$	$x_e' \times 10^3$	$w_e'' \text{ (cm}^{-1}\text{)}$	$x_e'' \times 10^3$
2170.21	6.20	1515.61	11.38

The $\bar{\nu}_{00}$ transition is observed at 64746.55 cm^{-1} . Calculate (a) the zero-point energies for the upper and lower states, and (b) the energy difference between the two electronic states. What is the corresponding wavelength?

Solution (a) From Eq. (5.15), we write the expression for the zero-point energies of the upper and lower states as

$$\text{Zero-point energy of the upper state} = \left(\frac{w_e''}{2} - \frac{w_e'' x_e''}{4} \right) \text{cm}^{-1}$$

$$\text{Zero-point energy of the lower state} = \left(\frac{w_e'}{2} - \frac{w_e' x_e'}{4} \right) \text{cm}^{-1}$$

Substituting the values of the respective constants from the problem, we get the zero-point energy of the upper state

$$\begin{aligned} &= \left(\frac{1515.61}{2} - \frac{1515.61 \times 11.38 \times 10^{-3}}{4} \right) \text{cm}^{-1} \\ &= (757.80 - 4.31) \text{cm}^{-1} = 753.49 \text{cm}^{-1} \end{aligned}$$

and zero-point energy of the ground state

$$\begin{aligned} &= \left(\frac{2170.21}{2} - \frac{2170.21 \times 6.20 \times 10^{-3}}{4} \right) \text{cm}^{-1} \\ &= (1085.1 - 3.36) \text{cm}^{-1} = 1081.74 \text{cm}^{-1} \end{aligned}$$

(b) Substituting these values of energies together with the value of ν_{00} from the problem into Eq. (5.15), we get the energy difference between the two electronic states:

$$\begin{aligned} \bar{\nu}_{\text{elec}} &= (64746.55 - 753.49 + 1081.74) \text{cm}^{-1} \\ &= 65074.80 \text{cm}^{-1} = 778.1 \text{kJ mole}^{-1} \end{aligned} \quad [1 \text{cm}^{-1} = 11.958 \text{J mole}^{-1}]$$

The corresponding wavelength is $1536.69 \text{ \AA}$.

Problem 5.4: The $0 \rightarrow 0$ transition in the electronic vibrational spectrum of C_2 arising from the ground $(^3\Pi_u)$ and excited $(^3\Pi_g)$ electronic states of C_2 is observed at 19378 cm^{-1} . The values of w_e and x_e for ground and excited electronic states of C_2 are 1641.4 cm^{-1} , 7.11×10^{-3} and 1788.2 cm^{-1} , 9.19×10^{-3} respectively. Calculate (a) the energy difference between the two minima of the Morse curves corresponding to the electronic states of the molecule, and (b) the force constants for the normal modes of vibration of C_2 in the ground and excited electronic states of the molecule.

Solution (a) In order to determine the energy difference between the two electronic states of C_2 , we are in need of the quantities $w_e' x_e'$ and $w_e'' x_e''$, from the data reported in the problem, we get

$$w_e' x_e' = 1641.4 \text{ (cm}^{-1}\text{)} \times 7.11 \times 10^{-3} = 11.67 \text{cm}^{-1}$$

$$w_e'' x_e'' = 1788.2(\text{cm}^{-1}) \times 9.19 \times 10^{-3} = 16.43 \text{ cm}^{-1}$$

Substituting the values of $w_e' x_e'$ and $w_e'' x_e''$ and also the wave number of 0-0 band into Eq. (5.15), we obtain

$$\begin{aligned} \bar{\nu}_{\text{elec}} &= \left[\bar{\nu}_{\text{elec-vib}} (V' = 0 \rightarrow V'' = 0) - \left(\frac{w_e''}{2} - \frac{w_e'' x_e''}{4} \right) + \left(\frac{w_e'}{2} - \frac{w_e' x_e'}{4} \right) \right] \text{cm}^{-1} \\ &= \left[19378 - \left(\frac{1788.2}{2} - \frac{16.43}{4} \right) + \left(\frac{1641.4}{2} - \frac{11.67}{4} \right) \right] \text{cm}^{-1} \\ &= (19378 - 889.99 + 817.78) \text{cm}^{-1} = 19306.79 \text{ cm}^{-1} = 230.85 \text{ kJ mole}^{-1} \end{aligned}$$

(b) The fundamental mode of vibration of C_2 in the ground and excited states is determined from Eq. (3.57), i.e.

$$\bar{\nu} = w_e (1 - x_e) \text{cm}^{-1}$$

Thus,

$$\bar{\nu} \text{ for ground state} = (1641.4 - 11.67) \text{ cm}^{-1} = 1629.7 \text{ cm}^{-1}$$

$$\bar{\nu} \text{ for excited state} = (1788.2 - 16.43) \text{ cm}^{-1} = 1771.7 \text{ cm}^{-1}$$

$$\mu_m = \frac{12 \times 12}{12 + 12} = 6 \text{ amu}$$

From Eq. (3.19), we now obtain the C-C force constant in the ground and excited states of the molecule.

$$k \text{ for the ground state} = \left[\frac{1629.7}{1303.16} \right]^2 \times 6 = 9.38 \text{ millidynes/\AA}$$

$$k \text{ for the excited state} = \left[\frac{1771.7}{1303.16} \right]^2 \times 6 = 11.09 \text{ millidynes/\AA}$$

Problem 5.5: (a) The frequencies assigned to the vibrational bands in the absorption spectrum of AgI near 3200 Å are listed here.

Frequencies (cm^{-1})	$V' \rightarrow V''$
31642	$0 \rightarrow 5$
31393	$0 \rightarrow 2$
30956	$1 \rightarrow 0$
31577	$0 \rightarrow 4$
31281	$0 \rightarrow 1$
30753	$2 \rightarrow 0$
31491	$0 \rightarrow 3$
31163	$0 \rightarrow 0$
30549	$3 \rightarrow 0$
31666	$0 \rightarrow 6$

- (i) Suggest assignment for the bands at 31256, 31086, 30769, 30868, 30656, 31157, 30953 cm^{-1} .
 (ii) Assign frequencies corresponding to the

$2 \rightarrow 2, 2 \rightarrow 3, 2 \rightarrow 1, 1 \rightarrow 3$ bands

(b) The frequencies assigned to the vibrational bands in the electronic absorption spectrum of nitrogen are listed below.

$V' \rightarrow V''$	Frequencies(cm^{-1})
$0 \rightarrow 0$	29662
$0 \rightarrow 1$	31652
$1 \rightarrow 0$	27957
$0 \rightarrow 3$	35463
$2 \rightarrow 0$	26281
$3 \rightarrow 0$	24634
$0 \rightarrow 2$	33593
$4 \rightarrow 0$	23022
$5 \rightarrow 0$	21425

- (i) Suggest assignment for the bands at 28271, 32082, 26624, 27226 cm^{-1} and (ii) assign frequencies corresponding to the $2 \rightarrow 2$, $3 \rightarrow 2$, $1 \rightarrow 3$ and $4 \rightarrow 2$ bands.

Solution (a) Based on the data in the problem, construct the Deslandres Table. The missing elements in the Table are generated on the basis of vibrational intervals between the adjacent elements in the first row and first column of the Table. The numbers in parenthesis represent the vibrational intervals.

V'' / V'	0		1		2		3
0	31163	(207)	30956	(203)	30753	(204)	30549
	(118)						
1	31281		31074		30871		30667
	(112)						
2	31393		31186		30983		30779
	(98)						
3	31491		31284		31081		30877
	(86)						
4	31577		31370		31167		30963
	(65)						
5	31642		31435		31232		31028
	(24)						
6	31666		31459		31256		31052

- (i) From the Table, the following bands are assigned to the frequencies in question:

$$2 \rightarrow 6, 2 \rightarrow 3, 3 \rightarrow 2, 3 \rightarrow 3, 3 \rightarrow 1, 2 \rightarrow 4, 3 \rightarrow 4.$$

- (ii) From the Table, the frequencies assigned to the bands in question are 30983, 31081, 30871, 31284.

(b) Proceeding as in the part (a) of this problem, we arrive at the following assignments:

(i) $2 \rightarrow 1, 2 \rightarrow 3, 3 \rightarrow 1, 5 \rightarrow 3$

(ii) 30212, 28565, 33758, 26953 cm^{-1}

5.3.4 Intensity Distribution in Vibrational Electronic Spectra From Franck–Condon Principle

According to the Franck–Condon principle, also sometimes called the vertical principle, the internuclear configuration of a diatomic molecule does not change appreciably during an electronic transition since the time scale of complete electron transition is of the order of $\sim 10^{-15}$ s and that of complete vibrational transition is of the order of $\sim 10^{-13}$ sec, i.e. the frequency of electronic transition is hundredfolds faster than that of vibrational transition. The molecule spends most of the time at the extreme ends of its vibration motion when the vibrational quantum number V is large and very little time in between since the vibrational kinetic energy is zero at the extreme ends. Quantum mechanically, the probability of transition $V' \rightarrow V''$ is determined from the quasi-moment that corresponds to the given transition.

$$M_{l(V''V')} = \int \psi_{V''}(r'') M_l \psi_{V'}(r') dr' \quad (5.16)$$

Here, $\psi_{v'}$ and $\psi_{v''}$ are the vibrational wave functions corresponding to the ground and excited electronic states of the diatomic molecule.

The form of the wave functions has been shown in Fig. 5.5. The nuclei are most likely to be found at distances apart given by the maxima of curve for each vibrational state. The vibrational wave functions have a perceptible magnitude in a certain interval of values of r . Due to this diffuseness, they overlap in the interval Δr and this, according to Eq. (5.16), leads to the possibility of a transition from a given level V'' not only to the upper lying level V''' but also to the adjacent levels as shown in Fig. 5.5, i.e. $V'' (= 0) \rightarrow V''' (0, 1, 2, 3 \dots)$, $0 \rightarrow 0$, $0 \rightarrow 1$, $0 \rightarrow 2$, $0 \rightarrow 3$, etc.

Quantum mechanically, the absorption or emission is an instantaneous process and occurs without any change in electronic configuration. Such transitions, are termed vertical and correspond to the arrows of Fig. 5.6. No change in bond length occurs in vertical transitions while in adiabatic transitions, length changes. Adiabatic transitions are strong in photoionisation processes. The two Morse curves shown in Fig. 5.6 have different curvatures, different vibrational intervals and different equilibrium distances. The square of the vibrational wave function is greatest at extreme ends of vibrational levels for larger V'' , suggesting that the probability of finding the nuclei is greatest there. The most probable transition is the vertical arrowed line which starts at the point corresponding to the internuclear distance in the ground state and terminates at the point where it meets the excited state curve at a vibrational level. Thus, the most probable internuclear distance for the vibrational levels other than $V'' = 0$ corresponds to the extreme ends and to the mid-point for $V'' = 0$. The relative intensity of the bands in the absorption or emission spectrum depends on the relative horizontal separations of the potential energy curves of the ground and excited-state molecules. Thus, the band associated with quantum transitions in which there is no change either in internuclear distance or the nuclear motion will have the highest intensity. Intensity distribution among the bands of an electronic transition not only differs from molecule to molecule but also from one progression to another of the same molecule. There are three possible main situations:

(i) Internuclear distances are equal in the lower and upper states, i.e. $r_{v'} = r_{v''}$, (ii) upper state internuclear distance is slightly greater than that in lower state, i.e. $r_{v''} > r_{v'}$, and (iii) upper-state internuclear bond distance is appreciably larger as compared to that in the lower state, i.e. $r_{v''} \gg r_{v'}$, involving the ground state and the first excited singlet states as shown in Fig. 5.7(a) – (c).

(a) CASE (I) When $r_e' = r_e''$, the transition $V'' = 0 \rightarrow V''' = 0$ is the most probable and the internuclear distance does not change during the transition. Consequently, an intense band is expected corresponding to this transition as shown in Fig. 5.7 (a). For other transitions $V'' (= 0) \rightarrow V''' (1, 2, 3, \dots)$, the probability of the successive transitions decreases sharply and the bond distance also changes which is contrary to the Franck–Condon principle. Consequently, weak bands with decreasing intensity are expected corresponding to these transitions as shown in Fig. 5.7 (a).

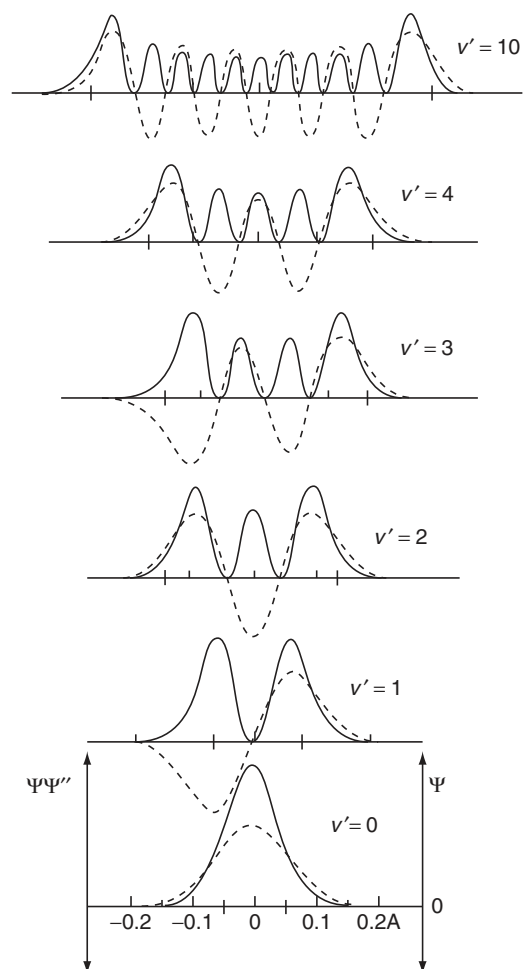


Fig. 5.5 Eigen functions (dashed curves) and probability densities (solid lines) of a harmonic oscillator for $V' = 0, 1, 2, 3 \dots$ and 10.

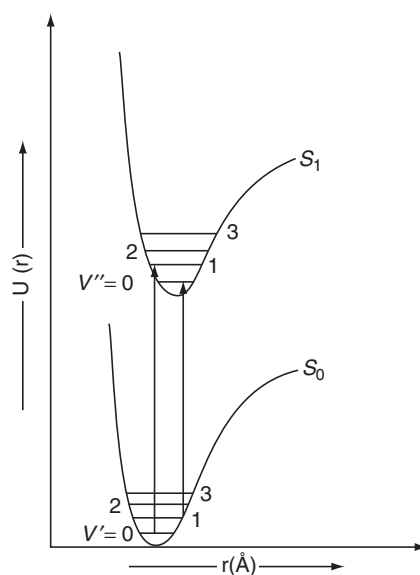


Fig. 5.6 Schematic diagram showing the probabilities of transition after the Franck–Condon principle.

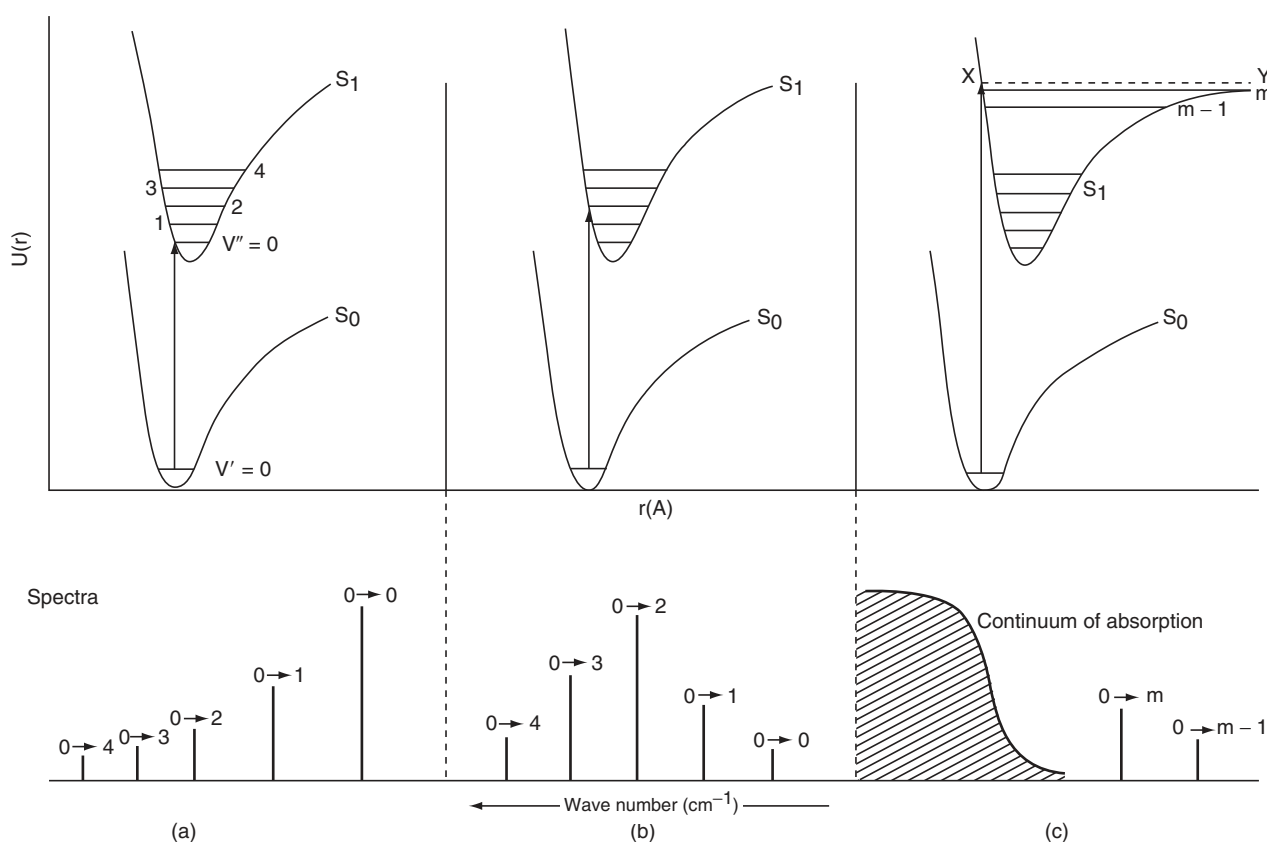


Fig. 5.7 Intensity distribution in absorption bands from Franck-Condon principle (a) internuclear distances are equal in upper and lower states (b) inter nuclear distance in the upper state is a little greater than in lower state (c) inter nuclear distance is considerable greater than that in the lower state.

(b) CASE (II) In the second case, where $r_e'' > r_e'$, the probability corresponding to the vertical transition $V' (= 0) \rightarrow V'' (= 2)$ is maximum and also the difference between internuclear distance in the ground and excited states corresponding to this transition is expected to be minimum. Consequently, the intensity of the band corresponding to this transition will be the maximum. The transitions from $V' (= 0)$ to lower than $V'' (= 2)$, i.e. $V'' (= 0, 1)$ states are (i) more probable, and (ii) differences in internuclear bond distances are small as compared to those from $V' (= 0)$ to higher than $V'' (= 2)$, i.e. $V'' (= 3, 4)$ states. Thus, the bands on the lower wave-number side of the ν_{20} band will be more intense than their counterparts on the higher wave-number side of the ν_{20} band. In general, the intensity of the bands corresponding to the $V' (= 0) \rightarrow V'' (0, 1)$ successive transitions increases and becomes maximum for $0 \rightarrow 2$ and then decreases for $V' (= 0) \rightarrow V'' (3, 4 \dots)$ successive transitions as shown in Fig. 5.7(b).

(c) CASE (III) When $r_e'' \gg r_e'$, the transition probability increases and the difference between the internuclear bond distance in the ground and excited states increases as the vibrational quantum number grows. Consequently, the intensity of the respective bands in the progression $V' (= 0) \rightarrow V'' (0, 1, 2, 3 \dots)$ will increase and becomes maximum at very high values of $V'' = m$ (Fig. 5.7c). The transition finishes at a state represented by the dotted line XY where the energy of the excited molecule exceeds its own dissociation energy. The molecule in this state will dissociate into atoms without any vibrations and atoms may take up any value of kinetic energy. All transitions from the ground state to the points above this level will lead to a continuum of absorption since such transitions are not quantised. The intensity distribution in such a case has been sketched in Fig. 5.7 (c).

Further, in case when $V' \neq 0$ in V' progressions, there are two bands with maximum intensity that correspond to the maxima of the wavefunction $\Psi_{v''}$ at the two turning points of the nuclei (Fig. 5.5). That is why we will have two intensity maxima in these series. The same is true when the initial level is V'' level (emission). For each value of the number of V'' (for $V'' > 0$), there will be two value of V' that correspond to two of the intense bands of the V' progressions in the series. The two maxima will coincide only if the equilibrium separations are the same in both the electronic states. At $V'' = 0$, we will have a series with one intensity maximum just as in case of absorption when the zero vibrational level ($V' = 0$) is the initial state of the molecule, and there is only one intensity maximum in the series.

5.4 ROTATIONAL FINE STRUCTURE OF ELECTRONIC-VIBRATION STRUCTURE OF A DIATOMIC MOLECULE

We know that the electronic spectra of diatomics consist of one or more series of convergent lines. These series of convergent lines constitute the vibrational coarse structure associated with each electronic transition. Normally, each of these lines is broad and diffuse, and under high resolution appears as a group of a large number of very close lines. Such a cluster of lines is termed *fine structure*.

Without taking into consideration the centrifugal distortion constant, let us determine the peculiarities of the rotational fine structure of the electronic spectrum of a diatomic molecule.

5.4.1 Selection Rules

The molecular electronic terms and selection rules for rotational fine structure have been discussed in detail in Chapter 2 on microwave spectroscopy under the title *hyperfine structure*. The selection rules for J depend upon the molecular electronic transition. For lower and upper electronic states, in which there is no electronic angular momentum about the bond axis, the selection rule is

$$\Delta J = \pm 1 \text{ only for } \sum_{\text{lower}}^1 \rightarrow \sum_{\text{upper}}^1 \text{ transition, } \Delta \Sigma = 0 \quad (5.17)$$

Thus, for such $^1\Sigma \rightarrow ^1\Sigma$ transitions, only P ($\Delta J = -1$) and R ($\Delta J = +1$) branches will appear in the electronic spectrum.

For all other transitions in which either the upper or the lower electronic states (or both) have angular momentum about the inter nuclear axis, the selection rule is

$$\Delta J = 0 \text{ or } \pm 1 \text{ and for both the cases } J = 0 \leftrightarrow J = 0 \text{ is forbidden.} \quad (5.18)$$

Thus, for such transitions, in addition to P - and R -branches, Q ($\Delta J = 0$) branch will also appear in the electronic spectrum. Note that for $\Lambda \neq 0$, the selection rule $\Delta J = 0$ or ± 1 and $J' = 0 \leftrightarrow J'' = 0$ is also allowed.

5.4.2 Transition Between Rotational Levels Associated with a Particular Vibrational Level in the Electronic Spectrum of a Diatomic Molecule

We have already proved that the frequencies of separate lines in the electronic spectrum of a diatomic molecule are represented by

$$\bar{\nu} = \bar{\nu}_{\text{elec}} + \bar{\nu}_{\text{vib}} + \bar{\nu}_{\text{rot}} \quad (\text{Eq. 5.6})$$

The frequencies of the individual rotational lines of a particular vibrational band characterised by vibrational quantum numbers V' and V'' , thus, can be represented by the formula

$$\begin{aligned} \bar{\nu}_{\text{rot-elec}} &= \bar{\nu}_{\text{elec}} + \bar{\nu}_{\text{vib}} + B_{V''}J''(J''+1) - B_{V'}J'(J'+1) \\ \bar{\nu}_{\text{rot-elec}} &= \bar{\nu}_{\text{elec-vib}(V'V'')} + B_{V''}J''(J''+1) - B_{V'}J'(J'+1) \end{aligned} \quad (5.19)$$

Here $B_{V''}$ and J'' refer to the upper electronic state and $B_{V'}$ and J' , to the lower electronic state of the diatomic molecule contrary to infrared spectroscopy where they belong to the same electronic state. Very often, when the electron is excited from the bonding orbital of the molecule in the ground state, the bond in the higher electronic state becomes weaker and longer. Further, since the quantity B , the rotational constant, is inversely proportional to the equilibrium moment of inertia and hence the square of the equilibrium bond distance of the molecule, it decreases during the electronic transition. Thus, in such a case, $B_{V''} < B_{V'}$. Sometimes, when the electron excitation is from the antibonding orbital of the molecule, the reverse happens, i.e. $B_{V''} > B_{V'}$. $\bar{\nu}_{\text{elec-vib}(V'V'')}$ is the wave number of an electronic vibrational transition. This corresponds to any of the transitions represented by $V' (= 0, 1, 2, \dots) \rightarrow V'' (0, 1, 2, 3, \dots)$, i.e. $0 \rightarrow 0, 0 \rightarrow 1, \dots, 1 \rightarrow 0, 1 \rightarrow 2$, etc. Thus, it represents the origin of a particular band. Applying the selection rules $\Delta J = \pm 1, \Delta J = 0, \pm 1; J' (= -0) \leftrightarrow J'' (= 0)$ to Eq. (5.19) for the spectral lines, we arrive at the expressions for the frequencies of P -, Q -, and R -branches of the electronic spectrum of the diatomic molecule

$$\begin{aligned} P: \Delta J &= -1, J'' - J' = -1 \text{ or } J' = J'' + 1 \\ \bar{\nu}_P &= \bar{\nu}_{\text{elec-vib}(V'V'')} + B_{V''}J''(J''+1) - B_{V'}(J''+1)(J''+2) \\ &= \bar{\nu}_{\text{elec-vib}(V'V'')} + (J''+1)[B_{V''}(J''+1) - B_{V'} - B_{V'}(J''+1) - B_{V'}] \end{aligned}$$

$$\text{or } \bar{\nu}_P = \bar{\nu}_{\text{elec-vib}(V'V'')} - (B_{V''} + B_{V'})J' + (B_{V''} - B_{V'})J'^2 \quad (5.20)$$

where $J' = 1, 2, 3 \dots J' \neq 0$ otherwise $J'' = -1$ which has no meaning.

Equation (5.20) reveals that no rotational line of the P -branch appears at the band origin $\bar{\nu}_P = \bar{\nu}_{\text{elec-vib}(V'V'')}$

$$R: \Delta J = +1, J'' - J' = +1, J'' = J' + 1$$

$$\bar{\nu}_R = \bar{\nu}_{\text{elec-vib}(V'V'')} + (B_{V''} + B_{V'})(J' + 1) + (B_{V''} - B_{V'})(J' + 1)^2$$

$$\text{where } J' = 0, 1, 2, \dots \quad (5.21)$$

Here too, no rotational line of the R -branch will appear at the band origin.

$$Q: \Delta J = 0, J'' - J' = 0, J'' = J', J' = 0 \leftrightarrow J'' = 0$$

$$\bar{\nu}_Q = \bar{\nu}_{\text{elec-vib}(V'V'')} + (B_{V''} + B_{V'})J' + (B_{V''} - B_{V'})J'^2$$

$$\text{where } J' = 1, 2, 3 \dots \quad (5.22)$$

since $J' = 0 \leftrightarrow J'' = 0$, no line from the Q -branch will appear at the origin. However, for $\Lambda \neq 0$, the rule $J' = 0 \leftrightarrow J'' = 0$ is also allowed and thus $J' = 0, 1, 2, 3, \dots$, the lines of Q -branch will start from the origin.

Equations (5.20) and (5.21) are clubbed together into

$$\bar{\nu}_{PR} = \bar{\nu}_{\text{elec-vib}(V'V'')} + (B_{V''} + B_{V'})m + (B_{V''} - B_{V'})m^2$$

$$\text{where } m = \pm 1, \pm 2, \pm 3 \dots \quad (5.23)$$

Here, m is negative for P -branch ($\Delta J = -1$) and positive for R -branch ($\Delta J = +1$). m can't be zero otherwise for P -branch $J'' = -1$ which is not possible.

The wave numbers of the rotational fine lines in the P - R - and Q -branches as worked out from Eqs (5.23) and (5.22) respectively for $B_{V''} (= 10 \text{ cm}^{-1}) < B_{V'} (= 12 \text{ cm}^{-1})$. 20 per cent difference between the two in the electronic-vibrational spectrum of the diatomic molecule have been listed in Table 5.2, and the corresponding spectrum is sketched in Fig. 5.8. We already know that even the higher rotational levels are

Table 5.2 Position of rotational fine lines relative to $\bar{\nu}_{\text{elec-vib}}$ for $B_{V''} < B_{V'}$ and 20 per cent difference between the two in the electronic vibrational structure of diatomic molecule, $B_{V''} = 10 \text{ cm}^{-1}$, $B_{V'} = 12 \text{ cm}^{-1}$, $\bar{\nu}_{PR} = \bar{\nu}_{\text{elec-vib}} + 22m - 2m^2$, m is positive for R -branch and negative for P -branch. $\bar{\nu}_Q = \bar{\nu}_{\text{elec-vib}} - 2J'(J' + 1)$.

m/J'	$\bar{\nu}_R (\text{cm}^{-1})$	$-\bar{\nu}_P (\text{cm}^{-1})$	$-\bar{\nu}_Q (\text{cm}^{-1})$
1	20	24	4
2	36	52	12
3	48	84	24
4	56	120	40
5	60	160	60
6	60	204	84
7	56	252	112
8	48	304	144
9	36	360	180
10	20	420	220

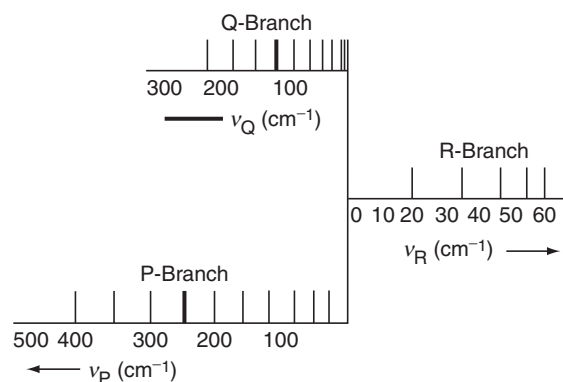


Fig. 5.8 Electronic vibrational spectrum of a diatomic molecule.

populated even at room temperature, consequently a large number of rotational lines appear in the P - and R -branches and wherever possible in the Q -branch also in the spectrum. The lines in the R branch become closely spaced on the high wave-number side and crowd together and eventually a maximum value of $\bar{\nu}_R$ is obtained at a particular value of m . This limiting position of the band corresponding to maximum value of $\bar{\nu}_R$ is called band head, and the lines become widely spaced on the low wave-number side of the band head called the tail of the band. This decline in total intensity away from the band head forms a line distribution in the band called shading or degrading of the band. The shading of a band towards longer wavelengths or low frequencies is termed red shading and the band is said to red-shaded as in the present case and violet-shaded if the shading is towards the lower wavelengths. The red shading is due to the dominance of m^2 over the $22m$ term. Further looking at the curve, it is found that the lines spread out in the P branch as m decreases. The Q -branch also follows the direction of the P -branch. However, the spacing between adjacent lines is much closer since $(B_{v''} - B_{v'})$ is numerically smaller than $(B_{v''} + B_{v'})$ and also there is no change in J' . The spacing between adjacent lines grows with J' . It may be noted that in many cases there is no band head. This occurs when the difference between $B_{v''}$ and $B_{v'}$ is slight. The characteristic band constant whose value corresponds to wave number of the band origin also called the zero line, i.e. $\bar{\nu}_{\text{elec-vib}(00)}$ is absent from the spectra of diatomics. The position of zero line in a band can be determined from the characteristic gap that disrupts the line sequence. The exact value of $\bar{\nu}_{\text{elec-vib}(00)}$ band can be determined from a detailed analysis of the rotational structure of the bands. The set of values of $\bar{\nu}_{\text{elec-vib}}$ so obtained aids in establishing the Deslandres formula for a given system of bands, i.e. determining the constant ν_{elec} and also the vibrational constants w_e and x_e for both the combining electronic terms.

The foregoing arguments are true for $B_{v''} < B_{v'}$. In case $B_{v''} > B_{v'}$, all the discussion is reversed and (i) the band head appears in the P -branch towards lower wave numbers or higher wavelengths away from the band origin $\bar{\nu}_{\text{elec-vib}(00)}$ and is shaded towards longer wave numbers, i.e. lower wavelengths away from the band head and is said to be violet shaded, (ii) the lines in the R -branch still appears on the higher wave-number side of the band origin and show an intense separation with m and (iii) the lines of the Q -branch spreads out to lower wavelengths or higher wave-number side of the band origin and the separation between adjacent lines increases with J' .

Problem 5.6: The fine structure line of C_2 band at 19378 cm^{-1} fits well into the equation

$$\bar{\nu}_{\text{rot-elec}} = [19378 + 3.3853m + 0.1201m^2] \text{ cm}^{-1}$$

(a) Find the value of the band head and position of the band head. (b) Calculate the separation between zero line and band head and state the direction of shading of the band. (c) Determine moments of inertia and internuclear distances in the two electronic states of the molecule.

Solution (a) The rotational fine structure of lines of a band is expressed by the relation

$$\bar{\nu}_{\text{rot-elec}} = \bar{\nu}_{\text{rot-elec}} + (B_{v''} + B_{v'})m + (B_{v''} - B_{v'})m^2, \text{ cm}^{-1} \quad (\text{Eq. 5.23})$$

Comparing Eq. (5.23) with the given relation, we obtain

$$\bar{\nu}_{\text{elec-vib}(v'=0 \rightarrow v''=0)} \text{ or } \bar{\nu}_{00} = 19378 \text{ cm}^{-1}$$

$$B_{v''} + B_{v'} = 3.3853 \text{ cm}^{-1}$$

$$B_{v''} - B_{v'} = 0.1201 \text{ cm}^{-1}$$

Solving these for $B_{v''}$ and $B_{v'}$, we get

$$B_{v''} = 1.7527 \text{ cm}^{-1}$$

$$B_{v'} = 1.6321 \text{ cm}^{-1}$$

The value of m at band head is given by

$$m = -\frac{(B_{v''} + B_{v'})}{2(B_{v''} - B_{v'})} = -\frac{3.3853(\text{cm}^{-1})}{2 \times 0.1201(\text{cm}^{-1})} = -14$$

The negative value of m reveals that the band head lies in the low wave-number side of the band origin or null line, i.e. P -branch of the spectrum. The band is shaded towards the high wave-number side or towards violet.

The position of the head, i.e. maximum value of $\bar{\nu}_{\text{rot-elec}}$ corresponding to $m = -14$ is determined from the equation.

$$\begin{aligned}\bar{\nu}_{\text{head}} &= [19378 + 3.3853(-14) + 0.1201(-14)^2] \text{cm}^{-1} \\ &= (19378 - 47.39 + 23.53) \text{cm}^{-1} \\ &= (19378 - 23.86) \text{cm}^{-1} \\ &= 19354.14 \text{cm}^{-1}\end{aligned}$$

- (b) The separation between band head and the null line is $(19354.14 - 19378) \text{cm}^{-1} = -23.86 \text{cm}^{-1}$. Thus the head is shaded towards violet.
- (c) The moments of inertia and bond distances in both the states of the molecule are determined from $B_{V''}$ and $B_{V'}$.

For the ground state, I'

$$I' = \frac{h}{8\pi^2 B_{V'} c} = \frac{16.8575}{1.6321} = 10.328 \text{ au.}$$

Since μ_m for $\text{C}_2 = \frac{12 \times 12}{12 + 12} = 6.0 \text{ amu}$, the bond length for C_2 in the ground state is

$$r' = \sqrt{\frac{I'}{\mu_m}} = \sqrt{\frac{10.328}{6}} = \sqrt{1.7213} = 1.311 \text{ \AA}$$

Similarly, for the excited state,

$$I'' = \frac{16.8575}{1.7527} = 9.618 \text{ au}$$

and

$$r'' = \sqrt{\frac{I''}{\mu_m}} = \sqrt{\frac{9.618}{6}} = \sqrt{1.603} = 1.266 \text{ \AA}$$

5.4.3 The Fortrat Diagram

It has already been stated that frequencies of the individual rotational lines of a band that is characterised by definite values of vibrational quantum numbers V' and V'' (that result because of electronic transitions between two electronic states of a diatomic molecule) are given by

$$\bar{\nu} = \bar{\nu}_{\text{elec-vib}(V'V'')} + B_{V''}J''(J''+1) - B_{V'}J'(J'+1) \quad (\text{Eq. 5.19})$$

Here, $B_{V''}$ and $B_{V'}$ correspond to two different electronic states, say Ψ''_{elec} and Ψ'_{elec} , of a diatomic molecule. It can be easily proved from Eq. (5.19) that the rotational frequencies of the P -, Q -, and R -branches in the electronic spectrum are given by

$$P: \bar{\nu}_P = \bar{\nu}_{\text{elec-vib}} - (B_{V''} + B_{V'})J' + (B_{V''} - B_{V'})J'^2 (\Delta J = -1) \quad (\text{Eq. 5.20})$$

$$Q: \bar{\nu}_Q = \bar{\nu}_{\text{elec-vib}} + (B_{V''} - B_{V'})J' + (B_{V''} - B_{V'})J'^2 (\Delta J = 0) \quad (\text{Eq. 5.21})$$

$$R: \bar{\nu}_R = \bar{\nu}_{\text{elec-vib}} + (B_{V''} + B_{V'})J' + (B_{V''} - B_{V'})J'^2 (\Delta J = +1) \quad (\text{Eq. 5.22})$$

and

$$\bar{\nu}_{PR} = \bar{\nu}_{\text{elec-vib}} + (B_{V''} + B_{V'})m + (B_{V''} - B_{V'})m^2 \quad (\text{Eq. 5.23})$$

where $m = \pm 1, \pm 2, \pm 3, \dots$, m is negative for P -branch and positive for R -branch. These three quadratics in J 's, represent three parabolas, i.e. P , Q and R and are usually termed *Fortrat parabolas*. Thus, the Fortrat diagram comprises parabolic curves corresponding to P -, Q - and R -branches of an electronic-vibrational band that is characterised by definite values of vibrational quantum numbers V' and V'' , and are constructed by plotting the frequencies of the rotational lines of $V' \rightarrow V''$ band against the rotational quantum numbers in the lower energy electronic state of the molecule. The Fortrat diagram for $B_{V''} (= 10 \text{ cm}^{-1}) < B_{V'} (12 \text{ cm}^{-1})$ and a 20 per cent difference

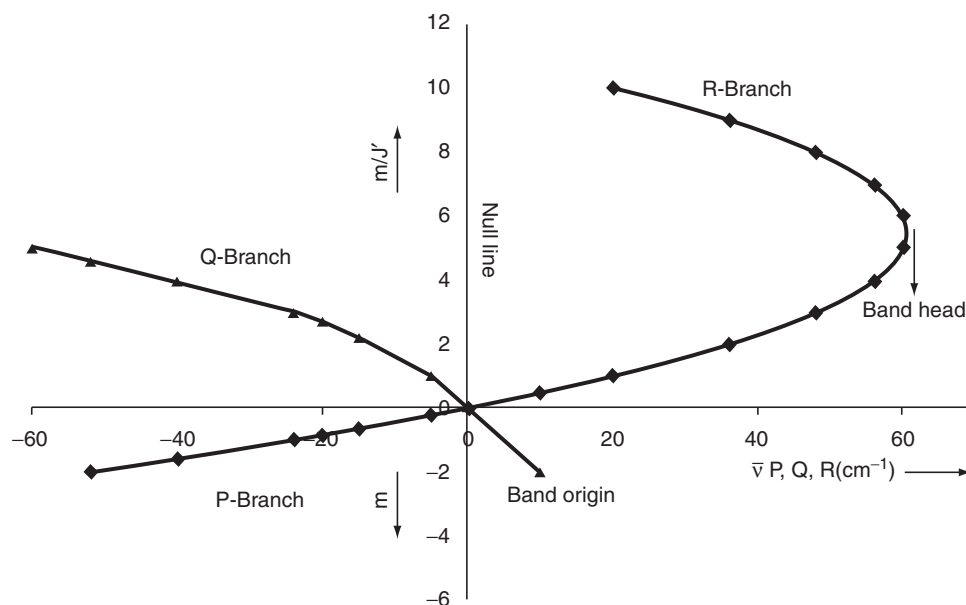


Fig. 5.9 Fortrat diagram of $B_{v''} (=12 \text{ cm}^{-1}) < B_{v'} (=10 \text{ cm}^{-1})$; 20 per cent difference between $B_{v''}$ and $B_{v'}$.

between the two is shown in Fig. 5.9. The position of the band head depends upon the difference between the values of $B_{v''}$ and $B_{v'}$.

The Fortrat diagram can be explained on the basis of arguments on the rotational fine structure of a vibrational-electronic transition of a diatomic molecule reported in Section 5.2. A usual property of the Fortrat diagram is that the band head is due to the turning point in the PR parabola. The problem arises as to which of the branches (R or P) has a turning point. This problem has been solved by the sign of quadratic term in the expression (5.23). The sign is determined as follows.

Differentiating Eq. (5.23) we get

$$\frac{d\bar{\nu}_{PR}}{dm} = (B_{v''} + B_{v'}) + 2m(B_{v''} - B_{v'})$$

At the tuning point, $\frac{d\bar{\nu}_{PR}}{dm} = 0$

$$\therefore (B_{v''} + B_{v'}) + 2m(B_{v''} - B_{v'}) = 0$$

or

$$m = -\frac{(B_{v''} + B_{v'})}{2(B_{v''} - B_{v'})} \text{ at the band head.}$$

Thus, the position of the band head depends on the difference between the values of $B_{v'}$ and $B_{v''}$,

- (i) For $B_{v''} < B_{v'}$ m is positive. Thus, the band head occurs in the R -branch.
- (ii) For $B_{v''} > B_{v'}$ m is negative. Thus, the band head lies in the region of m negative, i.e. in the P -branch.

Substituting the value of m in Eq. (5.23), we obtain the expression for the wave-number separation between the

$$\text{band head } \bar{\nu}_{PR} \text{ and the band origin } \bar{\nu}_{\text{elec-vib}}, \text{ i.e. } \bar{\nu}_{PR} - \bar{\nu}_{\text{elec-vib}} = -\frac{(B_{v''} + B_{v'})^2}{4(B_{v''} - B_{v'})} \quad (5.24)$$

$\bar{\nu}_{PR} - \bar{\nu}_{\text{elec-vib}}$ is positive for a band shaded to red ($B_{v''} < B_{v'}$), while it is negative for a band shaded to violet ($B_{v''} > B_{v'}$).

The value of J' at which the vertex on the band head of the Q -parabola lies is obtained by differentiating Eq. (5.22) with respect to J' , i.e.

$$\frac{d\bar{\nu}_Q}{dJ'} = (B_{v''} - B_{v'}) + 2(B_{v''} - B_{v'})J'$$

At the turning point of the parabola, $\frac{d\bar{\nu}_Q}{dJ'} = 0$

$$\therefore (B_{v''} - B_{v'}) + 2(B_{v''} - B_{v'})J' = 0 \quad \text{or} \quad J' = -\frac{1}{2} \quad (5.25)$$

Thus, unlike the PR band head, J' , i.e. the Q -band is independent of the values of $B_{v''}$ and $B_{v'}$. However, if the $(B_{v''} - B_{v'})$ difference is large, the spacing between the adjacent Q -lines increases rapidly, consequently the Q -head is not strongly expressed.

5.4.4 Simplification of the Analysis of Rotational Fine Structure in the Vibrational Electronic Spectrum

The analysis of the rotational spectrum of diatomics is simplified by setting up definite relations between frequencies of the rotational lines, in order to isolate individual rotational terms and rotational constants of the molecule. This is achieved by denoting the rotational term by $F(J)$, i.e. $F(J) = B_v J(J+1)$. Thus, in terms of $F(J)$, Eq. (5.19) can be expressed as

$$\bar{\nu}(J) = \bar{\nu}_{\text{elec-vib}} + F''(J) - F'(J) \quad (5.26)$$

The expressions for P -, Q -, and R -branches in terms of $F(J)$ will then appear as follows:

For P -branch: $\Delta J = -1$, $J'' - J' = -1$, $J'' = J' - 1$

$$\bar{\nu}_P = \bar{\nu}_{\text{elec-vib}} + B_{v''}(J' - 1)J' - B_{v'}J'(J' + 1).$$

or in terms of $F(J)$

$$\bar{\nu}_P(J') = \bar{\nu}_{\text{elec-vib}} + F''(J' - 1) - F'(J') \quad (5.27)$$

For R -branch: $\Delta J = +1$, $J'' = J' + 1$,

$$\bar{\nu}_R = \bar{\nu}_{\text{elec-vib}} + B_{v''}(J' + 1)(J' + 2) - B_{v'}J'(J' + 1)$$

or in terms of $F(J)$

$$\bar{\nu}_R(J') = \bar{\nu}_{\text{elec-vib}} + F''(J' + 1) - F'(J') \quad (5.28)$$

For Q -branch: $\Delta J = 0$, $J'' = J'$, $J'' = 0 \leftrightarrow J' = 0$

$$\bar{\nu}_Q = \bar{\nu}_{\text{elec-vib}} + B_{v''}J'(J' + 1) - B_{v'}J'(J' + 1)$$

or in terms of $F(J)$

$$\bar{\nu}_Q(J') = \bar{\nu}_{\text{elec-vib}} + F''(J') - F'(J') \quad (5.29)$$

From the above expressions (5.27 – 5.29), the following relations are obtained for separate lines.

$$\left. \begin{aligned} \bar{\nu}_Q(J') - \bar{\nu}_P(J') &= \bar{\nu}_R(J' - 1) - \bar{\nu}_Q(J' - 1) \\ &= F''(J') - F''(J' - 1) \\ &= B_{v''}(J' + 1)J' - B_{v''}J'(J' - 1) \\ &= 2B_{v''}J' \\ \bar{\nu}_Q(J' - 1) - \bar{\nu}_P(J') &= \bar{\nu}_R(J' - 1) - \bar{\nu}_Q(J') \\ &= F''(J') - F''(J' - 1) \\ &= B_{v''}J'(J' + 1) - B_{v''}(J' - 1)J' \\ &= 2B_{v''}J' \end{aligned} \right\} \quad (5.30)$$

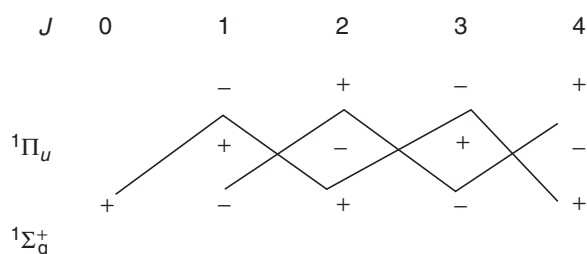
Equation (5.30) reveals that the frequency difference between two lines in a band is repeated twice and is a quantity that is a multiple of $2B_{v''}$ or $2B_{v'}$. Thus, the starting point in the analysis of rotational structure of a band is to determine the difference that satisfies the relations expressed by Eq. (5.30). Hence, we can directly find the

values of the constants $B_{v''}$ and $B_{v'}$ of the molecule and its rotational terms, e.g. for $J' = 1$, we obtain: $F''(1) - F''(0) = F''(1) = 2B_{v''}$ and $F'(1) - F'(0) = F'(1) = 2B_{v'}$.

These relations straight away give the constants $B_{v''}$ and $B_{v'}$ and the terms $F'(1)$ and $F''(1)$. For $J' = 2$, we have:

$$F''(2) - F''(1) = 4B_{v''} \text{ and } F'(2) - F'(1) = F(1) = 4B_{v'}$$

As has already been stated in the text that for $^1\Sigma \leftrightarrow ^1\Sigma$ transition, due to $\Delta J = \pm 1$, only P - and R -branches appear in the spectrum and the Q -branch is absent. However, in the $^1\Sigma \leftrightarrow ^1\Pi$ transition, in addition to P - and R -branches, the Q -branch also appears in the spectrum. But here the Λ -type doubling of Π term should also be taken into consideration. Since change in energy associated with Λ -doubling in Eqs.(5.20–5.22) is not taken into account, these formulae and also the relations in terms of $F(J)$ (5.27–5.30) derived from them are not very accurate. However, in spite of this, it in no way affects the number of branches in the spectrum corresponding to the combination $^1\Sigma - ^1\Pi$. The rotational Σ – terms are alternately positive and negative and the components of Λ -doubling of Π -term, i.e. Π_a and Π_b also have different signs. Based on the selection rules $\Delta J = 0, \pm 1$ and $+\leftrightarrow -$ only three combinations of each $^1\Sigma$ term, i.e. three simple branches are possible. These combinations can schematically be represented as follows.

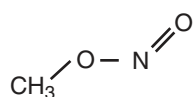


The rotational structure of bands in the combination of other terms is beyond the scope of the book. However, the results of some of the combinations are stated here.

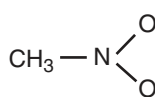
Combination	Branches
$\left. \begin{array}{l} ^3\Pi \leftrightarrow ^1\Pi \\ ^1\Pi \leftrightarrow ^1\Delta \end{array} \right\}$	six (two R -, two Q - and two P -branches)
$^2\Sigma \leftrightarrow ^2\Sigma$	Four (two R -, and two P -branches).
$^2\Sigma \leftrightarrow ^2\Pi$	Twelve

5.5 ELECTRONIC ABSORPTION SPECTRA OF POLYATOMICS

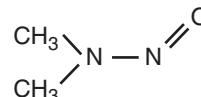
The vibrational and rotational structures in the electronic spectra of polyatomics is more complex than that of diatomics because a large number of constants, viz., vibrational and rotational, are involved in them. However, the rotational structure of the bands of symmetric linear molecules of the type CO_2 is close to that of diatomics. In spite of the complexities involved in vibrational and rotational structures in the electronic spectra of polyatomics, the spectra of polyatomics aid in assigning the fundamental modes of vibrations both in the ground and excited electronic states of the molecule as evidenced by the following examples. The ultraviolet-spectral data on methyl nitrite (I), nitromethane (II) and dimethyl nitrosoamine (III) as deduced from their near ultraviolet electronic absorption spectra in the vapour phase have been listed in Table 5.3.



(I)



(II)



(III)

Differences from 0–0 band are given within a parentheses. The intensities of bands decline progressively downwards.

Table 5.3 UV spectral data of methyl nitrite, nitromethane and dimethylnitrosoamine in the vapour phase.

Methyl nitrite		Nitromethane		Dimethylnitrosoamine	
$\bar{\nu}(\text{cm}^{-1})$	Assignment	$\bar{\nu}(\text{cm}^{-1})$	Assignment	$\bar{\nu}(\text{cm}^{-1})$	Assignment
27432 (1080)	$\nu'(\text{C-O})$	32777(1343)	$\nu'(\text{NO}_2)$		
		33213 (907)	$\nu'(\text{C-N})$		
28512	0-0	34120	0-0	26485	0-0
29481 (969)	$\nu''(\text{C-O})$	34955 (835)	$\nu''(\text{C-N})$	27469 (984)	$\nu''(\text{N-N})$
30465 (1953)	$2 \times \nu''(\text{C-O})$	35704(1584)	$2 \times \nu''(\text{C-N})$	28400 (1915)	$2 \times \nu''(\text{N-N})$
31367 (2885)	$3 \times \nu''(\text{C-O})$	36619(2499)	$3 \times \nu''(\text{C-N})$	29518(3033)	$3 \times \nu''(\text{N-N})$
32212 (3700)	$4 \times \nu''(\text{C-O})$				

Methyl nitrite weak band on the long-side wavelength side is comparable to the $\nu'(\text{C-O})$ fundamental in the infrared spectra. The other fundamentals are $1600 \nu'(\text{N=O})$, $800 \nu'(\text{N-O})$ and $600 \text{ cm}^{-1} \delta(\text{ONO})$. Thus, it is surmised that the bands in the progression are most likely to arise from the $\nu''(\text{C-O})$ in the first excited state. As expected, the $\nu''(\text{C-O})$ is lower than in the ground state. The combination tones with progressively decreasing intensities follow this band.

In case of nitromethane, the bands at 1377 , 658 and 918 cm^{-1} in its vapour phase spectrum is assigned to NO_2 symmetric stretching, NO_2 symmetric bending and C-N stretching modes respectively. The NO_2 bending mode is not involved with the progression. The progression is because of C-N stretching mode since the difference between the ground and excited state frequencies ($907 - 835 = 72 \text{ cm}^{-1}$) is of right order.

The 1023 cm^{-1} IR band of dimethylnitrosoamine increases in frequency on changing from non-polar to polar solvents and is assigned to the N-N stretching mode. Bands at 1489 and 1016 cm^{-1} in vapour phase IR spectrum are due to N=O and N-N stretching modes. Thus, the observed interval of 984 cm^{-1} in UV absorption spectrum of dimethylnitrosoamine can only be due to the $\nu''(\text{N-N})$ stretching mode.

Thus, it follows that electronic absorption spectroscopy is complementary to infrared- and Raman- spectroscopy or vice versa

5.6 THE ISOTOPE EFFECT IN MOLECULAR ELECTRONIC SPECTRA

This effect applies equally to molecular spectra with electronic excitation and to infrared-, and Raman-, spectra. The vibrational isotope effect is characterised by the difference in natural frequencies of the isotope molecules whereas the rotational effect, from their differences in moments of inertia. The isotope effect in molecular spectra is a sensitive and precise method of identifying isotopes and determining their relative abundances from their relative intensities in the spectrum, e.g. a number of isotopes $\text{H}^2(\text{D})$, C^{13} , N^{15} , O^{17} , O^{18} , etc., have been discovered by molecular spectroscopy.

5.6.1 Vibrational Isotope Effect

We know that

$$w_e = 1303.16 \sqrt{k / \mu_m}$$

and

$$x_e = \frac{h w_e}{4 D_e} = \frac{1303.16 h}{4 D_e} \sqrt{\frac{k}{\mu_m}}$$

Accordingly, the natural frequency and anharmonicity constant are inversely proportional to the square root of the of the reduced mass (μ_m) of the diatomic molecule, i.e. w_e or $x_e \propto \sqrt{\frac{1}{\mu_m}}$ while $w_e x_e$ to the reduced mass of molecule, i.e. $w_e x_e \propto \frac{1}{\mu_m}$.

Here, $\mu_m = \frac{m_1 m_2}{m_1 + m_2}$ and m_1 and m_2 are the masses of the atoms comprising the diatomic molecule.

In order to study this effect, a quantity *P rho* is introduced.

$$\rho = \sqrt{\frac{\mu_m^*}{\mu_m}} \quad (5.31)$$

where μ_m^* and μ_m are the reduced masses of the deuterated and undeuterated isotopes of the molecule.

The magnitude shift of zero line $(\Delta\nu_0)_{\text{vib}}$ in the spectra of diatomics can be determined from the Deslandres Table as follows.

$$\begin{aligned} \bar{\nu}_{\text{elec-vib}} = \bar{\nu}_{\text{elec}} + & \left[w_e'' \left(V'' + \frac{1}{2} \right) - w_e'' x_e'' \left(V'' + \frac{1}{2} \right)^2 \right] \\ & - \left[w_e' \left(V' + \frac{1}{2} \right) - w_e' x_e' \left(V' + \frac{1}{2} \right)^2 \right] \end{aligned} \quad (5.32)$$

$$\begin{aligned} \bar{\nu}_{\text{elec-vib}}^* = \bar{\nu}_{\text{elec}} + & \left[\rho w_e'' \left(V'' + \frac{1}{2} \right) - \rho^2 w_e'' x_e'' \left(V'' + \frac{1}{2} \right)^2 \right] \\ & - \left[\rho w_e' \left(V' + \frac{1}{2} \right) - \rho^2 w_e' x_e' \left(V' + \frac{1}{2} \right)^2 \right] \end{aligned} \quad (5.33)$$

Subtracting Eq. (5.32) from Eq. (5.33), we get

$$\begin{aligned} (\Delta\nu_0)_{\text{vib}} = \bar{\nu}_{\text{elec-vib}}^* - \bar{\nu}_{\text{elec-vib}} \\ = (\rho - 1) \left[w_e'' \left(V'' + \frac{1}{2} \right) - w_e' \left(V' + \frac{1}{2} \right) \right] \\ - (\rho^2 - 1) \left[w_e'' x_e'' \left(V'' + \frac{1}{2} \right)^2 - w_e' x_e' \left(V' + \frac{1}{2} \right)^2 \right] \end{aligned} \quad (5.34)$$

Disregarding the anharmonicity constant, Eq. (5.43) reduces to

$$(\Delta\nu_0)_{\text{vib}} = (\rho - 1) \left[w_e'' \left(V'' + \frac{1}{2} \right) - w_e' \left(V' + \frac{1}{2} \right) \right] \quad (5.35)$$

In order to determine $\Delta\nu_0$ for different transitions $(\rho - 1)$ for isotopes of the type $X_2^{(m_1, m_2)}$, $X^{m_1} X^{m_2^*}$ (e.g. $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, $^{12}\text{C}_2$, $^{12}\text{C}^{13}\text{C}$, $^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}$; etc.) is expressed as

$$\rho - 1 = \frac{\mu_m^*}{\mu_m} = \frac{\sqrt{m_2^*(m_1 + m_2)}}{\sqrt{m_2(m_1 + m_2^*)}} - 1 = \frac{\sqrt{m_2^*(m_1 + m_2)} - \sqrt{m_2(m_1 + m_2^*)}}{\sqrt{m_2(m_1 + m_2^*)}}$$

On rationalising and expressing $m_2^* - m_2 = \Delta m$ we obtain

$$\rho - 1 = \frac{\Delta m}{\sqrt{2m_2 + \Delta m} \left[\sqrt{2(m_2 + \Delta m)} + \sqrt{2(m_2 + \Delta m)} \right]} \quad (5.36)$$

Approximately, Δm is small compared to m_2 or m_1 (since $m_2 = m_1$), consequently (5.36) reduces to

$$\rho - 1 = \frac{\Delta m}{4m_2} \quad \text{or} \quad \frac{\Delta m}{4m_1} \quad (5.37)$$

With the aid of Eqs (5.35) and (5.37), one can study the vibrational isotope effect in the isotopic molecules of the type, $X_2^{m_1, m_2}$, $X^{m_1} X^{m_2^*}$. For more accurate results, the anharmonicity factor should be retained in Eq. (5.34). The second term of Eq. (5.34) then needs be multiplied by the quantity $(\rho^2 - 1)$ which is derived as follows.

We know that

$$\rho^2 = \frac{\mu_m^*}{\mu_m} = \frac{m_1 m_2^*}{m_1 + m_2^*} \times \frac{m_1 + m_2}{m_1 m_2}$$

or

$$\rho^2 = \frac{2m_2^*}{(m_1 + m_2^*)} \quad (\text{since } m_1 = m_2)$$

Thus,

$$\rho^2 - 1 = \frac{m_2^* - m_1}{(m_2^* - m_1) + 2m_1} = \frac{\Delta m}{\Delta m + 2m_1}$$

Δm being small compared to $2m_1$ can be disregarded in the denominator, consequently.

$$\rho^2 - 1 = \frac{\Delta m}{2m_1} \quad (5.38)$$

Problem 5.7: Prove that for molecular isotopes of the type, $X^{m_1}Y^{m_2}$, and $X^{m_1}Y^{m_2^*}$ (e.g. H^{35}Cl , H^{37}Cl), the term

$$\rho - 1 = \frac{m_1 \Delta m}{2m_2(m_1 + m_2)} \quad \text{where } \Delta m = m_2^* - m_2 \text{ and } m_2/m_2^* \gg m_1$$

Solution From Eq. (5.31), we write

$$\rho - 1 = \sqrt{\frac{\mu_m^*}{\mu_m}} - 1 = \sqrt{\frac{m_1 m_2^*}{m_1 + m_2^*} \times \frac{m_1 + m_2}{m_1 m_2}} - 1 = \frac{\sqrt{m_2^*(m_1 + m_2)} - \sqrt{m_2(m_1 + m_2^*)}}{\sqrt{m_2(m_1 + m_2^*)}}$$

On rationalising, we get

$$\begin{aligned} \rho - 1 &= \frac{m_2^*(m_1 + m_2) - m_2(m_1 + m_2^*)}{\sqrt{m_2(m_1 + m_2^*)} \left[\sqrt{m_2^*(m_1 + m_2)} + \sqrt{m_2(m_1 + m_2^*)} \right]} \\ &= \frac{m_1(m_2^* - m_2)}{\sqrt{m_2 m_2^*(m_1 + m_2^*)(m_1 + m_2)} + m_2(m_1 + m_2^*)} \end{aligned}$$

or

$$\rho - 1 = \frac{m_1 \Delta m}{\sqrt{m_2(m_2 + \Delta m)(m_1 + m_2 + \Delta m)(m_1 + m_2)} + m_2(m_1 + m_2 + \Delta m)}$$

Disregarding Δm relative to m_2 , we get

$$\rho - 1 = \frac{m_1 \Delta m}{\sqrt{m_2^2(m_1 + m_2)^2} + m_2(m_1 + m_2)} \quad \text{or} \quad \rho - 1 = \frac{m_1 \Delta m}{2m_2(m_1 + m_2)} \quad (5.39)$$

Problem 5.8 The values of w_e and x_e in the ground state ($^3\Pi_u$) and a particular excited state ($^3\Pi_g$) of C_2 are 1641.4 cm^{-1} , 7.11×10^{-3} respectively. Calculate the vibrational isotope shift of zero line for the transitions $V' \rightarrow V''$; $0 \rightarrow 0$, $0 \rightarrow 1$, $1 \rightarrow 1$, and $1 \rightarrow 2$ in the electronic spectra of the C_2 molecule.

Solution The isotopes of C_2 molecule are $^{12}\text{C } ^{12}\text{C}$ and $^{12}\text{C } ^{13}\text{C}$. In order to determine the vibrational isotope shift $(\Delta v_0)_{\text{vib}}$, the quantity $\rho - 1$ needs be determined first.

From Eq. (5.37), we get

$$\rho - 1 = \frac{\Delta m}{4m_1} = \frac{1}{4 \times 12} = 0.02.$$

Substituting this value of $(\rho - 1)$ together with the values of natural frequencies into Eq. (5.35), we obtain

$$(\Delta\nu_0)_{\text{vib}} = 0.02 \left[1788.2 \left(V'' + \frac{1}{2} \right) - 1641.4 \left(V' + \frac{1}{2} \right) \right]$$

The values of $(\Delta\nu_0)_{\text{vib}}$ in the asked transitions as deduced from the above expression are as follows:

Transition	$(\Delta\nu_0)_{\text{vib}}(\text{cm}^{-1})$
$V \rightarrow V''$	
$0 \rightarrow 0$	1.5
$0 \rightarrow 1$	37.5
$1 \rightarrow 1$	4.4
$1 \rightarrow 2$	40.1

Problem 5.9: The values of w_e in the ground state ($^1\Sigma$) and a particular excited state ($^3\Sigma$) of the terrestrial atmospheric O_2 are 1580.3 and 1432.6 cm^{-1} respectively. Calculate the isotope shift of zero line in a single progression of bands $V''(=0) \rightarrow V'(=0,1,2,3)$ in the electronic absorption or emission spectra of terrestrial atmospheric oxygen.

Solution The two isotopes of O_2 are $^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}$. Proceeding as in the above problem, we write

$$\rho - 1 = \frac{(18 - 16)}{4 \times 16} = 0.031$$

and

$$(\Delta\nu_0)_{\text{vib}} = 0.031 \left[1432.6 \left(V'' + \frac{1}{2} \right) - 1580.3 \left(V' + \frac{1}{2} \right) \right] \text{cm}^{-1}$$

The magnitude of $(\Delta\nu_0)_{\text{vib}}$ for the asked bands of the series as determined from the above expression are listed below.

Transition	$(\Delta\nu_0)_{\text{vib}}(\text{cm}^{-1})$
$V'' \rightarrow V'$	
$0 \rightarrow 0$	-2.229
$0 \rightarrow 1$	42.12
$0 \rightarrow 2$	86.53
$0 \rightarrow 3$	130.94

5.6.2 Rotational Isotope Effect

As already has been stated in Section 5.6, the rotational isotope effect is characterised by the difference in the moments of inertia of the isotopic molecules. Assuming the Franck–Condon principle holds good, we write

$$B \propto \frac{1}{\mu_m} \quad (5.40)$$

Thus, in order to study this effect in homonuclear diatomics of the type $X^{m_1}X^{m_2}$; $X^{m_1}X^{m_2^*}$, the quantity $(\rho - 1)$ defined by Eq. (5.38) is used here, i.e.

$$\rho^2 - 1 = \frac{\Delta m}{2m_1}$$

The frequencies of the individual rotation lines in the electronic–vibrational spectra of diatomics are given by

$$\bar{\nu}_{\text{rot-elec}} = \bar{\nu}_{\text{elec-vib}} + B_{V''} J''(J'' + 1) - B_{V'} J'(J' + 1) \quad (\text{Eq. 5.19})$$

Thus, the magnitude of shift of rotation line $(\Delta\nu_0)_{\text{rot}}$ in electronic spectra of diatomics can be determined as follows.

$$\bar{\nu}_{\text{rot-elec}}^* = \bar{\nu}_{\text{elec-vib}}^* + \rho^2 B_{V''}^* J''(J'' + 1) - \rho^2 B_{V'}^* J'(J' + 1) \quad (5.41)$$

Subtracting (5.19) from (5.41) and applying the selection rule $\Delta J = \pm 1$, i.e. $J'' - J' = +1$ or $J' = J + 1$, we obtain

$$(\Delta v_0)_{\text{rot}} = (\Delta v_0)_{\text{vib}} + \rho^2 [(B_{V''}^* - B_{V''})(J' + 1)(J' + 2) - (B_{V'}^* - B_{V'})J'(J' + 1)]$$

or

$$(\Delta v_0)_{\text{rot}} = (\Delta v_0)_{\text{vib}} + \rho^2 (J' + 1) \left[B_{V''} \left(\frac{B_{V''}^*}{B_{V''}} - 1 \right) (J' + 2) - B_{V'} \left(\frac{B_{V'}^*}{B_{V'}} - 1 \right) J' \right] \quad (5.42)$$

Since $B \propto \frac{1}{\mu_m}$

$$\therefore \frac{B_{V''}^*}{B_{V''}} \text{ or } \frac{B_{V'}^*}{B_{V'}} = \frac{\mu_m}{\mu_m^*} = \frac{1}{\rho^2}$$

Consequently, Eq. (5.42) yields

$$(\Delta v_0)_{\text{rot}} = (\Delta v_0)_{\text{vib}} - (\rho^2 - 1)(J' + 1)[B_{V''}(J' + 2) - B_{V'}J'] \quad (5.43)$$

Thus, the superposition of the rotational isotope effect on the vibrational isotope effect imparts an additional shift to the rotational lines in the spectrum. The rotational isotope shift, though measurable, is small compared to vibrational isotope shift because the difference between the rotational terms is small compared to the vibrational terms.

The isotope effect, both vibrational and rotational, has also been observed in polyatomics. However, an isotope shift of only those lines which are associated with the vibrations or rotations involving an isotope has been observed as expected theoretically also.

Problem 5.10: Using the required data from Problem 5.6 and Problem 5.8, calculate the rotational isomer shifts for the rotational transitions $J' \rightarrow J'' : 0 \rightarrow 1, 1 \rightarrow 2, 2 \rightarrow 3$ with $V' \rightarrow V'' : 0 \rightarrow 0$ transition in the electronic spectrum of C_2 .

Solution The data acquired from Problem 5.6 are $B_{V''} = 1.7527 \text{ cm}^{-1}$ and $B_{V'} = 1.6321 \text{ cm}^{-1}$ and from Problem 5.8 are $(\Delta v_0)_{\text{vib}(0 \rightarrow 0)} = 1.5 \text{ cm}^{-1}$

Here
$$\rho^2 - 1 = \frac{\Delta m}{2m_1} = \frac{1}{24} = 0.041$$

Substituting the value of $(\rho^2 - 1)$ and acquired data into Eq. (5.43), we obtain

$$(\Delta v_0)_{\text{rot}} = 1.5 - 0.041 (J' + 1) [1.7527 (J' + 2) - 1.6321 J'] \text{ cm}^{-1}$$

The values of $(\Delta v_0)_{\text{rot}}$ determined from the above expression for the asked transitions are listed here.

The rotational isotope shift decreases as the rotational quantum number J' increases.

J'	Transition	$(\Delta v_0)_{\text{rot}}$ (in cm^{-1})
0	$0 \rightarrow 1$	1.35
1	$1 \rightarrow 2$	1.20
2	$2 \rightarrow 3$	1.04

5.7 NUCLEAR SPIN AND INTENSITY ALTERNATION IN ELECTRONIC BAND STRUCTURE

Particles with odd half-integral spin quantum numbers are called *fermions*, e.g. protons and electrons. According to the Pauli exclusion principle, they are symmetric with respect to interchange of pair of particles, i.e.

$$\begin{array}{ccc} \Psi_{\text{elec}} & \xrightarrow{\text{exchange}} & \Psi_{\text{elec}} \\ (x, y, z) & & (x, y, z) \end{array}$$

On the other hand, the particles with integral spin quantum numbers, e.g. α particle ($s = 0$), photons ($s = 1$) are called *bosons* and they are anti-symmetric with respect to exchange of a pair of particles, i.e.

$$\begin{array}{ccc} \Psi_{\text{photon}} & \xrightarrow{\text{exchange}} & \Psi_{\text{photon}} \\ (x, y, z) & & (-x, -y, -z) \end{array}$$

The total wave function of a homonuclear diatomic molecule with nonzero spin such as H_2 , can be represented as

$$\Psi = \Psi_{\text{elec}} \Psi_{\text{vib}} \Psi_{\text{nuc}} \Psi_{\text{rot}}$$

Ψ should be either symmetric or asymmetric with respect to exchange of nuclei, i.e.

$$\begin{array}{ccc} \Psi & \xrightarrow{\text{exchange}} & \Psi \\ (x, y, z) & & (-x, -y, -z) \\ \Psi & \xrightarrow{\text{exchange}} & \Psi \\ (x, y, z) & & (x, y, z) \end{array}$$

Ψ_{elec} and Ψ_{vib} are symmetric with the interchange of pair of nuclei in the homonuclear diatomic molecule since Ψ_{elec} is dependent of the coordinates of the nuclei and Ψ_{vib} depends on the internuclear distance and is independent of the nuclear coordinates.

$$\left. \begin{array}{c} \Psi_{\text{elec}} \\ \Psi_{\text{vib}} \end{array} \right\} \xrightarrow{\text{Interchange}} \left. \begin{array}{c} \Psi_{\text{elec}} \\ \Psi_{\text{vib}} \end{array} \right\}$$

$$(x, y, z) \quad x, y, z$$

Thus, the wave function Ψ_{rot} can either be symmetric or asymmetric with the interchange of pair of nuclei in the homonuclear diatomic molecule and it is found that

$$\begin{array}{l} \Psi_{\text{rot}} \rightarrow \Psi_{\text{rot}} \text{ for even values of } J, \text{ i.e. } J=0, 2, 4 \\ (x, y, z) (x, y, z) \\ \Psi_{\text{rot}} \rightarrow \Psi_{\text{rot}} \text{ for odd values of } J=1, 3, 5. \\ (x, y, z) (-x, -y, -z) \end{array}$$

Let us now construct the nuclear spin wave functions for a homonuclear diatomic molecule with nonzero spin. If atoms are designated as 1 and 2 then the nuclear spin wave functions are

$$\text{and } \alpha(1) \alpha(2), \beta(1) \beta(2), \alpha(1) \beta(2), \text{ and } \beta(1) \alpha(2)$$

The wave functions $\alpha(1) \alpha(2)$ and $\beta(1) \beta(2)$ are symmetric while $\alpha(1) \beta(2)$ and $\beta(1) \alpha(2)$ are neither symmetric nor asymmetric with respect to the interchange of pair of nuclei (i.e. 1 and 2) in the molecule. The linear combination of wave functions gives

$$\left. \begin{array}{c} \alpha(1) \alpha(2) \\ \alpha(1) \beta(2) + \alpha(2) \beta(1) \\ \beta(1) \beta(2) \end{array} \right\} \text{symmetric nuclear wave function } \Psi_{\text{nuc}}^s$$

and $\alpha(1) \beta(2) - \alpha(2) \beta(1)$ asymmetric nuclear wave function Ψ_{nuc}^a

Thus, in view of the above arguments, the rotation levels of a given electronic state are not only affected by the spin of the electron but by the spin of the nucleus also. The total wave function Ψ is thus expressed as

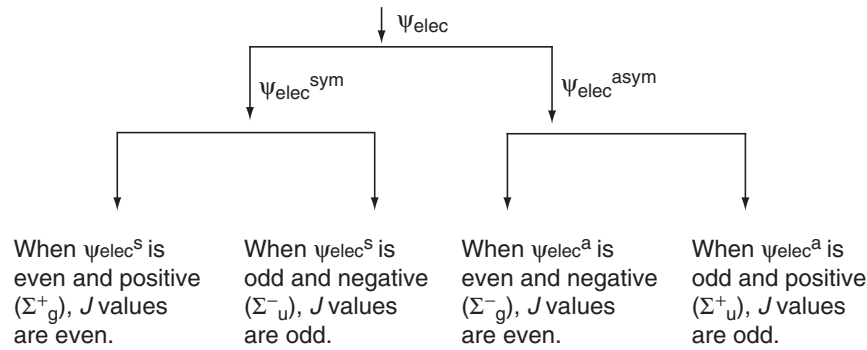
$$\Psi = \Psi_{\text{elec}} \Psi_{\text{nuc}}$$

where Ψ_{nuc} and Ψ_{elec} are the nuclear-spin and electron-spin wave functions of the nucleus and electron respectively.

According to the Pauli exclusion principle, Ψ must be symmetric with respect to exchange of two nuclei if they are bosons while asymmetric if the nuclei are fermions.

Let us first discuss the effect of two wave functions independent of each other on the rotational levels of a given electronic state. So the product of Ψ_{elec} and Ψ_{rot} , i.e. $\Psi' = \Psi_{\text{elec}} \Psi_{\text{rot}}$ will characterise the rotation term belonging to the corresponding electronic state of the molecule. Each of the functions may be positive or negative depending on whether the sign of the function changes with a change in sign of all coordinates of electron and nuclei (Ψ_{elec}) and with change of sign of coordinates of the nuclei alone, i.e. when the sense of rotation is reversed (Ψ_{rot}). It then turns out as shown in the Figure given below:

In case of Π -, Δ -, etc., terms, one of the components of Λ -type doubling of each rotational terms will be positive and other negative.



Further, when we consider the effect of Ψ_{nuc} on the rotational levels of a given electronic state, the product of Ψ_{nuc} and Ψ_{rot} will give a wave function $\Psi'' = \Psi_{\text{nuc}} \Psi_{\text{rot}}$ which characterises the rotation levels of a given electronic state.

If the spin quantum number of each nuclei is I then the total number of linearly independent spin functions corresponding to each nuclei $= 2I + 1$, since $M_I = I, I-1, \dots, -I$. Therefore, in a molecule the total number of wave functions $\Psi_{\text{nuc}}^s = (2I + 1)(2I + 1)$, the number of Ψ_{nuc}^s with respect to exchange of nuclei $= (2I + 1)(I + 1)$ and $\Psi_{\text{nuc}}^a = (2I + 1)I$,

Accordingly,

$$\frac{\text{Statistical weight of symmetric spin states, } N^s(\Psi_{\text{nuc}}^s)}{\text{Statistical weight of asymmetric spin states } N^a(\Psi_{\text{nuc}}^a)} = \frac{(2I + 1)(I + 1)}{(2I + 1)I} = \frac{I + 1}{I}$$

Thus, if

(i) $\Psi = \Psi_{\text{elec}}^s \Psi_{\text{nuc}}^s$, the symmetric rotational levels belonging to Ψ_{elec}^s is stronger for bosons

(ii) $\Psi = \Psi_{\text{elec}}^a \Psi_{\text{nuc}}^s$, the asymmetric rotational levels belonging to Ψ_{elec}^a are stronger in case of fermions

Let us now extend the treatment to homonuclear diatomics in which both the nuclei are either fermions or bosons.

In case of H_2 , where both the nuclei are fermions,

$$\Psi = \Psi_{\text{elec}}^s \Psi_{\text{nuc}}^a \text{ and } \Psi = \Psi_{\text{elec}}^a \Psi_{\text{nuc}}^s$$

Accordingly, Ψ_{rot}^a corresponding to Ψ_{elec}^a will be stronger as compared to Ψ_{rot}^s since Ψ_{nuc}^s has higher statistical weight than that of Ψ_{nuc}^a . Thus, in Σ_g^+ and Σ_u^- states, odd J levels are asymmetric and hence stronger while in Σ_g^- and Σ_u^+ states, even J levels are asymmetric and hence stronger. Thus, in case of H_2 (fermion), we write,

$$\frac{\text{Nuclear spin statistical weight of asymmetric levels, } N^a(\Psi_{\text{nuc}}^a)}{\text{Nuclear spin statistical weight symmetrical of levels, } N^s(\Psi_{\text{nuc}}^s)} = \frac{\text{Odd } J \text{ values (or even } J)}{\text{Even } J \text{ values (or odd } J)} = \frac{I + 1}{I},$$

$$= \frac{\frac{1}{2} + 1}{\frac{1}{2}} = \frac{3}{1}$$

i.e. odd number rotational levels in Σ_g^+ and Σ_u^- states are three times stronger than the even number rotational levels, while the reverse is true for Σ_g^- and Σ_u^+ states, i.e. $\frac{\text{even } J}{\text{odd } J} = \frac{3}{1}$.

Further, in case of diatomics with integral spins, i.e. bosons, say N_2 , D_2 , and O_2 ,

$$\Psi = \Psi_{\text{elec}}^s \Psi_{\text{nuc}}^s \text{ and } \Psi = \Psi_{\text{elec}}^a \Psi_{\text{nuc}}^a$$

Accordingly, Ψ_{rot}^s corresponding to Ψ_{elec}^s will be stronger in comparison to Ψ_{rot}^a since Ψ_{nuc}^s has higher statistical weight as compared to Ψ_{nuc}^a . Thus, in Σ_g^+ and Σ_u^- states, even J values are symmetric and hence stronger while in Σ_g^- and Σ_u^+ states, odd J values are symmetric and hence stronger.

Hence, in case of bosons, i.e. N_2 , D_2 , and O_2 , we write

$$\frac{\text{Nuclear spin statistical weight of symmetrical levels (stronger)}}{\text{Nuclear spin statistical weight of asymmetrical levels (weaker)}} = \frac{\text{Even } J (\text{or odd } J)}{\text{Odd } J (\text{or even } J)} = \frac{I+1}{I} = \frac{1+1}{1} = \frac{2}{1}$$

i.e. even-number rotational levels in Σ_g^+ and Σ_u^- states are two times stronger than odd-number rotational levels while the reverse is true for Σ_g^- and Σ_u^+ states, i.e. $\frac{\text{odd } J}{\text{even } J} = \frac{2}{1}$.

In case of O_2 , since $I = 0$ ($M_I = 0$), so asymmetric rotational levels are of weaker intensity or even missing in the spectrum.

The intensity alteration has also been observed in the rotational Raman spectra of bosons and fermions. The intensity alteration in these spectrum can also be explained on the aforesaid arguments.

In case of H_2 , the ground state $^1\Sigma_g^+$ is even and positive. So, even J values are symmetric, i.e. $\Psi = \Psi_{\text{elec}}^s \Psi_{\text{nuc}}^a$ while odd J values are asymmetric i.e. $\Psi = \Psi_{\text{elec}}^a \Psi_{\text{nuc}}^s$ consequently.

$$\frac{\text{odd } J}{\text{even } J} = \frac{I+1}{1} = \frac{3}{1}$$

The Stokes lines in the rotational Raman spectrum of H_2 follows this pattern of intensity alternation.

In case of N_2 and D_2 , $I = 1$, so the complete molecule wave function Ψ must be symmetric. Hence, symmetric rotational lines corresponding to $\Psi = \Psi_{\text{elec}}^s \Psi_{\text{nuc}}^s$ will be stronger. The electronic state $^1\Sigma_g^+$ is even and positive. So even J levels will correspond to Ψ_{elec}^s and odd J levels will correspond to Ψ_{elec}^a consequently

$$\frac{\text{even } J}{\text{odd } J} = \frac{I+1}{I} = \frac{1+1}{1} = \frac{2}{1}$$

i.e. even J lines will be two times stronger than the odd J lines.

In case of oxygen, since $I = 0$ ($M_I = 0$), so only symmetric nuclear spin function Ψ_{nuc}^s is possible. Thus, the complete molecular wave function $\Psi = \Psi_{\text{elec}}^s \Psi_{\text{nuc}}^s$ is possible while $\Psi = \Psi_{\text{elec}}^a \Psi_{\text{nuc}}^a$ is not possible. For O_2 , the ground state is $^3\Sigma_g^-$. It is even and negative, hence even J values are asymmetric and odd J values are symmetric. Consequently, rotational lines corresponding to even J values will be missing in the rotational Raman spectrum. The absence of these lines reveals that the spin of each of the nuclei of oxygen molecule is zero.

Now we know that in addition to isotope shift, the spectra of isotopic molecules are also influenced by nuclear spin of diatomics. The spins of diatomics with identical nuclei do not interact with one another or with the electrons of the molecule. Consequently, during a radiative transition of the molecule, the nuclear spin symmetry of the molecule does not change and the selection rule for space symmetry of rotational levels is $s \leftrightarrow a$, i.e. molecules in even J state tend to remain in even J state while in odd J state, tend to be in odd J state. Thus, the rule is absolutely true for molecules with zero spin, e.g. O_2 , C_2 , He_2 , etc. On the other hand, this rule is not true absolutely in diatomics with nonzero spins, e.g. H_2 , N_2 , D_2 , etc. Such types of molecules, i.e. molecules with nonzero spins, exist in two modifications, the characteristics of which are listed in Table 5.4. The statistical weight of the para modification being larger than the ortho, the spectral lines corresponding to the former will be more intense compared to the latter. However, such an alteration in intensity is missing in heterodiatomics. This difference is particularly strongly expressed when nuclear spin is zero. In this case, the para modification does not exist and hence in the absence of para term, every other line due to para form will be missing in the spectrum, e.g. $^{16}O^{16}O$. On the other hand, the spectra of $^{16}O^{17}O$ and $^{16}O^{18}O$ molecules show all lines permitted by the selection rule for the rotational quantum number J . This is illustrated in Fig. 5.10 showing the $0' \rightarrow 1''$ band of isotopic molecules

Table 5.4 Characteristic parameters for the ortho- and para- modifications of homonuclear diatomics with nonzero spin.

Modification	Nuclear spin	J levels occupied	Statistical weight
Ortho	$\uparrow\uparrow$	Odd	Large
Para	$\uparrow\downarrow$	Even	Small

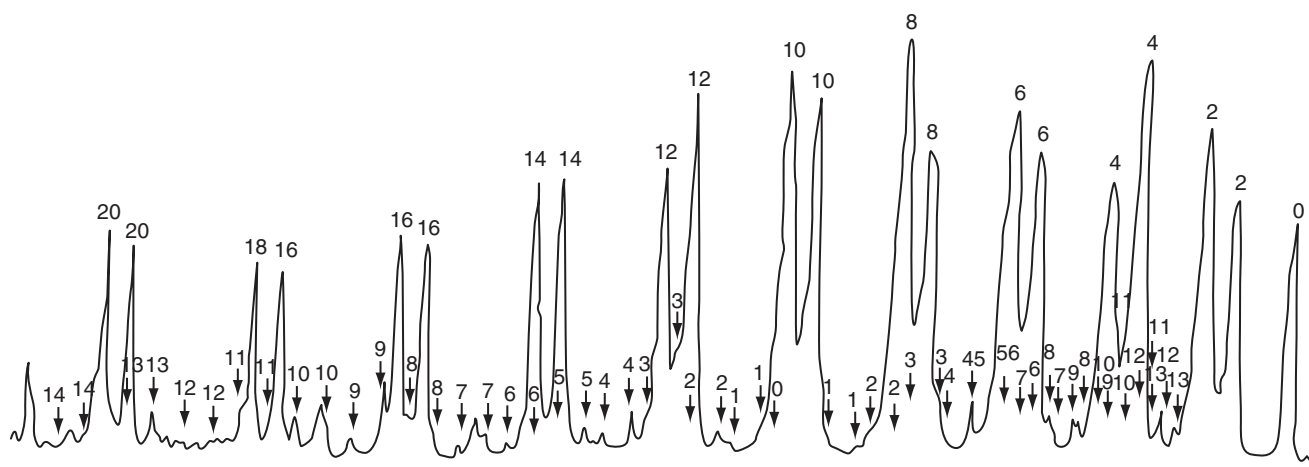


Fig. 5.10 Band ($0' 1''$) of isotopic molecules $^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}$ in the absorption spectrum of the terrestrial atmosphere. The lines of the $^{16}\text{O}^{18}\text{O}$ molecule are denoted by arrows. Intense doublets represent the P-branch of the band of $^{16}\text{O}^{16}\text{O}$.

$^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}$ in the absorption spectrum of terrestrial atmosphere (light source is sun). The two sets of doublets with different intensities are because of isotopic molecules $^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}$. The intensity difference is due to different relative abundance of the isotopic species.

The intense doublets with even values of J correspond to the P-branch of $0' 1''$ band of $^{16}\text{O}^{16}\text{O}$ molecule. The doublet structure of the lines is due to the interaction of nuclear spin with the rotation of the molecule. This structure results provided the nonpermissible $^2\sum_g^- \rightarrow ^1\sum_g^+$ transition is considered and the selection rule $\Delta J = 0, \pm 1$ rather than $\Delta J = 0, \pm 1, \pm 2$ is valid since the latter rule results for quadrupole radiation. This shows that atmospheric bands of O_2 are associated with magnetic dipole radiation but not with quadrupole radiation. The weak lines, both with even and with odd values of J in the second set of doublets, correspond to the $^{16}\text{O}^{18}\text{O}$ molecule. The asymmetric distribution of intensity in the bands of both the isotopes and also the presence of weak intermediate lines are because of the superposition of O_2 spectrum by the spectral lines of iron and water vapour.

Further, it is found that the ratio of the statistical weights for the ortho and para modifications and hence the ratio of their line intensities in the spectrum is given by

$$\frac{I_{\text{ortho}}}{I_{\text{para}}} = \frac{I+1}{I} \quad (5.44)$$

Thus, from the intensity measurements, it is possible to determine the nuclear spin and isotopic abundance in the molecule. The intensity ratio and nuclear spin of some homonuclear diatomics that exhibit ortho- and para-modification are listed in Table 5.5.

Table 5.5 Nuclear spin and ratio of line intensities of the ortho- and para- modifications in the spectra of homonuclear diatomics.

Molecule	Intensity ratio	Nuclear spin
$\text{H}_2, ^3\text{P}_2$	3:1	$\frac{1}{2}$
$\text{D}_2, ^{14}\text{N}_2$	2:1	1
$^7\text{Li}_2$	1.67:1	$\frac{3}{2}$
$^{35}\text{Cl}_2, ^{127}\text{I}_2$	1.4:1	$5/2$
$\left. \begin{array}{l} \text{He}_2, ^{12}\text{C}_2, \\ ^{16}\text{O}_2, ^{32}\text{S}_2 \\ ^{80}\text{Se}_2 \end{array} \right\}$	∞	0

Problem 5.11: The spin of a hydrogen molecule is $\frac{1}{2}$. Determine the per cent abundance of ortho- and para-modification of H_2 .

Solution From Eq. (5.44), we write

$$\frac{I_{\text{ortho}}}{I_{\text{para}}} = \frac{1 + \frac{1}{2}}{\frac{1}{2}} = \frac{3}{1}$$

$$\text{Amount of ortho modification} = \frac{3 \times 100}{4} = 75 \text{ per cent}$$

$$\text{And amount of para modification} = \frac{1 \times 100}{4} = 25 \text{ per cent}$$

Exercise: Draw the J levels for the following cases: (i) $\Sigma^+(\Lambda = 0)$ and $\Pi(\Lambda = 1)$, (ii) Σ_g^+ , Σ_u^- and Σ_g^- , Σ_u^+ (bosons), and (iii) Σ_g^+ , Σ_u^- and Σ_g^- , Σ_u^+ (fermions).

5.8 CONTINUOUS ABSORPTION AND EMISSION SPECTRA

5.8.1 Continuous Absorption Spectra

Molecular absorption electronic spectra of diatomic gases exhibit marked discrete linear band structure and in addition, a continuum is also observed particularly in polyatomics. Broadening of bands takes place at high temperature

and pressure. The former is called *Doppler broadening* and is expressed by $\Gamma_D = \frac{2\nu_{\text{obs}}}{c} \sqrt{\frac{2RT \ln 2}{M}} = 1.67 \frac{\nu_{\text{obs}}}{c} \sqrt{\frac{2RT}{M}}$

and the latter is known as *collision or impact broadening* and is given by $\Gamma_p = \frac{1}{\pi l_0} \sqrt{\frac{8RT}{M}}$ Here, l_0 is the mean

free path, M is the molecular mass, ν_{obs} is the observed frequency and T is the absolute temperature. Thus, it is possible to determine T from the former expression if Γ_D and ν_{obs} are known. For example, if ^{57}Fe line emitted from the surface of the sun is observed at 677.4 nm and has a bandwidth of 5.3 pm, the temperature of the sun's surface will be 6.3×10^7 K. It follows that when the pressure or temperature is increased, the separate lines in the rotational fine structure begin to broaden and at a certain stage, the width of rotational lines exceeds the interval between adjacent lines in the rotational fine structure. Consequently, the rotational fine structure starts disappearing and ultimately disappears completely. At sufficiently high pressure, the width of the separate rotational lines even exceeds the interval between the bands in the spectrum and a complete continuum results. Such a conversion of discrete linear band structure into a continuum occurs at high temperatures and pressures. However, a continuum is also observed at low temperatures and pressures. Thus, it follows that a continuum is not due to external parameters such as temperature and pressure but due to some internal causes also. One of the causes for continuum is that the rotational and vibrational motion is not quantised at least in one of the combining electronic states of the molecule in an electronic transition. Thus, a complete continuous absorption spectrum results when an electronic transition occurs from a ground electronic state to an unstable upper electronic state (i.e. a state without discrete rotational and vibrational levels) of the molecule as shown in Fig. 5.11(a). The molecule in the unstable state dissociates into atoms and the atoms fly away with kinetic energy. Since this kinetic energy of atoms is not quantised, a complete continuum results in the electronic absorption spectrum of the molecule. The lower limit of continuum will have energy $D'_0 = E_{\text{ex}}$, where E_{ex} is the total excitation energy of the products and D'_0 is the dissociation energy of the molecule in the ground state. The continuum also appears when transition takes place from a ground electronic state to an upper stable electronic state of the molecule as shown in Fig. 5.11(b). When the molecule crosses over from ground curve to the point 'X' in the upper curve by electronic excitation, it dissociates into separate atoms that fly apart with kinetic energy. Since the kinetic motion is not quantised, a complete continuum results. The lower limit of the continuum is $E_{\text{ex}} + D''_0 = D'_0$ (asymptote dashed line). Transitions to points below the asymptote, i.e. dissociation levels result into a successively deconverging discrete

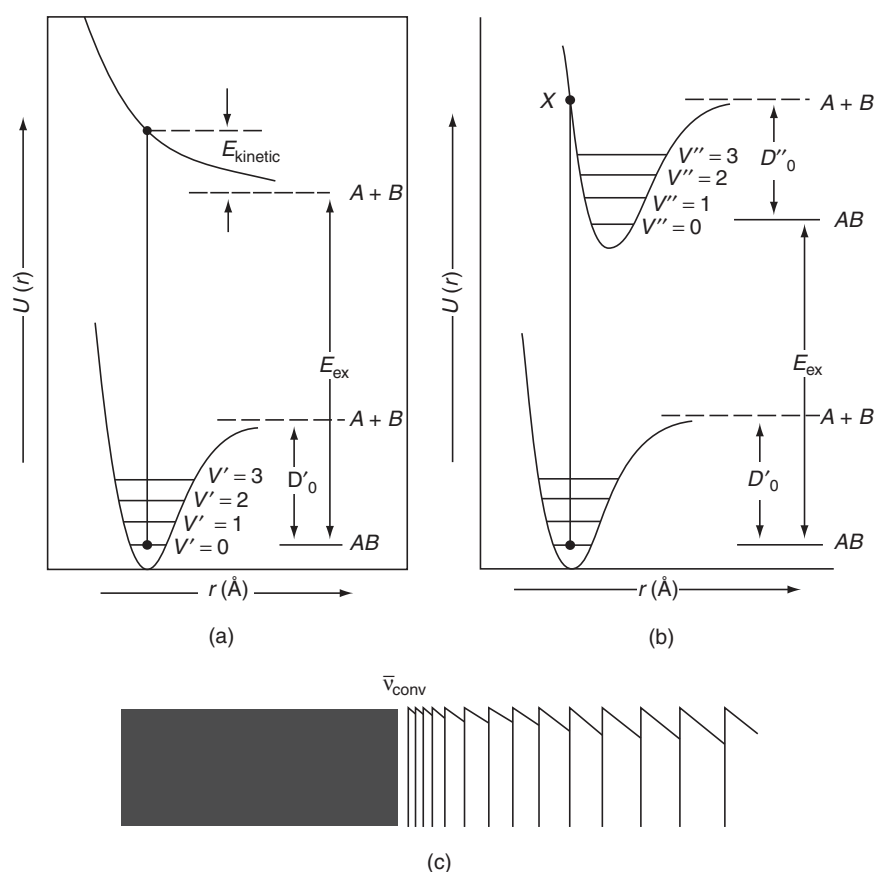


Fig. 5.11 Schematic diagram showing the photodissociation by excitation of a diatomic molecule from the ground stable state into (a) an upper unstable state, (b) an upper stable state, and (c) an absorption spectrum containing discrete and continuous portions.

bands. Such a spectrum in which continuum adjoins the convergence limit of discrete bands (V'' progression) has been observed in Cl_2 , Br_2 , I_2 , O_2 , ClO_2 , etc., and forms the basis of band convergence method for determination of dissociation energy of diatomics. [(Fig. 5.11(c))].

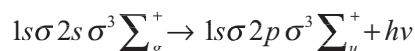
(i) When $r_e'' > r_e'$, there is one discrete region. This is due to the reason that the V'' progression breaks off before the convergence limit is attained since the probability of transition of molecule to the region above the dissociation level is negligibly small. (ii) When r_e'' (upper curve is repulsion curve and there is no minima in the unstable upper state) $\gg r_e'$ all transitions from all the V'' levels of ground state to the region above the dissociation level have maximum probability and complete continuum results since this region behaves like a repulsion curve, e.g. diatomics such HX , MeX , where $\text{X} = \text{Cl}$, Br , I , F and polyatomics such as N_2O , C_2O , COS , XCN , H_2O , H_2S , H_2O_2 , SO_3 , saturated hydrocarbons, alcohols, ethers, acids, etc.

5.8.2 Continuous Emission Spectra

The continuous emission spectra are the inversion of continuous absorption spectra of diatomics (A_2). They originate from the recombination of atoms, i.e. $A + A^* \rightarrow A_2 + h\nu$, e.g. temperature luminescence of halogens. The H_2 molecule when bombarded with electrons also exhibits continuous emission spectra but not when exposed to light (fluorescence). Continuous emission spectrum is due to the transition from the stable triplet state $1s\sigma 2s\sigma^3 \sum_g^+$ (excited by electron) to the unstable state $1s\sigma 2p\sigma^3 \sum_u^+$ and in this transition, the hydrogen molecule dissociates into two normal hydrogen atoms that fly away with unquantised kinetic energy. The absence of continuous emission spectrum when hydrogen is excited by light (fluorescence) is due to the fact that the transition $1 \sum_g^+ \rightarrow 3 \sum_g^+$ (ground stable of H_2) is forbidden. However, when excitation is by a free electron, the exchange of electron takes place according to the scheme:

1		2		3		1		3		2
$\uparrow$	+	$\downarrow$		$\uparrow$	$\rightarrow$	$\uparrow$		$\uparrow$	+	$\downarrow$
e		H_2		(1Σ)		H_2		(3Σ)		e

Consequently, the level $1s\sigma 2s\sigma^3 \sum_g^+$ is excited and a continuous emission spectrum in the 500–160 nm range results due to the transition,



The origin of continuous emission spectra of diatomics such as Xe_2 , He_2 , etc., is similar to that of the continuous emission spectrum of H_2 . Some diatomics, namely Hg_2 , Cd_2 , Zn_2 , exhibit continuous spectra with alternating maxima and minima of intensity, both in the absorption and emission mode. Vapours of MX (where M = alkali metals, X = halogens) also exhibit such a peculiar continuous absorption spectra. The continuous spectra of MX diatomics could be interpreted on the basis of transition from a ground stable state to the upper unstable state of the molecule represented by a horizontal line. All the transitions from different vibrational levels of the ground state to the upper state will have frequencies

$$\bar{\nu} = \bar{\nu}_{\text{elec-vib}} = \bar{\nu}_0 - w_e \left(V' + \frac{1}{2} \right) + w_e x_e \left(V' + \frac{1}{2} \right)^2 \quad (5.45)$$

The upper state being unstable, the transition to it results in the dissociation of molecules into separate atoms that fly apart with unquantised kinetic energy and a broad maximum results. According to Eq. (5.45), the maxima should coverage to a certain limit lying in the region of long wavelengths (V'' progressions). The distance between two maxima should approximately be equal to w_e . Note that if the repulsive curve is not horizontal but a steep one, the separate maxima will merge into a continuum with uniform distribution of intensity, e.g. NaCl, NaBr and KCl.

5.9 PREDISSOCIATION/DIFFUSE SPECTRA

The phenomenon of predissociation occurs due to the transfer of a molecule from a stable excited electronic state to an unstable electronic state of the molecule in an electronic absorption transition; the unstable state is the cause of predissociation. This process causes anomalous broadening of rotational lines which, in turn, results in diffuse bands within a progression in the electronic absorption spectra of gases. The diffuseness may build up slowly with diminishing wavelength in some cases and suddenly in other cases.

5.9.1 Mechanism of Predissociation in Diatomics

The electronic states of molecules are characterised by Morse potential energy curves. For predissociation to take place, the Morse curves corresponding to the stable excited electron state and unstable state of the molecule should intersect as shown in Fig. 5.12. Thus, the transition of a molecule from excited curve to an unstable curve will be the cause of pre-dissociation. Note that the repulsion curve of the excited state has no minimum or the minimum lies at a much greater internuclear distance than that of the ground state, i.e. $r'' \gg r'$.

According to the Franck–Condon principle which holds good for radiationless transitions also, the predissociation transition from excited curve to the repulsion curve is possible only near the points of intersection of the curves, since the vibrating molecule spends most of its time at the extreme ends of its vibrational motion, especially when the vibrational quantum number is large. The point/points of intersection must lie below the initial vibrational level of excitation and the lifetime of the excited molecule in vibrational states below and above the point of intersection is of the order of 10^{-8} s but the lifetime of the excited molecule which is $\tau = \alpha \tau_1$, where τ_1 is the lifetime of the ordinary excited state, $1 - \alpha$ is the probability of predissociation, in the vibrational levels immediately near the point of intersection, i.e. the region of predissociation decreases and the probability of transfer of molecule from stable to unstable state and hence predissociation increases. The transfer rate being faster than the rotational period ($\sim 10^{-11}$ s) but slower than the vibrational period (10^{-13} s), the predissociation will occur before the molecule rotates. Consequently, $\Gamma_{\text{rot}} \left(\Gamma_{\text{rot}} = \frac{h}{2\pi\tau} \right)$ width of rotational lines will increase and the fine structure of

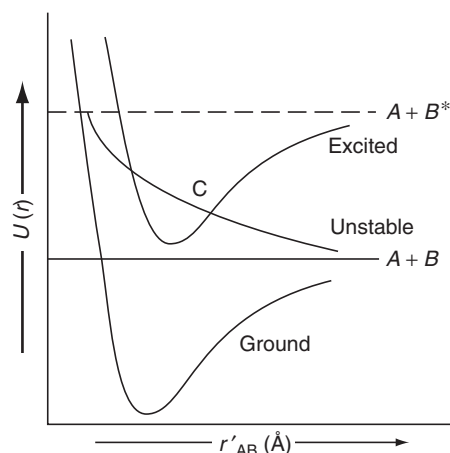


Fig. 5.12 Schematic diagram showing the predissociation of a diatomic molecule.

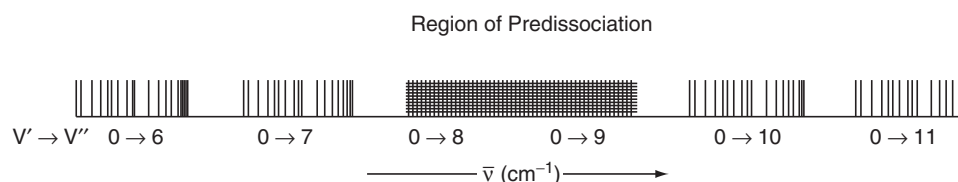


Fig. 5.13 Schematic diagram showing the predissociation spectrum. Rotation fine structure is seen both on the left-hand and right-hand sides of the predissociation region.

bands will disappear and the bands become diffuse but the vibrational coarse structure will not be affected. However, if the rate of transfer is faster than the vibrational period, the vibrational coarse structure will also be absent and a complete continuum will occur in the electronic absorption spectrum of the molecule. On the other hand, when the excited molecule is present in the vibrational levels away from the predissociation region, i.e. point of intersection of curves, the number of vibrations and rotations in the lifespan of the excited molecule will be 10^5 and 10^3 respectively as expected; since when excited molecule is present in these levels, it spends insufficient time near the point of intersection for appreciable dissociation to take place and a normal rotational fine structure will be observed for vibrational transitions both on the right- and left-hand sides of the predissociation region. The transitions below the point of intersection appear on the higher wavelength side of the predissociation region and lower wavelength side above the point of intersection as shown in Fig. 5.13.

Predissociation in diatomics also results when discrete vibrational or rotational levels of a certain upper electronic state of the molecule are overlapped by the dissociation continuum of lower electronic state, and radiationless transition occurs from discrete rotational or vibrational levels to dissociation continuum of the lower electronic state.

Further, the diffuseness of bands in a progression may set in suddenly or grow gradually with diminishing wavelength. The gradual increase in diffuseness of bands with diminishing wavelength in the absorption spectra of some diatomics, e.g. S_2 may be due to tunnelling effect, the probability of which increases as the distance of the initial vibrational level from the point of intersection of Morse curves increases. In such cases, no sharp predissociation limit, i.e. definite wavelength, is observed. However, when the diffuseness of bands in a progression sets in suddenly, a sharp predissociation limit (i.e. with a certain definite wavelength) is observed and the predissociation in such cases is termed *sharp predissociation*. The predissociation transitions take place only at $\Delta J = 0$, when $\Delta A = 0, \pm 1$, and $\Delta S = 0$. The positive levels combine with positive levels and negative levels combine with negative levels. Symbolically, $+\leftrightarrow +$; $-\leftrightarrow -$; $+\leftrightarrow -$. In case of diatomics having the same nuclei, the symmetric levels combine with symmetric levels and asymmetric levels with asymmetric levels, i.e. $s \leftrightarrow s$; $a \leftrightarrow a$; $s \leftrightarrow a$. When transition from the stable curve to the repulsive curve obeys the selection rules, spontaneous predissociation, i.e. spontaneous decay of the excited molecule is observed. Forbidden transitions are also possible under the influence of an external field and predissociation in such cases is called *induced predissociation*, e.g. predissociation induced by a magnetic field (e.g. in I_2) or induced by molecular collisions (e.g. in I_2 , Br_2 , N_2 , NO , S_2 , Se_2 , Te_2). The predissociation caused by molecular collisions is useful in understanding the mechanism of photochemical reactions.

5.9.2 Predissociation in Polyatomic Molecules

Predissociation in polyatomics occurs due to overlapping of higher vibrational levels of an electronic state by dissociation continuum adjoined to a lower dissociation limit of the same electronic state and the radiationless splitting of a particular atom or group of atoms takes place. This kind of predissociation is called *predissociation by vibration*.

The polyatomics dissociation differs from diatomics in that the interaction between atoms in polyatomics is characterised by potential-energy surfaces rather than the potential-energy curves. Thus, the region of predissociation in polyatomics is determined by the point of intersection of surfaces. However, the location of molecule in the predissociation region is not always a sufficient condition for predissociation. Moreover, the atoms must be in the phase of the motion that can cause the predissociation decomposition of the molecule. Both these conditions are to be satisfied simultaneously by the molecule for sharp predissociation which, of course, are not very frequently satisfied. However, sharp predissociation is also observed in the ultraviolet absorption spectrum of some polyatomics, e.g. NO_2 . The dissociation energy of NO_2 ($NO_2 \rightarrow NO + O$) as determined from predissociation limit is $70.8 \text{ kcal mole}^{-1}$. The value obtained from thermochemical data is $71.8 \text{ kcal mole}^{-1}$.

Predissociation in Emission Spectra The phenomenon of predissociation in emission spectra differs from predissociation in absorption spectra in that in some cases the bands are totally missing in the predissociation region and there is abrupt breaking off of the rotational lines in several bands. In the former, the predissociation limit is characterised by the abrupt breaking in the emission spectrum, e.g. S_2 , NO, N_2 , etc., for certain values of V and J determined for each series of bands (V) and for each band (J). Note that in some cases, e.g. S_2 , the bands absent in the predissociation region at low pressure appear at high pressure. This happens only in those cases where the mean lifetime of predissociating molecule becomes comparable with the time interval between two quenching collisions of an excited molecule with other molecules. The abrupt breaking off the rotational structure in the $0'0''$ emission band of CaH $\lambda = 3533.6 \text{ \AA}$. The sudden breaking off the rotational band structure observed in the emission spectrum of HgH and AlH is due to the splitting of the molecule under the interaction of the centrifugal force produced by the rotation of the molecule. This type of predissociation is termed *predissociation by rotation*. In predissociation by rotation, the higher rotational levels of a given vibrational level of a diatomic molecule are overlapped by the dissociation continuum belonging to the same electronic state, due to which radiationless decomposition of the molecule with no change of electronic state occurs.

5.10 DISSOCIATION ENERGY AND ITS DETERMINATION

The energy required to split a diatomic molecule into separate atoms comprising it is called the *dissociation energy* or *heat of dissociation*. It is designated as D and at absolute zero as D_0/D^0 . The heats of dissociation of diatomics are used for calculating the energies of splitting of complex molecules into atoms (heats of atomisation) which are of prime importance in determining the bond energies. The heat of dissociation of AB may be obtained from the heat of dissociation of A_2 and B_2 and the heat of formation of AB from the formula.

$$D_{AB} = \frac{1}{2}(D_{A_2} + D_{B_2}) - \Delta H_{AB} \quad (5.46)$$

where ΔH_{AB} is the heat of formation of AB , e.g. $D_{N_2}^0 = 225.09 \text{ kcal mole}^{-1}$, $D_{O_2}^0 = 117.96 \text{ kcal mole}^{-1}$, and $\Delta H_{NO} = 19.22 \text{ kcal mole}^{-1}$.

Thus,
$$D_{NO}^0 = \frac{1}{2}(225.09 + 117.96) - 19.22 = 152.3 \text{ kcal mole}^{-1}$$

Heat of dissociation can be measured experimentally by thermal and spectroscopic methods; the former gives an approximate while the latter gives an accurate value of dissociation energy. Thermal methods are based on the measurement of thermodynamic equilibrium (i.e., $X_2 \rightleftharpoons 2X$, $K_p = \frac{P_X^2}{P_{X_2}}$) as a function of temperature, e.g., Cl_2 , Br_2 , I_2 .

$D_{I_2}^0$ determined by this method is $35.514 \text{ kcal mole}^{-1}$. The other method based on thermodynamic equilibrium is the shock-wave method and is used for measurement of large values of heats of dissociation. This method is based on the relation between the rate of propagation of a shock wave through a gas and its state, i.e. temperature, density and pressure. The heat of dissociation measured by this method at absolute zero in case of N_2 is $225.09 \text{ kcal mole}^{-1}$. The other thermal methods, based on the measurement of rates of chemical processes at different temperatures, are called *kinetic thermal methods*. One of the examples of such methods is the *pyrolytic method* which deals with the rate of decomposition of substances.

The dissociation energy of a bond at a certain single temperature is given by

$$D = RT \ln \frac{10^{13}}{k} \quad (5.47)$$

where k is the specific rate constant. Dissociation energy of the C–I bond in various organic compounds was first of all measured by this method.

The spectroscopic methods differ from thermal methods in that the dissociation is achieved through electronic excitation of the molecule and its dissociation energy can be measured both in the ground and excited states. The two main spectroscopic methods employed to determine the dissociation energy of diatomics are band convergence and pre-dissociation limit methods. The former is most precise and gives accurate values of dissociation energy of diatomics.

5.10.1 Band-Convergence Method

Basically, the precision of the band-convergence method is based on the accurate determination of a vibration level of the excited molecule in an electronic transition in which the molecule breaks up into separate atoms with almost zero kinetic energy. This level is known as the *dissociation vibrational level* of the molecule in an electronic transition. Below this level, discrete but successively deconverging, bands appear while in the upper adjoining level, the molecule splits up into separate atoms and fly away with kinetic energy and a continuum results, the lower limit of which is the dissociation level. The continuum in the electronic absorption spectrum may appear due to the electronic transition from the ground electronic state either to stable or to an unstable upper electronic state of the molecule as shown in Figs 5.11 (b) and (a). In the former, the molecule splits up into separate atoms and flies away with kinetic energy and only a continuum results while in the latter, a convergent discrete-band structure followed by a continuum appears. This has been schematically shown at the bottom of Figs 5.11(a) and (b), i.e. Fig. 5.11(c). This method is based on the fact that the maximum vibrational energy of a molecule equals its dissociation energy. Only two vibrational levels are sufficient to prove this fact. We know that

$$E_V = hcw_e \left(V + \frac{1}{2} \right) - hcw_e x_e \left(V + \frac{1}{2} \right)^2$$

$$E_{V+1} = hcw_e \left(V + \frac{3}{2} \right) - hcw_e x_e \left(V + \frac{3}{2} \right)^2$$

Thus $E_{V+1} - E_V = hcw_e - 2hcw_e x_e (V + 1)$

When $(E_{V+1} - E_V) \rightarrow 0, V \rightarrow V_{\max}$

Thus, $V_{\max} = \frac{1 - 2x_e}{2x_e}$ and $D_e = E_{V_{\max}} = \frac{hcw_e}{4x_e} J = \frac{w_e}{4x_e}, \text{cm}^{-1}$

This convergence limit of bands in a progression (V') in the electronic absorption spectrum is related to the excitation energy E_{ex} of the products and heat of dissociation of the excited molecule D_0'' by the relation

$$\bar{\nu}_{\text{conv}} = \bar{\nu}_{\text{elec}} + D_0'' = E_{\text{ex}} + D_0'', \text{cm}^{-1}$$

or

$$D_0'' = \bar{\nu}_{\text{conv}} - E_{\text{ex}}, \text{cm}^{-1} \quad (5.48)$$

Thus, D_0'' can be determined if E_{ex} can be measured accurately from atomic spectroscopy. The convergent limit of bands is observed only in rare cases, e.g. diatomics Cl_2 , Br_2 , I_2 , O_2 , and ClO_2 , etc., otherwise it is determined by the Birge-Sponer method of extrapolation. The band convergence method and *Birge-Sponer methods* have already been discussed in detail in Chapter 3 on infrared spectroscopy. Note that the extrapolation method is applicable in case of vibrational structure of the spectrum and linear extrapolation always over-estimates the dissociation energy. This method is applicable for both the ground and excited states of the molecule. When no vibrational structure is observed and only a continuum results as in Fig. 5.11 (a), the lower limit of the continuum is taken as the convergent limit of the spectrum, e.g. HX ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{F}$) and a number of polyatomics: N_2O ; Cl_2O , COS , XCN , H_2O , H_2S , H_2O_2 , SO_3 , saturated hydrocarbons, alcohols, ethers, acids, etc.

Thus, $\bar{\nu}_{\text{conv}} = D_0'' = E_{\text{ex}} = D_0'$. Now the problem arises how to determine the dissociation energy of the molecule in the ground state. It can be determined provided the origin of the terms corresponding to the ground and excited states of the molecule are known. A number of cases are possible and only three of them are discussed here:

- (i) The ground and excited terms of the AB molecule originate from ground terms of atoms A and B . The excited molecule in such a case splits up into two atoms in the ground state as shown in Fig. 5.14(a). The dissociation energy of the molecule in the ground state D_0' is then given by

$$D_0' = E_{\text{ex}} + D_0'', \text{cm}^{-1} \quad (5.49)$$

- (ii) The ground term of the AB molecule originates from the ground terms of atoms A and B while the excited term of AB originates from the ground term of the atom A and excited term of the atom B . In such a case, the dissociation of the excited molecule will result into one normal atom A and other excited B^* while the dissociation of AB in the ground state will give rise to normal atoms A and B as shown in Fig. 5.14 (b). In this case,

$$E_{\text{ex}} + D_0'' = D_0' + E_{\text{ex}}(B^*)$$

or

$$D'_0 = E_{\text{ex}} + D''_0 - E_{\text{ex}}(B^*)$$

Using Eq. (5.48),

$$D'_0 = \bar{\nu}_{\text{con}} - E_{\text{ex}}(B^*), \text{ cm}^{-1} \quad (5.50)$$

Here, $E_{\text{ex}}(B^*)$ is the excitation energy of B^* .

Thus, in order to determine the dissociation energy of the molecule in the ground state in such case, the excitation energy of one of the atoms must be known, from atomic spectroscopy. This case is encountered in Cl_2 , Br_2 , I_2 , O_2 , etc.

- (iii) The ground term of the AB molecule originates from the ground term of the atom A and excited term of the atom B while the excited term of AB originates from the normal terms of atoms A and B . In such a case the excited molecule will dissociate to yield normal atoms A and B while the ground state molecule AB^* will split into one normal atom A and another excited atom B^* as shown in Fig. 5.14(c). In this case,

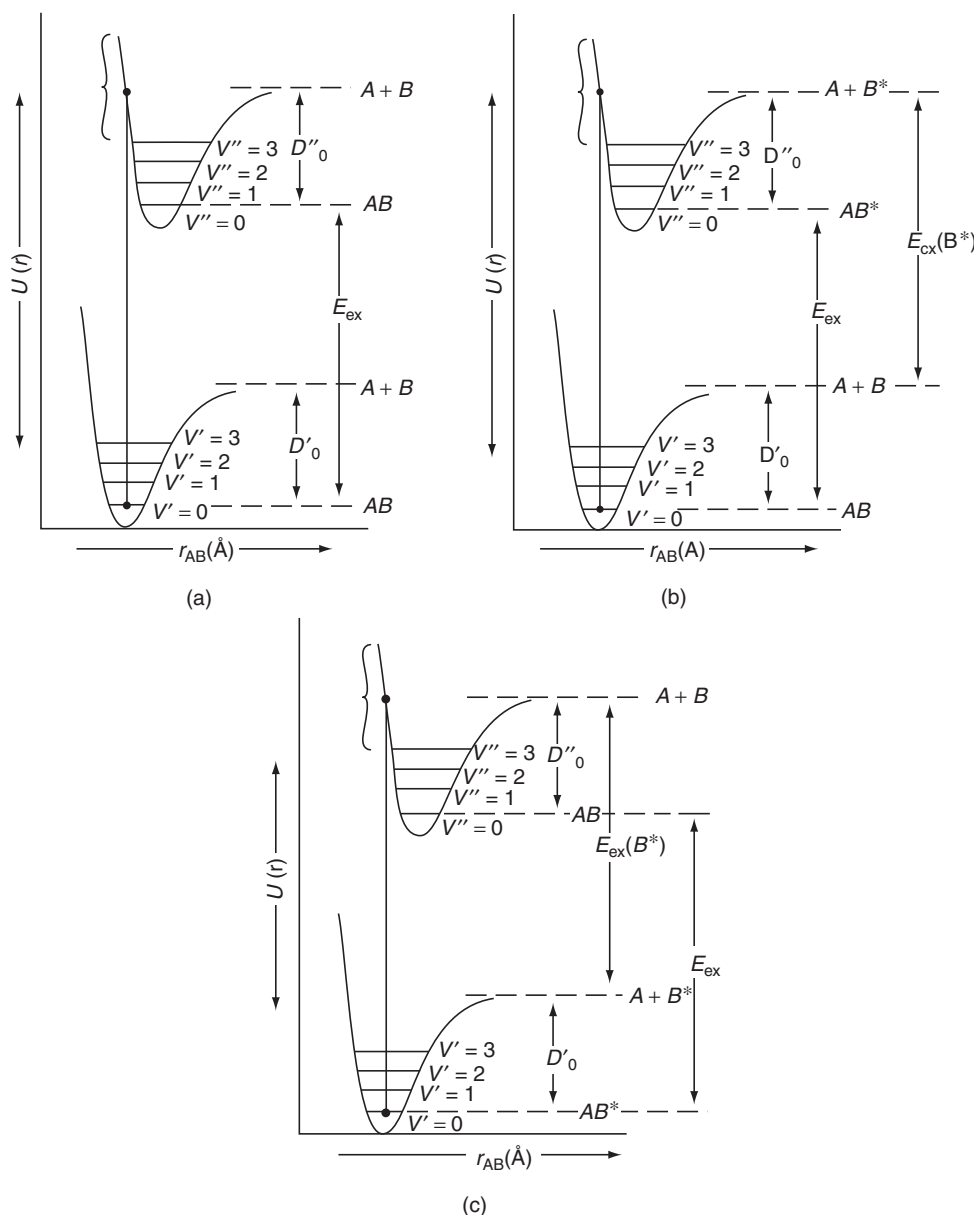


Fig. 5.14 Different cases of the photodissociation of diatomic molecules.

$$D'_0 - E_{\text{ex}}(B^*) = D''_0 + E_{\text{ex}}$$

or

$$D'_0 = D''_0 + E_{\text{ex}} + E_{\text{ex}}(B^*) = \bar{\nu}_{\text{conv}} + E_{\text{ex}}(B^*) \quad (5.51)$$

Thus, D'_0 can be determined provided $E_{\text{ex}}(B^*)$ is known from atomic spectroscopy.

Further, it is to be noted that the dissociation energy of diatomics can also be measured from the band progressions (V'') in the emission spectrum. In case of diatomics, the convergence limit directly gives the dissociation energy of the molecule in the ground state, D'_0 provided the ground term of the molecule originates from the normal terms of constituent atoms, i.e.

$$D'_0 = \bar{\nu}_{\text{elec}} - \bar{\nu}_{\text{conv}}, \text{cm}^{-1} \quad (5.52)$$

e.g. D'_0 for hydrogen has been found to be 103.24 kcal mole⁻¹.

Problem 5.12: In the electronic absorption of iodine vapour, the vibrational bands converge at 4995 Å. The excited state of iodine molecule dissociates into one normal atom ($^2P_{3/2}$) and other excited atom ($^2P_{1/2}$). The energy separation between the doublet ($^2P_{1/2} - ^2P_{3/2}$) as determined from atomic spectroscopy is 22 kcal g atom⁻¹. Calculate the dissociation energy of iodine molecule.

Solution According to band convergence method, the dissociation energy of a diatomic molecule is given by

$$D''_0 = \bar{\nu}_{\text{conv}} - E_{\text{ex}}, \text{cm}^{-1} \quad (\text{Eq. 5.48})$$

In case of I_2 , $E_{\text{ex}} = ^2P_{1/2} - ^2P_{3/2} = 22 \text{ kcal g atom}^{-1} = 92.4 \text{ kJ g atom}^{-1}$

Substituting the values of E_{ex} and $\bar{\nu}_{\text{conv}}$ in Eq. (5.48), we get

$$\begin{aligned} D''_0 &= \frac{6.62 \times 10^{-34} (\text{J.s}) \times 3 \times 10^{10} (\text{cm/s}) \times 6.023 \times 10^{23}}{4995 \times 10^{-8} (\text{cm})} - 92.4 (\text{kJ g atom}^{-1}) \\ &= (239.47 - 92.4) \text{ kJ mole}^{-1} \\ &= 147 \text{ kJ mole}^{-1} = 35.01 \text{ kcal mole}^{-1} \end{aligned}$$

The literature value is 36.46 kcal mole⁻¹.

Problem 5.13: The dissociation energy of O_2 determined by the band-convergence method at 0 K has been found to be 117.96 kcal mole⁻¹. The ground state ($^3\Sigma_g^-$) of the oxygen molecule originates from ^3P ground terms of the oxygen atom while that of the excited state ($^3\Sigma_u^-$) originates from the ^1D excited state of the oxygen atom and ^3P ground state of the oxygen atom. The energy difference between the doublet, as determined from atomic spectroscopy, is 45 kcal mole⁻¹. Calculate the convergence limit of progression (V'') in the electronic absorption spectrum of oxygen gas in Å, and cm⁻¹.

Solution Given $D''_0 = 117.96 \text{ kcal mole}^{-1}$

$$E_{\text{ex}} = ^1D - ^3P = 45 \text{ kcal mole}^{-1}$$

Substituting these values into Eq., (5.48) and rearranging, we get

$$\begin{aligned} \bar{\nu}_{\text{conv}} &= \frac{(117.96 + 45) \times 4.2 \times 10^3 (\text{J mole}^{-1})}{6.627 \times 10^{-34} (\text{J s}) \times (6.023 \times 10^{23}) \times 3 \times 10^{10} (\text{cm/s})} \\ &= \frac{684.43 \times 10^3 (\text{J mole}^{-1})}{11.96 (\text{J mole}^{-1} \text{ cm})} = 57226.58 \text{ cm}^{-1} \end{aligned}$$

$$\text{or} \quad \lambda = 1747 \text{ Å}$$

The experimentally observed value is 1758 Å.

Problem 5.14: The vibrational energy levels for the first eleven vibrational quantum numbers in the ground state as deduced from the gross structure of a band in the ultraviolet spectrum of CO can be represented by the expression

$$\bar{\nu} = 2170.21 \left(V' + \frac{3}{2} \right) - 13.46 \left(V' + \frac{3}{2} \right)^2, \text{cm}^{-1}$$

Calculate (a) the dissociation energy D'_e of the molecule in kJ mole^{-1} and kcal mole^{-1} , and (b) force constant for the fundamental mode of vibration of CO.

Solution (a) The dissociation energy can be determined by the Birge–Sponer method reported in Chapter 3 on infrared spectroscopy. Accordingly,

$$\bar{\nu}_{V'} = 2170.21 \left(V' + \frac{1}{2} \right) - 13.46 \left(V' + \frac{1}{2} \right)^2$$

$$\bar{\nu}_{V'+1} = 2170.21 \left(V' + \frac{3}{2} \right) - 13.46 \left(V' + \frac{3}{2} \right)^2$$

Thus,

$$\Delta G' = \bar{\nu}_{V'+1} - \bar{\nu}_{V'}$$

Generate the values of $\Delta G' = 0, 1, 2, 3, 4, 5, \dots, 8, 9$ and 10 and plot a graph between $\Delta G'$ and V' . From the graph, read off the value of the vibrational quantum number corresponding to $\Delta G' = 0$. Note that $V' = V'_{\text{max}}$ for $\Delta G' = 0$. Our value of V'_{max} has been found to be 79. Substituting the value of $V'_{\text{max}} = 79$ into the given equation, we obtain

$$\begin{aligned} \bar{\nu}_{V'} = D'_e &= 2170.21 \left(79 + \frac{1}{2} \right) - 13.46 \left(79 + \frac{1}{2} \right)^2, \text{cm}^{-1} \\ &= 2170.21 \times 79.5 - 13.46 \times (79.5)^2, \text{cm}^{-1} = 87461.13 \text{cm}^{-1} = 1045.86 \text{ kJ mole}^{-1} \\ &= 249 \text{ kcal mole}^{-1} \text{ (literature value is } 257 \text{ kcal mole}^{-1}\text{)}. \end{aligned}$$

(b) In order to determine the force constant, we must first determine the frequency of the fundamental mode of vibration of CO, i.e. $\bar{\nu}'$.

From Eq. (3.57),

$$\bar{\nu}' = w'_e (1 - x'_e), \text{cm}^{-1}$$

Substituting the values of w_e and $w_e x_e$ into the given equation, we obtain

$$\bar{\nu}' = 2170.21 - 13.46 = 2156.75 \text{ cm}^{-1}$$

For CO, the reduced mass $\mu'_m = \frac{16 \times 12}{16 + 12} \text{ amu} = \frac{192}{28} \text{ amu}$. Substituting the values of $\bar{\nu}'$ and μ'_m and into Eq. (3.19), we get

$$k' = \left[\frac{2156.75}{1303.16} \right]^2 \times \frac{192}{28} \text{ millidynes / \AA} = 18.78 \text{ millidynes / \AA}$$

Problem 5.15: The vibrational energy levels in the excited state, as deduced from the coarse structure of a band in the electronic absorption spectrum of CO, fits into the expression

$$\bar{\nu}'' = 1515.61 \left(V'' + \frac{1}{2} \right) - 17.25 \left(V'' + \frac{1}{2} \right)^2, \text{cm}^{-1}$$

Calculate (a) the dissociation energy D_e of the molecule in kJ mole^{-1} and kcal mole^{-1} , (b) force constant for the fundamental mode of vibration of CO, and (c) the energy corresponding to the electronic transition if the 0–0 band is observed at 64746.5 cm^{-1} . Use the required data from Problem 5.15 also.

Solution Proceeding as in Problem 5.15, we get;

$$(a) \quad \Delta G'' = 1515.61 - 34.50 (V'' + 1);$$

$$V''_{\max} = 42 \text{ and } D_e'' = 33255.61 \text{ cm}^{-1} = 397.670 \text{ kJ mole}^{-1} = 94.681 \text{ kcal mole}^{-1}$$

$$(b) \quad \bar{\nu}'' = (w_e'' - w_e'' x_e'') \text{ cm}^{-1} = (1515.61 - 17.25) \text{ cm}^{-1} = 1498.36 \text{ cm}^{-1}$$

$$\text{Therefore, } k'' = \left(\frac{1498.36}{1303.16} \right)^2 \times \frac{192}{28} \text{ millidynes/\AA} = 9.06 \text{ millidynes/\AA}$$

(c) In order to determine the energy corresponding to the electronic transition, we need the values of w_e' and $w_e' x_e'$. From Problem 5.15, we write $w_e' = 2170.21 \text{ cm}^{-1}$ and $w_e' x_e' = 13.46 \text{ cm}^{-1}$. Substituting these values together with w_e'' and $w_e'' x_e''$ and $\bar{\nu}_{00}$ into Eq. (5.15), we obtain

$$\begin{aligned} \bar{\nu}_{\text{elec}} &= 64746.5 - \left(\frac{1515.61}{2} - \frac{17.25}{4} \right) + \left(\frac{2170.21}{2} - \frac{13.46}{4} \right) \text{ cm}^{-1} \\ &= (64746.5 - 753.49 + 1081.74) \text{ cm}^{-1} \\ &= 65074.75 \text{ cm}^{-1}. \end{aligned}$$

Problem 5.16: The analysis of the vibrational coarse-rotational fine- structure of a band in the electronic spectrum of N_2^+ corresponding to the transition ${}^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ fits into the following expressions:

$$\begin{aligned} \bar{\nu}_{\text{elec-vib}} &= 25461.5 + \left[2419.84 \left(V'' + \frac{1}{2} \right) - 23.19 \left(V'' + \frac{1}{2} \right)^2 \right] \\ &\quad - \left[2207.19 \left(V' + \frac{1}{2} \right) - 16.136 \left(V' + \frac{1}{2} \right)^2 \right] \text{ cm}^{-1} \end{aligned} \quad (i)$$

$$\bar{\nu}_{\text{elec-rot}} = \left[\bar{\nu}_{\text{elec-vib}} + 4.015 m + 0.151 m^2 \right] \text{ cm}^{-1} \quad (ii)$$

Calculate (a) the zero-point energies of the ground and excited states of the molecule, (b) the 0-0 band, (c) the frequency and force constant for the fundamental modes of vibration in the lower and upper electronic states of the molecule, (d) the bond lengths of N_2^+ in the ground and excited states, (e) the value of the band head and its position, (f) separation between band head and zero line and the direction of shading, and (g) dissociation energies in the two electronic states of the molecule.

Solution (a) Zero-point energy of the upper state

$$= \left(\frac{w_e''}{2} - \frac{w_e'' x_e''}{4} \right) = \left(\frac{2419.84}{2} - \frac{23.19}{4} \right) \text{ cm}^{-1} = 1204.12 \text{ cm}^{-1}$$

Zero-point energy of the lower state

$$= \left(\frac{w_e'}{2} - \frac{w_e' x_e'}{4} \right) = \left(\frac{2207.19}{2} - \frac{16.136}{4} \right) \text{ cm}^{-1} = 1099.56 \text{ cm}^{-1}$$

(b) 0-0 band is determined from the given Eq. (i)

$$\begin{aligned} \bar{\nu}_{\text{elec-vib}}(V' = 0 \rightarrow V'' = 0) &= \left[25461.5 + \left(\frac{2419.84}{2} - \frac{23.19}{2} \right) - \left(\frac{2207.19}{2} - \frac{16.136}{2} \right) \right] \text{ cm}^{-1} \\ &= (25461.5 + 1204.12 - 1099.56) \text{ cm}^{-1} = 25566.06 \text{ cm}^{-1} \end{aligned}$$

(c) We know that $\bar{\nu}' = w_e' - w_e' x_e'$

$$\text{Thus, } \bar{\nu}' = (2207.19 - 16.136) \text{ cm}^{-1} = 2191.05 \text{ cm}^{-1}$$

$$\text{and } k' = \left[\frac{2191.05(\text{cm}^{-1})}{1303.16} \right]^2 \times \frac{196}{28} (\text{amu}) = 19.78 \text{ millidynes/\AA}$$

Similarly,

$$\bar{\nu}'' = (2419.84 - 23.19) \text{ cm}^{-1} = 2396.65 \text{ cm}^{-1} \text{ and}$$

$$k'' = \left[\frac{2396.65 (\text{cm}^{-1})}{1303.16} \right]^2 \times \frac{196}{28} (\text{amu}) = 23.67 \text{ millidynes/\AA}.$$

(d) Comparing Eq. (ii) with Eq. (5.23), i.e.

$$\bar{\nu}_{\text{elec-rot}} = \bar{\nu}_{\text{elec-vib}} + (B_{V''} + B_{V'})m + (B_{V''} - B_{V'})m^2; \text{ cm}^{-1}$$

we get $B_{V''} + B_{V'} = 4.015 \text{ cm}^{-1}$

$$B_{V''} - B_{V'} = 0.151 \text{ cm}^{-1}$$

Solving these equations for $B_{V''}$ and $B_{V'}$, we get

$$B_{V''} = 2.083 \text{ cm}^{-1} \text{ and}$$

$$B_{V'} = 1.932 \text{ cm}^{-1}$$

$\therefore$

$$I' = \frac{16.8575}{1.0932} (\text{au}) = 8.725 \text{ au}$$

and

$$I'' = \frac{16.8575}{2.083} (\text{au}) = 8.092 \text{ au}$$

Since μ_m for $\text{N}_2^+ = \frac{14 \times 14}{14 + 14} \text{ amu} = 7 \text{ amu}$, the bond length for N_2^+ in the lower state is

$$r' = \sqrt{\frac{I'}{\mu_m}} = \sqrt{\frac{8.725 (\text{au})}{7 (\text{amu})}} = \sqrt{1.246 (\text{\AA}^2)} = 1.116 \text{ \AA}$$

and for the upper state, it is

$$r'' = \sqrt{\frac{I''}{\mu_m}} = \sqrt{\frac{8.092 (\text{au})}{7 (\text{amu})}} = \sqrt{1.156 (\text{\AA}^2)} = 1.075 \text{ \AA}$$

(e) The value of m at the band head is given by

$$m = \frac{-(B_{V''} + B_{V'})}{2(B_{V''} - B_{V'})} = \frac{-4.015 (\text{cm}^{-1})}{2 \times 0.151 (\text{cm}^{-1})} = -13.29 \approx -13.$$

Thus, the frequency at the band head:

$$\begin{aligned} \bar{\nu}_{\text{head}} &= [25566.06 + 4.015 (-13) + 0.151 \times (-13)^2] \text{ cm}^{-1} \\ &= [25566.60 - 52.195 + 25.519] \text{ cm}^{-1} = 25539.384 \text{ cm}^{-1} \end{aligned}$$

(f) The separation between the band head and null line is $(25539.384 - 25566.06) \text{ cm}^{-1} = -26.676 \text{ cm}^{-1}$. The negative value of m and that of separation between band head and null line show that the band is shaded towards violet.

(g) The dissociation energies in the lower and upper states can be determined with the aid of Eq. (3.44), i.e.

$$\Delta G' = w'_e - 2w'_e x'_e (V' + 1)$$

Thus, for the lower level,

$$\Delta G' = 2207.19 - 32.272 \left(V' + \frac{1}{2} \right);$$

$$V'_{\max} = 67 \text{ and}$$

$$D'_e = \left[2207.19 \left(67 + \frac{1}{2} \right) - 16.136 \left(67 + \frac{1}{2} \right)^2 \right] \text{ cm}^{-1}$$

$$= 75465.675 \text{ cm}^{-1} = 9.34 \text{ eV} = 902.41 \text{ kJ mole}^{-1}$$

Similarly,

$$\Delta G'' = 2419.84 - 46.38 (V'' + 1);$$

$$V''_{\max} = 51 \text{ and}$$

$$D''_e = \left[2419.84 \left(51 + \frac{1}{2} \right) - 23.19 \left(51 + \frac{1}{2} \right)^2 \right] \text{ cm}^{-1}$$

$$= 63116.083 \text{ cm}^{-1} = 7.81 \text{ eV} = 754.742 \text{ kJ mole}^{-1}$$

Problem 5.17: Calculate the heat of dissociation of HX where X = F, Cl, Br, and I from the following data:

	<i>AB</i>	<i>D° (A₂)</i>	<i>D° (B₂)</i>	<i>−ΔH_{AB}</i>	
	HF	103.24	38.5	63.23	
The values of <i>D°</i> s	HCl	103.24	57.10	22.03	are in kcal mole ^{−1} .
	HBr	103.24	45.44	12.16	
	HI	103.24	35.57	1.09	

Solution Substituting the values of respective parameters into Eq. (5.46), we get $D^{\circ}_{\text{HF}} = 134.1 \text{ kcal mole}^{-1}$, $D^{\circ}_{\text{HCl}} = 102.2 \text{ kcal mole}^{-1}$, $D^{\circ}_{\text{HBr}} = 86.5 \text{ kcal mole}^{-1}$ and $D^{\circ}_{\text{HI}} = 70.5 \text{ kcal mole}^{-1}$.

5.10.2 Predissociation Limit Method

As has already been stated in Section 5.9, the process of predissociation occurs due to transfer of a molecule from a stable excited electronic state to an unstable electronic state of the molecule in an electronic absorption spectrum. The transfer of molecule to the latter results into diffuse bands due to anomalous broadening of rotation lines in a progression in the electronic absorption spectra of diatomic gases. The observed frequency corresponding to the predissociation limit yields the upper limit of the dissociation energy of the state causing the predissociation, i.e.

$$D_0'' \leq \bar{\nu}_{\text{pred}} \quad (5.53)$$

D_0'' can be very precisely determined provided it is possible to observe the break off of the rotational structure in several bands, i.e. vibrational levels of the molecule, e.g. H_2 , N_2 , P_2 , SO , etc. However, the state of the predissociation products of the molecule must be known and taken into consideration. The dissociation energy of P_2 by this method has been found to be $116.03 \text{ kcal mole}^{-1}$ on the assumption that the P_2 molecule dissociates in the predissociation region into atoms $\text{P}(^4\text{S})$ and $\text{P}(^2\text{D})$. The sharp limit of predissociation that coincides with the true dissociation limit is observed in the absorption spectrum of polyatomic NO_2 which dissociates as $\text{NO}_2 \rightarrow \text{NO} + \text{O}$. The dissociation energy from the predissociation method comes out to be $70.8 \text{ kcal mole}^{-1}$. Thermochemical data yields a value of $69.6 \text{ kcal mole}^{-1}$. The predissociation limit in the spectra of a majority of polyatomics is highly diffuse and in such cases only the upper limit of dissociation energy is obtained.

It is to be noted that predissociation limit, i.e. when predissociation begins, does not always give an upper limiting value for the corresponding dissociation limit of the state causing predissociation. Under certain circumstances, the predissociation limit may be appreciably higher than the dissociation limit belonging to it.

5.11 LOW RESOLUTION UV VISIBLE SPECTROSCOPY

5.11.1 Introduction

Historically, the simplest form of colourimetry, namely colour matching, as in the case of *pH* indicators has been known for a long time. However, colourimetry, or spectrophotometry, is comparatively a new technique. The invention of the spectroscope, an instrument which separates visible radiations/radiations of different wavelengths, i.e. disperses them into a spectrum for visual observation, in the closing decades of the nineteenth century brought with it an analytical approach which proved to be fruitful qualitatively in the beginning and both quantitatively and qualitatively later on. Gradually, few colourimetric methods were introduced for substances for which other techniques such as volumetric and gravimetric were unknown and unreliable. The rapid development of electrical measurement techniques in the years around 1930 resulted in the improvement of colourimetric methods. However, the use of spectral region on either side of the visible spectrum for analysis began only after 1930 in case of UV and after 1940 in case of IR radiations. Existence of IR radiation was demonstrated by W Herschel in 1800 and Julius used it for qualitative analysis in 1892. WW Coblentz in 1905 observed that certain atomic groups in molecules always gave characteristic absorption bands in definite positions that varied but little with the structure of the rest of the molecule. In 1913, Eva von Bahr resolved the rotational structure of HCl . There followed the demonstration of quantised rotational energy levels in molecules, which led to rapid progress in the analysis of their IR spectra and the determination, from the data, of molecular structure and moments of inertia. The wide spread of IR region for analytical purposes began around 1943. It was mainly developed for the analysis of polybutadiene during the Second-World War (1939–45). During this period, SBR (synthetic styrenebutadiene rubber) was the most important of the synthetic rubbers developed to replace unavailable natural rubber because of its structural resemblance with natural rubber, i.e. *cis*-poly 2-methyl-, 3-butadiene. In the case of UV region, though the discovery of UV radiation dates back to 1880, but its use for analytical purposes began only after 1930 and a reliable absorption spectrum in this region was obtained conveniently within a reasonable time in 1941.

As has already been stated that the electronic state of a molecule is associated with vibrational and rotational energy states, consequently, the electronic spectra of molecules in the vapour phase show simultaneously rotational and vibrational fine structures. Due to this, the electronic absorption line becomes a broad peak, i.e. a band containing rotational and vibrational fine structures. However, when a spectrum is recorded in solution phase, rotational and vibrational features in the spectra disappear due to solute–solvent interactions and a smooth curve is obtained. The vibrational fine structure is also observed in certain electronic transitions when the spectra of dilute solutions in nonpolar solvents or of vapours are recorded under high resolution, e.g. 260 nm transition of benzene shows vibrational fine structure as shown in Fig. 5.15. However, low-resolution electronic spectra of benzene does not show such a vibrational fine structure. Thus, the low-resolution spectrum of molecules in solution or vapour phase will consist of a smooth curve free of rotational and vibrational fine structures and is of interest to analysts for qualitative and quantitative analysis. Such a band is characterised by its intensity (i.e. absorbance) and position (i.e. wavelength). Most of the applications of low-resolution UV-visible spectroscopy are based on these two parameters and will be discussed later on.

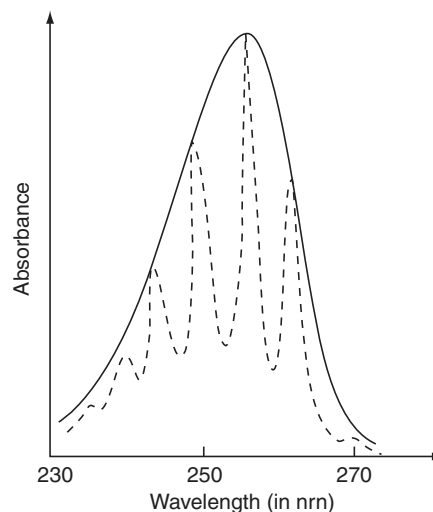


Fig. 5.15 Ultraviolet absorption spectrum of benzene. The dashed lines represent the vibrational coarse structure visible under high resolution.

5.11.2 Terms and Symbols Associated with UV/V Absorption Measurements of Molecules in Solution/Vapour Phase

Most of the terms and symbols and formulae involved in low-resolution spectroscopy of diatomic and polyatomic molecules in solution/gas phase have already been described in Chapter 1 on introduction. In addition, the terms which are routinely used in UV/V spectroscopy are described here.

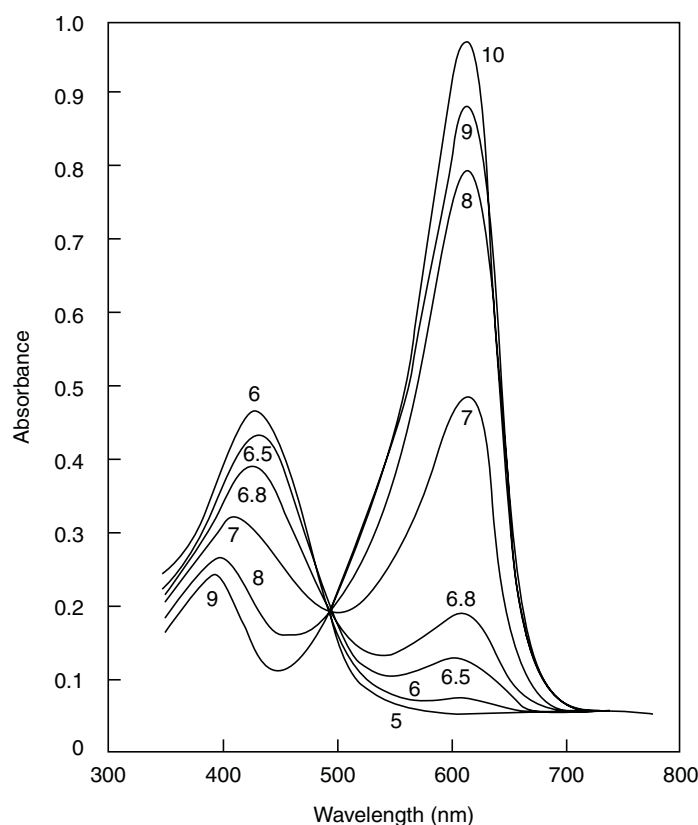
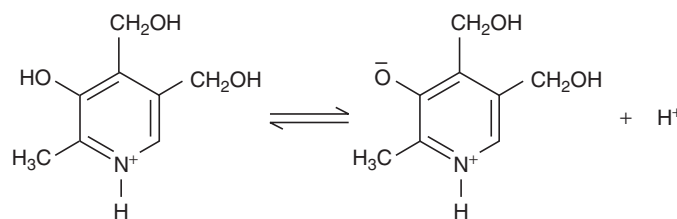


Fig. 5.16 The absorption spectra of phenolred at various pH values.

(a) Isosbestic Point pH affects the absorption spectrum of the reagents where the protonation of a functional group takes place. However, there is a point at which the absorption curves at different pHs intersect and at this point absorbance is independent of pH and degree of dissociation of the reagent (Fig. 5.16). This point at which all the curves at different pHs intersect is called the *isosbestic* or *isoabsorptive point* and is a characteristic of a system consisting of two chromophores which are interconvertible so that the total quantity is constant, i.e. the existence of an isosbestic point indicates that a chemical equilibrium exists between two species. The wavelength corresponding to the isosbestic point is known as *isosbestic wavelength*. The absence of an isosbestic point indicates a more complex system, e.g. Pyridonine, a molecule related to vitamin B₆ undergoes the following reversible reaction at pH < 7. UV absorption spectra of this reagent in the 220–350 nm range at various pHs exhibits three isosbestic points at $\lambda = 236, 266$ and 305 nm. Similarly, visible absorption spectra of phenolred in the 350–800 nm range at various pHs exhibits an isosbestic point at $\lambda = 495$ nm. Absorbance curves at various pHs (pH = 5–10) reveal that as the pH increases, the absorption at $\lambda = 610$ nm increases while at $\lambda = 430$ nm, it decreases. The curves at different pHs intersect at $\lambda = 495$ nm, the isosbestic point. The graph between absorbance and pH at the isosbestic wavelength will be S-shaped from which the pK value of the phenol can be determined. The pH value at which one half of the reagent is present in the acid and one half in the basic forms is the *pK value of the reagent*.



(b) Band Shifts and Intensity Changes The position and the intensity of the absorption band is not only affected by pH but also depends upon the nature of the solvent. The substituents present in the molecule also affect the electronic spectrum of the parent molecule via inductive effect, resonance effect, etc. Since inductive effect influences the charge densities on the atoms of the parent molecule (i.e. it affects the Coulomb integral only), either all the molecular orbitals are raised or lowered in energy relative to the parent molecule containing no substituent. However, the difference between HOMO and LUMO remains unchanged. Consequently, the band maximum of the transition is hardly influenced but the intensity of the band grows because of increase in the dipole length.

On the other hand, resonance or mesomeric effect shifts the band maximum. In resonance effect, the lone pair of the substituent participates in the bonding and tries to behave like an extended conjugation. As a result of this interaction, the energies of both the HOMO and LUMO are raised, but the effect is more pronounced in the former, because of which the energy difference between the HOMO and LUMO decreases. Consequently, the band maximum shifts to longer wavelength. The interaction of nonbonding electrons with σ orbital will be less as compared to π orbital. Thus, the resonance effect will be more pronounced in π - π^* transition than σ - σ^* transition. Greater the electronegativity of the hetero atom containing the lone pair, the more tightly it will be bound to the atom, and hence resonance effect will be small and $\lambda_{\max}$ of the original transition will be shifted slightly. The effect of substitution on the transition follows the order:



Further, the arrangement of the lone pair in space also affects the interaction. The interaction will be maximum if the orbitals are properly arranged, e.g. if n and π orbitals are parallel to each other, their interaction will be maximum and minimum if perpendicularly arranged. Due to this reason, the energies of π and π^* orbitals will be affected accordingly. The shift of the π - π^* absorption band will be maximum in the former case, i.e. parallel arrangement and minimum in the latter case, i.e. perpendicular arrangement of orbitals. Further, it is to be noted that the inductive and resonance effects due to substituents operate simultaneously and may act in the same direction or in the opposite direction. For example, both $-\text{NH}_2$ and $-\text{OH}$ groups decrease the energy of nonbonding electrons by inductive effect. The resonance of a lone pair of electrons in both these groups will increase the energy of the π^* anti-bonding orbital. Both the effects are acting in the same direction, i.e. increase the energy between the nonbonding and π^* anti-bonding molecular orbitals.

The shifts of absorption bands and their intensity changes are generally described in the literature using the terminology shown in Fig 5.17.

(c) Red Shift The shift of absorption maximum to longer wavelength due to substitution or solvent effect is called red shift. π - π^* transition of mesityloxide undergoes red shift as the polarity of the solvent increases, i.e. $\lambda_{\max} = 230.6$ in iso-octanol and $\lambda_{\max} = 237.6$ in chloroform. $\lambda_{\max}$ for thiophene in hexane is observed at 231 nm ($\epsilon_{\max} = 7100$) while for 2-bromothiophene, it is observed at 236 nm ($\epsilon_{\max} = 9100$). n - π^* transition of cyclohexanone in hexane is observed at 285 nm, ($\epsilon_{\max} = 14$) while in o-chloro, -bromo, -hydroxy cyclohexanones $\lambda_{\max}$ is observed at +307, +313, +302 nm, respectively in the axial conformation.

(d) Blue Shift The shift of absorption maximum to shorter wavelength due to substitution or solvent effect is called blue shift. n - π^* transition of mesityloxide undergoes blue shift as the polarity of the solvent increases, i.e. $\lambda_{\max} = 321$ nm in iso-octanol and $\lambda_{\max} = 314$ nm chloroform, n - π^* transition of cyclohexanone in hexane at 285 nm ($\epsilon_{\max} = 14$) is observed at 278, 280, 273 nm in o-chloro, -bromo, -hydroxycyclohexanones respectively in the equatorial conformation.

(e) Hyperchromic Effect The increase in absorption intensity due to solvent effect or substitution is called hyperchromic effect. For example, K (π - π^*) and B (Benzenoid) bands of aniline are observed at 230 ($\epsilon_{\max} = 8600$)

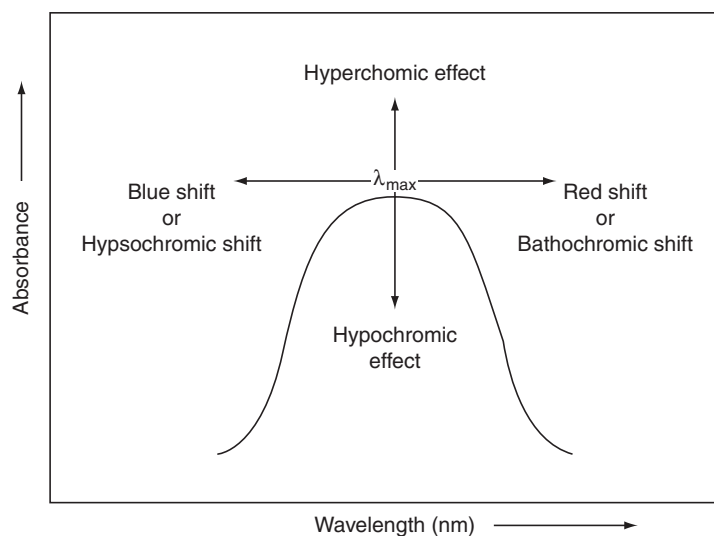


Fig. 5.17 Hypothetical plot between absorbance and wavelength describing the terminology related to the shifts of absorption maxima and their intensity changes.

and 280 nm ($\epsilon_{\max} = 1430$) respectively in water o-nitroaniline exhibits these bands at 283 ($\epsilon_{\max} = 5400$) and 358 nm ($\epsilon_{\max} = 4500$). In case of phenol $\pi-\pi^*$: $\lambda_{\max} = 210.5$ nm ($\epsilon_{\max} = 6200$) and B: $\lambda_{\max} = 270$ nm ($\epsilon_{\max} = 1450$) in water while in o-nitrophenol $\pi-\pi^*$: $\lambda_{\max} = 279$ nm ($\epsilon_{\max} = 6600$) and B: 351 nm ($\epsilon_{\max} = 3200$). The intensity of $n-\pi^*$ band of azomethine [$C_3H_7N=C(CH_3)_2$] increases as the polarity of the solvent increases, $\lambda_{\max} = 246$ nm ($\epsilon_{\max} = 140$) in cyclohexane and $\lambda_{\max} = 232$ nm ($\epsilon_{\max} = 200$) in ethanol. Here, the hyperchromic effect is caused by the solvent.

(f) Hypochromic Effect The decrease in absorption intensity due to solvent effect or substitution is called hypochromic effect. For example, furan shows an intense band at 200 nm ($\epsilon_{\max} = 10,000$) and a weak band at 252 nm ($\epsilon_{\max} = 1$). In 2-nitrofuran these bands appear 225 nm with $\epsilon_{\max} = 3400$ and at 315 nm with $\epsilon_{\max} = 8100$. These bands in 2-methoxyfuran appear at 225 nm ($\epsilon_{\max} = 2300$) and 270 nm ($\epsilon_{\max} = 12900$). The intensity of $n-\pi^*$ band of azomethine [$C_3H_7N=C(CH_3)_2$] decreases as the polarity of the solvent decreases, i.e. the $n-\pi^*$ transition of azomethine exhibits hypochromic effect as the polarity of the solvent decreases.

5.12 INTENSITY OF ABSORPTION BANDS

Recall from Part I that the intensity of an absorption band in the electronic absorption spectrum of a molecule depends on the transition probability corresponding to the band. The transition with high probability yields an intense band and the transition is said to be permissible, while the transition with low probability is said to be forbidden and results in a weak band. The intensity of an absorption band is measured in terms of different parameters. One such parameter is the *molar decadic extinction coefficient*. The intensity of the absorption band is measured in terms of molar extinction coefficient $\epsilon_{\max}$ at the value of wavelength of maximum absorption. It is a measure of the strength of the electric dipole transition involved and its value varies from 5×10^5 for the strongest bands to one or less for very weak bands. The other parameter is *the integrated intensity*. The integrated intensity of an absorption band is the molar extinction absorption coefficient integrated over the entire band and is given by

$$\text{Integrated absorption intensity} = \int_{\bar{\nu}_1}^{\bar{\nu}_2} \epsilon(\bar{\nu}) d\bar{\nu} \quad (5.54)$$

where $\bar{\nu}_1$ and $\bar{\nu}_2$ are the frequency limits in cm^{-1} . It is determined graphically by plotting ϵ against frequency (in cm^{-1}) and calculating the area of the band from the relation on

$$\int_{\bar{\nu}_1}^{\bar{\nu}_2} \epsilon(\bar{\nu}) d\bar{\nu} = \epsilon(\bar{\nu}) \times \Delta\bar{\nu}_{1/2} \quad (5.55)$$

where $\Delta\bar{\nu}_{1/2}$ is the width of the band in cm^{-1} and is temperature dependent. Accordingly, the integrated absorption intensity also depends upon temperature.

Another useful dimensionless parameter for expressing the intensity of the absorption band is the oscillator strength (f) and is linked to the integrated absorption intensity of the band by

$$f = \frac{2.303 \times 10^3 m_e c^2}{N_A e^2} \int_{\bar{\nu}_1}^{\bar{\nu}_2} \epsilon(\bar{\nu}) d\bar{\nu} = 4.33 \times 10^{-9} \int_{\bar{\nu}_1}^{\bar{\nu}_2} \epsilon(\bar{\nu}) d\bar{\nu} \quad (5.56)$$

where m_e is the mass of the electron in grams, e is the charge of the electron in electrostatic unit, $\bar{\nu}$ is the frequency expressed in wave numbers (cm^{-1}). The quantity 2.303 is the conversion factor from natural logarithm to the base-ten logarithm while the factor 10^3 is the number of cubic centimetres in a litre required by introduction of the molar absorption coefficient.

It is defined as the effective number of dispersion electrons, which are oscillating with a characteristic frequency ν_i . For example, the spectral lines emitted by an atom can be associated with the corresponding electronic oscillator strengths. The coefficient of integral is independent of temperature whereas the integrated absorption intensity is temperature dependent. Consequently the oscillator strength will also depend upon temperature.

For symmetric absorption bands,

$$f \sim 4.60 \times 10^{-9} (\epsilon_{\max} \Delta\bar{\nu}_{1/2}) \quad (5.56a)$$

Otherwise,

$$f \approx 4.33 \times 10^{-9} (\epsilon_{\max} \Delta\bar{\nu}_{1/2}) \quad (5.56b)$$

where the frequencies are measured in cm^{-1} and the value of ϵ_{max} is expressed in $\text{dm}^3 \text{ mole}^{-1} \text{ cm}^{-1}$ (or $10^3 \text{ mole}^{-1} \text{ cm}^2$, since $1 \text{ dm}^3 = 1000 \text{ cm}^3$).

Actually, ' f ' is a product of theoretical intensity of transition and integrated absorption intensity. The advantage of introducing oscillator strength is that it can be interpreted theoretically and can be calculated quantum mechanically. It is found that intense transitions have oscillator strengths of about unity. Values of ' f ' from 0.1 to 1 correspond to absorptivities in the range 10^3 to 10^5 depending on the width of the band.

The transition dipole moment is related to the observed oscillator strength by

$$M_t^2 = \frac{3he^2}{8\pi^2 m_e \nu} \cdot f \quad (5.57)$$

Substituting the values of the respective constants into Eq. (5.57), we obtain

$$\begin{aligned} M_t^2 &= \frac{3 \times (6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-2}) \times (1.602 \times 10^{-19} \text{ C})^2 f}{8 \times (3.14)^2 \times (9.10 \times 10^{-31} \text{ kg}) \nu (\text{s}^{-1})} \\ &= \frac{0.7107 \times 10^{-42} (\text{C}^2 \text{ m}^2) f}{\nu} \end{aligned}$$

$$\text{or} \quad M_t = 0.843 \times 10^{-21} \sqrt{f/\nu} \text{ (Cm)} \quad (5.57a)$$

$$\text{or} \quad M_t = 0.0958 \left[\frac{\epsilon_{\text{max}} \Delta \bar{\nu}_{1/2}}{\bar{\nu}_{\text{max}}} \right]^{1/2} \text{ (Debye)} \quad (5.57b)$$

Here, frequencies are in cm^{-1} and ϵ_{max} in $\text{dm}^3 \text{ mole}^{-1} \text{ cm}^{-1}$;
 $1 \text{ D} = 3.335641 \times 10^{-31} \text{ Cm}$

$$\text{or} \quad M_t = 0.31955 \times 10^{-30} \left[\frac{\epsilon_{\text{max}} \Delta \bar{\nu}_{1/2}}{\bar{\nu}_{\text{max}}} \right]^{1/2} \text{ Cm} \quad (5.57c)$$

As has already been defined in chapters 2 and 3,

$$M_t (M_{12} = M_{21}) = e \bar{r}_{12} = e \int \psi_{2r}^* \psi_1 dr$$

Accordingly, the effective dipole length is given by

$$\begin{aligned} \bar{r} = \bar{r}_{12} &= \frac{M_t}{e} = \frac{0.31955 \times 10^{-30} \left[\frac{\epsilon_{\text{max}} \Delta \bar{\nu}_{1/2}}{\bar{\nu}_{\text{max}}} \right]^{1/2} \text{ Cm}}{1.602 \times 10^{-19} \text{ C}} \\ &= 1.99469 \times 10^{-12} \left[\frac{\epsilon_{\text{max}} \Delta \bar{\nu}_{1/2}}{\bar{\nu}_{\text{max}}} \right]^{1/2} \text{ m} \end{aligned} \quad (5.58)$$

For example, from the charge-transfer band observed around 300 nm in the case of 2, 4-dinitrophenol-benzene system, we obtain $\Delta \bar{\nu}_{1/2} = 614 \text{ cm}^{-1}$, $\epsilon_{\text{max}} = 1960.8 \text{ dm}^3 \text{ mole}^{-1} \text{ cm}^{-1}$. Based on this data, we get

$$f = 4.33 \times 10^{-9} \times 1960.8 \times 614 = 5.2 \times 10^{-3}$$

$$M_t = 0.0958 \left[\frac{1960.8 \times 614}{333 \times 10^2} \right]^{1/2} = 0.57 \text{ D}$$

$$\text{and} \quad \bar{r} = \frac{M_t}{e} = \frac{0.57 (\text{D}) \times 3.335641 \times 10^{-30} (\text{Cm D}^{-1})}{1.602 \times 10^{-19} (\text{C})} = 1.186 \times 10^{-11} \text{ m} = 0.118 \text{ \AA}$$

To conclude, we can say that theoretically the oscillatory strength of a fully allowed transition is unity and ϵ is about 10^4 . So from the extent of deviation of experimental value of oscillator strength from unity, one can predict whether a given transition is forbidden or allowed. The values of oscillator strengths of the bands in the absorption spectrum of an aromatic carbonyl compound are listed in Table 5.6.

Table 5.6 Oscillator strengths for transitions in an aromatic carbonyl compound.

$\lambda_{\max}$	Transition	Oscillator strength f	$\epsilon_{\max}$ (in $\text{m}^2\text{mole}^{-1}$)
170	$\pi-\pi^*$	0.5 allowed	200
180	$n-\sigma^*$	0.02 forbidden	20
280	$n-\pi^*$	0.0004 forbidden	
350	$n-\pi^*$	10^{-5} forbidden	

Often bands with $\epsilon_{\max}$ values below $100 \text{ m}^2 \text{ mole}^{-1}$ result from forbidden while those with $\epsilon_{\max}$ above $1000 \text{ m}^2 \text{ mole}^{-1}$ result from allowed transitions.

5.12.1 Factors Affecting Position and Intensity of Absorption Bands

Both physical and chemical environmental factors influence the position and intensity of the absorption bands. The study of these effects aids in prescribing best analytical conditions for best optimum precision and sensitivity. The two types of effects that influence the wavelength of maximum absorption as well as intensity are intermolecular and intramolecular effects.

(a) Intramolecular Effects They are due to a change in the structure of a molecule that causes a change in the absorption spectrum. Optical isomers have identical spectra. Structural changes may be brought about by substitution which acts as mesomeric and inductive effects. Substitution may bring steric effects into operation which modifies the spectrum, e.g. 0-0 substituted stilbenes. Steric hindrance to coplanarity about a double bond causes an increase in the ground state energy but the energy of the excited state relatively remains unchanged. Consequently, a red shift results from the above results. Mild steric hindrance to coplanarity about a single bond has a small effect on the position of the absorption maxima but mild steric hindrance to coplanarity about a single bond strongly decreases the intensity and may cause either blue or red shift of the absorption maximum, e.g. p-nitroaniline shows absorption maximum at 375 nm ($\epsilon_{\max} = 16000$) while 2, 6-dimethyl-p-nitroaniline absorbs at 385 nm ($\epsilon_{\max} = 4840$). p-methylacetophenone absorbs at 252 nm ($\epsilon_{\max} = 15000$) while 2,4, 6-triethylacetophenone absorbs at 242 nm ($\epsilon_{\max} = 3200$). Extreme steric hindrance about a single bond prevents overlapping of the separated chromophores, i.e. prevents conjugation. Consequently, a blue shift is expected and has been observed indeed in many cases, e.g. dilactone produced from shelloic acid shows no absorption in UV region but an acid of this lactone absorbs at 227 nm ($\epsilon_{\max} = 5500$). The overlapping of double bond and carbonyl orbitals occurs since a constraint is released. One can make use of intramolecular effect for specific analytical purposes by modifying the structure of ligands to analyse inorganic ions colourimetrically, e.g. 4, 7-diphenyl-1, 10-phenanthralene is a better reagent for iron (II) and Cu (II) since it increases the molar extinction coefficient, thus giving higher sensitivity. Aromatic amines and phenols are determined calorimetrically by diazotisation to give coloured dye. The sensitivity of detection and limit of detection is far better in modified form.

(b) Intermolecular Effects They are due to solute-solvent interaction in the solution or interaction of other solutes in the solution with the solute under study. Solvents affect absorption by two or three mechanisms, namely their dielectric property, solvating power and/or hydrogen bonding. As the dielectric constant, i.e. polarity of the solvent, increases, the change in the instantaneous dipole moment during transition also increases, and consequently, the transition energy becomes less and absorption shifts to the longer-wavelength side. The molar decadic coefficient also changes to some extent.

Solvent effect is more pronounced in case of transitions involving a lone pair electrons as in pyridine, C = O compounds, NO₂ compounds, etc. Polar solvents or hydroxylic solvent solvate and hence stabilise the lone pair strongly. Consequently, more energy is required for excitation and the absorption moves to shorter-wavelength side. This effect is much more pronounced when the solute-solvent interaction is of H-bond type. Apart from these, the tautomeric equilibrium also depends upon solvent polarity, e.g. in ethylacetoacetate, the keto form has only a weak $n-\pi^*$ band ($\lambda_{\max} = 275 \text{ nm}$, $\epsilon_{\max} = 16$) of an isolated carbonyl group, while the $-\text{C}=\text{CH}-\text{C}=\text{O}$ unit in the enol form absorbs strongly ($\lambda_{\max} = 244 \text{ nm}$, $\epsilon_{\max} = 16000$). The percentage of enol form decreases as the polarity of the solvent increases.

(c) Effect of Temperature Temperature also affects the nature of the absorption spectra. Thionine and methylene blue show reversible shape of absorption curve in the temperature range 10–70 °C. When acetoacetic ester in petroleum ether is cooled with liquid air, a pure keto form (m.p. –39°C) crystallises out. At room temperature, it returns slowly to the equilibrium mixture. On vacuum distillation from a quartz flask, the first fraction distilled off is the lower-boiling enol form. The distilled off enol form, when allowed to stand, also changes to the equilibrium mixture of the two forms.

(d) Effect of Irradiation Irradiation can cause reversible changes due to photo-fading, rearrangement, photo-oxidation, isomerisation. Irradiation causes cis–trans isomerisation of thioindigo or stilbene. Ascorbic acid, when oxidised to dehydroascorbic acid, does not absorb in the ultraviolet range. Salts of quinoline show reversible effect on irradiation. Their colour changes in light and they regain their original colour when stored in dark. This effect is reversible but fading is irreversible. This is strongly shown by 10^{-5} M methylene blue and 0.02M ferrous ion at pH = 3. The strong blue solution becomes colourless when exposed to light and regains colour again. This is probably an oxidation–reduction reaction. The spectrophotometers which irradiate the analyte after dispersion have a specific advantage in this respect because amount of energy falling on the analyte is quite low and the effects would be reduced to a large extent.

5.13 SYMMETRY SELECTION RULES FOR POLYATOMIC MOLECULES

The probability of an electronic transition in polyatomics depends upon the change in a large number of factors, namely electron spin, orbital symmetry, momentum of the molecule, and electronic wave function involved in the transition. The probabilities due to these factors contribute to the total probability of an electronic transition which is defined by f , the oscillator strength of the transition under study and is given by

$$f = P_s P_o P_p P_m f_a \quad (5.59)$$

where P_s, P_o, P_p and P_m denote the spin-, orbital-, parity-, and momentum probabilities respectively. f_a is the oscillator strength of fully allowed $\pi - \pi^*$ transition and is the order of unity whereas the values of the P factors differ from unity. This formula forms the basis of selection rules for polyatomics.

(a) Electron Spin P_s When spin of an electron changes in an electronic transition, it is said to be spin forbidden. Thus, electronic transitions between states of same multiplicity ($2S + 1$) are allowed while between states of different multiplicity are forbidden, i.e. singlet–singlet, doublet–doublet, etc. transitions are highly allowed while singlet–triplet transitions are highly forbidden. The probability of S–T transitions is of the order of 10^{-5} for second row elements. This rule fails, i.e. S–T transitions are enhanced when heavy atoms such as iodine or paramagnetic molecules such as O_2 are added to the system under study, e.g. S–T transition is enhanced in the absorption spectrum (400–500 nm) of liquid naphthalene when ethyliodide is added to it as a solvent; and 2-naphthyl phenyl ketone in presence of O_2 (100 atm). In both the cases, vibration coarse structures has been observed in the S–T bands. The 0–0 band appears on the high wavelength side of the S–T band.

(b) Parity P_p We know that if electronic wave functions of a molecule that have the same charge remain unchanged when inverted at the midpoint of the internuclear axis, i.e. the centre of symmetry of the molecule, it is said to have an even parity and is designated as g (g stands for gerade) and odd parity u , (u stands for ungerade) when it changes sign on reflection at a plane through the centre of symmetry, e.g. wave functions corresponding to bonding π orbitals of symmetric ethylenes are ungerade while those corresponding to anti-bonding π^* orbitals are gerade.

According to parity selection rule (also called the *Laporte rule*), an electronic transition is permissible between states of different parity, i.e. the transition $g \leftrightarrow u$ is allowed while $g \leftrightarrow g$ and $u \leftrightarrow u$ are forbidden. In some cases weak transitions are observed, though they are parity forbidden. This is due to the coupling of vibrational motion of the nuclei with the electronic motion. Coupling of vibrational motion changes the symmetry of the molecule and hence the above rule is not vigorously followed. These types of transitions are called *vibronic transitions*. In aromatic hydrocarbons, the electronic transition is parity forbidden and the probability P_p is of the order of 10^{-1} for a condensed systems. The electron spin has no influence on the even–odd symmetry.

(c) Orbital Symmetry P_0 When two orbitals involved in an electronic transition simultaneously have large amplitudes in the same region of space, the transitions are called *space allowed* or *non-overlap*, otherwise *orbitally forbidden* as shown in Fig. 5.20. P_0 for $n-\pi^*$ transitions is 10^{-2} in carbonyl compounds or for second-row heteroatoms.

(d) Momentum P_m The electronic transition is said to be momentum forbidden when there is a large change in the linear or angular momentum of the molecule in the electronic transition: P_m for condensed ring compounds falls in the range $10^{-1}-10^{-3}$.

Thus, it is inferred that the transitions that strictly obey the selection rules are said to be highly allowed and give rise to intense bands in the electronic absorption spectra of molecules. Otherwise they are highly forbidden, i.e. the probability of occurrence is very low and results in very weak bands in the observed spectra.

5.14 MECHANISM OF ABSORPTION AND OF COLOUR

We know that the electrons in the atoms of the molecules occupy electronic states of certain energy values and the UV/V radiations change the electronic configuration of the molecules. If E_1 and E_2 are the energies of the electronic ground and excited states, the frequency of transitions ν between these two levels under resonance

condition is given by $\pm \Delta E = h\nu = hc\bar{\nu} = hc\frac{1}{\lambda}$, where $\Delta E = E_2 - E_1$ for absorption or $\Delta E = E_1 - E_2$, for emission.

In organic molecules, the absorption of light causes the electrons to move from a low-energy orbital to a high-energy orbital whereas in inorganic molecules, partially filled d -orbitals of transition metal ions are involved in electronic transitions. The latter will be discussed in detail under a separate heading entitled 'Inorganic Spectroscopy'.

5.15 ELECTRON TRANSITIONS IN ORGANIC MOLECULES

In organic molecules, transitions occur between bonding and anti-bonding molecular orbitals. Bonding orbitals result due to the linear combination of atomic orbitals when their wave functions are added, i.e. $\Psi_{\text{bonding}} = \Psi_a + \Psi_b$, while the anti-bonding orbitals are formed due to the linear combination of atomic orbitals when their wave functions are subtracted, i.e. $\Psi_{\text{anti-bonding}} = \Psi_a - \Psi_b$. Ψ_a and Ψ_b are the wave functions of the atomic orbitals. Ψ_σ and Ψ_{σ^*} are the wave functions of the bonding and anti-bonding molecular orbitals. Bonding orbitals have lower energy (more stable) than the combining atomic orbitals while the reverse is true for the anti-bonding molecular orbitals. Accordingly, $E_{\text{bonding}} < E_{\text{anti-bonding}}$.

There are three types of molecular orbitals in organic molecules, namely sigma orbitals, pi-orbitals and non-bonding orbitals.

(a) Sigma Orbitals These orbitals are formed by the linear combination of $1s$ [$\Psi(1s)$] and of $2p$ [$\Psi(2p_z)$] atomic orbitals lying along the axis joining the atoms. The resulting molecular orbitals are shown in Fig. 5.18. Bonding and anti-bonding orbitals are denoted by the symbols σ and σ^* respectively.

(b) Pi-orbitals They are formed by the sidewise overlapping of $2p_y$ [$\Psi(2p_y)$] atomic orbitals. The overlapping gives rise to a bonding and anti-bonding orbitals as shown in Fig. 5.19. Bonding and anti-bonding p -orbitals are denoted by the symbols π and π^* respectively.

The six molecular orbitals in benzene are formed by the overlap of the six $2p$ atomic orbitals, three of these are π orbitals and three are π^* orbitals as shown in Fig. 5.20. The ultraviolet absorption spectrum of benzene in the range 180–280 nm shows three bands corresponding to three $\pi - \pi^*$ transitions.

(c) Nonbonding Orbitals Hetero-atoms in molecules have electrons in orbitals associated with them and these orbitals do not participate in a bonding system of the molecules and hence are known as anti-bonding orbitals. They are denoted by the symbol n , e.g. there are two electrons in the nonbonding $2p$ orbital (n orbitals) on the oxygen atom as shown in Fig. 5.21. The absorption of radiation causes one of these electrons to move either to a σ^* or π^* orbital.

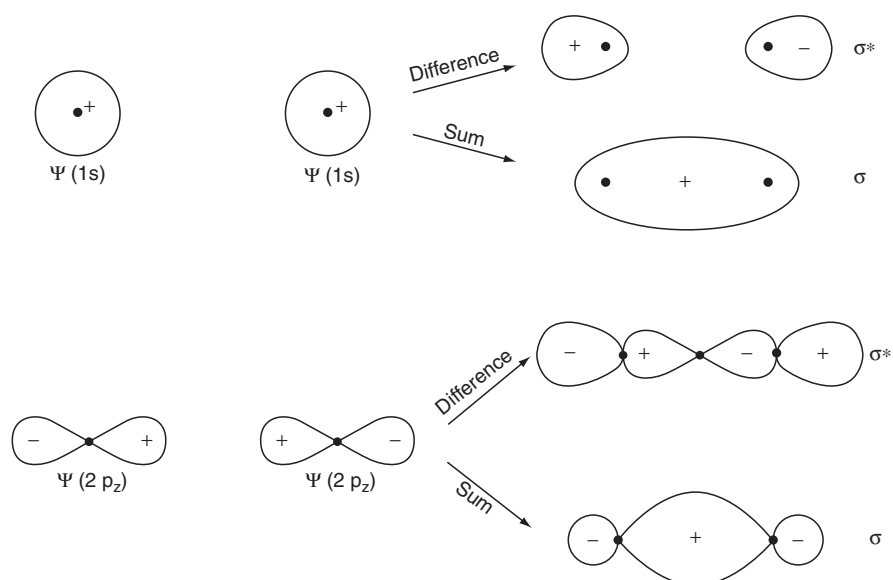


Fig. 5.18 Schematic diagram for the formation of sigma orbitals from two 1s and two 2p_z atomic orbitals.

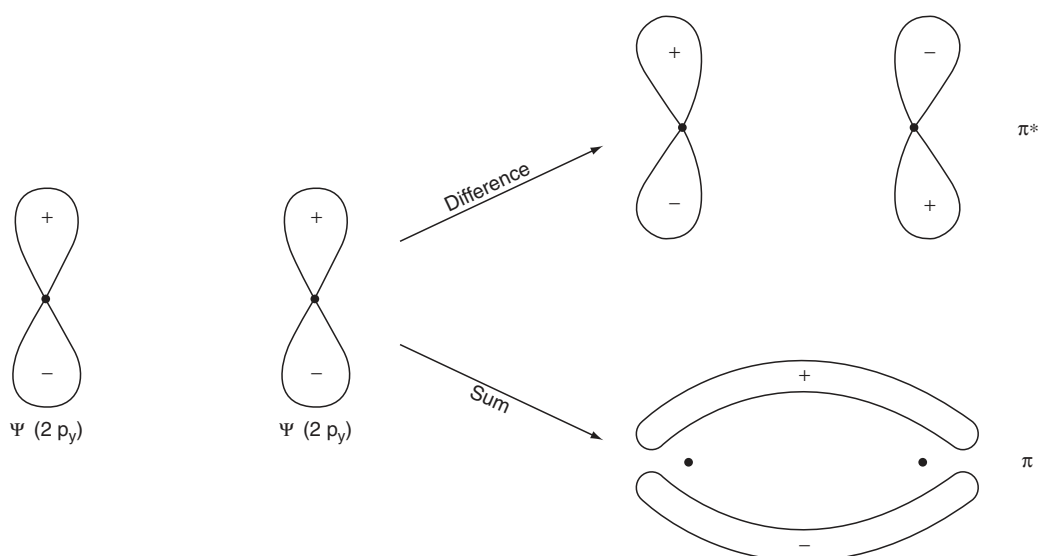


Fig. 5.19 Schematic diagram for the formation of pi-orbitals from two 2p_y atomic orbitals.

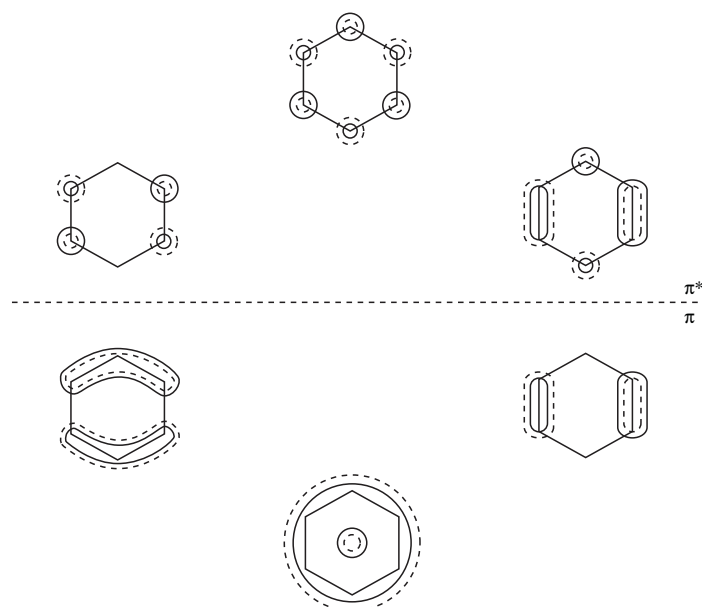


Fig. 5.20 Schematic diagram for the π bonding and π^* anti-bonding orbitals in benzene. Solid contours represent the negative parts of the wave function while dotted contours are for positive parts of the wave function.

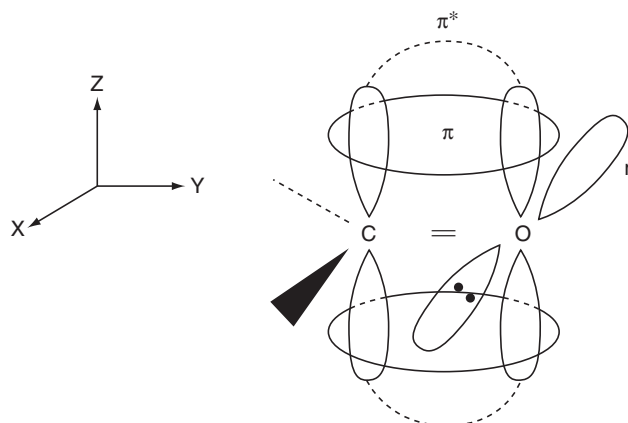


Fig. 5.21 Representation of the n , π and π^* orbitals associated with the carbonyl group. π and π^* orbitals lie in the YZ plane while n orbital ($2p$) points along the X -axis.

From the foregoing discussion, it is evident that four types of electronic transitions in molecules are possible and these have been classified as follows: $\sigma - \sigma^*$, $n - \sigma^*$, $n - \pi^*$ and $\pi - \pi^*$. It can be seen that for a molecule containing σ , π^* and n orbitals, the lowest energy transition is likely to be $n - \pi^*$. But it is possible that for molecules with a high degree of conjugation, the π orbital can have higher energy than the n orbital and thus $\pi - \pi^*$ transition would then have one of lowest energy. The energy of these transitions follows the order: $\sigma - \sigma^* > n - \sigma^* > n - \pi^* > \pi - \pi^*$. The $\pi - \pi^*$ transitions in conjugated carbon systems are of particular chemical interest. The wavelength of radiation needed for $\sigma - \sigma^*$ and $n - \sigma^*$ transitions is often shorter than 200 nm and hence not handy from a practical point of view. The schematic energy-level diagram showing these transitions is given in Fig. 5.22.

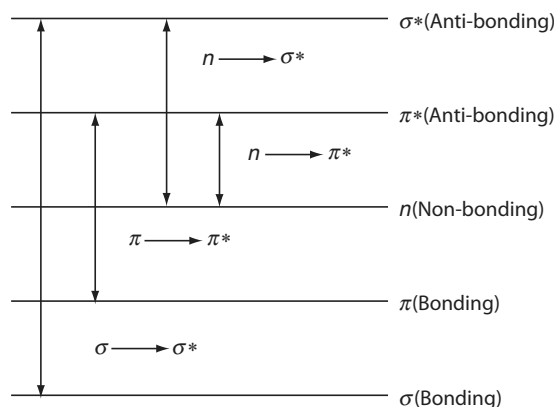


Fig 5.22 Schematic energy- level diagram showing various electronic transitions.

The Mulliken's notations corresponding to molecular orbital symbols for electronic transitions in organic molecules are given below:

Mulliken's notations	Molecular orbital notations
$N \rightarrow V$	$\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$
$N \rightarrow Q$	$n \rightarrow \pi^*$, $n \rightarrow \sigma^*$
$N \rightarrow R$	Photo-ionisation, i.e. the excitation energy is so high that the electron leaves the molecule

N —denotes the ground state; V , Q , R , etc. denote the excited states, $N \rightarrow R$ denotes the Rydberg transition. The group theory and Platt's symbols for electronic transitions are not used in the text. Readers wanting to learn about these symbols may consult any book on electronic spectroscopy.

5.15.1 Characteristics of Various Types of Electronic Transitions

The electronic transitions are characterised by their energies and intensities and the effect of various parameters such as temperature and nature of solvent on them. The solvent effects are especially useful in identifying the electronic transitions.

(a) $N \rightarrow V$ Transitions This type of transition results when an electron moves from a bonding orbital to an anti-bonding orbital. The excited state is polarised. This means that the transitions are accompanied by a considerable change of the dipole moment and the corresponding band is of high intensity. The most common types of $N \rightarrow V$ transitions are $\sigma - \sigma^*$, and $\pi - \pi^*$, transitions. $\sigma - \sigma^*$ transitions lie in the vacuum ultraviolet (< 200 nm) region and generally do not appear when spectra are recorded on commercial spectrophotometers since absorption of UV radiation by atmospheric oxygen starts at ≈ 195 nm (Schumann–Runge band system) and most spectrometers are limited to this wavelength limit, e.g. saturated hydrocarbons exhibit $\sigma - \sigma^*$ transitions. $\sigma - \sigma^*$ transition of CH_4 is observed at 122 nm while that of ethane is at 135 nm. $\pi - \pi^*$ transitions require a lower transition energy as compared to $\sigma - \sigma^*$ transitions and lie in the near ultraviolet (200–400 nm) and sometimes even in the near infrared ($4000\text{--}12000\text{ cm}^{-1}$) region of the spectrum. The intensity of $\pi - \pi^*$ transitions is high, the molar decadic extinction coefficient usually exceeds 1000.

In polar solvents, the $\pi - \pi^*$ absorption shifts to longer wavelengths. The shift increases as the polarity of the solvent increases. The shift is probably because of more stabilisation of excited state than that of the ground state due to solvation and hydrogen bonding. [Fig. 5.23(a)]. The hydrogen bonding causes much larger spectral shifts than most other solvent–solute effects, e.g. unsaturated organic molecules with double and triple bonds exhibit $\pi - \pi^*$ transitions: $\pi - \pi^*$ transition of ethylene is observed at 165 nm ($\epsilon_{\text{max}} = 10000$) and that of acetylene at 173 nm ($\epsilon_{\text{max}} = 6000$). The substitution of an electron-attracting group in the molecule increases the double-bond character, and consequently the absorption shifts to longer wavelengths.

It is observed that introduction of one more double-bond conjugated to the first one, shifts the $\pi - \pi^*$ transition to longer wavelength by about 30 nm. Moreover, in highly conjugated π -electron systems, the movement of electron in the conjugated system can be compared to a particle in a one-dimensional box. The energies of the

levels are given by $E_n = \frac{h^2 n^2}{8m_e a^2}$, where $n = 1, 2, 3, \dots$, a is the effective length of the molecule. In lycopene, there are eleven conjugated double bonds and $\lambda_{\text{max}} = 474$ nm. Thus, the total number of π -electrons = 22. Two electrons with opposite spins can reside in one energy level. Thus, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are 11 and 12 respectively. Accordingly, the energy of transition is

$$\Delta E = E_{12} - E_{11} = \frac{h^2}{8m_e a^2} [12^2 - 11^2] = \frac{23h^2}{8m_e a^2}$$

or
$$h\nu = \frac{hc}{\lambda} = \frac{23h^2}{8m_e a^2}$$

or
$$a = \left[\frac{23h\lambda}{8m_e c} \right]^{1/2}$$

Substituting the values of the respective constants and $\lambda = 474$ nm, we get

$$a = \left[\frac{23 \times (6.26 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-2}) \times (474 \times 10^{-9} \text{ m})}{8(9.1 \times 10^{-31} \text{ kg}) \times (3 \times 10^8 \text{ m s}^{-1})} \right]^{1/2} = [3.30 \times 10^{-18} \text{ m}^2]^{1/2}$$

$$= 18.1 \times 10^{-10} \text{ m} = 18.1 \text{ \AA}$$

In case of butadiene, $\lambda_{\text{max}} = 217$ nm. The number of π electrons = 4. So according to electron-free model $a = 573$ pm [i.e. two C = C bonds ($= 2 \times 135$ pm $= 270$ pm + one C—C bond ($= 154$) pm + the distance of carbon radius at each end $= 2 \times 77.0$ pm ($= 154$ pm) $= 578$ pm.]

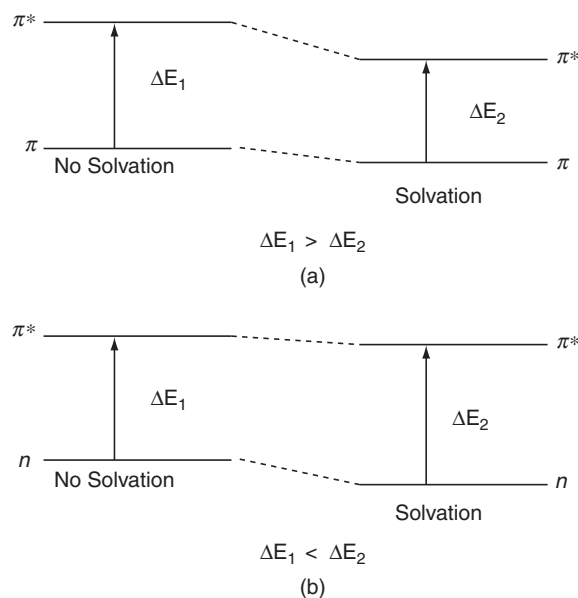
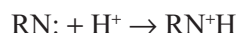


Fig. 5.23 Schematic diagram showing the effect of solvation on (a) $\pi - \pi^*$, and (b) $n - \pi^*$ transitions.

(b) N–Q Transitions This type of transition results when an electron moves from a nonbonding orbital (more polar) to an anti-bonding orbital (less polar). The most common types of N–Q transitions are $n - \pi^*$ and $n - \sigma^*$ transitions. These transitions are observed at longer wavelengths as compared to $\pi - \pi^*$ transitions but the corresponding molar decadic coefficients in $n - \pi^*$ transitions are usually lower than 100 and $>100 < 1000$ in case of $n - \sigma^*$ transitions, e.g. unsaturated molecules containing hetero atoms such as O, N or S exhibit $n - \pi^*$ transitions. $n - \pi^*$ transitions in acetone and acetaldehyde are observed at 279 nm ($\epsilon_{\max} = 15$) and 290 nm ($\epsilon_{\max} = 17$) respectively in *n*-hexane. On the other hand, saturated molecules containing hetero atoms such as O, N, S with lone-pair electrons exhibit $n - \sigma^*$ and $\sigma - \sigma^*$ transitions. $[(\text{CH}_3)_3\text{N}]$ shows bands at 227 nm and 99 nm corresponding to $n - \sigma^*$ and $\sigma - \sigma^*$ transitions respectively. $n - \sigma^*$ transition of methanol is observed at 177 nm ($\epsilon_{\max} = 200$) in hexane while that of 1-hexanethiol is observed at 224 nm ($\epsilon_{\max} = 126$) in cyclohexane.

In polar solvents, the absorption shifts to shorter wavelengths in both the $n - \sigma^*$ and $n - \pi^*$ transitions because of more stabilisation of ground state than that of the excited state due to solvation and hydrogen bonding [Fig. 5.23(b)]. The substitution of an electron-repelling group in the unsaturated molecules containing hetero atom, decreases the double-bond character, and consequently the absorption will shift to shorter wavelengths.

Note that when spectrum of an amine like RN: where $\text{R} = (\text{CH}_3)_3-, (\text{C}_2\text{H}_5)_3-,$ for $n - \sigma^*$, C_5H_5- (for $n - \pi^*$) is recorded in acidic medium, the band $\rightarrow$ corresponding to $n - \pi^*$ or $n - \sigma^*$ (as the case may be) transition is not observed due to protonation of the nitrogen atom:



This has been fixed as one of the criteria to differentiate between $n - \pi^*$ and $\pi - \pi^*$ transitions.

(c) Rydberg or Atomic Transition When the excitation energy lies in the vacuum ultraviolet region, photo-ionisation of the molecule occurs [i.e. $X + h\nu \rightarrow X^+ + e^-$] and intense narrow bands appear in the spectrum.

5.15.2 Colour

Colour is a property of light which reaches our eyes but not a property of the substance we see. Since substances absorb certain wavelengths from the light incident upon them and reflect others, the colour of an opaque substance depends upon the kind of light which it reflects to the eye. If a substance reflects all colours it receives, we say it is white. We call it black if it absorbs all the wavelengths of light that fall upon it. However, the colour of transparent substances depends upon the colour of light which they transmit. Any two colours which combine to form white light are said to be complementary. The rotating colour wheel of various complementary colours is shown in Fig. 5.24 and visual responses of colours are given in Table 5.24.

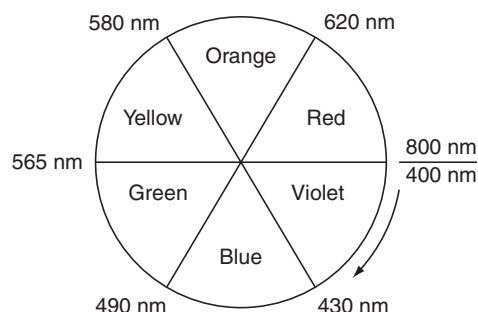


Fig 5.24 Rotating colour wheel of the various complementary colours. The apparent colour is across the wheel from the actual colour absorbed.

Table 5.7 Visual responses of colour.

Colour absorbed	Wavelength (in nm)	Apparent colour of substance
UV	< 300	Colourless
Violet	380–435	Yellowish green
Blue	435–480	Yellow
Greenish blue	480–490	Orange
Bluish Green	490–500	Red
Green	500–560	Purple, rose, magenta
Yellowish green	560–580	Violet
Yellow	580–595	Blue
Orange	595–650	Greenish blue
Red	650–780	Bluish green
Infrared	> 780	Colourless

(a) Organic and Inorganic Colours Organic colours are obtained by lowering the transition energies until the visible region is reached, while inorganic colours are obtained when the transition energies are increased from zero until the visible energies are reached. The organic chemist makes use of $\pi - \pi^*$ transitions to explain the colour of organic compounds while inorganic chemists make use of the partially filled d -orbitals of transition metal ions to explain the colour of complexes, and will be discussed later on under the heading entitled 'electronic absorption spectra of inorganic molecules'.

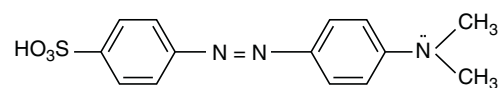
(b) Chromophores Certain unsaturated chemical groups which when substituted in hydrocarbons impart them colour, were christened as chromophores by Witt in 1876, i.e. *a covalently unsaturated group responsible for electronic absorption is called a chromophore (or chromophoric group)*. The chromophores are of interest to chemists from the point of view of elucidation of structure and related properties of the molecules. Some of the chemical chromophores along with their respective absorption maxima and molar extinction coefficients are listed in Table 5.8.

Table 5.8 Typical chromophore groups.

Group	System	Solvent	$\lambda_{\max} (nm)$	$\log \epsilon_{\max} \times 10^5$	Transition
>C=C<	Ethylene	Vapour	165	417609	$\pi - \pi^*$
			193	400000	$\pi - \pi^*$
$-\text{C} \equiv \text{C}-$	Acetylene	Vapour	173	377815	$\pi - \pi^*$
>C=O	Acetone	Vapour	166	420412	$\pi - \pi^*$
		<i>n</i> -Hexane	189	295424	$\pi - \pi^*$
			279	117609	$n - \pi^*$
>C=O	Acetaldehyde	Vapour	160	430103	$\pi - \pi^*$
			180	400000	
		<i>n</i> -Hexane	290	123045	$n - \pi^*$
>C=S			205	strong	
			495	weak	
S=O	Cyclohexylmethylsulphoxide	Ethanol	210	317609	
$-\text{N} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{O} \end{smallmatrix}$	Nitromethane	Ethanol	271	126951	$n - \pi^*$
		Methanol	201, 274	369897, 123045	
$-\text{ONO}_2$	Butylnitrate	Ethanol	270	123044	$n - \pi^*$
$-\text{ONO}$	Butylnitrite	<i>n</i> -Hexane	220	416136	$\pi - \pi^*$
			356	193951	$\pi - \pi^*$
>C=N	Acetoxime	Water	190	369897	$\pi - \pi^*$
$-\text{C} \equiv \text{N}$	Acetonitrile	Vapour	167	?	$n - \pi^*$
$-\text{N}=\text{N}-$	Azomethane	Ethanol	338	60206	$n - \pi^*$
$=\text{N}_2$	Diazomethane	Vapour	410	47713	
$-\text{N}_3$			220	217609	
			287	130103	
$-\text{COOH}$	Acetic acid	Water	204	177816	$n - \pi^*$

Methyl orange has a very long conjugated system of delocalised π -electrons, and it absorbs in the visible region at $\lambda_{\max} = 460 \text{ nm}$. The conjugation of π -electrons in this molecule is extended by the chromophore $-\text{N}=\text{N}-$ as is evident from the structure of methyl orange given here. High conjugation is responsible for the colours of many

other dyestuffs and natural pigments. Lycopene, the red pigment in tomatoes, has an absorption maximum at around 485 nm due to the presence of eleven conjugated ethylenic bonds. Ultraviolet spectra of organic compounds are therefore associated with delocalised π -electrons.



Structure of methyl orange

(c) Auxochromes or Auxochromic Groups Saturated groups with nonbonded electrons, which when attached to chromophores alter both the wavelength and intensity of the absorption band corresponding to $\pi - \pi^*$ transition of chromophores, are termed auxochromes or auxochromic groups. These groups do not show absorption bands on their own in the 200 – 800 nm range. The most typical auxochromes are $\ddot{\text{N}}\text{H}_2$, $\ddot{\text{N}}\text{R}_2$, $\ddot{\text{O}}\text{H}$, $\ddot{\text{O}}\text{R}$, $\ddot{\text{S}}\text{H}$. The substitution of electron-repelling groups, especially those having unpaired electrons, shifts the wavelength of $\pi - \pi^*$ transitions to shorter wavelengths. The effect of some auxochromes on the benzene chromophore is given in Table 5.9.

Table 5.9 Effect of auxochromes on absorption of benzene.

Compound	Solvent	Ethylenic Band		Benzenoid band	
		λ_{max} (in nm)	$\text{Log} \epsilon_{\text{max}}$	λ_{max} (in nm)	$\text{Log} \epsilon_{\text{max}}$
Benzene	Cyclohexane	198	3.90	255	2.36
Diphenylether	Cyclohexane	255	4.04	272	3.30
				278	3.25
Phenol	Water	210.5	3.79	270	3.16
Thiophenol	<i>n</i> -Hexane	236	4.00	269	2.85
Aniline	Water	230	3.93	280	3.16
Anilinium cation	Aq. acid	203	3.87	254	2.20
Chlorobenzene	Ethanol	210	3.88	257	2.23
Phenolate ion	Aq. base	235	3.97	287	3.42

The number of isolated double bonds in organic molecules does not practically influence the position of the band but intensity of the band increases proportionately. However, when the number of conjugate double bonds increases, the band corresponding to $\pi - \pi^*$ transition shifts to longer wavelength side of the spectrum and ultimately at some limiting value of the conjugation chain length, the absorption maxima shifts to the visible region and the compounds become coloured. The effect of conjugation chain length on λ_{max} in case of organic molecules is shown in Tables 5.10 and 5.11.

Table 5.10 Values of λ_{max} molecules with different conjugation chain lengths.

Compound	λ_{max} (in nm)				
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
$\text{CH}_3 - (\text{CH}=\text{CH})_n - \text{COOH}$ (in alcohol)	204	254	294	327	—
$\text{CH}_3 - (\text{CH}=\text{CH})_n - \text{CHO}$ (in alcohol)	220	271	315	353	393
$\text{CH}_3 - (\text{CH}=\text{CH})_n - \text{C}_6\text{H}_5$ (in benzene)	306 (24)	334 (40)	358 (75)	384 (86)	420 (114)

*The quantities within parenthesis are values of $\epsilon_{\text{max}} \times 10^{-3}$.

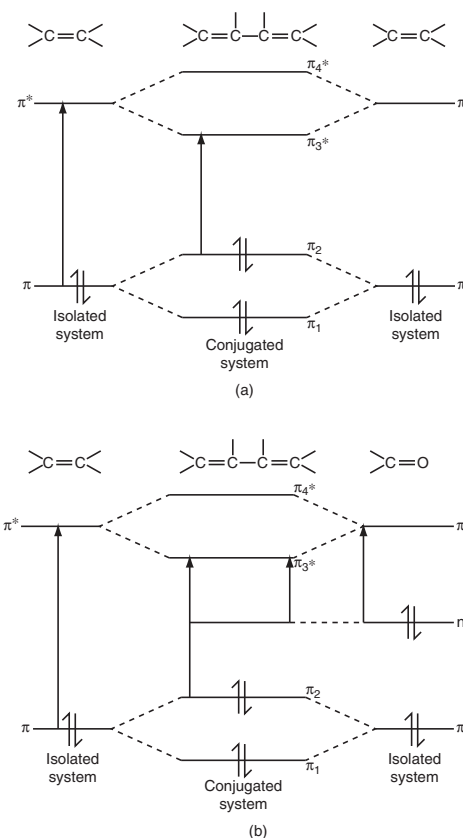
Table 5.11 Values of $\lambda_{\max}$ and $\epsilon_{\max}$ for a series of hydrocarbons with number of conjugated bonds increasing from compound to compound.

Compound	Number of conjugated bonds	$\lambda_{\max}$ (in nm)	$\epsilon_{\max} \times 10^{-3}$	Colour
Butadiene	2	217	21	Colourless
Hexatriene	3	258	35	Colourless
Decatetraene	4	310	42	Colourless
Vitamin A ₁	5	326	4.66*	Colourless
Tetradecaheptaene	6	360	70	Colourless
α -Carotene	10	445	145	Orange
Lycopene	11	476	191	Red
*log $\epsilon_{\max}$				

The absorption band due to $\pi - \pi^*$ transition in such conjugated systems, i.e. enes, is called a *K* (Konjugierte) band and in these conjugated systems there is one common *K*-band instead of several bands. Thus, the length of the conjugated system can be deduced from the position and intensity of the *K*-band as is evident from Tables 5.10 and 5.11. The *K* bands of enes are independent of the polarity of the solvent.

The electronic transition is accompanied by a change of dipole moment, and thus depending on the polarity induced in the excited state, the absorption band may have high or low intensity. In long conjugated systems, the excited dipolar states have large dipole moments and hence intense *K*-bands are observed in these systems. Values of $\epsilon_{\max}$ for *K*-bands lie in the range of $10^4 - 10^5$. On the other hand, less energy is required to excite π electrons in conjugated molecules, and as the conjugation increases, the excitation energy decreases, i.e. the absorption shifts to longer wavelength side of the spectrum (Fig. 5.25a).

Carbonyl compounds such as ketones, aldehydes, esters, etc., not only show intense *K*-bands but also a low-intensity band called *R* (Radikalartig) band due to $n - \pi^*$ transition, (Fig. 5.25b). The former moves to the longer wavelength side, while the latter to shorter wavelength with the polarity of the solvent. In general, chromophores having one electron pair on the hetero atom give rise to *R*-bands. Since *R*-bands are of low intensity they are called forbidden bands. $\epsilon_{\max}$ of *R*-bands is <100 . *K*-bands of carbonyl compounds, differ from those of enes in that the former depend on the polarity of the solvent (undergo red shift), while the latter are independent of it. Absorption data for some conjugated enes and carbonyl compounds are compared here in Table 5.12.

**Fig 5.25** Molecular orbital energy relationships between isolated and conjugated. (a) C = C group in dienes, and (b) C = C and C = O groups in α, β -unsaturated ketones.**Table 5.12** Absorption data for some conjugated enes and carbonyls.

System	<i>K</i> -band ($\pi - \pi^*$)		<i>R</i> -band ($n - \pi^*$)	
	$\lambda_{\max}$ (in nm)	$\epsilon_{\max}$	$\lambda_{\max}$ (in nm)	$\epsilon_{\max}$
1,3-Butadiene (in hexane)	217	21000	—	—
1,3-Cyclohexadiene (in hexane)	256	8000	—	—
Methylvinylketone (in ethanol)	212.5	7080	320	20.9
Acrolein (in water)	210	11482	315	25.7
Crotonaldehyde (in ethanol)	220	14792	322	28.2
Acetone (in hexane)	188	900	279	15

Aromatics or hetero-aromatics show three absorption bands, say at wavelengths λ_{E_1} , $\lambda_{E_2/K}$ and λ_B , due to $\pi-\pi^*$ transitions. The absorptions and intensities corresponding to these bands follow the order.

$$\lambda_B > \lambda_{E_2/K} > \lambda_{E_1}$$

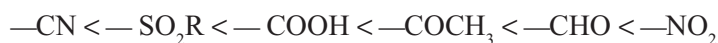
and

$$\epsilon_{\max}^B (10^2 - <10^3) < \epsilon_{\max}^{E_2/K} (10^3 - <10^4) < \epsilon_{\max}^{E_1} (10^4 - 10^5)$$

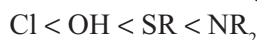
The band at λ_B is called the *benzenoid band* and is regarded as a representative of the 'forbidden' biradical transition. *B*-bands generally show a vibrational fine structure which often disappears or is reduced in polar solvents. The other two bands at wavelengths $\lambda_{E_2/K}$ and λ_{E_1} are called *ethylenic (E) bands* and like the *B*-band they may also show vibrational fine structure. Any substituent capable of conjugation causes a red shift of the *K*-band, *B*-band and an increase in the intensity of the bands of the parent molecule. These effects vary from substituent to substituent. When a chromophore, i.e. NO_2 , $\text{C}=\text{O}$, etc., is attached to an aromatic ring, the *B*-bands undergo more red shift as compared to $E_{2/K}$ bands. When an *R*-band due to $n-\pi^*$ transition is also observed along with the $\pi-\pi^*$ transitions of the aromatics, the *R*-band moves to longer wavelengths. Vibrational fine structure may not be observed in the spectra of substituted aromatics.

When an auxochromic group NH_2 , OH , etc., is attached to the aromatic molecules; *B* and *E* bands, i.e. E_1 and E_2 , undergo red shift. The intensity of the *B*-band of the parent molecule also increases while that of the E_2 band does not show any definite trend. The effect of auxochromic substitution on *B* and *E* bands of benzene is demonstrated in Table 5.9.

In case of benzene, the effect of ortho-, para- and meta-substituents on the red shift may be arranged in the following two series:



and



Thus, it is evident that the magnitude of red shift increases as the conjugating power of the substituent increases. When different kinds of substituents are in the para position, the *K*-bands of benzene are strongly red shifted as is evident from the spectral data indicated below:

The red shift of *K*-band of benzene due to conjugation effect of various substituents affords a method for the determination of the position of the substituent in the benzene ring, which is required for analysis of mixtures of meta- and para-substituted compounds.

The absorption data of some substituted and unsubstituted aromatics and hetero aromatics is compared in Table 5.13.

Table 5.13 Absorption data of some typical substituted and unsubstituted aromatics and hetero aromatics.

System	<i>E₁</i> -band ($\pi-\pi^*$)		<i>K/E₂</i> -band ($\pi-\pi^*$)		<i>B</i> -band ($\pi-\pi^*$)		<i>R</i> -band ($\pi-\pi^*$)		Solvent
	$\lambda_{\max}$ (in nm)	$\epsilon_{\max}$ (10^3)	$\lambda_{\max}$ (in nm)	$\epsilon_{\max}$ (10^3)	$\lambda_{\max}$ (in nm)	$\epsilon_{\max}$ (10^3)	$\lambda_{\max}$	$\epsilon_{\max}$	
Benzene	184	60	204	7.9	256	0.2			
Naphthalene	221	133	286	9.3	312	0.289			
Anthracene	256	180	375	9.0	submerged				
o-nitroaniline			283	5.4	412	4.5			
o-nitrophenol			279	6.6	351	3.2			
m-nitroaniline			280	4.8	358	1.45			
m-nitrophenol			274	6	333	1.96			
p-nitroaniline			381	13.5	submerged				
p-nitrophenol			318	10	submerged				
Styrene			244	12	282	0.45			Ethanol
Benzaldehyde			244	15	280	1.5	328	20	Ethanol

System	$\lambda_{\max}$ (<i>K</i> -band) (in nm)
Benzene	200
Aniline	230
Nitrobenzene	269
p-dinitrobenzene	266
p-nitroaniline	381
m-nitroaniline	280

System	E_1 -band ($\pi-\pi^*$)		K/E_2 -band ($\pi-\pi^*$)		B -band ($\pi-\pi^*$)		R -band ($\pi-\pi^*$)		Solvent
	$\lambda_{\max}$ (in nm)	$\epsilon_{\max}$ (10^3)	$\lambda_{\max}$ (in nm)	$\epsilon_{\max}$ (10^3)	$\lambda_{\max}$ (in nm)	$\epsilon_{\max}$ (10^3)	$\lambda_{\max}$	$\epsilon_{\max}$	
Acetophenone			240	13	278	1.1	319	50	Ethanol
Nitrobenzene			252	10	280	1	330	125	Hexane
Quinoline	228	40	270	3.162	315	2.5			Cyclohexane
Acridine	250	20	358	10					Ethanol

Further, the lower members of the acene series have typical benzenoid absorption bands with the following characteristics (benzene is given for comparison).

The larger the number of six-membered rings fused together in a linear manner, (I) the stronger the bathochromic shift of light absorption and more intense the absorption band. At the same time, the stability of the compound decreases sharply, its aromaticity is diminished, and it becomes increasingly unsaturated and closes to a polyenic hydrocarbon with conjugated bonds. This is easily understandable since only one ring of an acene has a sextet of electrons. When the system of any acene, say anthracene, is symmetrical, the two electrons in the sextet are mobile and migrate from one end of the system to the other as shown below:

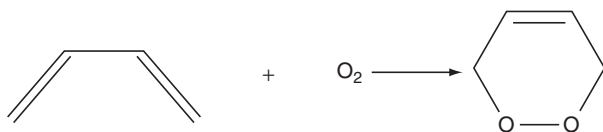
The arrow indicates the migration of a pair of electrons of the sextet.

The angular condensed hydrocarbons, (II) beginning with phenanthrene, contain a larger number of completely aromatic rings and the path covered by the pair of electrons from the sextet is shorter.

These hydrocarbons absorb light in a larger wavelength region of the spectrum, are more stable and aromatic.

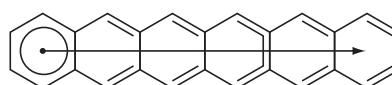
Solutions of the red-coloured hydrocarbon rubrene (9,10,11,12-tetraphenyltetracene) are decolourised in sunlight by atmospheric oxygen due to the formation of peroxide (III) shown below.

This rubrene peroxide decomposes in vacuum at 140–150 °C into molecular oxygen and rubrene. The evolved oxygen in the active singlet state adds on to the conjugated C—C π -bonds, i.e.

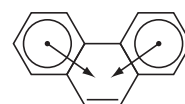


Based on the ultraviolet spectral data of all classes of organic compounds, i.e. fused-ring systems, many steroids, terpenes, heterocyclic compounds and their derivatives, etc., rules have been worked out from which one can predict the position of the absorption maximum in some organic systems. The rules will be discussed in detail in the application part under the title 'Structural Elucidation'.

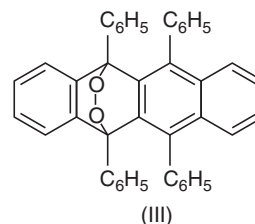
System	$\lambda_{\max}$ (in nm)	$\epsilon_{\max}$
Benzene	225	230
Naphthalene	314	316
Anthracene	380	7900
Tetracene	480	11,000
Pentacene	580	12,600



(I)



(II)



(III)

5.16 INORGANIC ELECTRONIC ABSORPTION SPECTROSCOPY

Before discussing the electronic absorption spectra of inorganic molecules, the basic theories that laid the foundation of electronic absorption spectroscopy of inorganic substances need be introduced here in brief.

All the five d -orbitals, i.e. d_{xy} , d_{yz} , d_{zx} , d_{z^2} , $d_{x^2-y^2}$, in an isolated transition metal ion in the gaseous state and that of an ion in a spherical electronic field are degenerate but the orbitals in the latter are at a higher energy level compared to the former because of electron repulsion between metal-ion electron density and spherical field of negative charge. The splitting of energy levels or orbitals of a metal ion under the influence of an electric field of the oppositely charged ions surrounding it as in a crystal is called *crystal field splitting*. The details and extent of splitting depend on the symmetry and the strength of the crystalline electric field. According to this theory, there is no

overlapping between the orbitals of the neighbouring ions and the central metal ion under consideration and only repulsion is operative between the negative charge of the surrounding ions and electrons of the central metal ion, i.e. the model assumes that the bonds between metal ions and oppositely charged ions surrounding it are of ionic nature. This model also describes the properties of complexes where the metal ion is under the influence of the electric field created by the ligands (L). But this ionic or electrostatic model is not realistic since in complexes of transition metal ions in which the transition metal atoms, say M, are surrounded by a definite number of bound groups called ligands (arranged in one of several definite symmetries: octahedral, tetrahedral, tetragonal or square planar) whose charge clouds exert a marked influence on the electronic configuration of the transition element. These bound groups may be monoatomic or polyatomic ions such as Cl^- , F^- , CN^- , etc., or neutral polar molecules usually having one or more lone pairs of electrons, e.g. H_2O , NH_3 , CO , etc. The overlapping of electron clouds of ligands with that of the central metal ion removes the degeneracy of some orbitals of the metal ion which have the same energy values in the absence of the electric field of the ligand. This lifting of degeneracy of some orbitals of the metal ion by the electric field of the ligand in the metal complexes is called *ligand-field splitting*. In other words, we can say that in some complexes in which we have assumed electrons to be entirely in the atomic d -orbitals of the metal, may they actually spread out and spend some time in the orbitals belonging to the ligand and vice versa. Thus, there are three kinds of interactions involving M and L: (i) $\text{L} \rightarrow \text{M}$, σ overlap of orbitals, (ii) $\text{L} \rightarrow \text{M}$, π - overlap of orbitals, and (iii) $\text{M} \rightarrow \text{L}$, back bonding (π^*) interactions, i.e. $d\pi$ - $p\pi$ back bonding due to π -overlap of full d -orbitals of M with empty p -orbitals of L. These interactions give rise to considerable covalency to $\text{M}-\text{L}$ bonds which are now made up of $\text{M}-\text{L}$ molecular orbitals. Accordingly, the lone pair orbitals of ligand are combined with s , p and d orbitals of M to give bonding, anti-bonding and sometimes nonbonding orbitals in the complexes. The electrons from the ligands then occupy the bonding orbitals and impart covalency to the complexes. The remaining electrons partially fill the anti-bonding orbitals.

Both the theories explain the splitting of d -orbital degeneracy of isolated metal ions in different ways, but they give rise to the same general pattern of energy levels: The ligand field theory may thus be visualised as crystal field theory with superimposed molecular orbital concepts i.e. the ligand field theory is a modification of the crystal field theory in which we drop the assumption that partially filled electron shell in one consisting of pure d orbitals. Instead there is overlap between the d orbitals of metal and orbitals of the ligand atoms. The theory deals with three broad categories: (i) crystal field strength is less than the spin-orbit ($L-S$) coupling (ii) crystal-field strength is of intermediate strength in comparison to spin-orbit coupling and electron repulsion terms e^2/r_{ij} , and (iii) crystal-field strength is greater than the repulsion terms, i.e. e^2/r_{ij} . Complexes of rare earths (4f) belong to the category (i) while complexes of first transition group and covalent complexes belong to categories (ii) and (iii) respectively.

5.16.1 Energy Levels in Transition Metal Complexes

Let us consider an ion with single d electron, i.e. d^1 configuration subjected to an external electric field (crystal field) of octahedral symmetry. The five d -orbitals, viz., d_{xy} , d_{yz} , d_{zx} , d_{z^2} , $d_{x^2-y^2}$ of a metal ion in the gaseous state are degenerate, i.e. they have the same energy values. The single d -electron can occupy any one of the five d -orbitals and the probability of occupancy is the same for all the d -orbitals. In the octahedral environment, out of the five orbitals the two d_{z^2} and $d_{x^2-y^2}$ correspond to high electron density along the axes while the remaining three d_{xy} , d_{yz} , d_{zx} correspond to high electron density along the 45° lines between the axes as shown in Fig. 5.26. Thus, when a d electron is present in one of the d -orbitals along the axes, i.e. d_{z^2} and $d_{x^2-y^2}$, there will be stronger repulsion between the electron cloud of the d electron and that of the ligand. The repulsion will be less if the electron is present in one of the d -orbitals that are directed between the ligands with minimum charge density on the axes, i.e. d_{xy} , d_{yz} and d_{zx} . Consequently, d_{z^2} and $d_{x^2-y^2}$ are high-energy orbitals as compared to the d_{xy} , d_{yz} and d_{zx} orbitals in an octahedral environment. Not all the five d -orbitals are degenerate in the octahedral environment but split into two groups: one group of triply and a second group of doubly degenerate levels. The single electron in the $d_{x^2-y^2}$ orbitals is being repelled by four ligands, while the electron in the d_{z^2} orbital is only being repelled by two ligands. Thus, the energy of $d_{x^2-y^2}$ increases relative to that of d_{z^2} and if the ligand field is sufficiently strong, the difference in energy between these two orbitals becomes larger than the energy needed to pair the electrons. The group of d_{xy} , d_{yz} and d_{zx} orbitals is labeled as t_{2g} or $d\epsilon$ orbitals while that of d_{z^2} and $d_{x^2-y^2}$ as e_g or $d\gamma$. Thus, the five d -levels are said to 'split into e_g and t_{2g} with t_{2g} as the lower energy level; where the symbol 'g' stands for gerade, 't' for a set of triply degenerate orbitals and 'e' for a set of doubly degenerate orbitals. The subscript '2' indicates anti-symmetry with respect to the rotation axis other than the principal axis. The energy of the two splitted levels is expressed in terms of the crystal-field parameters D and q , where ' q ', is the magnitude of the charge on the ligands and ' D ' is a measure of the polarisability of the central metal ion. Since, in practice, it is

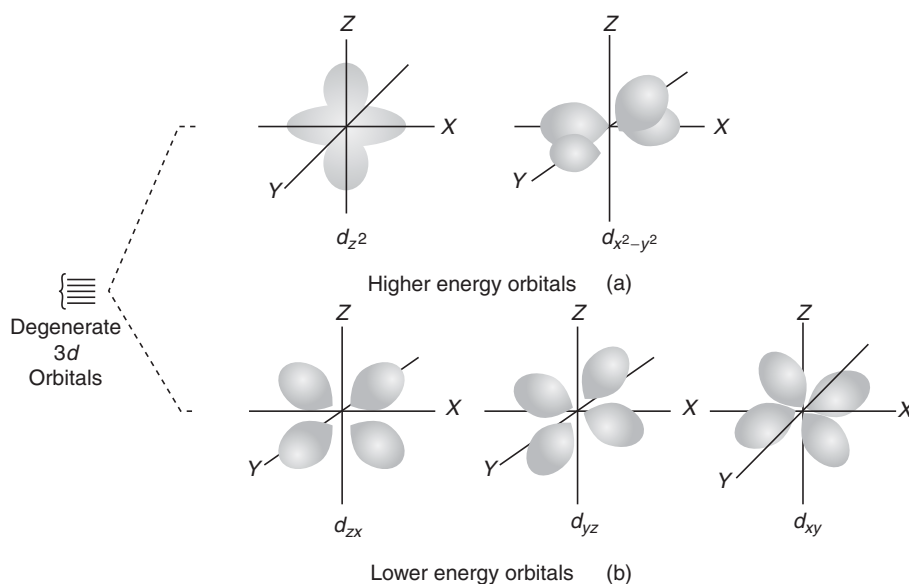


Fig. 5.26 High electron density 3d orbitals (a) along the axes, and (b) along 45° lines between the axes in a octahedral environment.

not possible to separate D and q , a single adjustable parameter Dq is considered. The energy of e_g level, $E(e_g) = +6Dq$ and that of t_{2g} level $E(t_{2g}) = -4Dq$ (with respect to the energy of the degenerate levels, i.e. the bary centre of the degenerate levels; each neighbour contributes to the blended value in proportion to its overlap at the bary centre). Thus, the energy difference Δ_0 between e_g and t_{2g} levels of an ion with d^1 configuration in an octahedral crystal field is $10Dq$.

The energy level splitting of an ion with a single d electron in an octahedral crystal field is shown in Fig. 5.27. The crystal field splitting of d -orbitals of metal ions in other crystal field symmetries, shown in Fig. 5.28, show that the energy difference between the two separated groups of orbitals of metal ions in various crystal-field symmetries follows the trend:

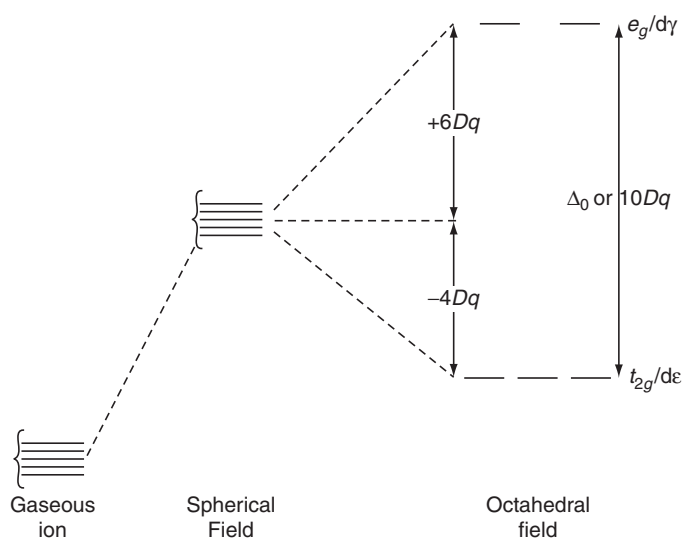


Fig. 5.27 Splitting of five degenerate 3d orbitals in an octahedral field.

Square planar > Tetragonal > Octahedral > Tetrahedral

$$1.30\Delta_0$$

$$\Delta_0$$

$$0.45\Delta_0$$

The magnitude of Δ can be obtained from the spectra of transition metals. The frequency ν of absorption band due to $d-d$ transition in a transition metal complex with d^1 configuration under resonance condition is given by $\Delta E = h\nu$. Thus, knowing ν , we can determine Δ , e.g. the absorption maximum in $[\text{Ti}^{III}(\text{H}_2\text{O})_6]^{3+}$ is observed at $\lambda = 500 \text{ nm}$. Therefore, $\Delta_0 = 500 \text{ nm} = 20,000 \text{ cm}^{-1} = 239.4 \text{ kJ mole}^{-1}$. The magnitude of Δ depends on two quantities: (i) the nature of the ligands, and (ii) the d -electron configuration of the metal ion, which can vary for the same element in different oxidation states. Note that for ions with more than one d electron, several electron transitions are possible, giving rise to more than one absorption band. However, these transitions usually fall in or near the

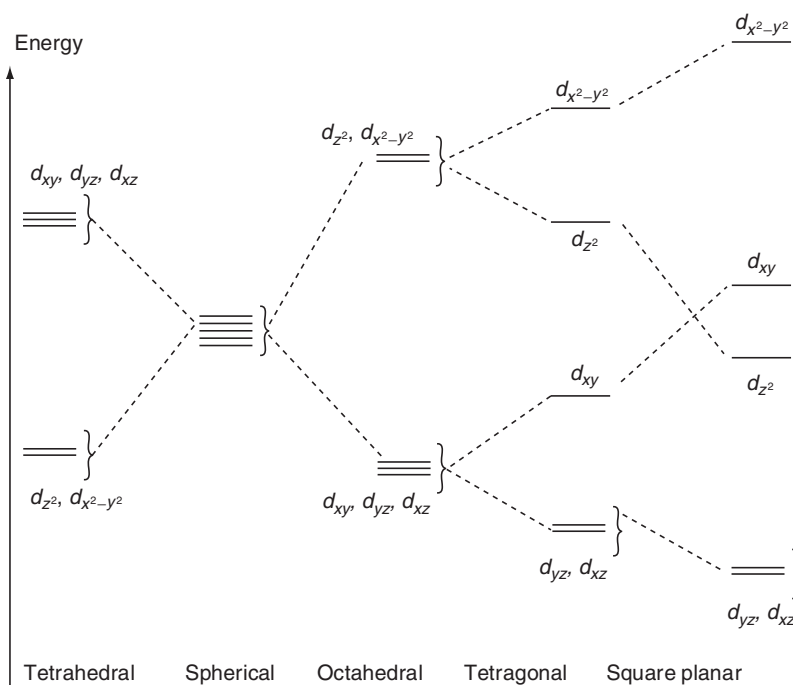


Fig. 5.28 Splitting of 3d orbitals for various symmetries.

visible region. For the transition metal ions having the same electronic configuration d^n , i.e. same charge, the value of Δ_0 is affected by the nature of the ligands which controls the strength of the ligand field. This explains the variation in colour within a given oxidation state for an ion of different ligands. On the basis of Δ values, ligands have been arranged in the form of a series called the *spectrochemical series* $\text{CO} \approx \text{CN}^- > \text{NO}_2^- > \text{O-phenanthroline} > \text{dipyridyl} > \text{ethylenediamine} > \text{pyridine} \approx \text{NH}_3 > \text{EDTA} > \text{oxalate} \approx \text{H}_2\text{O} > \text{OH}^- > \text{F}^- > \text{NO}_3^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$.

Strong ligand field... →

Weak ligand field

Blue end of spectrum... →

Red end of spectrum

Low wavelength... → High wavelength.

The splitting produced by strong CN^- ligands is approximately twice that produced by weak ligand fields. The spectrochemical series is useful to explain the colour of the transition metal complexes, e.g. NiSO_4 is pale green, $[\text{Ni}(\text{en})_3]^{2+}$ is deep blue; $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ is pale blue, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is blue, and CuSO_4 salt is colourless, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is blue while aquo ion $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green.

The value of Δ_0 increases as the charge on the metal ion grows, i.e. $\Delta_0(\text{M}^{3+}) > \Delta_0(\text{M}^{2+})$. e.g. $d^3 [\text{Cr}^{III}(\text{H}_2\text{O})_6]^{3+}$ ($\Delta_0 = 17400 \text{ cm}^{-1}$) $> d^4 [\text{Cr}^{II}(\text{H}_2\text{O})_6]^{4+}$: ($\Delta_0 = 13100 \text{ cm}^{-1}$); $d^4 [\text{Mn}^{III}(\text{H}_2\text{O})_6]^{3+}$: ($\Delta_0 = 21000 \text{ cm}^{-1}$) $> d^5 [\text{Mn}^{II}(\text{H}_2\text{O})_6]^{4+}$ ($\Delta_0 = 7800 \text{ cm}^{-1}$):

The magnitude of Δ_0 also grows on descending a group of transition elements, e.g. $\Delta_0[\text{Co}(\text{NH}_3)_6]^{3+} = 23000 \text{ cm}^{-1} < \Delta_0[\text{Rh}(\text{NH}_3)_6]^{3+} = 34000 \text{ cm}^{-1} < \Delta_0[\text{Ir}(\text{NH}_3)_6]^{3+} = 41000 \text{ cm}^{-1}$.

Further, note that any nonlinear molecule possessing orbital degeneracy being unstable, distorts itself in such a way so as to remove degeneracy and become stable. This is called *Jahn–Teller effect*. Distortions are significant when orbitals are directed towards ligands, i.e., e_g orbitals in octahedral and t_{2g} orbitals in tetrahedral complexes. The distortions from t_{2g} orbitals in octahedral and from e orbitals in tetrahedral complexes are too small to be observed, since these orbitals do not point toward ligands. This effect in former cases lifts the degeneracy of the upper level due to which asymmetric absorption band rather than a symmetric one appears in the electronic absorption spectra of transition metal complexes.

5.16.2 Crystal Field Stabilisation Energy

Fig. 5.27 shows that the energy of e_g orbitals increases by an amount $+6Dq$ and that of the t_{2g} orbitals decreases by $-4Dq$ compared to the energy of degenerate orbitals, under the influence of octahedral crystal field, i.e. an electron from metal ion, placed in t_{2g} orbitals stabilises the system by $-4Dq$ (where negative sign refers to stabilisation) while an electron in the e_g orbitals destabilises the system by $+6Dq$ (where the positive sign refers to destabilisation). Thus according to electrostatic model, an ion gets stabilised under the influence of an octahedral crystal

field and the actual energy of stabilisation is called stabilisation energy (CFSE). CFSE not only depends on the symmetry of field but also on its strength.

The CFSEs of ions with different electronic configurations of 3d orbitals: $d^0, d^1, d^2, \dots, d^{10}$, i.e. M^{2+} ion of the first transition series in an octahedral crystal field can be computed with the help of the following rules:

- An electron from a metal ion placed in t_{2g} orbital stabilises the system by $-4Dq$ and in an e_g orbital destabilises the system by $+6Dq$.
- Each electron from a metal ion placed in t_{2g} orbital contributes to the stability of the system while in the e_g orbital, contributes to the destabilisation of the system.
- In weak crystalline fields, i.e. high spin octahedral complexes, the 3d- electrons are distributed among the available orbitals in such a way that maximum number of electrons remain unpaired while in strong crystalline fields, i.e. low-spin octahedral complexes, the distribution is carried out to have maximum number of paired electrons, i.e. minimum number of unpaired electrons among the available d-orbitals.

$$\text{Mathematically, CFSE (octahedral)} = -0.4n_{t_{2g}} + 0.6n_{e_g} \quad (5.60a)$$

where $n_{t_{2g}}$ and n_{e_g} are the number of electrons in t_{2g} and e_g orbitals respectively.

Table 5.14 Crystal-field stabilisation energies of Ca^{++} to, Zn^{++} ions in weak and strong octahedral fields.

		Ca^{++}	Sc^{++}	Ti^{++}	V^{++}	Cr^{++}	Mn^{++}	Fe^{++}	Co^{++}	Ni^{++}	Cu^{++}	Zn^{++}
3d-electronic		d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
ConFiguRation												
Distribution for high Spin (i.e weak field) ConFiguRation:	e_g	—	—	—	—	1	2	2	2	2	3	4
	t_{2g}	0	1	2	3	3	3	4	5	6	6	6
CFSE:	$-10Dq$	0	4	8	12	6	0	4	8	12	6	0
Distribution forLow spin (i.e high field) configura-tion	t_{2g}	0	1	2	3	4	5	6	6	6	6	6
	e_g	—	—	—	—	—	—	—	1	2	3	4
CFSE:	$-10Dq$	0	4	8	12	16	20	24	18	12	6	0

According to the above rules, the crystal field stabilisation energies of M^{2+} ions with $d^0, d^1, d^2, \dots, d^9, d^{10}$ configurations in low-, and high-, spin octahedral complexes have been calculated and are recorded in Table 5.14.

Thus, according to the simple electrostatic model, all M^{2+} ions except Ca^{++} , Mn^{++} and Zn^{++} , i.e. d^0, d^5 , and d^{10} configuration, will be stabilised in a weak crystalline octahedral field while in a strong crystalline octahedral field only d^0 and d^{10} configurations will not be stabilised.

In tetrahedral complexes, there are four ligands (bulky) instead of six (small in size) and the direction of approach of ligands does not coincide either with the e or t_2 orbitals. The subscript 'g' is not considered in tetrahedral complexes since they lack centre of symmetry. Each of these facts reduces the octahedral splitting by a factor of 2/3. Thus, the tetrahedral splitting Δ_t is roughly $\frac{4}{9}$ of the octahedral splitting Δ_o , i.e. $\Delta_t = \frac{4}{9}\Delta_o$. Since $\Delta_t < \Delta_o$, the tetrahedral complexes are of high spin. Moreover, e is the lower energy level and t_2 is the upper energy level in these complexes, i.e. the energy-level diagram for tetrahedral complexes is the inverse of those for octahedral complexes. The rules to calculate the CFSEs of metal ions with $d^0, d^1, d^2, \dots, d^{10}$ configurations in weak octahedral fields equally apply to high spin tetrahedral complexes except that an electron in the e orbital stabilises the system by $6Dq$ and in the t_2 orbital destabilises the system by $+4Dq$.

Accordingly, Eq. (5.60a) for tetrahedral complexes is expressed as $\text{CFSE (tetrahedral)} = -0.6n_e + 0.4n_{t_2}$ (5.60b).

The values of CFSEs determined with the aid of Eq. (5.60b) are compared with those of CFSEs in an octahedral field in Table 5.15. Table 5.15 reveals that all M^{2+} ions, except those with d^0, d^5 and d^{10} configurations, are stabilised in high-spin tetrahedral as well as in high-spin octahedral complexes also.

Table 5.15 Crystal field stabilisation energies of Ca^{++} to Zn^{++} ions in high-spin tetrahedral and octahedral complexes.

Number of d -electrons (M^{2+})	Distribution of electrons in high spin tetrahedral field		Tetrahedral CFSE	Octahedral CFSE
	e	t_2	Δ_t^*	Δ_o
$d^0 (\text{Ca}^{++})$	—	—	0.0	0.0
$d^1 (\text{Sc}^{++})$	1	—	−0.6	−0.4
$d^2 (\text{Ti}^{++})$	2	—	−1.2	−0.8
$d^3 (\text{V}^{++})$	2	1	−1.2 + 0.4 = −0.8	−1.2
$d^4 (\text{Cr}^{++})$	2	2	−1.2 + 0.8 = −0.4	−0.6
$d^5 (\text{Mn}^{++})$	2	3	−1.2 + 1.2 = 0.0	0.0
$d^6 (\text{Fe}^{++})$	3	3	−1.8 + 1.2 = −0.6	−0.4
$d^7 (\text{Co}^{++})$	4	3	−2.4 + 1.2 = 1.2	−0.8
$d^8 (\text{Ni}^{++})$	4	4	−2.4 + 1.6 = −0.8	−1.2
$d^9 (\text{Cu}^{++})$	4	5	−2.4 + 2.0 = −0.4	−0.6
$d^{10} (\text{Zn}^{++})$	4	6	−2.4 + 2.4 = 0.0	0.0

$\Delta_t = E(e) + E(t_2)$. These CFSE values can also be expressed in terms of Dq .

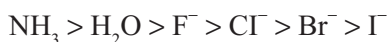
5.16.3 Charge Transfer Inter-Ligand Transitions in Transition Metal Complexes

Recall from Chapter 3 on infrared spectroscopy that charge-transfer complexation occurs with the transfer of an electron from the donor molecule to the acceptor molecule. The colour of transition-metal complexes is attributed to $d-d$ transitions. But there are compounds which have no d electrons but still have intense colours, e.g. permanganate (VII) ion, (intense purple, d^0), chromate (VI) ion (yellow, d^0), mercury (II) iodide (brick red d^{10}), bismuth (III) iodide (red, orange $d^{10}s^2$). The colours of these types of complexes are attributed partly to electron transfer from a ligand orbital to a metal orbital and vice versa with the absorption of light. Such electron- or charge-transfer processes are designated as $L \rightarrow M$ and $M \rightarrow L$ electron transfer respectively. The energy of charge-transfer transitions is generally higher than those of the $d-d$ transitions and the charge-transfer band generally appears in the ultraviolet or far ultraviolet region of the spectra. But if the metal is readily oxidisable and the ligand easily reducible and vice versa, the charge-transfer transitions may occur in the visible region. The charge-transfer spectra are very intense and mask the $d-d$ transitions e.g., $d-d$ transitions of metal iodide complexes are hard to observe since the iodide ion is readily oxidisable. The CT transitions in MnO_4^- and CrO_4^{2-} are attributed to the transfer of an electron from nonbonding orbital of an oxygen atom to manganese or chromium (i.e. $n \rightarrow \pi^*$) subsequently reducing the metals in the excited state. Alternatively the transition may occur with transfer of an electron from the π -bonding molecular orbital of oxygen to the molecule orbital which actually is the metal atomic orbital. In pyridine complex of iridium (III), the metal being easily oxidisable, the charge-transfer transition involves the transfer of an electron from the atomic orbital of iridium to an empty π^* anti-bonding orbital in pyridine. Charge transfer in gaseous sodium chloride takes place from the ion pair $\text{Na}^+ \text{Cl}^-$ to an excited state consisting of sodium and chloride atoms provided the Franck-Condon principle is obeyed, i.e. $r(\text{Na}^+ \text{Cl}^-) = r(\text{NaCl})$. Intra-ligand transitions such as $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ in metal complexes are affected by coordination and occur in UV region of the spectrum.

5.16.4 Ligand-Field Stabilisation Energy

In ML_6 octahedral complex, as a result of strong $L \rightarrow M$ sigma overlap, the energy of e_g level increases and hence Δ_o value also increases while due to $L \rightarrow M$ π -overlap, the energy of t_{2g} level increases but the Δ_o value decreases. The $M-L$ backbonding lowers the t_{2g} level but increases the Δ_o value. Thus, the net effect of these $M \rightarrow L$ and $L \rightarrow M$ interactions affects the Δ_o value and hence the stabilisation energies, called the ligand-field stabilisation energies (LFSE) as opposed the CFSE, e.g. CN^- and CO , being strong π -acceptor ligands favour strong $M \rightarrow L$ backbonding interaction due to which these ligands cause large splitting in the energy range of 3.72 eV ($= 30,000 \text{ cm}^{-1}$). On the other hand, the anionic ligands with lone pair of electrons such as Br^- , I^- called donors to the π -orbitals of metal, i.e. $L \rightarrow M$ π -interactions cause small splittings in the energy range of 1.24 eV ($= 10,000 \text{ cm}^{-1}$). Thus, the neutral ligands with lone pair of electrons, which have no π -bonding capacity, may cause intermediate range of splitting. According to the electrostatic model, this result is unexpected since the halogen anions I^- and Br^-

with their negative charge should give smaller splitting than a neutral ligand like NH_3 or H_2O . The answer to this discrepancy lies in the covalence effect. The lone pair of NH_3 or H_2O in the sp^3 hybrid orbital interacts with the empty metal hybrid orbital. In contrast, the filled p -orbitals on the halide ligand interact strongly with the empty d -orbitals of M , i.e. electric charge is transferred from ligand to metal. These types of $L \rightarrow M$ interactions give rise to charge transfer transitions. The charge-transfer from a ligand lowers the positive charge on the metal and reduces the D term in ' $10Dq$ '. For the same metal, the greater the reducing power of the ligand, e.g. $\text{I}^- > \text{Br}^- > \text{Cl}^-$, the lower will be the energy of the charge-transfer transition. Similarly, for the same L , the greater the oxidising power of the metal ion, the lower will be the energy of charge-transfer transition. Thus, for metal ions having same charge, the value of Δ_0 is affected by the nature of the ligand which controls the strength of the ligand field. On the basis of Δ_0 values, ligands are arranged in the form of a series called the spectrochemical series reported in Section 5.16.1. The order of σ -bond interaction of some typical ligands with metal ions based on spectral studies on octahedral ML_6 complexes is



The order of π -repulsion is:



5.16.5 Selection Rules for Transitions Between Energy States of Transition Metal Complexes

Before discussing the spectra of inorganic systems, it is nice to summarise the selection rules worked out quantummechanically in Section 5.2. The energy difference Δ_0 between the two separated groups of orbitals, i.e. e_g and t_{2g} , is identified with the $d-d$ electronic transitions in the transition-metal complexes. The $d-d$ electronic transitions in the complexes are either said to be allowed or forbidden according to the following selection rules.

(a) Spin or Multiplicity Selection Rule Electronic transition between states of different multiplicity are said to be multiplicity or spin forbidden, i.e. $\Delta S \neq 0$, is forbidden while between states of same multiplicity are said to be spin allowed, i.e. $\Delta S = 0$ is allowed. In other words, we can say that electronic transitions in which the spin of an electron does not change are multiplicity allowed while those in which it changes are forbidden.

(b) Laporte Parity Rule According to this rule, the only possible transition is between even and odd terms: a term is said to be even or odd depending on whether the sum of the azimuthal quantum numbers of all electrons in the atom is even or odd. Thus, the transition in which $\Delta l/\Delta L = 0$ are Laporte forbidden while for which $\Delta l/\Delta L = \pm 1$ are Laporte allowed, e.g. for Ca , $s^2 \rightarrow s^1 p^1$, $\Delta l/\Delta L = \pm 1$, the transition is allowed and $\epsilon_{\text{max}} = 5000-10000 \text{ lit mole}^{-1} \text{ cm}^{-1}$, while $d-d$ transitions in transition metals are forbidden since $\Delta l = 0$. However electronic spectra of very low intensity, i.e. $\epsilon_{\text{max}} = 5-10 \text{ lit mole}^{-1} \text{ cm}^{-1}$, are observed because of relaxation in the Laporte rule. Accordingly, transitions within a given group of p or d orbitals are Laporte forbidden if the molecule has a centre of symmetry. Thus, $d-d$ transitions in perfect octahedral complexes are forbidden and many complexes are colourless except the following.

(a) If the centre of symmetry is distorted due to mixing of d and p orbitals of the complex, then the transitions are no longer pure $d-d$ in character. The transitions actually occur between d levels with different amounts of p character. The intensity of transition is roughly proportional to the amount of mixing and $\epsilon_{\text{max}} = 20$ to $50 \text{ lit mole}^{-1} \text{ cm}^{-1}$, e.g. tetrahedral complexes, namely $[\text{MnBr}_4]^{2-}$ and unsymmetrically substituted octahedral complexes such as $[\text{Co}(\text{NH}_3)_5 \text{Cl}]^{2+}$, are both coloured.

(b) According to the Laporte rule, the complexes with perfect octahedral symmetry (O_h), i.e. centre of symmetry should be colourless, e.g. $[\text{Co}(\text{NH}_3)_6]^{3+}$ or $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, but the observations are contrary to the rule, i.e. these complexes are not colourless. In such cases due to the normal vibrations of the $M-L$ bond of the octahedral complex, some of the molecules lose their centre of symmetry and mixing of d and p orbitals occurs in the unsymmetrical configuration. Consequently, a very low transition with $\epsilon_{\text{max}} \sim 5$ to $25 \text{ lit mole}^{-1} \text{ cm}^{-1}$ is observed. Such transitions are said to be vibronically allowed and the effect is called *vibronic coupling*. In general, we can say that Laporte allowed transitions are very intense while Laporte forbidden transitions vary from weak intensity if the complex is noncentrosymmetric to very weak if it is centrosymmetric. The selection rules are summarised in Table 5.16.

Table 5.16 Summary of selection rules for transitions between energy states of transition metal complexes.

Laporte	Spin	Type of transition	$\epsilon_{\max}$ (lit mole ⁻¹ cm ⁻¹)	Example
Allowed	Allowed	Charge transfer	10,000	$[\text{TiCl}_6]^{3-}$
Partly allowed, some p - d mixing	Allowed	$d-d$	500	$[\text{CoBr}_4]^{2-}$ $[\text{CoCl}_4]^{2-}$
Forbidden	Allowed	$d-d$	8–10	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$; $[\text{V}(\text{H}_2\text{O})_6]^{3+}$
Partly allowed, some p - d mixing	Forbidden	$d-d$	4	$[\text{MnBr}_4]^{2-}$
Forbidden	Forbidden	$d-d$	0.02	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

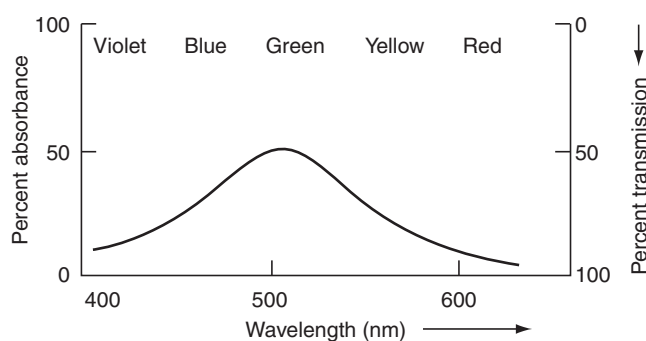
It is to be kept in mind that spin-allowed transitions are broad while spin-forbidden transitions are usually sharp. This is due to the fact that multiplicity allowed $t_{2g} \rightarrow e_g$ transitions give rise to an excited state in which $M-L$ distance is larger than in the ground state. Thus, according to Franck–Condon principle, a broad band is observed. This fact may provide an aid in the assignment of bands in the electronic spectra of complexes.

5.16.6 Bandwidths

The bandwidth of an absorption band due to $d-d$ transitions in the electronic absorption spectrum of transition metal complexes in solution phase not only broadens due to super imposition of vibrational and rotational levels but also due to the Jahn–Teller effect and spin-orbit coupling. Bandwidths have been found to be of the order of 1000–3000 cm⁻¹ but rarely narrower bands (width ~100 cm⁻¹) are observed.

5.17 ELECTRONIC ABSORPTION SPECTRA OF TRANSITION METAL COMPLEXES WITH $d^1, d^2, d^3, \dots d^9$ CONFIGURATIONS IN OCTAHEDRAL AND TETRAHEDRAL FIELDS

Most metal salts are colourless except those of transition elements. Colour variation not only takes place between elements, but also between oxidation states of the same elements and sometimes within oxidation states, e.g. anhydrous CuSO_4 is colourless while $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is light blue and $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ is dark blue. The origin of colour of transition metals and their compounds lies in their partially filled d -orbitals. The $d-d$ transition under the influence of light gives rise to an absorption band in the electronic absorption spectra of transition elements. For ions with more than one d electron, several transitions are possible giving rise to more than one absorption band. These bands fall in or near the visible region. The colour of a compound is seen provided the absorption takes place over a wide range of wavelengths and the colour which we see is determined by the colour or colours of white light which are transmitted, i.e. not absorbed by the compound, as shown in Fig. 5.29. Figure 5.29 shows

Fig. 5.29 Electronic absorption spectrum of Ti^{3+} ion in visible region.

that a single transition occurs with the absorption of the green component ($\lambda_{\text{max}} = 500 \text{ nm}$) of visible light and the colour transmitted is purple, i.e. violet-red.

Before describing the electronic spectra of transition metal ions with different electronic configurations, i.e. d^1 , d^2 , $d^3 \dots d^{10}$, it is nice to summarise ground terms for d^1 to d^{10} transition metal ions, the pattern of splitting of free electronic states under the tetra- and octahedral-fields and the terms arising for s , p and d electronic configurations in the form of Tables 5.17–5.19 respectively for ready reference. The deductions of the terms for free ions are not discussed here and the readers interested in these aspects can consult any textbook on general inorganic chemistry such as *A New Concise Inorganic Chemistry* by J D Lee:

Table 5.17 Spectroscopic ground terms for d^1 to d^{10} transition-metal ions.

Ion	Electronic Configuration d^n	Ground Terms	m_l	$\Sigma m_l = M_L$	S
			2 1 0 -1 -2		
Ti ³⁺	d^1	^2D		2	$\frac{1}{2}$
V ³⁺	d^2	^3F		3	1
Cr ³⁺	d^3	^4F		3	$1\frac{1}{2}$
Cr ²⁺	d^4	^5D		2	2
Mn ²⁺	d^5	^6S		0	$2\frac{1}{2}$
Fe ²⁺	$d^6(4)$	^5D		2	2
Co ²⁺	$d^7(3)$	^4F		3	$1\frac{1}{2}$
Ni ²⁺	$d^8(2)$	^3F		3	1
Cu ²⁺	$d^9(1)$	^2D		2	$\frac{1}{2}$

The quantities within parenthesis are the number of holes on the vacancies.

Table 5.18 Spectroscopic terms arising for s , p and d electronic configurations.

Electronic Configuration	Ground state terms	Excited state terms
s^1	^2S	
s^2	^1S	
p^1, p^5	^2P	
p^2, p^4	^3P	$^1S, ^1D$
p^3	^4S	$^2P, ^2D$
p^6	-	^1S
d^1, d^9	^2D	-
d^2, d^8	^3F	$^3P, ^1G, ^1D, ^1S.$
d^3, d^7	^4F	$^4P, ^2H, ^2G, ^2F, ^2D, ^2P.$
d^4, d^6	^5D	$^3H, ^3G, ^3F, ^3D, ^3P, ^1I, ^1G, ^1F, ^1D, ^1S.$
d^5	^6S	$^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G, ^2F, ^2D, ^2P, ^2S.$
d^{10}	^1S	-

When the subshell is more than half filled, the terms are worked out by considering the holes, i.e. the vacancies in the various orbitals, rather than the large number of electrons actually present, e.g. the number of holes in the electronic configurations p^4 , p^5 , d^8 and d^9 are 2, 1, 2 and 1 respectively.

Table 5.19(a) Transformation of spectroscopic terms of free ions with s^1 , p^1 , d^1 , f^1 and g^1 electronic configurations into Mulliken states under the octahedral and tetrahedral fields of ligands.

Electronic structure of free ion	Spectroscopic terms	Mulliken terms octahedral field	Tetrahedral field
s^1	S	A_{1g}	A_1
p^1	P	T_{1g}	T_1
d^1	D	$E_g + T_{2g}$	$E + T_2$
f^1	F	$A_{2g} + T_{1g} + T_{2g}$	$A_2 + T_1 + T_2$
g^1	G	$A_{1g} + E_g + T_{1g} + T_{2g}$	$A_1 + E + T_1 + T_2$

The singly degenerate s -orbital is referred to as a_{1g} , where 'a' indicates the value of degeneracy, i.e. $a = 1$. The triply degenerate set of ungerade p -orbitals is referred to as t_{1u} . The former being spherical and the latter directional along X , Y and Z -axes, are not splitted under the influence of tetrahedral or octahedral field. The splitting of d , f and g orbitals into a number of degenerate groups of orbitals under the influence of octahedral or tetrahedral field are denoted by small letters, e.g. the five $3d$ orbitals are subdivided into two groups: the high-energy group contains two e_g orbitals and the low-energy group contains three t_{2g} orbitals. The terms and symbols such as A_{1g} , A_1 , T_{1g} , T_1 , A_{2g} , A_2 , T_2 , etc., are due to Mulliken and originate in group theory. The subscript g is not written in terms of tetrahedral complexes since they lack centre of symmetry.

Table 5.19(b) Energy of the various Mulliken states corresponding to the d^1 , d^2 , d^3 d^9 , electronic configuration of transition-metal ions in octahedral and tetrahedral fields of the ligands.

ConFiguRation (Environ-ment)	Group state Spectroscopic terms	Mulliken states ${}^2T_{2g}/{}^5T_{2g}$	Energy(E)
$d^1(O)/d^6(O)$		${}^2E_g/{}^5E_g$	$+6Dq$
or	${}^2D/{}^5D$		
$d^3(T)/d^4(T)$		${}^2T_{2g}/{}^5T_{2g}$	$-4Dq$
$d^3(O)/d^4(O)$		${}^2T_{2g}/{}^5T_{2g}$	$+4Dq$
or	${}^2D/{}^5D$		
$d^1(T)/d^6(T)$		${}^2E_g/{}^5E_g$	$-6Dq$
$d^2(O)/d^7(O)$		${}^3A_{2g}(F)/{}^4A_{2g}(F)$	$+12Dq$
or	${}^3F/{}^4F$		
$d^8(T)/d^3(T)$		${}^3T_{1g}(P)/{}^4T_{1g}(P)$	
		${}^3T_{2g}(F)/{}^4T_{2g}(F)$	$+2Dq$
		${}^3T_{1g}(F)/{}^4T_{1g}(F)$	$-6Dq$
$d^8(O)/d^3(O)$		${}^3T_{1g}(P)/{}^4T_{1g}(P)$	
or	${}^3F/{}^4F$		
$d^2(T)/d^7(T)$		${}^3T_{1g}(F)/{}^4T_{1g}(F)$	$+6Dq$
		${}^3T_{2g}(F)/{}^4T_{2g}(F)$	$-2Dq$
		${}^3A_{2g}(F)/{}^4A_{2g}(F)$	$-12Dq$

For tetrahedral environment, the subscript g is ignored. The transition corresponding to $d^1(O)/d^6(O)$ is ${}^2T_{2g} \rightarrow {}^2E_g/{}^5T_{2g} \rightarrow {}^5E_g$.

The splitting of seven $4f^1$ degenerate orbitals of an ion in an octahedral crystal field is shown in Fig. 5.30. The sevenfold degenerate level splits up into triply degenerate t_{1g} level, triply degenerate t_{2g} level and a singly degenerate a_{2g} level. The t_{1g} level is stabilised by $-6Dq$ while the levels t_{2g} and a_{2g} are destabilised by $+2Dq$ and $+12Dq$ respectively relative to the energy level of seven degenerate orbitals.

d^1 -ion The most simple and interesting example of an ion with a d^1 electronic configuration is that of Ti^{3+} which is produced as follows. The electronic structure of titanium with an atomic number (Z) of 22 is $Ar. 3d^2.4s^2$

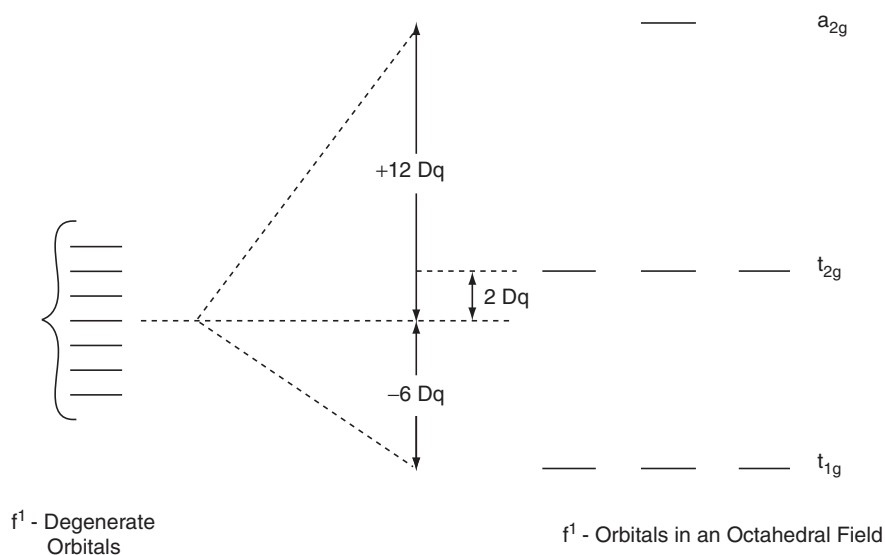


Fig. 5.30 Splitting of $4f^1$ degenerate orbitals under the influence of an octahedral field.

where Ar represents the inner shell structure. The Ti^{3+} ion with an electronic configuration of $\text{Ar } 3d^1$ results when three electrons are lost by the titanium atom, i.e. $\text{Ar } 3d^2 4s^2 \xrightarrow{-3e} \text{Ar } 3d^1$. This uncomplexed, Ti^{3+} ion has five degenerate $3d$ orbitals, i.e. $d^1: d_{xy}^1, d_{yz}^1, d_{zx}^1, d_{x^2-y^2}^1, d_{z^2}^1$, $d_{xy}^1 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$, $d_{xy}^1 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$, $d_{xy}^1 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$, $d_{xy}^1 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$ as shown in Fig. 5.31 (a). The probability of a single electron residing in each of the five degenerate orbitals is the same. When six ligands, say $6\text{H}_2\text{O}$, approach a Ti^{3+} ion, its five $3d$ degenerate orbitals split up into two degenerate groups of low and high energy under the influence of electrostatic octahedral field of the ligands. The low-energy group (called the ground state) consists of three t_{2g} (i.e. d_{xy} , d_{yz} , and d_{zx}) and is stabilised by $-4Dq$ while the high-energy group (called the excited state) consists of two e_g (i.e. $d_{x^2-y^2}$ and d_{z^2}) degenerate orbitals and is destabilised by $+6Dq$ with respect to the bary centre of the five degenerate orbitals. The single electron from the five $3d$ degenerate orbitals goes into the lower energy group, i.e. ground state as shown in Fig. 5.31(b). When such a system is exposed to light of energy $h\nu$ such that $\Delta_0 = h\nu$, the electron moves from the lower t_{2g} to the upper e_g state; the probability of residing the electron in both the d -orbitals is equal, [Fig. 5.31 (c)] through $d-d$ transition, i.e. $t_{2g} \rightarrow e_g$. The energy corresponding to this transition gives to an absorption band in the middle of the visible region having an absorption maximum around 500 nm [Fig. 5.29.]. The asymmetry in the band arises due to the splitting of the excited state because of Jahn–Teller distortion. The purple colour of the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion results

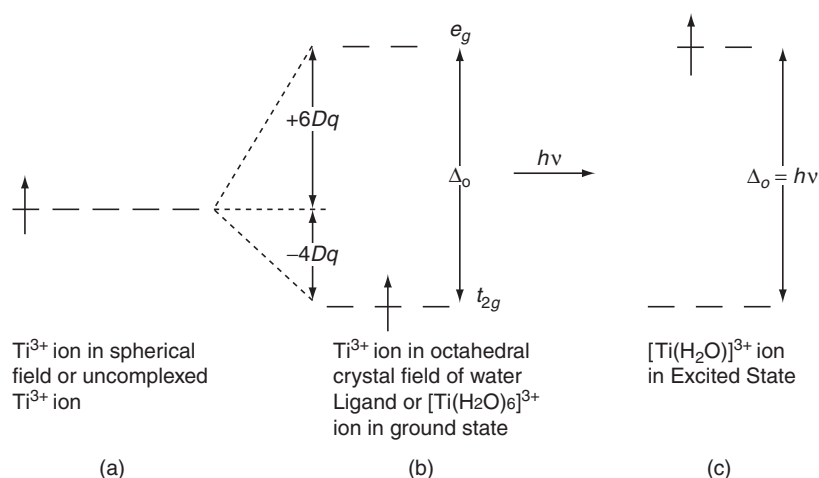


Fig. 5.31 Energy-level diagram illustrating the origin of electronic absorption spectrum of d^1 -ion in an octahedral field of a ligand.

because absorption of light by the system occurs in the blue, green and yellow regions while transmission takes place mainly in the red and violet regions of the spectrum.

The electronic absorption spectrum of an octahedral complex of d^1 -ion can also be expressed in terms of the ground-state spectroscopic term for a free d^1 -ion, and the Mulliken terms corresponding to it in an octahedral environment is as follows: The ground state spectroscopic term for a virgin ion with d^1 -configuration is ^2D . In an octahedral field of the ligand, the ^2D state splits up into the $^2T_{2g}$ and ^2E_g Mulliken states. The former originates from the triply degenerate set of t_{2g} orbitals, i.e. $t_{2g}^1: d_{xy}^1, d_{yz}^1, d_{zx}^1; d_{xy}^1, d_{yz}^1, d_{zx}^1$ and is stabilised by $-4Dq$, while the latter originates from the doubly degenerate set of e_g orbitals. The electronic configuration of ^2E_g is $e_g^1: d_{z^2}^1, d_{x^2-y^2}^1, d_{z^2}^1, d_{x^2-y^2}^1$ and is destabilised by $+6Dq$ by the octahedral field of the ligand. Accordingly, the lower-energy $^2T_{2g}$ state corresponds to the single electron residing in one of the t_{2g} orbitals and the upper-energy ^2E_g state corresponds to the single electron residing in one of the e_g orbitals. The energy-level diagram showing the ^2D ground state term and its splitting into Mulliken states under the influence of the octahedral field of the ligand is shown in Fig. 5.32. The slope of the T_{2g} line is $-4Dq$ and that of E_g line is $+6Dq$. The difference between the two slopes ΔE , is $10Dq$ or Δ_0 . The absorption of photons of light $h\nu$ by the system promotes the electron from the $^2T_{2g}$ state to the ^2E_g state provided $\Delta_0 = h\nu$. Consequently, a single absorption band at 20400 cm^{-1} results corresponding to the $^2T_{2g} \rightarrow ^2E_g$ transition in the absorption spectrum of aquo ion $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ with d^1 -configuration. Further, since $E(^2E_g) - E(^2T_{2g}) = 6Dq - (-4Dq) = 10Dq$, therefore $10Dq = 20400\text{ cm}^{-1}$. Moreover, Fig. 5.32 reveals that the magnitude of splitting and hence the energy of $d-d$ transition depends on the nature of the ligand and grows with the strength of the ligand and the same has been observed indeed experimentally. For example, the electronic absorption spectra of some octahedral complexes of Ti with d^1 -configuration indicated below in the tabular form show that the magnitude of splitting, i.e. Δ_0 , fits into the spectrochemical series, i.e. $\text{CN}^- > \text{H}_2\text{O} > \text{F}^- > \text{Cl}^-$.

The energy-level diagrams for the electronic absorption spectrum of d^1 ion in a tetrahedral field of a ligand have been shown in Figs 5.33 and 5.34. In a tetrahedral field, the two splitted groups of five $3d$ degenerate orbitals, i.e. $d^1: d_{xy}^1, d_{yz}^1, d_{zx}^1, d_{x^2-y^2}^1, d_{z^2}^1, d_{xy}^1, d_{yz}^1, d_{zx}^1, d_{x^2-y^2}^1, d_{z^2}^1, d_{xy}^1, d_{yz}^1, d_{zx}^1, d_{x^2-y^2}^1, d_{z^2}^1$ (the corresponding spectroscopic term is ^2D) are inverse of that in an octahedral field of the ligand. The low-energy

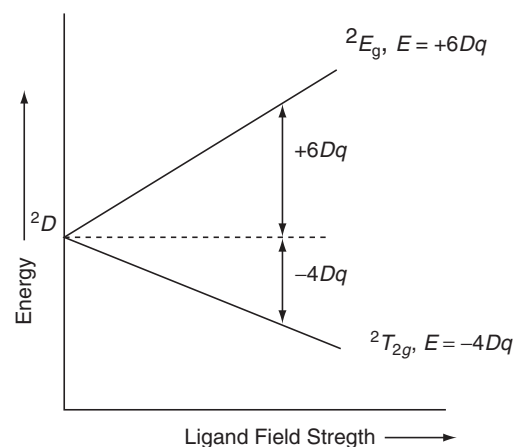


Fig. 5.32 Energy-level diagram for the spitting of ^2D spectroscopic term of an ion with d^1 -configuration into Mulliken terms in an octahedral field of a ligand.

Ion	Absorption maxima (in cm^{-1})
$[\text{TiCl}_6]^{3-}$	13000
$[\text{TiF}_6]^{3-}$	18900
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	20300
$[\text{Ti}(\text{CN})_6]^{3+}$	22300

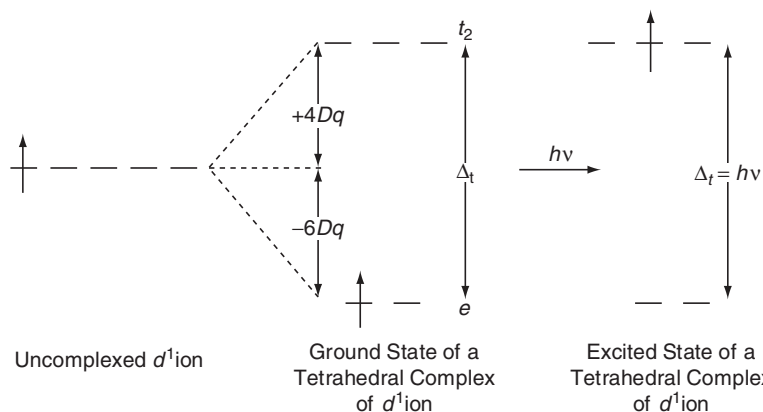


Fig. 5.33 Energy-level diagram illustrating the origin of electronic absorption spectrum of d^1 ion in a tetrahedral field of a ligand.

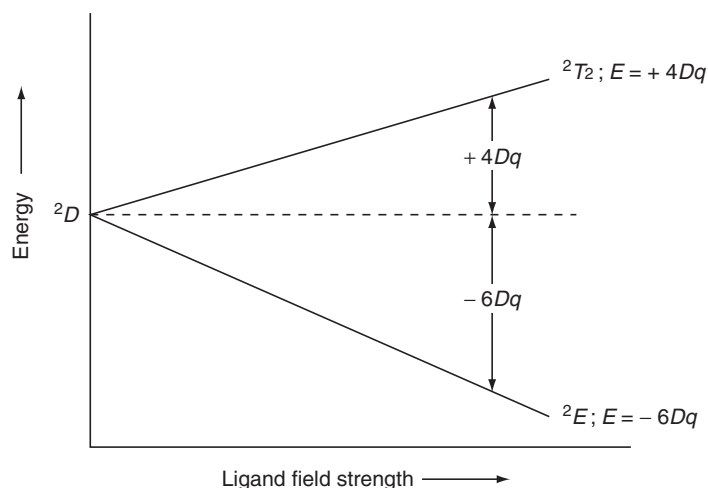
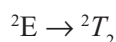


Fig. 5.34 Energy-level diagram for the splitting of ^2D spectroscopic term of an ion with d^1 configuration into Mulliken terms in a tetrahedral field of a ligand.

group of two degenerate e orbitals (i.e. $e^1: d_{z^2}^1, d_{x^2-y^2}^1, d_{z^2}^1, d_{x^2-y^2}^1$; the Mulliken term corresponding to this set is ^2E) is stabilised by $-6Dq$ while the high-energy group of three t_2 orbitals (i.e. $t_2^1: d_{xy}^1, d_{yz}^1, d_{zx}^1$;.....) the Mulliken term corresponding to this set is $^2T_2$) is destabilised by $+4Dq$ with respect to the bary centre of the five $3d$ degenerate orbitals by the tetrahedral field of the ligand. Accordingly, the low-energy group of e orbitals constitutes the ground state and high-energy group of t orbitals constitutes the excited state of the system. Thus, when such a system is exposed to light of energy $h\nu$ such that $\Delta_t = h\nu$, the electron jumps from ground to the excited state giving rise to an absorption band in the spectrum by $d-d$ transition.



or



Further, Fig. 5.34 reveals that just like an octahedral complex of d^1 ion, the magnitude of splitting Δ_t of a d^1 ion in a tetrahedral field of the ligand depends on the nature of the ligand and increases as the strength of the ligand field increases.

It is to be noted that for tetrahedral complexes, the $d-d$ absorption bands are considerably more intense than in octahedral complexes. The reason being that tetrahedral complexes lack centre of symmetry, while the symmetry in octahedral complexes is slightly distorted because of the vibronic effect. In other words, we can say that in tetrahedral complexes the $d-d$ transitions are Laporte-forbidden due to the absence of centre of symmetry while Laporte-allowed in octahedral complexes.

(a) d^9 ion The common example of an ion with, d^9 electronic configuration is that of Cu^{2+} . The electronic structure of copper with atomic number (Z) of 29 is $\text{Ar } 3d^{10}4s^1$. The Cu^{2+} ion with an electronic configuration of $\text{Ar } 3d^9$ results when two electrons are removed from the copper atom, i.e. $\text{Ar } 3d^{10}4s^1 \xrightarrow{-2e} \text{Ar } 3d^9$. The free ion having a d^9 electronic configuration has five $3d$ degenerate orbitals (i.e. $d^9: d_{xy}^1 d_{yz}^2 d_{zx}^2 d_{z^2}^2 d_{x^2-y^2}^2$; $d_{xy}^2 d_{yz}^1 d_{zx}^2 d_{z^2}^2 d_{x^2-y^2}^2$; $d_{xy}^2 d_{yz}^2 d_{zx}^1 d_{z^2}^2 d_{x^2-y^2}^2$; $d_{xy}^2 d_{yz}^2 d_{zx}^2 d_{z^2}^1 d_{x^2-y^2}^2$; the spectroscopic term corresponding to this set of d -orbitals is ^2D , Figs 5.35(a). and 5.36). On complexing with six ligands, $6\text{H}_2\text{O}$ for example, the five $3d$ degenerate orbitals split up into two degenerate sets, the low-energy and high-energy sets under the influence of the octahedral field of the ligand. The low-energy set consists of three t_{2g} , while the high-energy set consists of two e_g orbitals. The ground state is stabilised by $-6Dq$ and represents an electronic configuration $t_{2g}^6 e_g^3: t_{2g}^6 d_{x^2-y^2}^2 d_{z^2}^1$, $t_{2g}^6 d_{x^2-y^2}^1 d_{z^2}^2$; the Mulliken term corresponding to this configuration is ^2E_g , while the excited state is destabilised by $+4Dq$ with an electronic configuration $t_{2g}^5 e_g^4: d_{xy}^1 d_{yz}^2 d_{zx}^2 e_g^4$, $t_{2g}^5 e_g^4: d_{xy}^2 d_{yz}^1 d_{zx}^2 e_g^4$, $d_{xy}^2 d_{yz}^2 d_{zx}^1 e_g^4$; the Mulliken state corresponding to this configuration is $^2T_{2g}$. The single positive hole (o) resides in one of the two e_g orbitals as shown in Figs 5.35(b) or in ^2E_g level; Fig. 5.36. On absorption of light of photon $h\nu$ such that $\Delta_0 = h\nu$, the single hole from the e_g orbitals of ground state (or from the ^2E_g level) crosses over to the t_{2g} orbitals by a $d-d$ transition

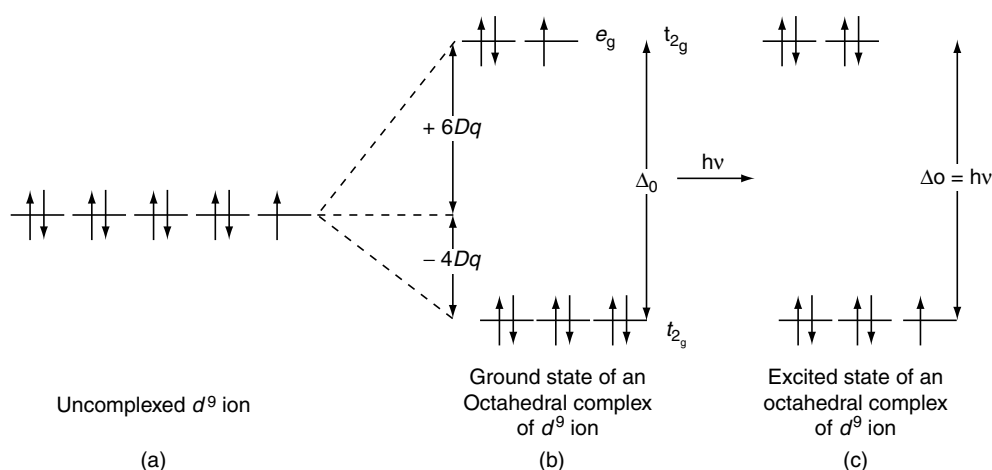


Fig. 5.35 Figure illustrating the origin of $d-d$ transition in d^9 -ion in an octahedral field of the ligand.

(or to the ${}^2T_{2g}$ level); Figs 5.35(c) and 5.36. The energy corresponding to this $d-d$ transition, i.e. $t_{2g} \rightarrow e_g$ or $t_{2g}^6 e_g^3 [\equiv {}^2E_g] \rightarrow t_{2g}^5 e_g^4 [\equiv {}^2T_{2g}]$ will give rise to an absorption band in the electronic absorption spectrum of d^9 ion in an octahedral field and the same has been observed indeed as an asymmetric band around 794 nm in the spectrum of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion. The asymmetry in the band has been attributed to Jahn–Teller distortion. The pale blue colour of aquo ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ results because absorption of white light occurs in the red region while a transmission occurs mainly in the blue region of the spectrum. Again, it is evident from Fig. 5.36, that alike d^1 octahedral and tetrahedral complexes the magnitude of splitting Δ_0 between two sets of orbitals in d^9 octahedral complexes depends on the strength of the ligand and increases as the strength of the ligand increases.

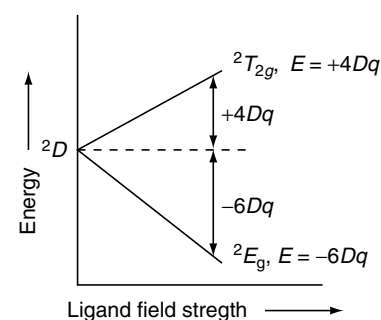


Fig. 5.36 Energy-level diagram of d^9 -ion in an octahedral field of a ligand in terms of ${}^2D$ spectroscopic term and the Mulliken terms corresponding to it.

In tetrahedral complexes of a d^9 ion, the energy-level diagrams are the inverse of that of a d^9 ion in an octahedral field of the ligand [Figs. 5.37 and 5.36]. The spectroscopic term corresponding to the five $3d$ degenerate orbitals for free d^9 -ion is ${}^2D$. The ground state of the complex can be written as $e^4 t_2^5 : e^4 d_{xy}^1 d_{yz}^2 d_{zx}^2, e^4 d_{xy}^2 d_{yz}^1 d_{zx}^2, e^4 d_{xy}^2 d_{yz}^2 d_{zx}^1$; the Mulliken state corresponding to this configuration is ${}^2T_2$ while the excited state can be written as $e^3 t_2^6 : e^3 d_{xy}^2 d_{yz}^2 d_{zx}^2, e^3 d_{xy}^2 d_{yz}^2 d_{zx}^2, e^3 d_{xy}^2 d_{yz}^2 d_{zx}^2$; the Mulliken state corresponding to this configuration is ${}^2E$. In this case the absorption of light of photon $h\nu$ such that $\Delta_t = h\nu$, causes the single electron to move from e [Fig. 5.37(b)] to t_2 level [Fig. 5.37(c)]. Accordingly, the $e \rightarrow t_2$ or $e^4 t_2^5 [\equiv {}^2T_2] \rightarrow e^3 t_2^6 [\equiv {}^2E]$ transition will result in a single band in the electronic absorption spectrum of d^9 -ion in a tetrahedral field of the ligand and the same has been observed indeed in the spectrum of cupric tetra-ammine, i.e. $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and that of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$. Thus the intense blue

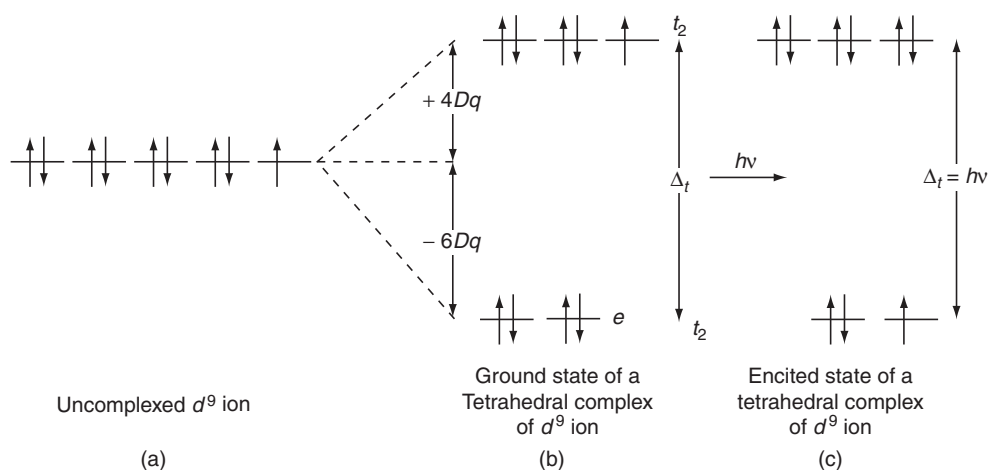


Fig. 5.37 Energy-level diagram illustrating the origin of electronic absorption band due to $d-d$ transition in d^9 -tetrahedral complexes.

colour of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is due to the single absorption band of Cu^{2+} falling in the red end of the spectrum, while the pale blue colour of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ is due to the absorption band in the infrared with only a tail in the red end of the spectrum. The blue colour of the solid salt of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is due to the absorption band around 12000 cm^{-1} . The Cu^{2+} ion in the salt has octahedral environment of oxygen atoms. On the other hand, in anhydrous copper sulphate with a weak ligand field of SO_4^{2-} , the absorption band appears in the infrared and thus salt is colourless.

(b) d^4 ion Cr^{2+} and Mn^{3+} ions have a d^4 -configuration. Cr^{2+} with an electronic structure of $\text{Ar}3d^4$ is generated from Cr atom having an atomic number (Z) 24 and electronic structure $\text{Ar}3d^5 4s^1$ by the removal of two electrons from it, i.e. $\text{Ar}3d^5 4s^1 \xrightarrow{-2e} \text{Ar}3d^4$, while three electrons are removed from the Mn atom with an atomic number (Z) 25 and electronic structure $\text{Ar} 3d^5 4s^2$ to form Mn^{3+} with an electronic structure $\text{Ar}3d^4$, i.e. $\text{Ar}3d^5 4s^2 \xrightarrow{-3e} \text{Ar}3d^4$. The energy-level diagrams for the absorption spectrum of high-spin d^4 octahedral complexes is qualitatively analogous to that d^9 ion in the octahedral field as shown in Figs 5.35 and 5.36. In Fig. 5.36, the multiplicity 2 is to be replaced by 5. The five degenerate 3d orbitals of d^4 ion are $d^4: d_{xy}^1 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$; $d_{xy}^1 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$; $d_{xy}^1 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$; $d_{xy}^1 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$; $d_{xy}^1 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$. The ground state spectroscopic term corresponding to this configuration is ^5D [Figs 5.38(a) and 5.36]. In an octahedral field of the ligand, the degenerate orbitals split up into two degenerate sets: one of high energy and the other low energy. The low-energy set consists of three degenerate t_{2g} orbitals while the high-energy set consists of two e_g orbitals; the former is stabilized by $-4Dq$ in contrast to latter which is destabilised by $+6Dq$ by the octahedral field of the ligand. Accordingly, the low-energy set of orbitals constitutes the ground state which is represented as $t_{2g}^3 e_g^1: t_{2g}^3 d_{x^2-y^2}^1 d_{z^2}^1, t_{2g}^3 d_{x^2-y^2}^1 d_{z^2}^1$; the Mulliken term corresponding to this configuration is ^5E_g (Fig. 5.38b and 5.36 and the high-energy set constitutes the excited state which is represented as $t_{2g}^2 e_g^2: d_{xy}^1 d_{yz}^1 d_{zx}^1 e_g^2; d_{xy}^1 d_{yz}^1 d_{zx}^1 e_g^2; d_{xy}^1 d_{yz}^1 d_{zx}^1 e_g^2$; the Mulliken term corresponding to this configuration is $^5T_{2g}$ [Figs. 5.38 (c) and 5.36]. In Fig. 5.36, the multiplicity 2 is to be replaced by 5. Thus the absorption band will result due to the crossover of one hole from the e_g level to the t_{2g} level through $d-d$ transition provided $\Delta_0 = h\nu$, i.e. $e_g \rightarrow t_{2g}$ or $t_{2g}^3 e_g^1 [^5E_g] \rightarrow t_{2g}^2 e_g^2 [^5T_{2g}]$.

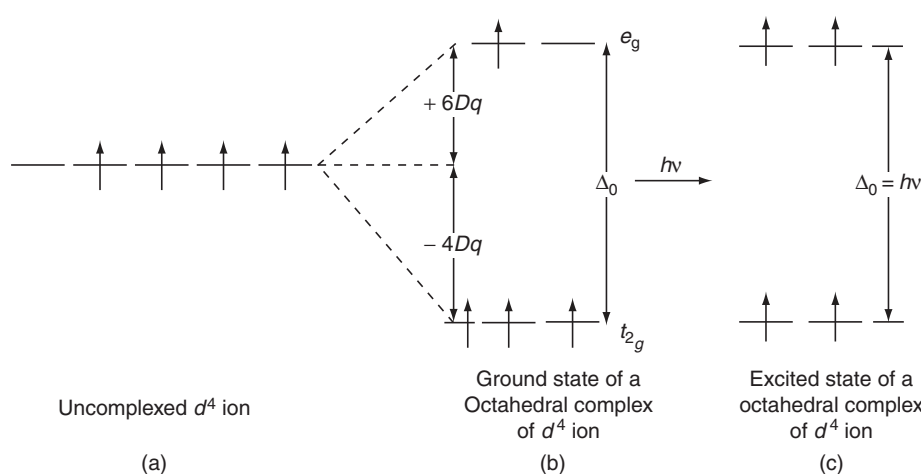


Fig. 5.38 Energy-level diagram illustrating the origin of $d-d$ transition in octahedral complexes with d^4 -configuration.

As examples, aquo ion $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ shows an absorption band at about 13900 cm^{-1} ($= 719 \text{ nm}$). The absorption maximum falls mainly in the red region and transmission is maximum in the violet region of the spectrum. This is sufficient to impart violet colour to the aquo ion of Cr^{2+} . In case of $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$, absorption band with maximum at 21000 cm^{-1} ($\approx 476 \text{ nm}$) appears in the green region of the spectrum. Thus, the pink colour of aquo ion, i.e. $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$, results due to the transmission of white light occurring mainly in the orange and red regions of the spectrum.

The treatment for the electronic absorption spectrum of d^4 ion in a tetrahedral field of a ligand is left an exercise for the students. As a hint, the energy-level diagrams of d^4 high spin tetrahedral complexes are the inverse of that of d^4 octahedral complexes but qualitatively similar to that of d^9 octahedral complexes. The $d-d$ transition is because of the transfer of a single hole from t_2 to e level under the influence of light of photon $h\nu$ provided $\Delta_t = h\nu$. The ground state (stabilised by $-4Dq$) of the system is represented as $e^2 t^2: e^2 d_{xy}^1 d_{yz}^1 d_{zx}^1, e^2 d_{xy}^1 d_{yz}^1 d_{zx}^1$,

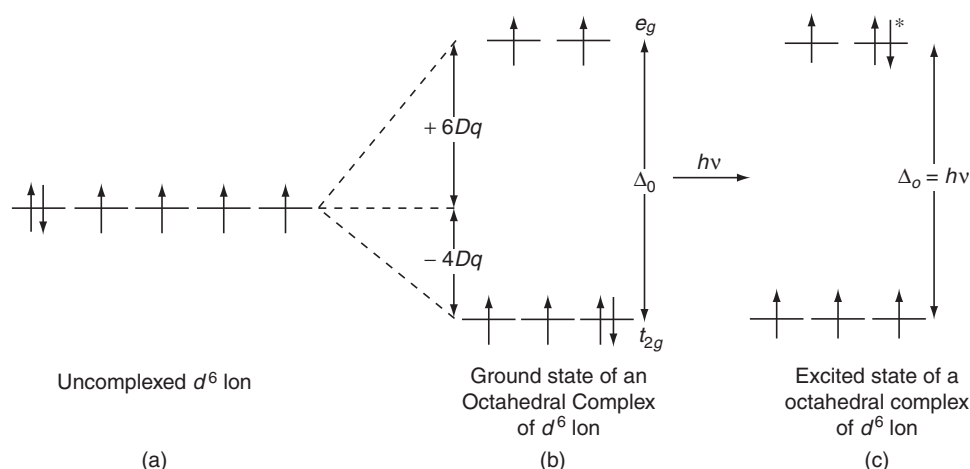


Fig. 5.39 Energy-level diagram depicting the origin of $d-d$ transition in octahedral complexes with d^6 electronic configuration.

$e^2 d_{xy}^1 d_{yz}^1 d_{zx}^1$; the Mulliken term corresponding to it is ${}^5T_2$ and the excited state (destabilised by $+6Dq$) is represented as $e^1 t^3: e^1 d_{xy}^1, d_{yz}^1, d_{zx}^1; e^1 d_{xy}^1 d_{yz}^1 d_{zx}^1; e^1 d_{xy}^1 d_{yz}^1 d_{zx}^1, d_{xy}^1 d_{yz}^1 d_{zx}^1$, the Mulliken term corresponding to this configuration is ${}^5E$.

(c) d^6 ion The common examples of ions with a d^6 electronic configuration are Fe^{2+} and Co^{3+} . The electronic structure of the Fe atom with an atomic number (Z) of 26 is $\text{Ar } 3d^6 4s^2$ and that of Co having an atomic number 27 is $\text{Ar } 3d^7 4s^2$. Fe^{2+} results when two electrons are removed from Fe atom, i.e. $\text{Ar } 3d^6 4s^2 \xrightarrow{-2e} \text{Ar } 3d^6$ while Co^{3+} results when three electrons are expelled from the Co atom, i.e. $\text{Ar } 3d^7 4s^2 \xrightarrow{-3e} \text{Ar } 3d^6$. The energy-level diagrams illustrating the origin of absorption spectrum of d^6 ion in an octahedral field of a ligand are shown in Figs 5.39 and 5.32. In Fig. 5.32, multiplicity 2 is to be replaced by 5.

In an octahedral field of the ligand, the five degenerate $3d$ orbitals of a d^6 ion, i.e. $d^6: d_{xy}^2 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$, $d_{xy}^1 d_{yz}^2 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$, $d_{xy}^1 d_{yz}^1 d_{zx}^2 d_{x^2-y^2}^1 d_{z^2}^1$, $d_{xy}^1 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^2 d_{z^2}^1$, the ground-state spectroscopic term corresponding to this configuration is ${}^5D$. [Fig. 5.39(a)], split into the low, i.e. t_{2g} and high, i.e. e_g energy degenerate groups. The former group is stabilised by $-4Dq$ by the octahedral field of the ligand and represents the ground state of the system which is written as, $t_{2g}^4 e_g^2: d_{xy}^2 d_{yz}^1 d_{zx}^1 e_g^2, d_{xy}^1 d_{yz}^2 d_{zx}^1 e_g^2, d_{xy}^1 d_{yz}^1 d_{zx}^2 e_g^2$, the Mulliken term corresponding to it is ${}^5T_{2g}$ while the latter group is destabilised by $+6Dq$ and represents the excited state which is written as $t_{2g}^3 e_g^3: t_{2g}^3 d_{x^2-y^2}^1 d_{z^2}^2; t_{2g}^3 d_{x^2-y^2}^2 d_{z^2}^1$; the Mulliken term corresponding to this configuration is ${}^5E_g$. [Figs 5.39(b) and 5.32]. On absorption of light of photon $h\nu$ such that $\Delta_0 = h\nu$, only the paired electron from the $t_{2g}[{}^5T_{2g}]$ state which has opposite spin to all the other electrons moves to the $e_g[{}^5E_g]$ state through $d-d$ transition [Figs 5.39(c) and 5.32]. This $d-d$ transition, i.e. $t_{2g} \rightarrow e_g$ or $t_{2g}^4 e_g^2[{}^5T_{2g}] \rightarrow t_{2g}^3 e_g^3[{}^5E_g]$, gives to an absorption band in the electronic absorption spectrum of an octahedral complex with d^6 electronic structure. Other transitions that involve inversion of spins are forbidden and hence may give rise to weak bands in the spectrum. The arguments pertaining to Fig. 5.32 hold good for octahedral complex of d^6 ion also, i.e. the magnitude of splitting of five degenerate orbitals into two sets of orbitals depend on the nature of the ligand and it increases as the strength of the ligand increases.

As an example, the absorption spectrum of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ in aqueous solution shows an asymmetric absorption band with a maximum at $10,400 \text{ cm}^{-1}$ ($= 962 \text{ nm}$) that falls into the infrared with only its tail in the red region of the spectrum. This tail in the red region is responsible for the pale green colour of the aquo ion $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$. The asymmetry in the absorption band in this case is due to splitting of the energy level ${}^5E_g$ into two non degenerate energy levels because of Jahn–Teller effect. The example of a low-spin octahedral complex of the Fe^{2+} is $[\text{Fe}(\text{CN})_6]^{4-}$ i.e. the ferrocyanide ion. The examples of high-spin and low-spin octahedral complexes of Co^{3+} are $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ with $\Delta_0 = 23000 \text{ cm}^{-1}$, $[\text{Co}(\text{CN})_6]^{3-}$ respectively.

The energy-level diagrams of d^6 high-spin tetrahedral complexes are the inverse of that of d^6 -octahedral complexes. The ground state is represented as $e^3 t^3: d_{x^2-y^2}^1 d_{z^2}^2 t^3; d_{x^2-y^2}^2 d_{z^2}^1 t^3$; the Mulliken term corresponding to it is ${}^5E$ and is stabilised by $-6Dq$ while the excited state is represented as $e^2 t^4: e^2 d_{xy}^2 d_{yz}^1 d_{zx}^1; e^2 d_{xy}^1 d_{yz}^2 d_{zx}^1; e^2 d_{xy}^1 d_{yz}^1 d_{zx}^2$; the Mulliken term ${}^5T_2$ originates from this configuration is destabilised by $+4Dq$ by the tetrahedral field of the ligand. The absorption band in the spectrum results from the transfer of only one electron without any change of spin

from e level to t_2 level through $d-d$ transition, i.e. $e \rightarrow t_2$ or $e^3 t_2^3 [\equiv {}^5E] \rightarrow e^2 t_2^4 [\equiv {}^5T_2]$. As an example, $[\text{FeCl}_4]^{2-}$ in aqueous solution shows a crystal field broad absorption band around 4000 cm^{-1} in near IR region.

Finally, (i) the effect of strength of octahedral and tetrahedral ligand fields on the splitting of five degenerate $3d$ -orbitals in ions with d^1 , d^4 , d^6 , and d^9 , electronic configurations and (ii) the allowed $d-d$ transitions responsible for the single absorption band in the spectra of the high-spin octahedral and tetrahedral transition metal complexes have been summarised by L E Orgel in a qualitative way in the form of a diagram known as the *Orgel diagram* [Fig. 5.40]. The right half of the diagram is applicable to octahedral d^1 , d^6 as well as to tetrahedral d^4 , d^9 high-spin complexes. The spectra of these complexes show only one band due to a $d-d$ transition which, is assigned as $T_{2g} \rightarrow E_g$ for d^1 , d^6 octahedral and $E \rightarrow T_2$ for d^4 , d^9 tetrahedral complexes. The left half of the diagram describes the spectra of d^1 , d^6 tetrahedral and of d^4 , d^9 octahedral complexes. The spectra of these complexes also exhibit only one band due to $d-d$ transition which is assigned as $E \rightarrow T_2$ for d^1 , d^6 , tetrahedral and $E_g \rightarrow T_{2g}$ for d^4 , d^9 octahedral complexes.

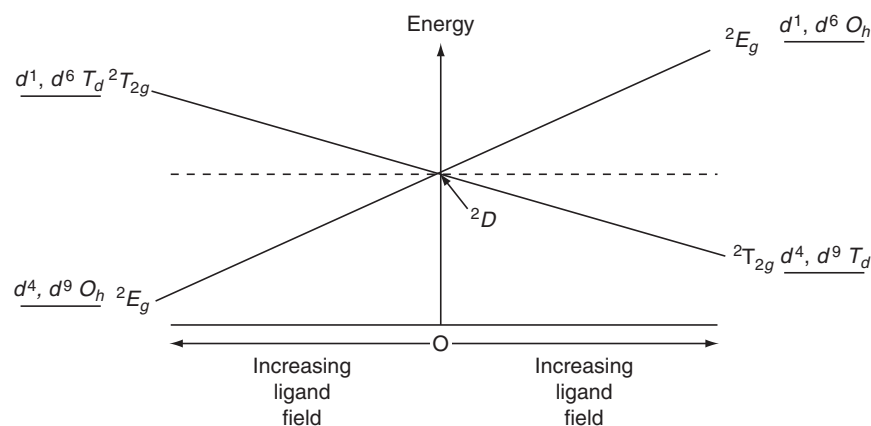


Fig. 5.40 Orgel combined energy-level diagram for ions with d^1 , d^6 , d^4 , d^9 electronic configurations in an octahedral (O_h) and a tetrahedral (T_d) fields of a ligand. Subscript g is omitted in T_d cases.

The Orgel energy-level diagram for d^2 -, d^3 -, d^7 -, and d^8 -ions in an octahedral and a tetrahedral environment of a ligand is shown in Fig. 5.41. States between ${}^3P$ and ${}^3F$ are not indicated since they have different multiplicity. Thus, transitions to these states are spin forbidden and usually not observed. The two T_{1g} states, i.e. $T_{1g}(P)$ and ${}^3T_{1g}(F)$ are slightly curved lines because they have the same symmetry and they interact with each other. This inter-electronic repulsion lowers the energy of the lower state and increases the energy of the higher state. The effect is much more pronounced on the left of the diagram since both the states are close in energy. In the absence of isoelectronic repulsions, the energy states would be linear and cross each other and at the cross point, the two electrons in one atom may have the same symmetry and energy. But according to noncrossing rule, two states of the same symmetry can't cross each other. Remember that in case of d^7-O_h and d^8-T_d complexes, the transition lines should be drawn to the left-hand side of the cross point of ${}^3A_{2g}(F)$ and ${}^3T_{1g}(P)$ lines. This will give rise to

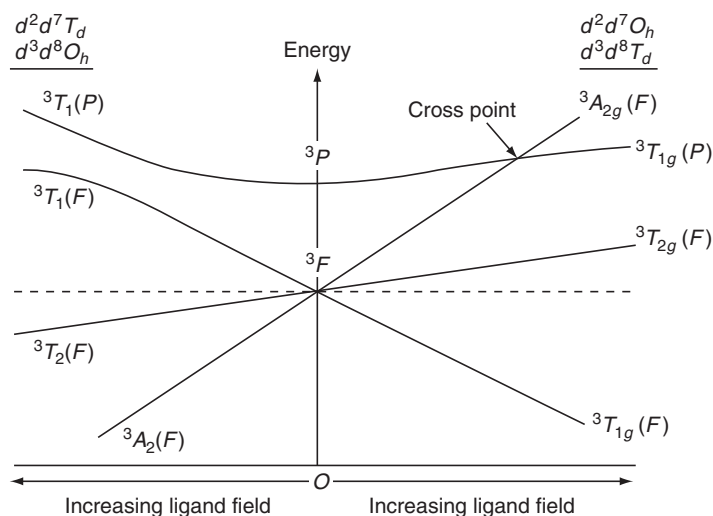


Fig. 5.41 Orgel energy-level diagram for d^2 , d^3 , d^7 , and d^8 octahedral and tetrahedral complexes. The suffix g is omitted in tetrahedral cases. For d^3 and d^8 systems, the spectroscopic terms are ${}^4F$ and ${}^4P$ all the Mulliken terms have a multiplicity of four.

${}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$, and ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$, transitions. For d^2-O_h and d^3-T_d complexes, the transition lines are drawn to the right-hand side of the cross point. Accordingly, the following transitions will result: ${}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$, ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$. If this sounds like gibberish, do not worry, you will see some examples.

(d) d^2 ion The simplest examples of a d^2 ion is V^{3+} . It is formed when three electrons are removed from the vanadium atom with an atomic number (Z) of 23, i.e. $Ar\ 3d^34s^2 \xrightarrow{-3e} Ar\ 3d^2$. The energy-level diagram showing the origin of absorption spectrum of d^2 -ion in an octahedral field of a ligand, the five degenerate $3d$ orbitals of a bare ion [Fig. 5.42 (a)] split up into three low energy t_{2g} and two high-energy e_g orbitals. Two electrons occupy two of the three t_{2g} orbitals. [Fig. 5.42(b)] On absorption of light of photon $h\nu$ such that $h\nu = \Delta_0$, the electrons from t_{2g} orbitals cross over to e_g orbitals as shown in Fig. 5.42(c). The electrons in d_{xz} or d_{yz} orbitals require less energy to move to the d_{z^2} orbital as compared to the $d_{x^2-y^2}$ orbital. This discrepancy arises because the former transition, i.e. d_{xz} or $d_{yz} \rightarrow d_{z^2}$ gives a $d_{xy}^1d_{z^2}^1$ arrangement in which the electron cloud of the two electrons is

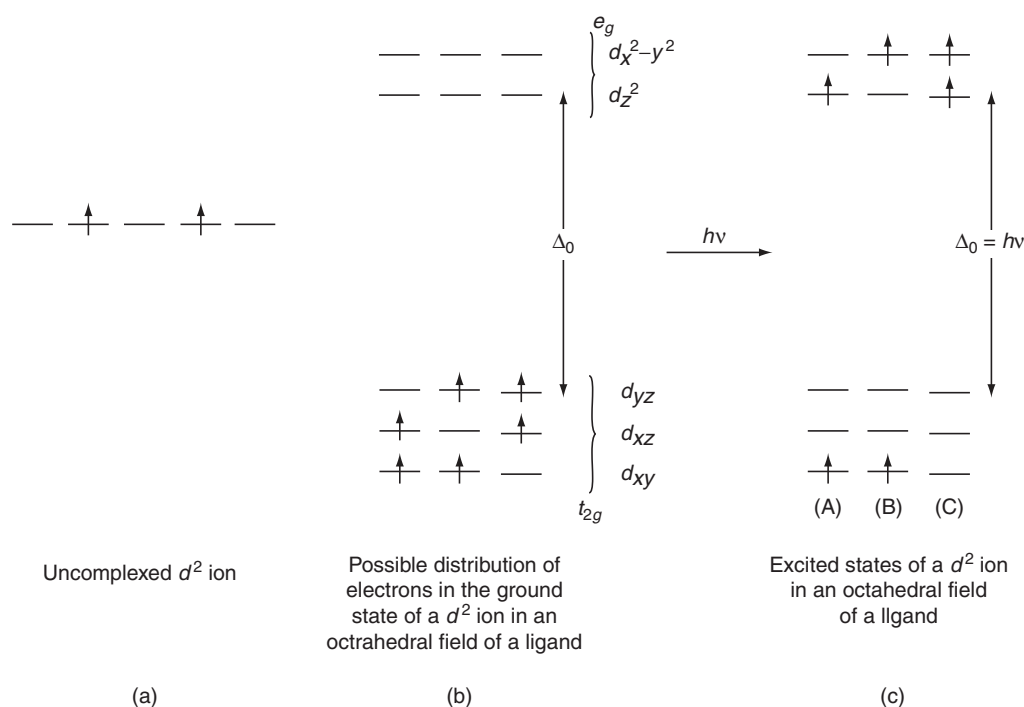


Fig. 5.42 Schematic diagram illustrating the origin of $d-d$ transitions in octahedral complexes of an ion with d^2 -configuration.

uniformly spread in the X, Y, Z directions. Such a uniform spread of electron density reduces the interelectronic repulsion compared to that of the $d_{xy}^1d_{x^2-y^2}^1$ arrangement where the electrons are confined only in the (XY) plane. Thus the two permissible $d-d$ transitions arising due to the transfer of an electron from t_{2g} orbitals to e_g orbitals are: $d_{xz}/d_{yz} \rightarrow d_{z^2}$ [Fig. 5.42(c), A] and $d_{xy}/d_{yz} \rightarrow d_{x^2-y^2}$ [Fig. 5.42(c), B]. The third allowed $d-d$ transition, i.e. $d_{xy}d_{yz}/d_{xz}d_{yz}/d_{yz}d_{xy} \rightarrow d_{z^2}d_{x^2-y^2}$ results because of the simultaneous promotion of both the electrons from t_{2g} orbitals to e_g orbitals [Fig. 5.42(c), C]. The other possible transitions involving the reversal of spin of one of the electrons such as $d_{xy}(\uparrow)d_{xz}(\uparrow) \rightarrow d_{z^2}(\downarrow)d_{x^2-y^2}(\uparrow)$; $d_{yz}(\uparrow)d_{xy}(\uparrow) \rightarrow d_{z^2}(\uparrow)d_{x^2-y^2}(\downarrow)$ are multiplicity forbidden. Such transitions may give rise to very weak bands in the spectrum. Thus only three absorption bands, corresponding to $d_{xz}/d_{yz} \rightarrow d_{z^2}$, $d_{yz}/d_{xz} \rightarrow d_{z^2}$ and $d_{xy}d_{xz} \rightarrow d_{x^2-y^2}d_{z^2}$ transitions are expected in the electronic absorption spectrum of a d^2 -ion in an octahedral field of the ligand.

The absorption spectrum of octahedral complexes of an ion with d^2 configuration can also be described by spectroscopic terms of a bare d^2 -ion and their splitting into Mulliken terms in an octahedral field of a ligand.

The spectroscopic states of a bare ion with d^2 -electronic configuration arise because of interelectronic repulsions between d electrons and are

Ground state: ${}^3F$

Excited states: ${}^3P, {}^1G, {}^1D, {}^1S$.

The transitions from the ^3F ground state to the ^1G , ^1D or ^1S states being multiplicity forbidden, will be very weak. The only important allowed transition is $^3F \rightarrow ^3P$. The energy of the ^3F state for Ti^{2+} , V^{3+} and Cr^{3+} free ions is zero and that of the ^3P state for the respective ions are 10600, 13250, and 15700 cm^{-1} .

In an octahedral field of the ligand, the ^3F state splits up into the triply degenerate $^3T_{1g}(F)$; (the origin of this state is the orbital set $t_{2g}^2 : d_{xy}^1 d_{yz}^1 d_{zx}^1, d_{xy}^1 d_{yz}^1 d_{zx}^1, d_{xy}^1 d_{yz}^1 d_{zx}^1$, i.e. the ground state of the system), triply degenerate $^3T_{2g}(F)$ (the origin of the state is $t_{2g}^1 e_g^1 : d_{xy}^1 d_{z^2}^1, d_{xz}^1 d_{x^2-y^2}^1, d_{yz}^1 d_{x^2-y^2}^1$) and singly degenerate $^3A_{2g}(F)$; (the arrangement $e_g^2 : d_{z^2}^1 d_{x^2-y^2}^1$ produces a singly degenerate $^3A_{2g}$ state), Mulliken states while the ^3P state is not affected by the ligand field and transforms to the triplet $^3T_{1g}(P)$ [the arrangement $t_{2g}^1 e_g^1(P) : d_{xy}^1 d_{x^2-y^2}^1, d_{xz}^1 d_{z^2}^1, d_{yz}^1 d_{z^2}^1$ produces triply degenerate $^3T_{1g}(P)$ state] Mulliken state. The energies of these states as a function of Dq can be calculated by evaluating the electrostatic perturbation of the ligand on the d -orbitals. Splitting of the spectroscopic states of the bare d^2 ion into Mulliken states under the influence of an octahedral field of a ligand have been shown diagrammatically in Fig. 5.43. Accordingly, the absorption spectra of octahedral complexes of d^2 -ions should consist of three absorption bands corresponding to the d -d transitions indicated below:

Mulliken	Energy	Transition	Transition energy
$^3T_{1g}(F)$	$-6Dq$	$^3T_{1g}(F) \rightarrow ^3T_{2g}(F)$	$8Dq$
$^3T_{2g}(F)$	$+2Dq$	$^3T_{1g}(F) \rightarrow ^3T_{1g}(P)$	—
$^3T_{1g}(P)$	—		
$^3A_{2g}(F)$	$+12Dq$	$^3T_{1g}(F) \rightarrow ^3A_{2g}(F)$	$18Dq$

However in practice, the absorption spectra of complexes of V^{3+} ion contain only two bands. As an example, in aquo ion $[V(H_2O)_6]^{3+}$, the absorption bands are observed at 17000 cm^{-1} ($= 588$ nm) and 24000 cm^{-1} (417 nm) (Fig. 5.44). The discrepancy between the theoretically expected and observed spectral data arises because of the submersion of high energy bands corresponding to the $^3T_{1g}(F) \rightarrow ^3T_{1g}(P)$ and $^3T_{1g}(F) \rightarrow ^3A_{2g}(F)$ transitions, i.e. the overlapping of the high-energy bands occurs since the transitions take place close to the crossover point between $^3A_{2g}(F)$ and $^3T_{1g}(P)$ terms on the energy-level diagram [Fig. 5.43].

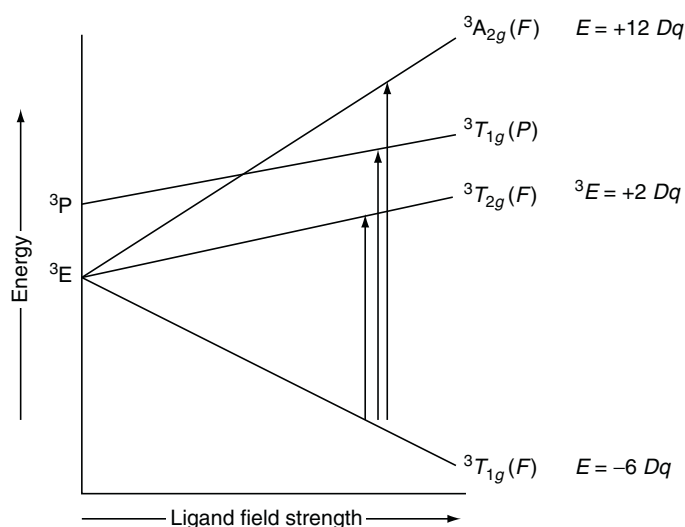


Fig. 5.43 Energy-level diagram for the splitting of ^3P and ^3F spectroscopic terms of a bare ion, with d^2 -configuration into Mulliken terms in an octahedral field of a ligand.

Further, in order to determine Δ_0 we proceed as follows:

$$\text{Since } E(^3T_{2g}) - E(^3T_{1g}) = 2Dq - (-6Dq) = 8Dq = 17000 \text{ cm}^{-1}.$$

$$\text{Therefore } \Delta_0 = 10Dq = \frac{17000(\text{cm}^{-1}) \times 10}{8} = 2125 \text{ cm}^{-1}.$$

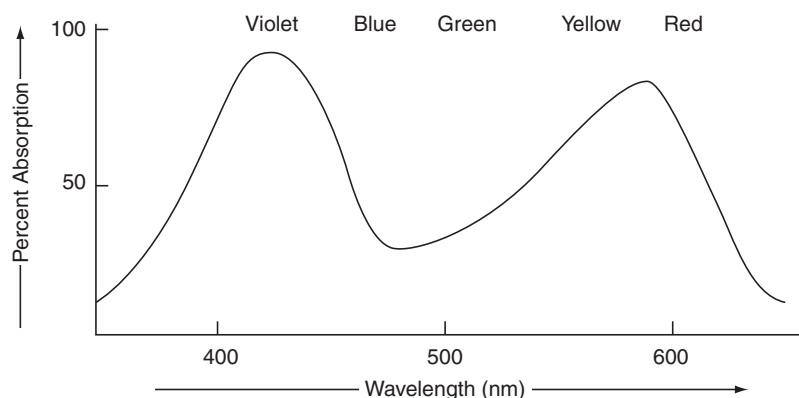


Fig. 5.44 Ultraviolet visible spectrum of $[V(H_2O)_6]^{3+}$ ion.

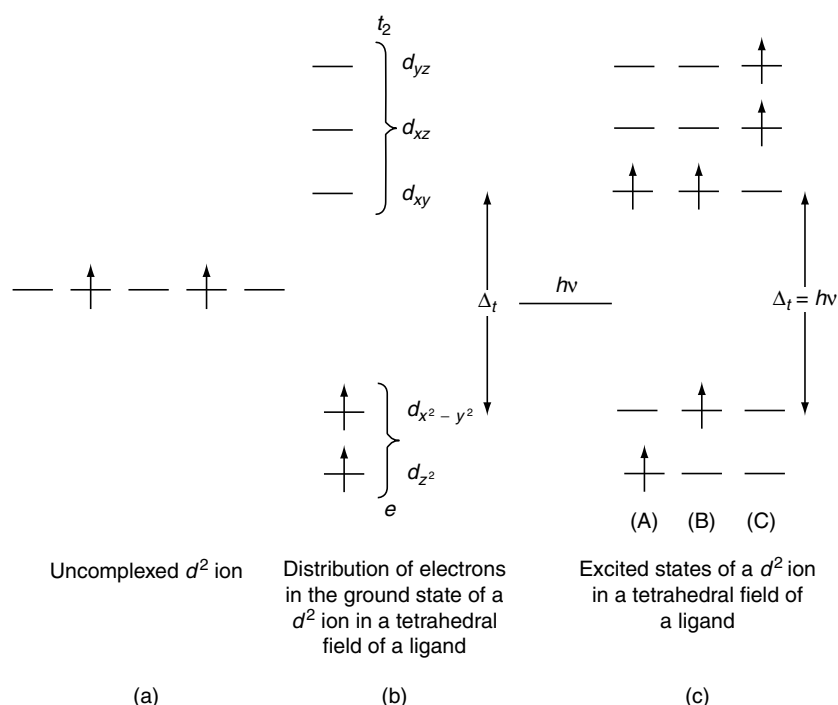


Fig. 5.45 Schematic energy-level diagram, illustrating the origin of electronic absorption spectrum of d^2 -ion, in a tetrahedral field of a ligand. Here in case (b), for convenience t^2 (---) is represented as t_2 [=] and e (--) as e [=]. This is so in the incoming diagrams also.

In tetrahedral complexes of a d^2 -ion the energy level diagrams are the inverse of that of d^2 -ion in an octahedral field of the ligand as shown in Figs 5.45 and 5.46.

On absorption of light, the electrons from e level [Fig. 5.45(b)] shift to t_2 -orbitals according to the arrangements A, B and C [Fig. 5.45(c)]. The electrons in the $d_{x^2-y^2}$ orbital require less energy to crossover to the d_{xy} orbital than from the d_{z^2} orbital since the former transition results in lower electron repulsion $d_{z^2}^1 d_{xy}^1$ arrangement compared to $d_{x^2-y^2}^1 d_{xy}^1$ arrangement due to the logic discussed earlier in octahedral d^2 -complexes. Thus the two permissible one electron $d-d$ transitions are $d_{z^2} \rightarrow d_{xy}$ and $d_{z^2} \rightarrow d_{xz}$ and $d_{x^2-y^2} \rightarrow d_{xy}$. The third allowed $d-d$ transition arising, because of the simultaneous promotion of both the electrons from e to t_2 orbitals, is $d_{z^2} d_{x^2-y^2} \rightarrow d_{xy} d_{xz}$ or $d_{xz} d_{yz}$ or $d_{yz} d_{xy}$. The other possible transitions involving the reversal of spin of one of the electrons such as $d_{z^2}(\uparrow) d_{x^2-y^2}(\uparrow) \rightarrow d_{xy}(\downarrow) d_{xz}(\uparrow)$; $d_{z^2}(\uparrow) d_{x^2-y^2}(\uparrow) \rightarrow d_{xy}(\uparrow) d_{xz}(\downarrow)$

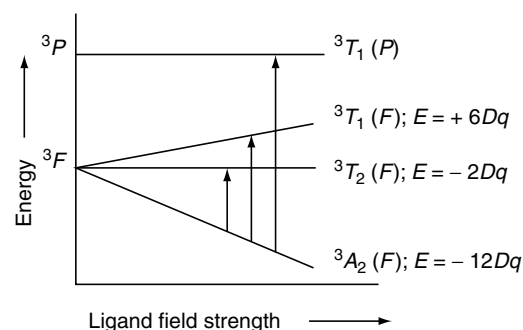


Fig. 5.46 Energy-level diagram for the splitting of ^3P and ^3F spectroscopic terms of an ion with d^2 -configuration into Mulliken terms in a tetrahedral field of a ligand.

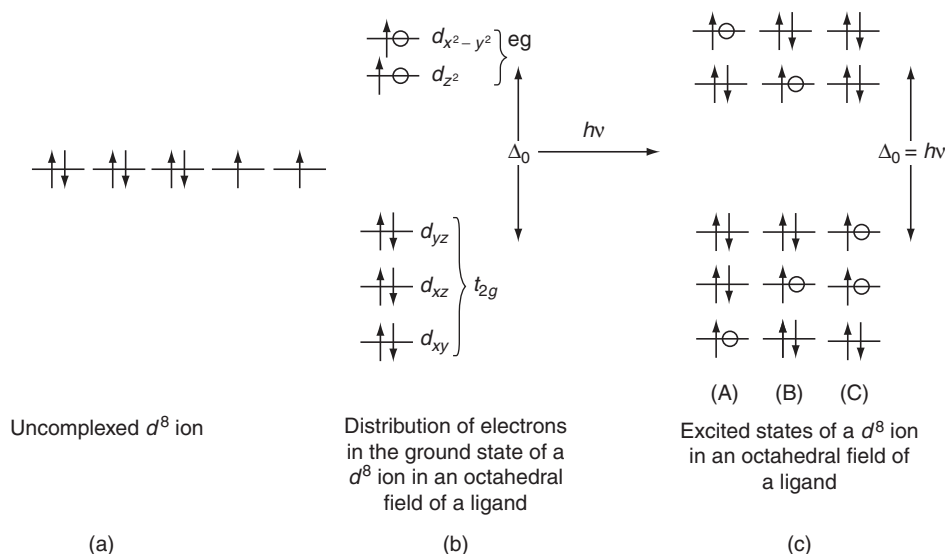


Fig. 5.47 Schematic energy-level diagram showing the origin of $d-d$ electronic transitions of d^8 -ion in an octahedral field of a ligand. Open circles represent holes.

are spin forbidden. Such transitions may give rise to very weak bands. Accordingly, three absorption bands corresponding to the $d_{x^2-y^2} \rightarrow d_{xy}/d_{yz}/d_{zx}$, $d_{z^2} \rightarrow d_{xy}/d_{yz}/d_{zx}$, and $d_{x^2-y^2}d_{z^2} \rightarrow d_{xy}d_{yz}$ transitions are expected in the electronic spectrum of high spin tetrahedral complexes of metal ions with d^2 configuration.

The description of Figure 5.46 is left as an exercise for the students. As a hint, the absorption spectra of high spin d^2 -tetrahedral complexes should contain three bands corresponding to ${}^3A_2(F) \rightarrow {}^3T_2(F)$, ${}^3A_2(F) \rightarrow {}^3T_1(F)$ and ${}^3A_2(F) \rightarrow {}^3T_1(P)$, $d-d$ transitions. In this case no overlapping of high-energy bands will take place since there is no crossover of ${}^3T_1(P)$ and ${}^3T_1(F)$ lines. The red-purple colour of tetrahedral ferrate ion $[\text{Fe}^{\text{VI}}(\text{O}_4^{2-})]^{4+}$ (stable in strongly alkaline solution) results since transmission of white light occurs mainly in the red and violet regions of the spectrum.

(a) d^8 ion The d^8 -configuration occurs in Ni^{2+} . This ion with electronic structure $\text{Ar } 3d^8$ is formed from Ni atom with an atomic number (Z) of 28 by removing two electrons from it, i.e. $\text{Ar } 3d^8 4s^2 \xrightarrow{-2e} \text{Ar } 3d^8$. On complexing with six-ligand molecules, the five $3d$ degenerate orbitals split into two degenerate sets: the low-energy (t_{2g}) and high-energy (e_g) sets due to electrostatic octahedral field of a ligand. The energy-level diagram for the d^8 -ion in an octahedral field is shown in Fig. 5.47. There are two holes in the e_g orbitals. The $d-d$ transitions are due to the transfer of holes from e_g to t_{2g} orbitals under the influence of light of photon $h\nu$. The transition which gives rise to a $d_{z^2} d_{xy}$ arrangements, in which the electron cloud of electrons is uniformly spread in the X , Y and Z directions which reduces the inter-electronic repulsion, is more probable as compared with the $d_{x^2-y^2} d_{xy}$ arrangement where the electrons are confined only to the XY plane.

Thus, the two possible $d-d$ transitions ($d_{xy}/d_{yz}/d_{zx} \rightarrow d_{z^2}$; $d_{xy}/d_{yz}/d_{zx} \rightarrow d_{x^2-y^2}$) arising due to the transfer of a hole from e_g orbitals to t_{2g} orbitals are: $d_{z^2} \rightarrow d_{xy}/d_{yz}/d_{zx}$; $d_{x^2-y^2} \rightarrow d_{xy}/d_{yz}/d_{zx}$. The third possible $d-d$ transition that results due to the simultaneous promotion of both the electrons from the t_{2g} to e_g states and simultaneously the migration of the two holes from e_g orbitals to t_{2g} orbitals is $d_{z^2}d_{x^2-y^2} \rightarrow d_{xy}d_{yz}$ or $d_{yz}d_{xy}$ or $d_{xy}d_{xz}$. Accordingly, three absorption bands corresponding to the $d_{xy} \rightarrow d_{z^2}$, or $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz}d_{yz} \rightarrow d_{z^2}d_{x^2-y^2}$ transitions are expected in the metal complexes of d^8 ion. The energy-level diagram in terms of spectroscopic terms, i.e. and ${}^3F$ of d^8 -ion and their splitting into Mulliken terms in an octahedral field of a ligand is presented in Fig. 5.48. The lines ${}^3T_{1g}(P)$ and ${}^3T_{1g}(F)$ do not cross because they are of the same symmetry.

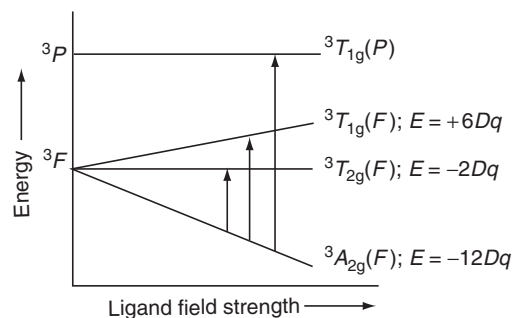


Fig. 5.48 Energy-level diagram for the splitting of ${}^3P$ and ${}^3F$ spectroscopic terms of an ion with d^8 configuration into Mulliken terms in an octahedral field of a ligand.

The Mulliken terms indicated in Fig. 5.48 originates from the following arrangements of t_{2g} and e_g orbitals

Mulliken term	Arrangement of orbitals	
${}^3A_{2g}(F)$	$t_{2g}^6 e_g^2 : d_{xy}^2 d_{yz}^2 d_{zx}^2 d_{z^2}^1 d_{x^2-y^2}^1$,	[From Fig. 5.47(b)]
${}^3T_{2g}(F)$	$t_{2g}^5 e_g^3 : d_{xy}^2 d_{yz}^2 d_{zx}^1 d_{z^2}^2 d_{x^2-y^2}^1$,	
	$d_{xy}^1 d_{yz}^2 d_{zx}^2 d_{x^2-y^2}^1 d_{z^2}^2$,	
	$d_{xy}^2 d_{yz}^1 d_{zx}^2 d_{x^2-y^2}^1 d_{z^2}^2$,	[From Fig. 5.47(c);(B)]
${}^3T_{1g}(F)$	$t_{2g}^5 e_g^3 : d_{xy}^2 d_{yz}^2 d_{zx}^1 d_{z^2}^1 d_{x^2-y^2}^2$,	
	$d_{xy}^1 d_{yz}^2 d_{zx}^2 d_{z^2}^1 d_{x^2-y^2}^2$	
	$d_{xy}^2 d_{yz}^1 d_{zx}^2 d_{z^2}^1 d_{x^2-y^2}^2$,	[From Fig. 5.47(c);(A)]
${}^3T_{1g}(P)$	$t_{2g}^4 e_g^4 : d_{xy}^2 d_{yz}^1 d_{zx}^1 d_{z^2}^2 d_{x^2-y^2}^2$,	
	$d_{xy}^1 d_{yz}^2 d_{zx}^1 d_{z^2}^2 d_{x^2-y^2}^2$	
	$d_{xy}^1 d_{yz}^1 d_{zx}^2 d_{z^2}^2 d_{x^2-y^2}^2$.	[From Fig. 5.47(c);(C)]

According to Fig. 5.48, the three absorption bands are expected in the electronic spectra of d^8 -octahedral complexes corresponding to the transitions indicated below.

Mulliken state	Energy	Transition	Transition energy
${}^3A_{2g}(F)$	$-12Dq$	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	$10Dq$
${}^3T_{2g}(F)$	$-2Dq$	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	$18Dq$
${}^3T_{1g}(F)$	$+6Dq$	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	—
${}^3T_{1g}(P)$	—		

and the same has been experimentally observed indeed.

For example, the absorption spectra of octahedral complexes of Ni^{2+} ion with various ligands such as H_2O , NH_3 , etc, i.e. $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$ shown in Fig. 5.49, conform to the theoretically expected spectra. The three absorption bands fall in the regions $8000\text{--}13000\text{ cm}^{-1}$ ($1250\text{--}769\text{ nm}$), $15000\text{--}19000\text{ cm}^{-1}$ ($666.6\text{--}526.3\text{ nm}$) and $25000\text{--}29000\text{ cm}^{-1}$ ($400\text{--}344.8\text{ nm}$). The exact positions depend on the quantities Δ_0 and β .

The $\epsilon_{\max}$ of these bands is generally below 20. In the case of $[Ni(H_2O)_6]^{2+}$ ion, the middle peak shows sign of splitting into two peaks because of Jahn–Teller distortion. The amine of nickel $[Ni(NH_3)_6]^{2+}$ complex ion is blue whereas the aquo ion $[Ni(H_2O)_6]^{2+}$ is green. The absorption spectra of ions show that Δ_0 is larger for ammonia

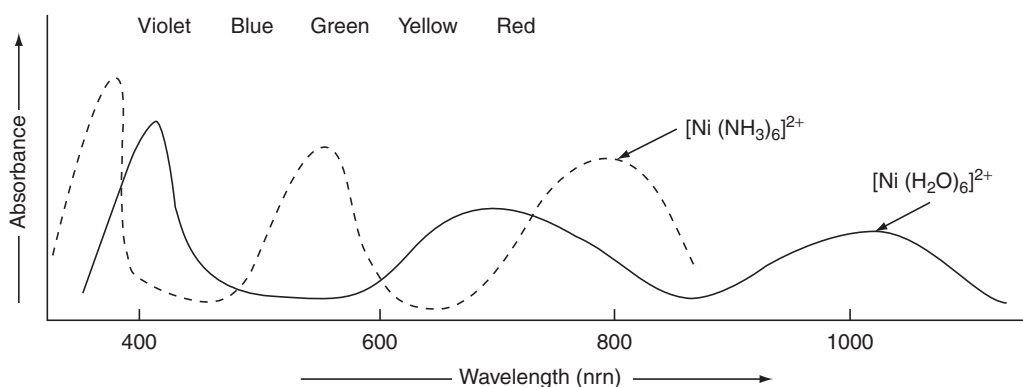


Fig. 5.49 Electronic absorption spectra of high spin hexa-aquo and hexa-amine complexes of Ni^{2+} ion.

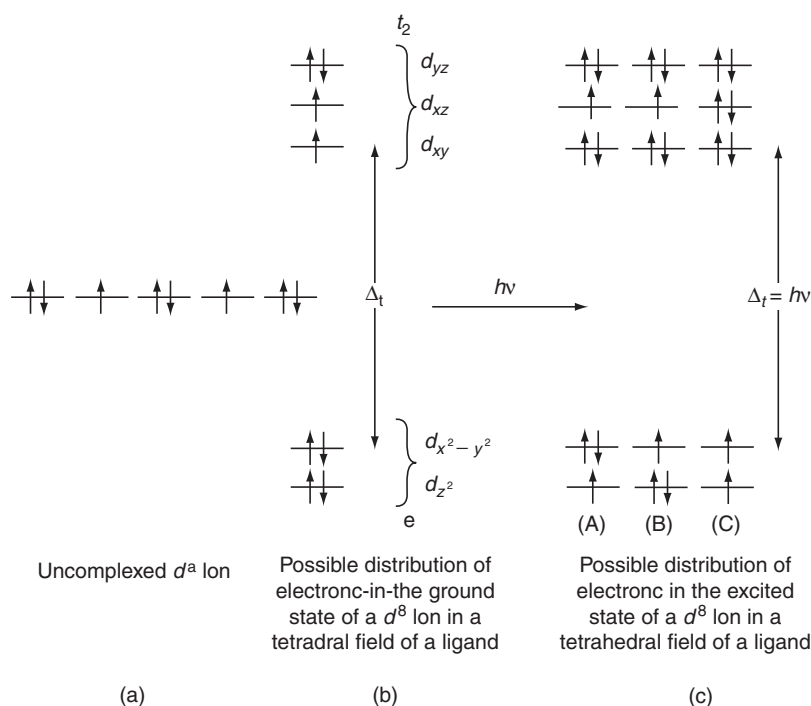


Fig. 5.50 Schematic diagram showing the origin of $d-d$ transition in d^8 -tetrahedral complexes.

than for water. For $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion, the band maxima are at 8700, 14500 and 25300 cm^{-1} . Thus in this case $E(^3T_{2g}) - E(^3A_{2g}) = -2Dq - (-12Dq) = 8700 \text{ cm}^{-1}$. Hence $10Dq = 8700 \text{ cm}^{-1}$. For $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ion, the absorption maximum corresponding to $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ transition lies at around 12907 cm^{-1} . Accordingly $10Dq = 12907 \text{ cm}^{-1}$.

The treatment for the origin of d^8 tetrahedral complexes is left an exercise for the students. As a hint, the diagram for the origin of $d-d$ transitions in these complexes is shown in Fig. 5.50 and the energy-level diagram showing splitting of ^3F and ^3P spectroscopic states in Mulliken terms is similar to that of d^2 octahedral complexes except that $E = -2Dq$ for $^3T_2(F)$ shown in Fig. 5.43 in a qualitative way. Two transitions due to the transfer of an electron with antiparallel spin from e to t_2 orbitals are $d_{z^2} \rightarrow d_{xy}$ transition, gives higher interelectronic repulsion arrangement $d_{xy}d_{z^2-y^2}(A)$ and $d_{x^2-y^2} \rightarrow d_{xy}$ transition, results in lower interelectron repulsion arrangement $d_{z^2}d_{xy}(B)$. The third possible transition is due to the simultaneous migration of two electrons with anti-parallel spins. The Mulliken terms originates from the electronic configuration of e and t_2 orbitals in Fig. 5.50.

$$\begin{aligned}
 ^3T_1(F) & \quad e^4 t_2^4 : e^4 d_{xy}^1 d_{yz}^1 d_{zx}^2, e^4 d_{xy}^2 d_{yz}^1 d_{zx}^1, e^4 d_{xy}^1 d_{yz}^2 d_{zx}^1. \\
 ^3T_2(F) & \quad e^3 t_2^5 : e^3 (d_{z^2}^2 d_{x^2-y^2}^1) d_{xy}^2 d_{yz}^2 d_{zx}^2, e^3 d_{xy}^1 d_{yz}^2 d_{zx}^2, e^3 d_{xy}^2 d_{yz}^2 d_{zx}^1. \\
 ^3T_1(P) & \quad e^3 t_2^5 : e^3 (d_{z^2}^1 d_{x^2-y^2}^2) d_{xy}^2 d_{yz}^1 d_{zx}^2, e^3 d_{xy}^1 d_{yz}^2 d_{zx}^2, e^3 d_{xy}^2 d_{yz}^2 d_{zx}^1. \\
 ^3A_2(F) & \quad e^2 t_2^6 : e^2 d_{xy}^2 d_{yz}^2 d_{zx}^2.
 \end{aligned}$$

The three-spin allowed transitions in T_d complexes of Ni^{2+} are $^3T_1(F) \rightarrow ^3T_2(F)$; $^3T_1(F) \rightarrow ^3A_2(F)$; and $^3T_1(F) \rightarrow ^3T_1(P)$. For example, the absorption spectrum of $[(\text{C}_6\text{H}_5)_3\text{AsO}\{\text{NiCl}_2\}]$ in benzene shows two bands at 7800 cm^{-1} and at 14000–16000 cm^{-1} . The complex has distorted tetrahedral structure. The two absorption bands are attributed to the following transitions:

$$^3T_1(F) \rightarrow ^3A_2(F), 7800 \text{ cm}^{-1}$$

$$^3T_1(F) \rightarrow ^3T_1(P), 16000 \text{ cm}^{-1}$$

Accordingly,

$$E(^3A_2) - E(^3T_1) = 12Dq - (-6Dq) = 18Dq = 7800 \text{ cm}^{-1}.$$

$$\text{Hence, } 10Dq = \frac{7800(\text{cm}^{-1}) \times 10}{18} = 4333 \text{ cm}^{-1}$$

infrared region. Note that the band of lowest energy is often masked by absorption of either the organic part of the molecule or the solvent. The other example of d^8 tetrahedral complex is that of $[\text{Ni}(\text{Cl})_4]^{2-}$ in CH_3NO_2 . It shows an absorption band at 608 nm (16450 cm^{-1}) as a shoulder ($\epsilon=10$) and two equally intense bands ($\epsilon=35$) at 654 nm (15290 cm^{-1}) and 705 nm (14190 cm^{-1}). Thus the green colour of this complex is attributed to absorption in the yellow–red regions and hence transmission in green region of spectrum of white light. The first cationic tetrahedral complex of Ni^{2+} was with phosphoramidate, i.e. $\text{O}-\text{P}[\text{N}(\text{CH}_3)_2]_3$ abbreviated as HMPA. The similarity of the spectrum of $[\text{Ni}(\text{Cl})_4]^{2-}$ was used to establish tetrahedral structure.

The energy-level diagram for transition/s in metal complexes with d^3 ion in terms of its spectroscopic terms and their transformation into Mulliken terms under the influence of octahedral field of an ligand is similar to that of d^8 octahedral complexes except that the multiplicity 3 is to be replaced by 4 and the origin of Mulliken terms will also be different [Fig. 5.48]. The origin of these terms, as worked out from Fig. 5.51, is expressed here.

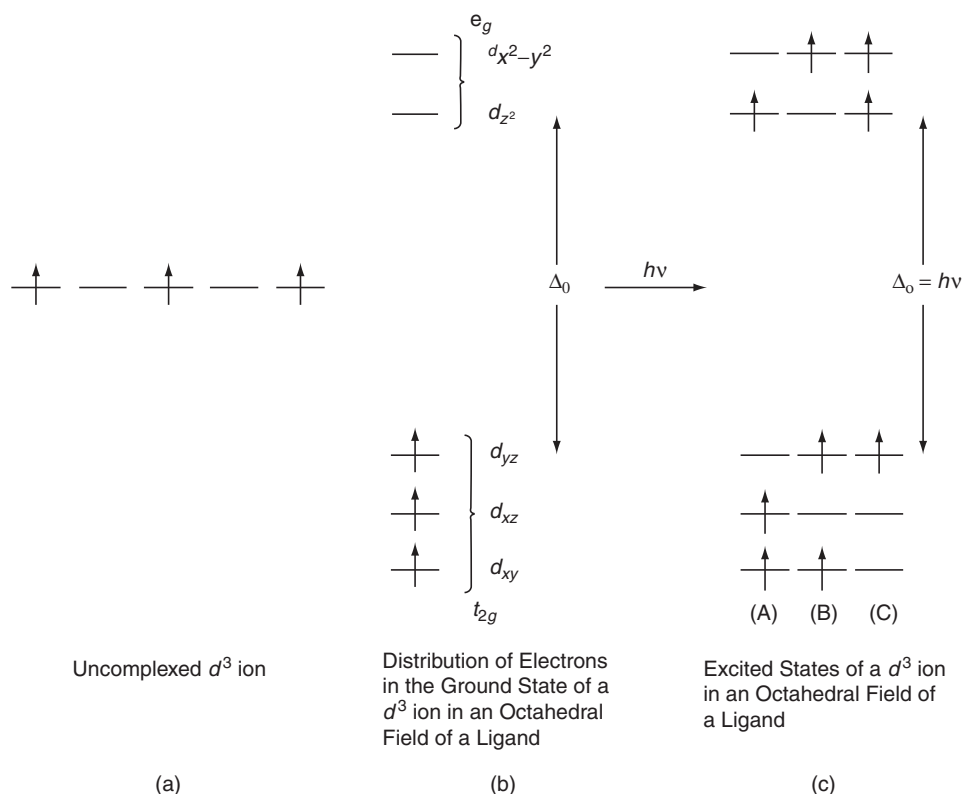
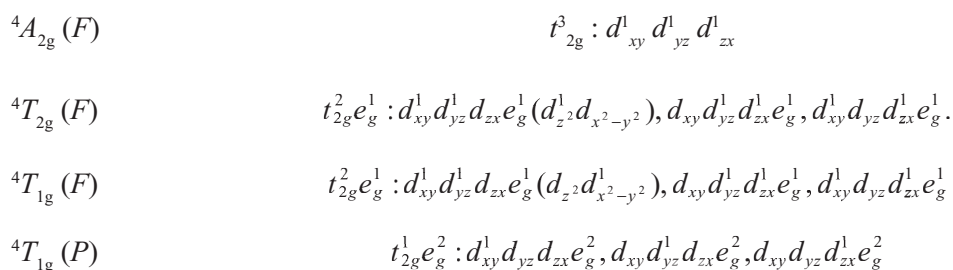


Fig. 5.51 Schematic diagram illustrating the origin of electronic transitions in octahedral complexes of d^3 ion.



Accordingly, the following transitions are possible in the d^3 octahedral complexes:

Mulliken Term	Energy	Transition	Transition energy
${}^4A_{2g}(F)$	$-12Dq$	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$	$+10Dq$
${}^4T_{2g}(F)$	$-2Dq$	${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$	$+18Dq$
${}^4T_{1g}(F)$	$+6Dq$	${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$	—
${}^4T_{1g}(P)$	—		

Thus, the electronic absorption spectra of d^3 octahedral complexes should contain three bands and the same has been observed indeed. For example, the observed absorption spectrum of $[\text{Cr}(\text{F})_6]^{3-}$ ion exhibits three bands at about 34400 cm^{-1} ($\approx 290.7\text{ nm}$), 22700 cm^{-1} ($\approx 440.5\text{ nm}$) and 14900 cm^{-1} ($\approx 671.1\text{ nm}$) while that of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion shows three bands at 37879 cm^{-1} ($\approx 264\text{ nm}$), 24570 cm^{-1} (407 nm) and 17241 cm^{-1} ($\approx 580\text{ nm}$). The Δ_0 values for these complexes can be worked out as follows:

For $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion in an aqueous medium, we have $E({}^4T_{2g}) - E({}^4A_{2g}) = -2Dq - (-12Dq) = 10Dq$, hence $\Delta_0 = 10Dq = 17241\text{ cm}^{-1}$ and for $[\text{Cr}(\text{F})_6]^{3-}$ we have $E({}^4T_{2g}) - E({}^4A_{2g}) = -2Dq - (-12Dq) = 10Dq$, hence $\Delta_0 = 10Dq = 14,900\text{ cm}^{-1}$ and for $[\text{Cr}(\text{F})_6]^{3-}$ we have $E({}^4T_{2g}) - E({}^4A_{2g}) = -2Dq - (-12Dq) = 10Dq$, hence $\Delta_0 = 10Dq = 14,900\text{ cm}^{-1}$. Accordingly, H_2O is a strong ligand as compared to F^- as expected on the basis of spectrochemical series.

The bluish green colour of Cr^{3+} octahedral complexes results because blue/green components of white light remain relatively unabsorbed. Another example of d^3 ion is V^{2+} . $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ aquo ion shows absorption bands at 358, 541 and 910 nm. In this case, the violet colour of light remains relatively unabsorbed. For this complex, $10Dq = \Delta_0 = 10990\text{ cm}^{-1}$. Thus Cr^{3+} forms a stronger octahedral complex with water relative to V^{2+} as expected.

For d^3 tetrahedral complexes, the diagram showing the origin of $d-d$ transition/s, i.e. transfer of an electron/s from e to t_2 orbitals, is shown in Fig. 5.52 and the energy-level diagram showing the splitting of ${}^4F$ and ${}^4P$ spectroscopic terms into Mulliken terms in a tetrahedral field of a ligand is similar to that of d^2 octahedral complexes (Fig. 5.43) except the multiplicity and the orbital arrangements giving rise to Mulliken terms. The origin of Mulliken terms as worked out from Fig. 5.52 is listed here.

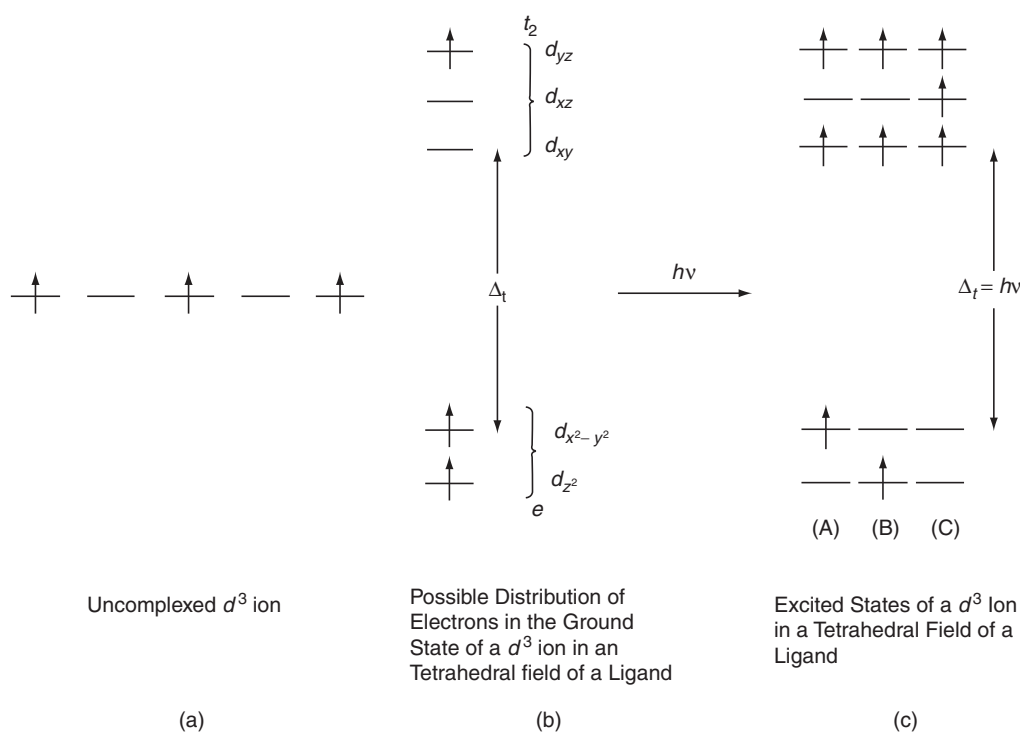


Fig. 5.52 Diagram illustrating the origin of $d-d$ transitions in d^3 ion in a tetrahedral field of a ligand.

$$\begin{aligned}
{}^4T_1(F) & e^2 t_2^1 : e^2 d_{xy}^1 d_{yz}^1 d_{zx}^1, e^2 d_{xy}^1 d_{yz}^1 d_{zx}^1, e^2 d_{xy}^1 d_{yz}^1 d_{zx}^1 \\
{}^4T_2(F) & e^1 t_2^2 : e^1 (d_{z^2}^1 d_{x^2-y^2}^1) d_{xy}^1 d_{yz}^1 d_{zx}^1, e^1 d_{xy}^1 d_{yz}^1 d_{zx}^1, e^1 d_{xy}^1 d_{yz}^1 d_{zx}^1 \\
{}^4T_1(P) & e^1 t_2^2 : e^1 (d_{x^2-y^2}^1 d_{z^2}^1) d_{xy}^1 d_{yz}^1 d_{zx}^1, e^1 d_{xy}^1 d_{yz}^1 d_{zx}^1, e^1 d_{xy}^1 d_{yz}^1 d_{zx}^1 \\
{}^4A_2 & t_2^3 : d_{xy}^1 d_{yz}^1 d_{zx}^1
\end{aligned}$$

Accordingly, the absorption spectra of d^3 -tetrahedral complexes should give rise to three bands corresponding to the $d-d$ transition/s indicated below.

Mulliken term	Energy	Transition	Transition energy
${}^4T_1(F)$	$-6 Dq$	${}^4T_1(F) \rightarrow {}^4T_2(F)$	$+8 Dq$
${}^4T_2(F)$	$+2 Dq$	${}^4T_1(F) \rightarrow {}^4T_1(P)$	—
${}^4T_1(P)$	—	—	—
${}^4A_2$	$12 Dq$	${}^4T_1(F) \rightarrow {}^4A_2$	$18 Dq$

(g) d^7 -ion Co^{2+} with an electronic configuration $\text{Ar } 3d^7$ is an important example of d^7 -ion. It is produced by ejecting two electrons from the cobalt atom ($Z = 27$) having an electronic configuration of $\text{Ar } 3d^7 4s^2$, i.e. $\text{Ar } 3d^7 4s^2 \xrightarrow{-2e} \text{Ar } 3d^7$. The origin of $d-d$ transitions in d^7 -octahedral complexes has been shown in Fig. 5.53. Two-one electron transitions of the type $d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xz} \rightarrow d_{z^2}$ occur due to the migration of an electron without change of spin from t_{2g} to e_g orbitals. The third possible transition of the type $d_{xy} d_{yz} \rightarrow d_{z^2} d_{x^2-y^2}$ is due to the simultaneous crossover of two electrons without change of spin from t_{2g} to e_g orbitals. Accordingly, the absorption spectra of d^7 -octahedral complexes should contain three absorption bands.

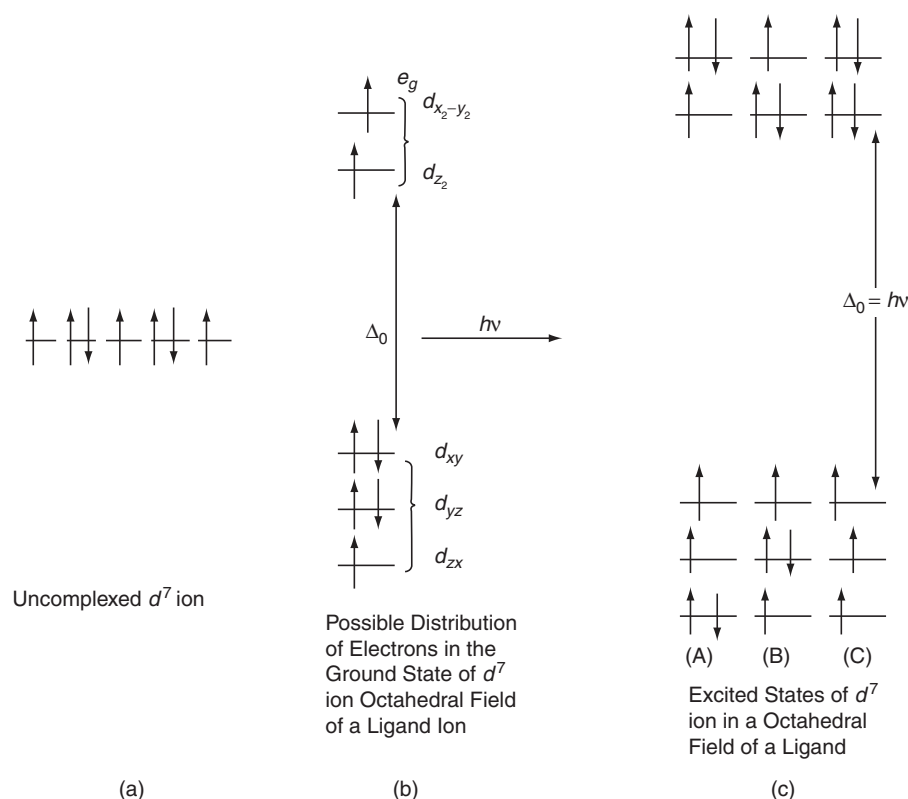


Fig. 5.53 Schematic diagram depicting the origin of $d-d$ transition in d^7 -octahedral complexes.

Further the energy-level diagram showing the splitting of ${}^4F$ and ${}^4P$ spectroscopic terms of d^7 -ion into Mulliken terms under the influence of an octahedral field of a ligand is similar (except the multiplicity and arrangement of orbitals due to $d-d$ transition) to that of d^2 -octahedral complexes (Fig. 5.43). The arrangements of orbitals that give rise to Mulliken terms as deduced from Fig. 5.53 are indicated below.

$$\begin{aligned}
{}^4T_{1g}(F) & t_{2g}^5 e_g^2 : d_{xy}^1 d_{yz}^2 d_{zx}^2 e_g^2, d_{xy}^2 d_{yz}^2 d_{zx}^1 e_g^2, d_{xy}^2 d_{yz}^2 d_{zx}^1 e_g^2. \\
{}^4T_{2g}(F) & t_{2g}^4 e_g^3 : d_{xy}^1 d_{yz}^2 d_{zx}^1 e_g^3 (d_{z^2}^2 d_{x^2-y^2}^1), d_{xy}^2 d_{yz}^2 d_{zx}^1 e_g^3, d_{xy}^1 d_{yz}^2 d_{zx}^2 e_g^3.
\end{aligned}$$

$${}^4T_{1g}(P) \quad t_{2g}^4 e_g^3 : d_{xy}^1 d_{yz}^1 d_{zx}^2 e_g^3 (d_{z^2}^2 d_{x^2-y^2}^1), d_{xy}^2 d_{yz}^1 d_{zx}^1 e_g^3, d_{xy}^1 d_{yz}^2 d_{zx}^1 e_g^3.$$

$${}^4A_{2g}(F) \quad t_{2g}^3 e_g^4 : d_{xy}^1 d_{yz}^1 d_{zx}^1 e_g^4.$$

According to the energy-level diagram of d^7 octahedral complexes, three absorption bands are expected to correspond to the following transitions:

Mulliken term	Energy	Transition	Transition Energy
${}^4T_{1g}(F)$	$-6Dq$	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	$8Dq$
${}^4T_{2g}(F)$	$+2Dq$	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	—
${}^4T_{1g}(P)$	—		
${}^4A_{2g}(F)$	$+12Dq$	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	$18Dq$

and the same has been observed indeed. For examples, $[\text{Co}(\text{F})_6]^{4-}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, etc.; the absorption spectrum of the former shows three bands at 7150 cm^{-1} (1398.3 nm), 15200 cm^{-1} (658 nm) and 19200 cm^{-1} (521 nm) while that of latter (Fig. 5.54) exhibits a well-resolved low-intensity band at about 8000 cm^{-1} (1250 nm) and a high-intensity multiple absorption band consisting of three overlapping peaks at about $20,000 \text{ cm}^{-1}$. The three peaks in the multiplet

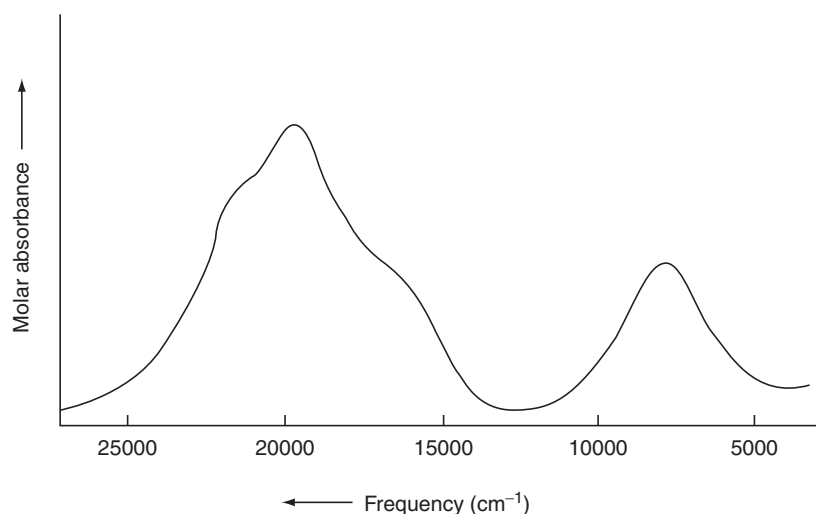


Fig. 5.54 Electronic absorption spectrum of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ in aqueous medium.

are at about 16000 cm^{-1} (625 nm), 19417 cm^{-1} (515 nm) and 21598 cm^{-1} (463 nm). The closeness of the peaks at 19417 and 21598 cm^{-1} indicates that the ligand field strength of water causes transitions close to the crossover point of ${}^4T_{1g}(P)$ and ${}^4A_{2g}$ terms. Thus, the three absorption bands at 8000 , 19417 and 21598 cm^{-1} correspond to the three electronic transitions, viz., ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and respectively. The extra band at about 16000 cm^{-1} is attributed either to spin-orbit coupling effects or transitions to doublet states. Further, in order to find Δ_0 , i.e. $10Dq$; we write as

$$E[{}^4T_{2g}(F)] - E[{}^4T_{1g}(F)] = +2Dq - (-6Dq) = 8Dq = 8000 \text{ cm}^{-1}$$

$$\text{Hence} \quad 10Dq = \frac{8000(\text{cm}^{-1}) \times 10}{8} = 10000 \text{ cm}^{-1}.$$

The pinkish violet colour of octahedral complexes of Co^{2+} ions is attributed to the fact that transmission of white light occurs in the red region of the spectrum, i.e. $> 15,000 \text{ cm}^{-1} < 10,000 \text{ cm}^{-1}$.

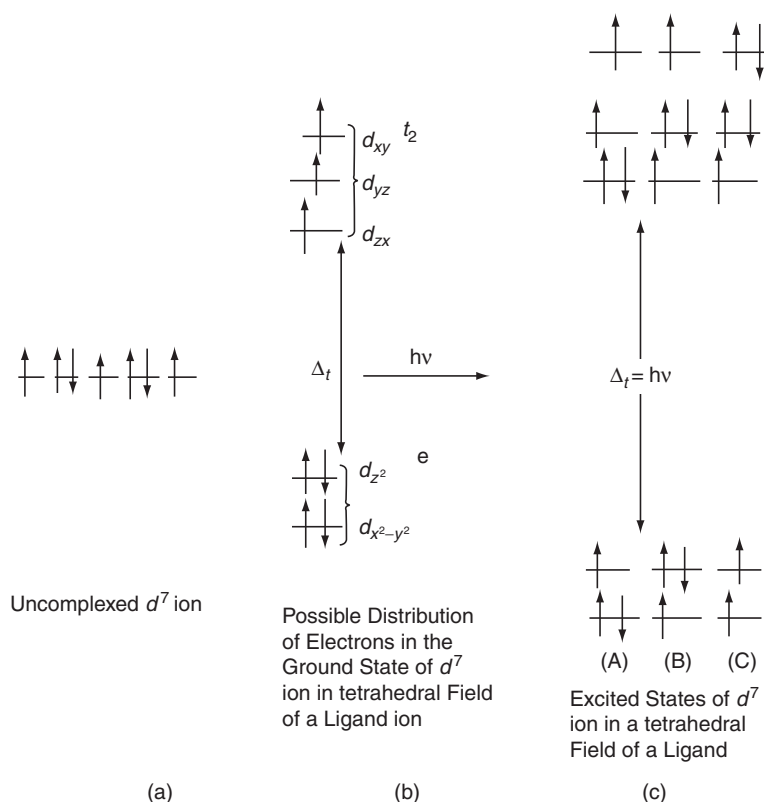


Fig. 5.55 Schematic diagram illustrating the origin of $d-d$ transitions of d^7 -ion in a tetrahedral field of a ligand.

Further, for $[\text{Co}(\text{F})_6]^{4-}$, $8Dq = 7150 \text{ cm}^{-1}$, hence $\Delta_0 = 10 Dq = \frac{7150(\text{cm}^{-1}) \times 10}{8} = 8938 \text{ cm}^{-1}$.

Since, $\Delta_0(\text{H}_2\text{O}) > \Delta_0(\text{F}^-)$, therefore H_2O is a strong ligand than F^- as expected according to spectrochemical series. The three non-overlapping bands of $[\text{Co}(\text{F})_6]^{4-}$ at 7150 , 15200 and 19200 cm^{-1} correspond to the ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$, ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$ and ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ transitions respectively.

The splitting of five degenerate orbitals of d^7 -ion into e and t_2 sets of orbitals under the influence of tetrahedral environment of a ligand as well as the origin of two-one electron transitions, i.e. $d_{z^2} \rightarrow d_{xz}$ and $d_{x^2-y^2} \rightarrow d_{yz}$ and one-two electron transition, i.e. $d_{z^2}d_{x^2-y^2} \rightarrow d_{xy}d_{yz}$ that take place due to the transfer of electron/s without change of spin from e to t_2 orbitals is shown in Fig. 5.55. The energy-level diagram showing the splitting of spectroscopic terms ${}^4F$ and ${}^4P$ of d^7 -ion in tetrahedral environment into Mulliken terms (with multiplicity of 4) is similar to that of d^2 -tetrahedral complexes (Fig. 5.46), except the multiplicity, and the arrangements of orbitals giving rise to Mulliken terms. The origin of Mulliken terms is indicated below.

$${}^4A_2(\text{F}) \quad e^4 t_2^3 : d_{z^2}^2 d_{x^2-y^2}^2 d_{xy}^1 d_{yz}^1 d_{zx}^1$$

$${}^4T_2(\text{F}) \quad e^3 t_2^4 : e^3 (d_{z^2}^1 d_{x^2-y^2}^2) d_{xy}^2 d_{yz}^1 d_{zx}^1, e^3 d_{xy}^1 d_{yz}^2 d_{zx}^1, e^3 d_{xy}^1 d_{yz}^1 d_{zx}^2$$

$${}^4T_1(\text{F}) \quad e^3 t_2^4 : e^3 (d_{z^2}^1 d_{x^2-y^2}^2) d_{xy}^2 d_{yz}^1 d_{zx}^1, e^3 d_{xy}^1 d_{yz}^2 d_{zx}^1, e^3 d_{xy}^1 d_{yz}^1 d_{zx}^2$$

$${}^4T_1(\text{P}) \quad e^2 t_2^5 : e^2 d_{xy}^1 d_{yz}^2 d_{zx}^2, e^2 d_{xy}^2 d_{yz}^1 d_{zx}^2, e^2 d_{xy}^2 d_{yz}^2 d_{zx}^1$$

Thus, according to energy-level diagram of d^7 -ion in tetrahedral environment (Fig. 5.46), the absorptions spectra of d^7 -tetrahedral complexes should consist of three absorption bands corresponding to the transitions indicated below.

Mulliken term	Energy	Transition	Transition energy
${}^4A_2(F)$	$-12Dq$	${}^4A_2(F) \rightarrow {}^4T_2(F)$	$+10Dq$
${}^4T_2(F)$	$-2Dq$	${}^4A_2(F) \rightarrow {}^4T_1(F)$	$+18Dq$
${}^4T_1(F)$	$+6Dq$	${}^4A_2(F) \rightarrow {}^4T_1(P)$	—
${}^4T_1(P)$	—		

For example, the electronic absorption spectrum of $[\text{Co}(\text{Cl})_4]^{2-}$ [Fig. 5.56] shows two bands at 15000 cm^{-1} (666.5 nm ; _{visible}) and 5800 cm^{-1} (1724 nm ; _{near IR}), and are assigned to ${}^4A_2(F) \rightarrow {}^4T_1(P)$ and ${}^4A_2(F) \rightarrow {}^4T_1(F)$ transitions respectively. The band of lowest energy is expected in the IR region and will correspond to transition ${}^4A_2(F) \rightarrow {}^4T_2(F)$. In order to determine $10Dq$, we write, $E[{}^4T_1(F)] - E[{}^4A_2(F)] = +6Dq - (-12Dq) = 18Dq = 5800\text{ cm}^{-1}$.

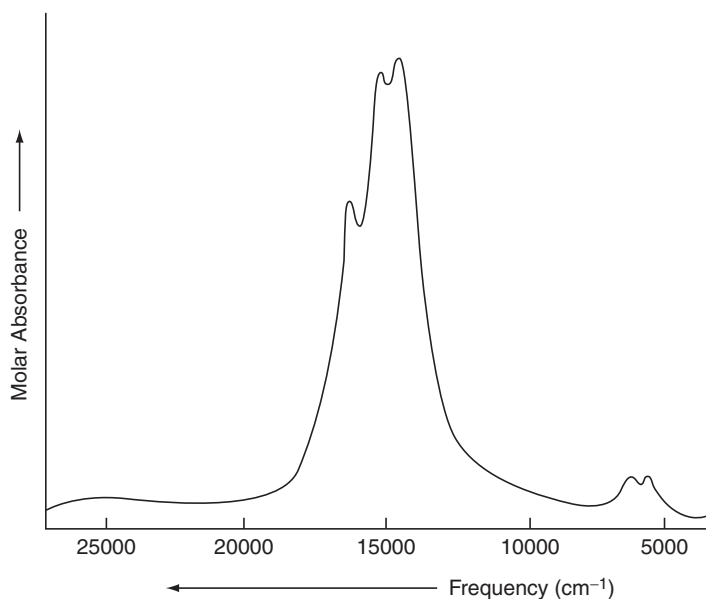


Fig. 5.56 Electronic absorption spectrum of $[\text{Co}(\text{Cl})_4]^{2-}$ in aqueous medium.

$$\text{Hence, } 10Dq = \frac{5800(\text{cm}^{-1}) \times 10}{18} = 3222\text{ cm}^{-1}.$$

Thus, the band of lowest energy should appear at about 3200 cm^{-1} .

The band at 15000 cm^{-1} (666.5 nm) falls in the red and green regions of the spectrum. The characteristic blue component of white light remains unabsorbed and hence imparts deep blue colour to $[\text{Co}(\text{Cl})_4]^{2-}$, the high-spin tetrahedral complex of Co^{2+} ion.

(h) d^5 -ion Mn^{2+} , Fe^{3+} and Co^{4+} are some of the examples of ions with an electronic configuration of $\text{Ar } 3d^5$. They are produced by the removal of two, three and four electrons from their respective atoms. In an octahedral field of a weak ligand, the five degenerate $3d$ orbitals split into two degenerate set of orbitals, the lower-energy set and the higher-energy set: the former comprises three t_{2g} orbitals while the latter contains two e_g orbitals. Three unpaired electrons with parallel spins reside in the lower set while the remaining two unpaired electrons reside in the upper set. The t_{2g} orbitals stabilises the system by $-12Dq$ while the e_g orbitals destabilises the system by $12Dq$. On absorption of light photon $h\nu$, such that $\Delta_0 = h\nu$, any $d-d$ electron transition between two energy states will occur with a reversal of spins. Hence like all other spin forbidden transitions, the absorption bands arising

due to the transitions involving reversal of only one spin will be extremely weak, while involving reversal of two spins will be too weak to be observed and can be ignored.

The possible spectroscopic energy states for an ion with d^5 configuration are

Ground state	${}^6S$
Eleven excited states	${}^4G, {}^4F, {}^4D, {}^4P, {}^2I, {}^2H, {}^2G, {}^2F, {}^2D, {}^2P, {}^2S.$

The order of energy of spectroscopic states with a multiplicity of four is $G < F < D < P$.

The four excited states with a multiplicity of four ($2 \times \frac{3}{2} + 1 = 4$) involve only reversal of one spin while the states with a multiplicity of two ($2 \times \frac{1}{2} + 1 = 2$) involve reversal of two spins. Thus, the transitions from the ground state ${}^6S$, to Mulliken states with a multiplicity of two are spin forbidden and can be ignored. The only important transitions are from ${}^6S$ to ${}^4G$, ${}^4F$, ${}^4D$ and ${}^4P$ states respectively. In an octahedral field of a ligand, the ground and excited states split into Mulliken states as reported in Table 5.20. Accordingly, ten extremely weak bands are expected in the absorption spectrum of a d^5 -ion in an octahedral field of a ligand, for example in the electronic absorption spectrum of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ shown in Fig. 5.57, extremely weak bands are observed, the molar extinction coefficient ϵ being about 0.02–0.03 $\text{lit mole}^{-1} \text{cm}^{-1}$, which is approximately 250–333 times small compared to spin-allowed transitions. Some of the bands are sharp while other are broad. Spin-allowed bands are invariably broad. The positions of the bands are at about 18900 cm^{-1} ($\approx 529 \text{ nm}$), 24970 cm^{-1} ($\approx 402 \text{ nm}$), 25300 cm^{-1} ($\approx 395 \text{ nm}$), 29700 cm^{-1} ($\approx 337 \text{ nm}$), 23100 cm^{-1} ($\approx 433 \text{ nm}$) and 28000 cm^{-1} ($\approx 357 \text{ nm}$), i.e. the absorption region falls mainly in the violet, blue and green regions of the spectrum of white light, which is sufficient to

Table 5.20 The transformation of spectroscopic states of d^5 -ion into Mulliken states in an octahedral field of a ligand.

Spectroscopic states	Mulliken states
${}^6S$	${}^6A_{1g}$
${}^4G$	${}^4T_{1g}, {}^4T_{2g}, {}^4E_g, {}^4A_{1g}$
${}^4P$	${}^4T_{1g}$
${}^4D$	${}^4T_{2g}, {}^4E_g$
${}^4F$	${}^4A_{2g}, {}^4T_{1g}, {}^4T_{2g}$

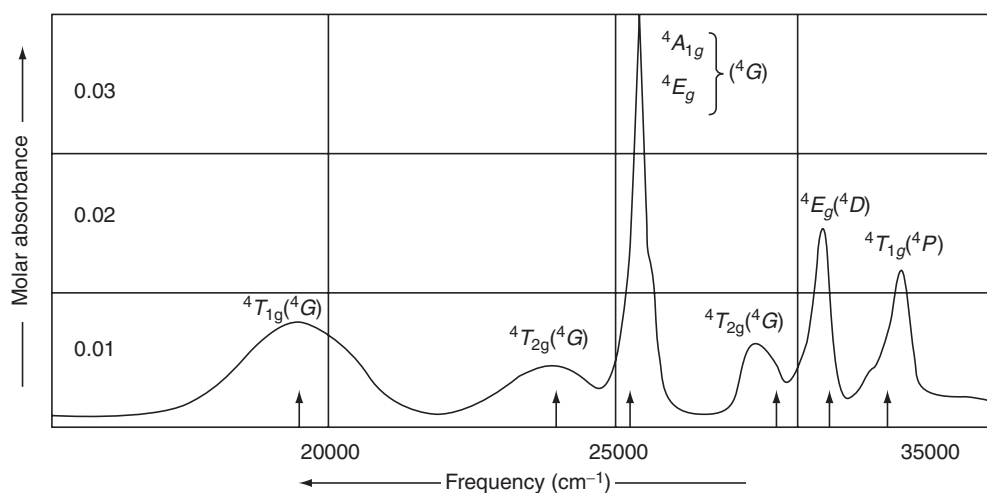


Fig. 5.57 Electronic absorption spectrum of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$.

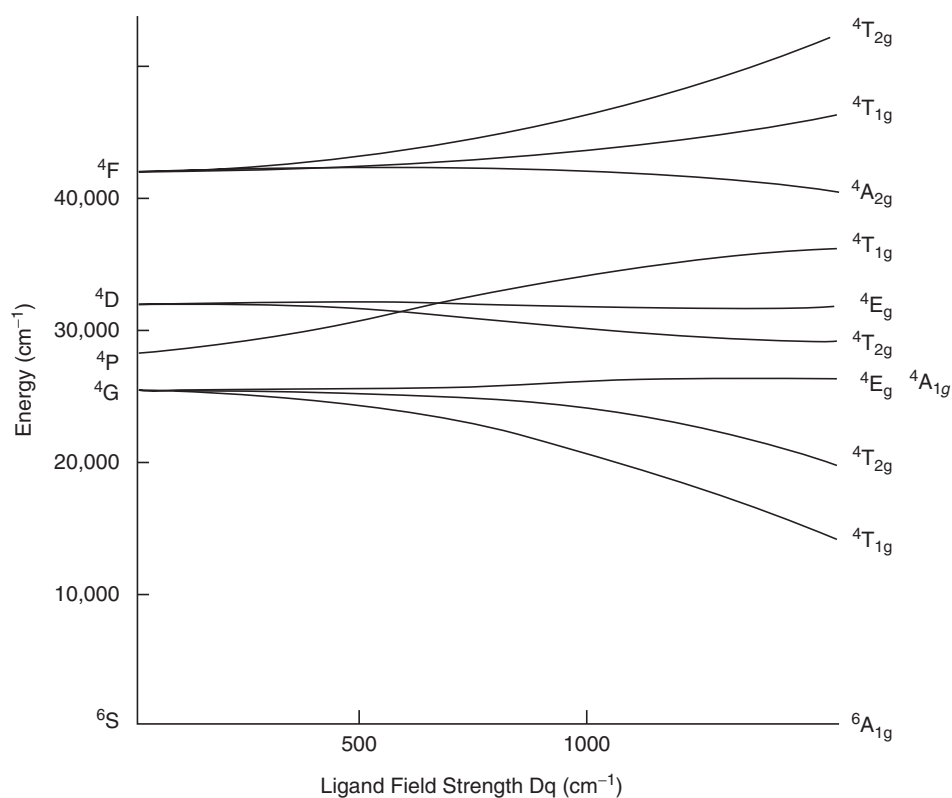


Fig. 5.58 The Orgel energy-level diagram for Mn^{2+} ion in an octahedral field of water ligand.

impart pale pink colour to most of the Mn(II) salts. $[\text{MnF}_6]^{4-}$ and $[\text{FeF}_6]^{3-}$ are the other examples of octahedral complexes of ions with d^5 -configuration. Iron(III) alum has pale violet colour.

The energy of the Mulliken states, corresponding to the respective spectroscopic states, increases from left-hand side to right-hand side.

The Orgel energy-level diagram of Mn^{2+} ion in the octahedral field of water has been shown in Fig. 5.58. The Orgel diagram reveals that ${}^6S$ state is not split and transforms to ${}^6A_{1g}$ state which is drawn along the horizontal axis. The ${}^4E_g(G)$, ${}^4A_{1g}$, ${}^4E_g(D)$ and ${}^4A_{2g}(F)$ terms also appear as horizontal lines on the diagram indicating that their energies are also independent of the crystal field of the ligand. Since the ligand in a complex oscillates about mean position, so the crystal field strength $10Dq$ varies about a mean value. Thus, the energy for a particular transition varies about a mean value. Hence, the absorption peaks are broad. The degree of broadening of the peaks is related to the slope of the lines on the Orgel diagram. Transitions between states of zero slopes, i.e. horizontal lines, will give rise to intense bands and any deviation of excited state from zero slope will contribute to broadening of the sharp band. Accordingly, the transitions from the ${}^6A_{1g}$ state to ${}^4E_g(G)$, ${}^4A_{1g}$, ${}^4E_g(D)$, and ${}^4A_{2g}(F)$ states respectively will yield sharp bands while to ${}^4T_{1g}(G)$, and ${}^4T_{2g}(G)$ states will give broad bands.

Accordingly, the bands are assigned as follows.

The Orgel energy-level diagram for tetrahedral complexes of d^5 -ion is inverse of that of d^5 -ion in an octahedral field of the ligand. According to Laporte selection rule, tetrahedral complexes such as $[\text{Mn}^{II}\text{Br}_4]^{2-}$ lacks a centre of symmetry, so mixing of p and d orbitals can take place. This is true for all tetrahedral complexes. For example, $[\text{CoCl}_4]^{2-}$ is deep blue in colour as compared with $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion.

The Orgel energy-level diagrams are no doubt useful for interpreting the absorption spectra of high-spin complexes but they are applicable only for spin-allowed transitions when the number of observed bands is greater than or equal to the number of empirical quantities: crystal field splitting Dq , modified Racah parameter B' and bending constant x .

The low-spin complexes can also be expressed on an Orgel energy-level diagram but commonly Tanabe-Sugano diagrams are used for interpretation of low-spin as well as high-spin

Transition	Band positions (cm^{-1})
${}^6A_{1g} \rightarrow {}^4T_{1g}$	18900
${}^6A_{1g} \rightarrow {}^4E_g(G)$ ${}^6A_{1g} \rightarrow {}^4A_{1g}$	24970 and 25300
${}^6A_{1g} \rightarrow {}^4E_g(D)$	29700
${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$	23100
${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$	28000

complexes. Due to space problem, these diagrams are not reported here. They are well documented in standard textbooks on inorganic spectroscopy and in the literature: Y Tanabe and S Sugano, J. Phys. Soc. Japan, 9(1964) 753, 766; RS Drago, *Physical Methods in Inorganic Chemistry*, Chapman and Hall Ltd. London, 1965.

5.18 RACAH PARAMETERS

The various Mulliken's energy states of the same multiplicity corresponding to the high spin, low and high energy spectroscopic terms of free ions having d^2 , d^3 , d^7 and d^8 configurations under the influence of octahedral or tetrahedral field of ligand are not linear as is evident from the Orgel energy-level diagrams. This nonlinear behaviour of the various energy levels of the same multiplicity in the Orgel energy-level diagram arises because of inter-electronic repulsion of d -electrons, also called configuration interaction, between them. The electron–electron repulsion lowers the energy of the lower state and increases the energy of the higher state by the same amount called the *bending constant* x . The nonlinear behaviour is much more pronounced in the regions where the states are close in energy. In absence of isoelectronic repulsions, the energy states would be linear and cross each other, and at the cross point, the two electrons in one atom may have the same symmetry and energy. But according to noncrossing rule, two states of the same symmetry cannot cross each other, i.e. two states of different symmetry cross each other, e.g. $^3A_{2g}$ and $^3T_{1g}(P)$. The magnitude of inter-electron repulsion between various states in the gaseous ion is measured in terms of parameters called Racah parameters and are designated as B and C . For states of different multiplicity, both the B and C parameters are necessary to explain the positions of bands in the spectrum. While in many cases, for terms of same multiplicity, only the quantity B suffices. The energy difference between spectroscopic terms of highest spin multiplicity is expressed as ' nB ' where n is an integer. Both n and B vary for different ions. For most transition metal ions, B is about 700–1000 cm^{-1} and C is approximately four times B , i.e. $C \approx 4B$. The values of B (in cm^{-1}) for bare transition metal ions are given in Table 5.21.

The effective value of the Racah interelectronic repulsion term in the complex is denoted by B' and is always less than that for free ion value because of covalent character between metal ion and ligand in the complex rather

Table 5.21 The values of Racah parameter B (in cm^{-1}) for virgin transition metal ions.

Metal	M^{2+}	M^{3+}
Ti	695	–
V	755	861
Cr	810	918
Mn	860	965
Fe	917	1015
Co	971	1065
Ni	1030	1115

than only electrostatic interaction where the ligands are considered as point charges and there is no covalency in the metal–ligand bond. The covalence effect, also called *nephelauxetic effect*, causes the delocalisation of electron density on metal ion on to ligand and thus reduction in the electron–electron repulsion of d -electrons in the complexed metal ion compared to the repulsions in the gaseous state. This causes a decrease in the energy difference between two spectroscopic terms of same multiplicity in the complex relative to that in the gaseous ion. A percentage lowering of the upper spectroscopic state in the complex compared to the energy of the upper state in the free gaseous ion is given by

$$\beta^0 = \frac{(B - B')}{B} \times 100 \quad (5.61)$$

where B equals the energy value of upper spectroscopic state in the free gaseous ion and B' is the experimental energy value of upper state in the complex.

Most often the quantity β is used instead of β^0 and is defined as

$$\beta = \frac{B'}{B} \quad (5.62)$$

Here, β is called the *nephelauxetic ratio*. β decreases as delocalisation increases and is always less than unity. It usually varies from 0.7 to 0.9.

5.18.1 Determination of Dq and β for Transition-Metal Ions in Octahedral and Tetrahedral Fields

The magnitude of Dq depends upon a number of factors and the contribution from each factor depends upon the nature of the transition-metal complex. The various factors which contribute to the magnitude of Dq are perturbation caused by electrostatic interactions, the $M-L$ σ bond, the $L-M$ $P\pi$ bond, the $M-L$ $P\pi$ bond and metal electron–ligand electron–electron repulsions. Information regarding the metal ion–ligand interaction can be obtained from the evaluation of Dq and β . Theoretical expressions relating the energies of the various Mulliken states of transition-metal ions to the Dq value of the ligand in octahedral or tetrahedral field can be employed to determine β and Dq provided the spectral data on the complexes are available.

(a) M^{2+} Ions with d^8 Configuration in an Octahedral Field. The energies E (in cm^{-1}) of the various Mulliken states for M^{2+} ions with d^8 configuration relative to the spherical field are related to Dq , the strength of the ligand field, on the assumption that the ligands behave only as point charges or point dipoles, by the expressions.

$$E = -2Dq \quad \text{for } {}^3T_{2g} \quad (5.63)$$

$$E = -12Dq \quad \text{for } {}^3A_{2g} \quad (5.64)$$

$$6Dq p - 16(Dq)^2 + [-6Dq - p] E + E^2 = 0 \quad \text{for } {}^3T_{1g}(F) \text{ and } {}^3T_{1g}(P) \quad (5.65)$$

The roots of the quadratic Eq. (5.65) will correspond to the energies of ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ Mulliken states. Here, p is the energy of higher energy spectroscopic term, i.e. ${}^3P$ state or ${}^3T_{1g}(P)$ Mulliken state.

For spin-free octahedral M^{2+} complex irrespective of the nature of the ligand; the energy difference between the first two states, i.e. ${}^3T_{2g}$ and ${}^3A_{2g}$ is $10Dq$ [i.e. ${}^3T_{2g} - {}^3A_{2g} = -2Dq - (-12Dq) = 10Dq$]

The energy difference between two spectroscopic terms of Ni^{2+} gaseous ion is 15840 cm^{-1} , i.e. $E({}^3P) - E({}^3F) = 15B = 15840 \text{ cm}^{-1}$. The above expressions hold good perfectly for an Ni^{2+} ion. The energy of the upper spectroscopic term ${}^3P_0$, i.e. $E({}^3P)$, i.e. $E[{}^3T_{1g}(P)]$ is obtained from the energy of the transition ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$.

Substituting the values of $E({}^3P)$ and Dq into the quadratic equation, we obtain the value of p , the energy difference between the two spectroscopic terms of Ni^{2+} ion in an octahedral field of the ligand, i.e. $p = 15B'$.

Once B and B' are known, the values of β° and β are determined from Eqs (5.61) and (5.62) respectively. In order to determine the position of the bands corresponding to the $[{}^3A_{2g} \rightarrow {}^3T_{1g}(F)]$ and $[{}^3A_{2g} \rightarrow {}^3T_{1g}(P)]$ transitions, substitute the value of p for the complexed ion and Dq into the quadratic expression (5.65). The values of two roots of the equation will give the energies of the ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ states. Using these values, one can obtain the position of the above said two bands in the spectrum. For other metal ions, these expressions become complicated due to spin-orbit (so.) coupling. so. coupling splits the three t_{2g} orbitals as shown in Fig. 5.58. It also lowers the energy of ground state and lowering depends upon the magnitude of so. coupling. This lowering because of so. coupling affects the energies of the spectral bands also. Thus, the contribution of $\Delta_{\text{so.}}$ to Δ_t value should be taken into account in order to have accurate values of Dq and β . Hence, so coupling in the excited state does not create any problem since transitions in both the split levels often occur and the average of the two energies can be considered. When the ground state splits, only the lower level is populated. Thus accurate values of Dq and β can be obtained for ions even without taking into consideration $\Delta_{\text{so.}}$, the contribution due to so. coupling to Δ_t , in which the ground state is A or E , e.g. Ni^{2+} . Jahn–Teller distortions also affect the energies of the levels and hence the values of Dq and β . So in order to improve upon the values of Dq and β , contribution from this effect to Δ_t should also be considered.

Note that complications due to so. coupling and Jahn–Teller distortion are insignificant, in case of Ni^{2+} , Mn^{2+} (high spin), Co^{3+} (low spin) and Cr^{3+} octahedral complexes, thus accurate values of Dq and β can be obtained from spectral data. Ti^{3+} has only minor complications from so. coupling and Jahn–Teller distortions. The magnitude of splitting because of so. coupling becomes appreciable in tetrahedral complexes and tends to that of tetrahedral crystal field splitting, i.e. $\Delta_{\text{so.}} \rightarrow \Delta_t = \frac{4}{9}\Delta_0$. Thus, in such cases contributions due to so. coupling to Δ_0 must be considered to obtain accurate values of Dq and β from positions of the absorption bands in the spectrum.

Problem 5.18: Calculate the values of Dq , β , β° , the theoretical energies corresponding to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions for Ni^{2+} octahedral complexes from the spectral data given below.

Variation number	Ligand	Absorption maxima (cm ⁻¹)		
1	H ₂ O	8500	15400 (13495)	26000
2	NH ₃	10750	17500	28200
3	HC(O) N(CH ₃) ₂	8503	13605 (14900)	25000

The energy difference between the two spectroscopic terms for gaseous Ni²⁺ ion is 15840 cm⁻¹.

Solution The electronic structure of Ni²⁺ ion is 3d⁸. With the aid of energy diagram for 3d⁸ configuration, the bands are assigned to the various transitions as under.

Ligand	³ A _{2g} → ³ T _{2g}	³ A _{2g} → ³ T _{1g} (F)	³ A _{2g} → ³ T _{1g} (P)
H ₂ O	8500	15400(13495)	26000
NH ₃	10750	17500	282000
HC(O)N(CH ₃) ₂ N(CH ₃) ₂	8503	13605(14900)	25000

The absorption data is in cm⁻¹.

H₂O: The following steps are followed to obtain the results

(i) The spectroscopic terms for Ni²⁺ gaseous ion are ³P and ³F. The energy difference between two spectroscopic terms is 15840 cm⁻¹, i.e.

$$E(^3P) - E(^3F) = 15 \beta = 15840 \text{ cm}^{-1}.$$

(ii) Dq is determined from the energy of the lowest energy transition ³A_{2g} → ³T_{2g}.

$$E(^3T_{2g}) - E(^3A_{2g}) = 8500 \text{ m}^{-1} = 10 Dq$$

or
$$Dq = \frac{8500 \text{ cm}^{-1}}{10} = 850 \text{ cm}^{-1}.$$

(iii) The energy of the upper spectroscopic term $E(^3P)$ is obtained from the ³A_{2g} → ³T_{1g}(P). transition as follows:

$$E[^3T_{1g}(P)] - E[^3A_{2g}] = 26000 \text{ cm}^{-1}$$

Since
$$^3A_{2g} = -12 Dq$$

Therefore,
$$E[^3T_{1g}(P)] = 26000 \text{ cm}^{-1} - 12 Dq = 26000 \text{ cm}^{-1} - 12 \times 850 \text{ cm}^{-1} = 15800 \text{ cm}^{-1}.$$

(iv) On substituting the value of $E(^3P) = 15800 \text{ cm}^{-1}$ and $Dq = 850 \text{ cm}^{-1}$ into Eq. (5.65), we get

$$p = \frac{15.75 \times 10^7 \text{ cm}^{-1}}{10700} = 14719.6 \text{ cm}^{-1}$$

Thus, the energy difference between two spectroscopic terms when the ion is under the octahedral field of H₂O is

$$p = 15 \beta = 14719.6 \text{ cm}^{-1}.$$

(v) From Eq. (5.62), we obtain

$$\beta = \frac{14719.6 \text{ cm}^{-1}}{15840 \text{ cm}^{-1}} = 0.929.$$

and from Eq. (5.61), we obtain

$$\beta^0 = \left\{ \frac{15840 \text{ cm}^{-1} - 14719.6 \text{ cm}^{-1}}{15840 \text{ cm}^{-1}} \right\} \times 100 = 7.07 \text{ per cent}$$

(vi) In order to obtain the energy of the ³T_{1g}(P) and ³T_{1g}(F) states, put the values of $p = 14719.6 \text{ cm}^{-1}$ and $Dq = 850 \text{ cm}^{-1}$ into Eq. (5.65). On simplification, we arrive at the following equation.

$$E^2 - 1.9819 \times 10^4 E + 6.350 \times 10^7 = 0$$

Solving for E , we obtain

$$E = \frac{(1.9819 \pm 1.1777)10^4}{2} = 15798 \text{ and } 4021 \text{ cm}^{-1}$$

Thus the energy of ³T_{1g}(P) state = 15798 cm⁻¹ and of ³T_{1g}(F) state = 4021 cm⁻¹.

(vii) The position of the absorption bands corresponding to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, transitions will be

$$E = [{}^3T_{1g}(P)] - E[{}^3A_{2g}] = 15798 \text{ cm}^{-1} + 12 Dq$$

$$= 15798 \text{ cm}^{-1} \times 12 \times 850 \text{ cm}^{-1} = 25998 \text{ cm}^{-1}$$

$$E[{}^3T_{1g}(F)] - E[{}^3A_{2g}] = 4021 \text{ cm}^{-1} + 12 \times 850 \text{ cm}^{-1} = 14221 \text{ cm}^{-1}.$$

NH₃ Using the required data from the problem and proceeding as in case of H₂O, we obtain

(i) $E({}^3F) - E({}^3P) = 15 B = 15840 \text{ cm}^{-1}$

(ii) $10750 \text{ cm}^{-1} = 10 Dq$; or $Dq = 1075 \text{ cm}^{-1}$

(iii) $E[{}^3T_{1g}(P)] = 28200 \text{ cm}^{-1} - 12 \times 1075 \text{ cm}^{-1} = 15300 \text{ cm}^{-1}$

(iv) $p = 15B' = \frac{11.692 \times 10^7}{8.85 \times 10^3} = 13211 \text{ cm}^{-1}$

(v) $\beta = \frac{13211 \text{ cm}^{-1}}{15840 \text{ cm}^{-1}} = 0.834$

and $\beta^0 = \frac{15840 \text{ cm}^{-1} - 13211 \text{ cm}^{-1}}{15840 \text{ cm}^{-1}} \times 100 = 16.6 \text{ per cent}$

(vi) $p = 13211 \text{ cm}^{-1}$; $Dq = 1075 \text{ cm}^{-1}$

$$E^2 - 1.966 \times 10^4 E + 6.672 \times 10^7 = 0$$

$$E = \frac{(1.966 \pm 1.094) \times 10^4}{2} \text{ cm}^{-1} = 15295 \text{ cm}^{-1}, 4355 \text{ cm}^{-1}$$

Thus

$$E[{}^3T_{1g}(P)] = 15295 \text{ cm}^{-1}$$

and

$$E[{}^3T_{1g}(F)] = 4355 \text{ cm}^{-1}.$$

(vii) $E[{}^3T_{1g}(P)] - E[{}^3A_{2g}] = 15295 \text{ cm}^{-1} + 12 \times 1075 \text{ cm}^{-1} = 28195 \text{ cm}^{-1}$

and $E[{}^3T_{1g}(F)] - E[{}^3A_{2g}] = 4355 \text{ cm}^{-1} + 12 \times 1075 \text{ cm}^{-1} = 17255 \text{ cm}^{-1}.$

HC(O)N(CH₃)₂ Using the required spectral data from the problem and proceeding as in case of H₂O, we get,

(i) $E({}^3F) - E({}^3P) = 15 B = 15840 \text{ cm}^{-1}$

(ii) $8503 \text{ cm}^{-1} = 10 Dq$

or

$$Dq = 850.3 \text{ cm}^{-1}$$

(iii) $E[{}^3T_{1g}(P)] = 25000 \text{ cm}^{-1} - 12 \times 850.3 \text{ cm}^{-1} = 14796 \text{ cm}^{-1}$

(iv) $p = 15B' = \frac{13.1867 \times 10^7}{9.695 \times 10^3} = 13601.5 \text{ cm}^{-1}$

(v) $\beta = \frac{13601.5 \text{ cm}^{-1}}{15840 \text{ cm}^{-1}} = 0.858$

and $\beta^0 = \frac{15840 \text{ cm}^{-1} - 13601.5 \text{ cm}^{-1}}{15840 \text{ cm}^{-1}} \times 100 = 14.1 \text{ per cent}$

(vi) $p = 13601.5 \text{ cm}^{-1}$, $Dq = 850.3 \text{ cm}^{-1}$

$$E^2 - 1.8703 \times 10^4 E + 5.7824 \times 10^7 = 0$$

$$E = \frac{(1.8703 \pm 1.0886) 10^4}{2} \text{ cm}^{-1} = 14794.5 \text{ cm}^{-1}, 3908.5 \text{ cm}^{-1}$$

Thus,

$$E[{}^3T_{1g}(P)] = 14794.5 \text{ cm}^{-1}$$

and

$$E[{}^3T_{1g}(F)] = 3908.5 \text{ cm}^{-1}$$

(vii) $E[{}^3T_{1g}(P)] - E[{}^3A_{2g}] = 14794.5 \text{ cm}^{-1} + 12 \times 850.3 \text{ cm}^{-1} = 24998 \text{ cm}^{-1}$

and

$$E[{}^3T_{1g}(F)] - E[{}^3A_{2g}] = 3908.5 \text{ cm}^{-1} + 12 \times 850.3 \text{ cm}^{-1} = 14112 \text{ cm}^{-1}.$$

(b) M^{3+} and M^{2+} Ions with d^3 - and d^7 Configurations Respectively in an Octahedral field of a Ligand. The energies E (in cm^{-1}) of the various $d-d$ transitions of M^{3+} ion (with d^3 -configuration) and of M^{2+} ion (with d^7 -configuration) in an octahedral field of a ligand are shown in Figs 5.59 (a) and (b). Thus, the Racah parameters and bending constants of d^3 and d^7 ions in an octahedral field can be determined from the expressions deduced from the Figs 5.59 (a) and (b) respectively. For d^3 ions, the expressions are

$$E[{}^4A_{2g} \rightarrow {}^4T_{2g}(P)] = 12 Dq + 15 B' + x \text{ (in } \text{cm}^{-1}) \quad (5.66)$$

$$E[{}^4A_{2g} \rightarrow {}^4T_{1g}(F)] = 18 Dq - x \text{ (in } \text{cm}^{-1}) \quad (5.67)$$

$$E[{}^4A_{2g} \rightarrow {}^4T_{2g}] = 10 Dq \text{ (in } \text{cm}^{-1}) \quad (5.68)$$

For d^7 ions, the expressions are

$$E[{}^4T_{1g} \rightarrow {}^4T_{2g}(F)] = 8 Dq + x \quad (5.69)$$

$$E[{}^4T_{1g} \rightarrow {}^4A_{2g}(F)] - E[{}^4T_{1g} \rightarrow {}^4T_{2g}(F)] = 10 Dq \quad (5.70)$$

$$E[{}^4T_{1g} \rightarrow {}^4T_{1g}(P)] = 15B' + 2x + 6 Dq \quad (5.71)$$

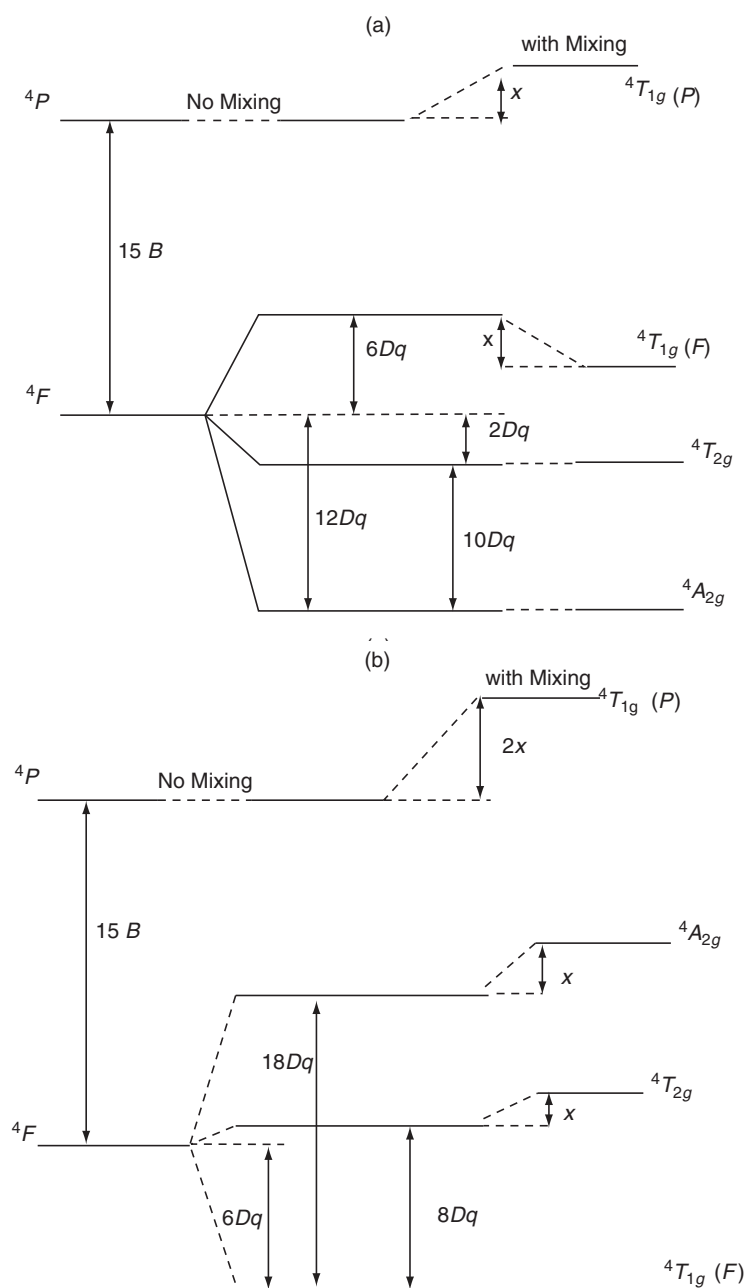


Fig. 5.59 The splitting of ${}^4F$ and ${}^4P$ spectroscopic terms of (a) d^3 , and (b) d^7 ions in an octahedral field of ligand.

Problem 5.19: The electronic absorption spectrum of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion shows three bands at 37879, 24570 and 17241 cm^{-1} . Assign these bands to the various transitions involved in the spectrum of the compound and calculate the values of the Racah parameters and that of the bending constant. $B = 918\text{ cm}^{-1}$ for virgin Cr^{3+} ion.

Solution According to Fig 5.59 (a), the bands at 37879, 24570 and 17241 cm^{-1} correspond to the ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (P), ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F) and ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transitions respectively. In order to determine B' , the values of Dq and x need to be computed first.

From Eq. (5.68) we write

$$E[{}^4A_{2g} \rightarrow {}^4T_{2g}] = 10 Dq = 17241\text{ cm}^{-1}$$

or
$$Dq = 1724.1\text{ cm}^{-1}$$

Substituting the values of $Dq = 1724.1\text{ cm}^{-1}$ into Eq. (5.67) we obtain

$$E[{}^4A_{2g} \rightarrow {}^4T_{1g} (F)] = 18 Dq - x = 24570\text{ cm}^{-1}$$

or
$$\begin{aligned} x &= (18 Dq) - 24570\text{ cm}^{-1} \\ &= (18 \times 1724.1 - 24570)\text{ cm}^{-1} \\ &= (31033.8 - 24570)\text{ cm}^{-1} = 6463.8\text{ cm}^{-1} \end{aligned}$$

Substituting the values of Dq and x into Eq. (5.66), we obtain

$$E[{}^4A_{2g} \rightarrow {}^4T_{1g} (P)] = 12 Dq + 15 B' + x = 37879\text{ cm}^{-1}$$

or
$$12 \times 1724.1\text{ cm}^{-1} + 15 B' + 6463.8\text{ cm}^{-1} = 37879\text{ cm}^{-1}$$

or
$$15 B' = (37879 - 6463.8 - 20689.2)\text{ cm}^{-1} = 10726\text{ cm}^{-1}$$

or
$$B' = 715\text{ cm}^{-1}$$

Thus, by Eq. (5.62);

$$\beta = \frac{B'}{B} = \frac{715\text{ cm}^{-1}}{918\text{ cm}^{-1}} = 0.778.$$

and from Eq. (5.61),
$$\beta^0 = \frac{(918 - 715)\text{ cm}^{-1}}{918\text{ cm}^{-1}} \times 100 = 22.1\text{ per cent}$$

Problem 5.20. The electronic absorption spectrum of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ shows three bands at 8000, 16000 and 19417 cm^{-1} . Calculate the values of Racah parameters as well as that of Dq and bending constant. $B = 917\text{ cm}^{-1}$ for bare Co^{2+} ion.

Solution From Fig 5.59 (b) and Eqs. [5.69 – 5.71], we write

$$E({}^4T_{1g} \rightarrow {}^4T_{2g}) = 8000\text{ cm}^{-1} = 8 Dq + x$$

$$E[{}^4T_{1g} \rightarrow {}^4A_{2g} (F)] - E[{}^4T_{1g} \rightarrow {}^4T_{2g}] = 10 Dq = (16000 - 8000)\text{ cm}^{-1} = 8000\text{ cm}^{-1}$$

and
$$E[{}^4T_{1g} \rightarrow {}^4T_{1g} (P)] = 15 B' + 2x + 6Dq = 19417\text{ cm}^{-1}$$

Solving these Eqs, for Dq , x and B' , we get

$$Dq = 800\text{ cm}^{-1}, x = 1600\text{ cm}^{-1} \text{ and } B' = 761.1\text{ cm}^{-1}$$

Thus,
$$\beta = \frac{761.1\text{ cm}^{-1}}{917\text{ cm}^{-1}} = 0.78 \text{ and } \beta^0 = \frac{(917 - 761)\text{ cm}^{-1}}{917\text{ cm}^{-1}} \times 100 = 21.6\text{ per cent}$$

(c) M^{2+} ions with d^7 Configuration in tetrahedral field. The transition energies E_s (in cm^{-1}) of the various $d-d$ transitions of Co^{2+} ion in tetrahedral field are related to Δ_t by the following expressions.

$$E_1 = \Delta_t \text{ for } {}^4A_2 \rightarrow {}^4T_2 \quad (5.72)$$

$$E_2 = 1.5 \Delta_t + 7.5 B' - Q \text{ for } {}^4A_2 \rightarrow {}^4T_1 (F) \quad (5.73)$$

$$E_3 = 1.5 \Delta_t + 7.5 B' + Q \text{ for } {}^4A_2 \rightarrow {}^4T_1 (P) \quad (5.74)$$

$$Q = \frac{1}{2} \sqrt{(0.6 \Delta_t - 15 B')^2 + 0.64 \Delta_t^2} \quad (5.75)$$

The spectroscopic ground terms of M^{2+} ion with d^7 configuration, i.e. Co^{2+} , are ${}^4F$ and ${}^4P$. The Mulliken terms corresponding to ${}^4F$ are ${}^4A_2$, ${}^4T_2$ and ${}^4T_1 (F)$ while ${}^4T_1 (P)$ for ${}^4P$. The energy difference between spectroscopic terms of Co^{2+} gaseous ions is 14565 cm^{-1} , i.e. $15 B = 14565 \text{ cm}^{-1}$. The above expressions can be used to determine the values of Δ_t and β for Co^{2+} ion in tetrahedral field from the spectral data as follows:

Addition of Eqs. (5.73) and (5.75) yields.

$$\Delta_t = \frac{E_2 + E_3 - 15 B'}{3} \quad (5.76)$$

Subtracting Eq. (5.73) from Eq. (5.74), we obtain

$$Q = \frac{1}{2} (E_3 - E_2) \quad (5.77)$$

Squaring both sides of Eq. (5.75) and rearranging the resultant expression, we obtain

$$4Q^2 = \Delta_t^2 - 18 B' \Delta_t + 225 (B')^2 \quad (5.78)$$

Substitute the values of Δ_t and Q from Eqs. (5.76) and (5.77) respectively into Eq. (5.78), and solve for B' . Once B' is known, the value of Δ_t can be obtained from Eq. (5.76) and β° and β from Eqs. (5.61) and (5.62) respectively.

Problem 5.21: The electronic absorption spectrum of $[\text{Co}(\text{Cl})_4]^{2-}$ yields two bands at 15000 and 5800 cm^{-1} . The former has been assigned to ${}^4T_2 \rightarrow {}^4T_1 (P)$ while the latter to ${}^4A_2 \rightarrow {}^4T_1 (F)$ transitions. Calculate the values of the Racah parameters for Co^{2+} ion in the tetrahedral field due to chloride ions.

Solution Here, $E_3 = 15000 \text{ cm}^{-1}$ and $E_2 = 5800 \text{ cm}^{-1}$.

From Eq. (5.77), we obtain

$$Q = \frac{1}{2} (E_3 - E_2) \text{ cm}^{-1} = \frac{1}{2} (15000 - 5800) \text{ cm}^{-1} = \frac{9200}{2} \text{ cm}^{-1} = 4600 \text{ cm}^{-1}$$

Substituting the values of E_3 and E_2 into Eq. (5.76), we get

$$\Delta_t = \frac{(5800 + 15000) \text{ cm}^{-1} - 15 B'}{3} = \frac{20800 \text{ cm}^{-1} - 15 B'}{3} = 5[1387 \text{ cm}^{-1} - B']$$

Substituting $Q = 4600 \text{ cm}^{-1}$ and $\Delta_t = 5 [1387 \text{ cm}^{-1} - B']$ into Eq. (5.75), we obtain a quadratic in B' , i.e.

$$4 \times (4600)^2 = 25 (1387 - B')^2 - 18 \times B' \times 5 (1387 - B') + 225 B'^2$$

Simplification and rearrangement of the above expression yields

$$68 B'^2 - 38836 B' - 7309155 = 0$$

Solving the quadratic for B' , we get

$$B' = \frac{38836 \pm 59128.6}{136} \text{ cm}^{-1}$$

Thus,

$$B' = \frac{97964.6}{136} = 720 \text{ cm}^{-1}$$

The negative root is not considered.

For

$$B' = 720 \text{ cm}^{-1},$$

$$\Delta_i = 5 (1387 \text{ cm}^{-1} - 720 \text{ cm}^{-1}) = 3335 \text{ cm}^{-1}.$$

Since,

$$\Delta_i = E_1; \text{ therefore, } E_1 = 3335 \text{ cm}^{-1}$$

$E_1 (= 3335 \text{ cm}^{-1})$ corresponds to the ${}^4A_2 \rightarrow {}^4T_2$ (F) transition. A band at 3300 cm^{-1} has indeed been reported in the infrared region of the spectrum.

The nephelauxetic ratio β is obtained from Eq. (5.62), i.e.

$$\beta = \frac{B'}{B} = \frac{720 \text{ cm}^{-1}}{971 \text{ cm}^{-1}} = 0.74$$

and the value of parameter β^0 from Eq. (5.61), i.e.

$$\beta^0 = \frac{(971 - 720) \text{ cm}^{-1}}{971 \text{ cm}^{-1}} \times 100 = 25.8 \text{ per cent}$$

5.19 BASIC PRINCIPLES OF A DOUBLE BEAM UV-VISIBLE SPECTROPHOTOMETER

The self-explanatory block diagram indicating the basic elements of an UV-visible spectrophotometer is shown in Fig. 5.60. The spectrophotometer consists of radiation source, two cells, one for sample solution and the other called reference or blank cell for solvent only. The radiation from the source is passed through each of these cells separately, and analysed and detected using a rotating prisim and a photomultiplier. The given range of wavelengths is scanned for both the beams with a suitable optical arrangement of series of mirrors, prisms and diffraction gratings not shown in the Fig. 5.60. The radiation is made to fall alternately on the detector

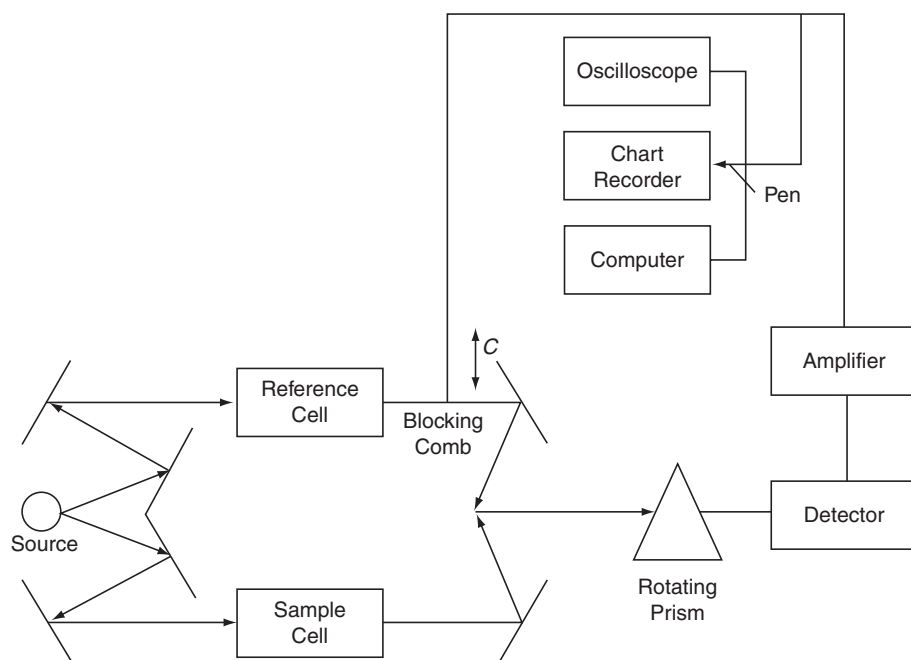


Fig. 5.60 Block diagram of a double beam UV-visible/infrared spectrophotometer.

with the help of a pair of rotatable chopping mirrors. When two beams have the same intensity, there is no resultant signal from the detector and the blocking or compensating comb C is withdrawn from the reference beam. When the radiation is absorbed by the sample at a particular wavelength, the comb C moves into the reference beam so that the emergent beams retain the same intensity. The movement of the comb which is connected to the chart recorder/computer/oscilloscope and the amplifying assembly is a measure of absorption of radiation by the sample at a given wavelength. Thus, the absorption spectra are plot of absorption against wavelength or a plot of $\log \epsilon$ against wavelength. The plot between $\log \epsilon$ and wavelength has an advantage over the plot between absorbance and wavelength especially in related compounds. The absorption intensity of related compounds is about the same but the parameter ϵ brings out the differences better. This is probably so when a large part of the molecule does not contribute to absorption which is due to chromophore only, but certainly contributes to the molecular mass. When the molecular mass is not known then specific absorption coefficient is used.

(a) Monochromators and Windows A monochromator is a device to isolate a band of wavelengths, usually much narrower than is obtained by a filter. Glass is the material used for prisms, windows and lenses in the visible region. Fused silica or quartz prisms, windows and lenses are used both in the UV and visible region out to 185 nm. Lithium fluoride is used out to 110 nm and calcium fluoride or sapphire out to 125 nm. Reflection grating monochromators are used both in the UV and visible region.

(b) Sources of Radiation Sources of radiation in the UV-visible region of the spectrum are 400 W high pressure Xe discharge lamp (300–1000 nm). Tungsten filament lamps in quartz envelopes (near ultraviolet), Tungsten filament lamps (300–1000 nm), high pressure hydrogen or helium discharge lamps (300–200 nm or below); 1 mm of H_2 or He, emits a continuum useful out to 100–60 nm. UV spectrum out to 185 nm can be studied by flushing out air with nitrogen since atmospheric O_2 starts absorbing at around is 195 nm. Lower wavelengths than this require evacuated path.

(c) Detectors Three types of photosensitive devices, called detectors, used to detect-radiations are Barrier layer or photovoltaic cells. Photoconductive cells permit operation down to 1μ (near infrared). Phototubes or Photo-emissive (vacuum) Tubes These tubes are more sensitive than photovoltaic cells, and photomultiplier tubes. (The sensitivity of a photo-emissive cell can be increased by employing the photomultiplier tube.) Photographic detection is still a very useful means of obtaining ultraviolet spectra, particularly for high-resolution studies.

(d) Sample Preparation and Cells The solvent used for the test solution should not absorb radiation in the region of electromagnetic spectrum under investigation. Some of the most commonly used solvents along with their lowest wavelength limit (in nm) for 1 cm cell are acetonitrile (190), water (191), cyclohexane (195), hexane (201) or any other saturated hydrocarbon, methanol (203), ethanol (204), ether (215), methyl chloride (220) chloroform (237), carbon tetrachloride (257), carbon disulphide (380), acetone (330), benzene (285), toluene (290), dioxane (220). Cells used for the determination of spectra in solution vary in path length from 1 to 10 cm. However cells are generally of 1 cm thickness and *effective thickness*, also called *optical thickness*, is changed by changing the concentration of the sample. Microcells with an internal width of 2 mm and a path length of 0.1 mm are used when only a small amount of solution is available. Glass cells are used in the visible region while for UV region, cells made of quartz are used. When cell thickness is not mentioned, it is taken as 1 cm. Solid samples are examined as thin films (cast or painted or evaporated), KBr pellets or 'Nujolmulls'. Reflectance studies are made on solids.

The samples for investigation are very dilute solutions, though gases can be used. They are held in fused quartz cells, usually of 1.0 to 100 mm path length. Path lengths of 0.5–120 m can be achieved by using cells containing mirrors. These cells are equipped with gas inlets and outlets. Cell jackets are available through which liquids may be circulated for temperature control. The sensitivity of detection is 10^{-6} – 10^{-7} g. For UV spectral studies, the instrument is evacuated for air since atmospheric oxygen UV absorption starts at wavelengths less than 200 nm (i.e. in 195 nm, Schumann–Runge band systems; such studies may be covered under vacuum UV spectroscopy).

Note that the block diagram of IR single and double-beam spectrophotometers applies equally to UV-visible spectrophotometers but the sources and detectors and the materials used for prisms and the specifications of the grating are different. Moreover, in IR the monochromator is placed before the detector and after the sample to avoid stray light while in UV-visible, it is kept before the sample.

The more elaborated block diagram for double-beam UV-visible spectrophotometer applies equally to IR-double-beam spectrophotometer, but again here the sources and the detectors and the materials used for prisms and specifications of the grating used are different. The IR spectra are recorded in the transmission mode while the UV-visible spectra are recorded in the absorption mode.

(e) Wavelength Calibration Wavelengths are checked from both sides by a mercury arc source which gives lines at 690.7, 579.1, 577.0, 546.1, 496.0, 491.6, 435.8 and 404.7 nm, potassium flame which gives lines at 769.9 and 766.5 nm or even a hydrogen lamp for a quick check. Hydrogen gives three lines at 656, 486.1 and 379.9 nm. The wavelength is usually set by rotating the prism or grating or a mirror. The other sources for wavelength checking are rare earth glasses (holmium, dysmium, etc.) or vapour absorption bands of benzene or any line source like neon, Ar, Kr, cadmium, etc. Wavelength of the red cadmium line in air, 760 mm pressure and 15°C is 6438.4696 Å and is used as a primary standard. Wavelengths of such sources along with their intensities both in the UV and visible regions are given in standard data books such as '*Handbook of Chemistry and Physics*' by CRC Press.

(f) Calibration of Photometric Scale The photometric scale is checked by liquid standards such as KNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ or K_2CrO_4 solutions. The complete prescriptions are given in standard data books together with absorbance values. Solid standards with well-defined absorbances marked on them are also available, e.g. rhodiumised glass or silica or other set of neutral absorbance filters. A dye suspended in gelatin and sandwiched between two glass plates acts as an absorption filter. Coloured solutions of inorganic salts and organic dyes in rectangular cells

Table 5.22 Absorption characteristics of some common filters

Colour of filter	Absorption band (in nm or m μ)
Yellow	450
Red	575
Purple	450–650
Orange	500
Blue	480
Green	575–700

can also act as filters. Coloured glass filters are preferred as compared to solution filters because of their greater thermal stability. Characteristics of some common filters are described in Table 5.22.

The filters transmit radiations of some desired wavelength which correspond to the absorption maximum but absorb wholly or partially other unwanted wavelengths. Coloured glasses are used as filters in the visible region. The other class of filters which function on the interference phenomenon, called interference filters, are also in use. Such a type of filter consists of a layer of transparent material such as magnesium fluoride or calcium fluoride which is coated on each side with a semitransparent thin film of silver. The wavelength bands are isolated and called band pass, i.e. width of the transmission band at half the peak transmission are much narrower (10–15 nm) and the peak transmittances much greater (40–60 per cent) than in case with glass filters (i.e. 35–50 nm; 5–20 per cent decreasing with improved spectral isolations). Multi-layer interference filters have transmissions of 50–70 per cent and bandwidths of 1.0–5.0 nm. Filters of one type or another are available which, alone or in combination, allow a selection of wavelength bands at almost any region of the spectrum, from x-rays through the infrared. The band of wavelengths isolated by filters is much broader than that obtained by a monochromator.

5.19.1 Spectrographs

A spectrograph is an instrument for producing a spectrogram, a photographic image of the spectrum. Both absorption and emission high-resolving power spectrographs are employed to record the spectra of gases. The self-explanatory flowsheet diagram of

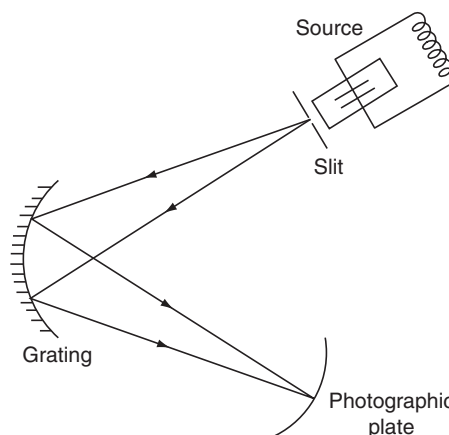


Fig. 5.61 Block diagram of a simple high-resolution ultraviolet or visible spectrograph.

a simple high-resolution spectrograph is shown in Fig. 5.61. The dispersing element of the spectrograph is a grating. Source of radiation for absorption studies is a discharge lamp and for emission spectrum, samples are excited either thermally or electrically and the spectrum is recorded photographically. The photographic plate or film is mounted so that successive wavelengths are focussed at the successive points. Thus, an entire spectral region can be photographed simultaneously. The whole spectrograph is housed in an evacuated tank to allow air to be removed, since atmospheric oxygen UV absorption starts around 195 nm (Schumann–Runge band systems) [Vacuum UV spectroscopy]. The rotational fine structure of the electronic bands, even for many diatomics, is not clearly resolved if the resolving power of the spectrograph is not very high. So, spectrographs with focal lengths of several metres are used.

5.20 APPLICATIONS OF LOW RESOLUTION UV-VISIBLE SPECTROSCOPY

Chemical analysis or the art of qualitative identification of different substances and determining their amounts in a quantitative way, is of great importance for the progress of science and technology. Just like other spectroscopic techniques, namely IR, NMR, etc., UV Visible spectroscopy also meets the above qualifications. Wavelength position of the absorption band is a criterion for the identification of chemical species and as such is used for qualitative analysis. Variation of absorption with polarisation of radiation throws light on the internal structure of the molecule. If the incident radiation used in an absorption experiment is polarised, only those transitions with similarly oriented dipole moment vector will occur. In a powder, the molecules or complex ions are randomly oriented.

All allowed transitions will be observed, for there will be a statistical distribution of crystals with dipole moment vectors aligned with the polarised radiations. However, suppose, for example, a formaldehyde crystal, with all molecules arranged so that their Z-axes are parallel, is examined. When the Z-axis of the molecules in the crystal are aligned parallel to the plane of polarisation of light in the Z-direction, light will be absorbed for $\pi\text{--}\pi^*$ transition. Light of this wavelength polarised in other planes will not be absorbed. If this crystal is rotated so that Z-axis is perpendicular to the plane of polarisation of light, no light is absorbed. This behaviour supplements the assignment of the band to $\pi\text{--}\pi^*$ transition. Intensity of light absorbed is a measure of the quantity of the absorbers present and is useful for quantitative analysis. Based on these parameters, some of the qualitative, quantitative and biological applications of this technique are described here.

5.20.1 Qualitative Applications

The qualitative applications are based on the position of the absorption maxima and factors affecting it, e.g. temperature, pH, concentration, solvent, etc.

(a) Identification of Molecular Species The visible UV spectra are distinguishable for many different species. Solutions of hydrated cobalt ion are pink while those of cobalt ion formed in excess of chloride ions are blue. The absorption spectra of these two ions, i.e. $\text{Co}[(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$, are completely different as shown in Fig. 5.62. The absorption maximum in the former is at 515 nm and 667 nm in the latter.

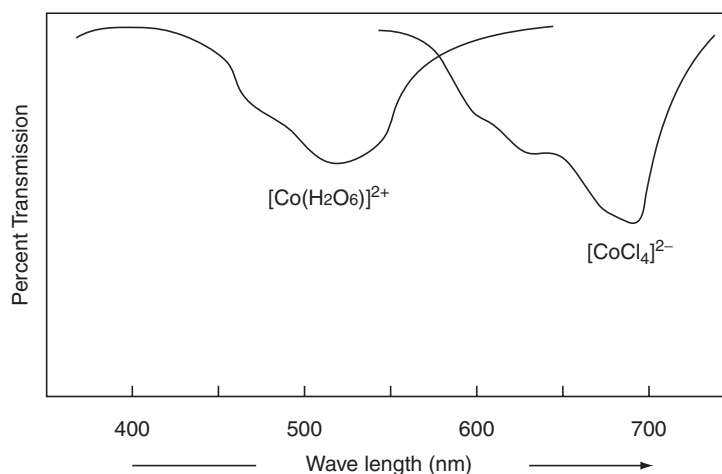
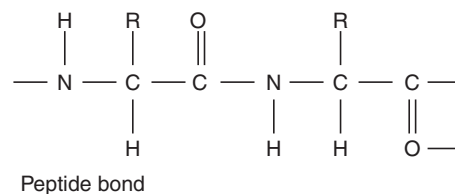


Fig. 5.62 The absorption spectra of two complex ions of cobalt.

(b) Search for Extraterrestrial Life on Planets Among the more novel and fascinating uses of UV absorption spectra is the plan to search for extraterrestrial life using automated instrumentation in space probes such as Viking missions to Mars and other planets. Molecules, such as proteins that contain peptide bonds, absorb in a band centred around 195 nm in the UV. Water molecule shows $n-\sigma^*$ band at 167 nm ($\epsilon_{\max} = 7000$).

If a sample dug by the probe showed these absorptions, it would be suspected of containing a biological material and water. Thus, one can infer from these type of data whether water and life in the present/past was possible on Mars and on other planets or not. Such type of data could also give scientists clues about how life on Earth began and the origin of life on Earth.



(c) Study of Environmental Effects on Molecular Systems Molecules are generally affected by their environments. UV/visible spectral shifts provide valuable information about these effects since UV/visible spectra are sensitive to intermolecular interactions such as solvent effects that modify the electronic states of the molecule or ion, e.g. molecular iodine dissolves in nonpolar solvents such as carbon tetrachloride (CCl_4) or cyclohexane (C_6H_{12}) with very little interactions between I_2 and solvent molecules. These solutions of iodine have a characteristic purple colour similar to the colour of solid and gaseous iodine ($\lambda_{\max} = 520 \text{ nm}$). However, in solvents such as pyridine ($\text{C}_5\text{H}_5\text{N}$), the colour changes to reddish brown with the change in the absorption spectrum. The change is due to the interaction of iodine with the pyridine molecule and affects one or more of the electronic states of iodine changing their energies and thereby changing the frequencies of the radiation absorbed.

(d) Structural Elucidation Structural information such as bond-distances and angles can't be deduced from most UV/Visible absorption spectra but it provides a valuable tool in the identification of unsaturated organic compounds and in elucidation of their structure. However, it has no match to infrared spectroscopy. According to Prof. Woodward, no single tool has had more dramatic impact upon organic chemistry than infrared measurements.

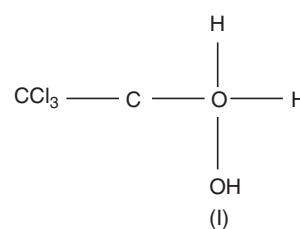
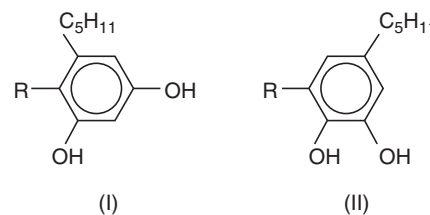
Position of the absorption band and its intensity is used for identification of the compound. The certainty of identification can be improved by measuring the spectrum in a number of solvents or solution conditions such as pH of both the known and unknown. According to Hartley's rule, 'compounds having similar structure would have similar absorption spectra'.

Sometimes (but not always like IR, NMR, etc.) a direct comparison of absorption spectrum of an unknown compound with those of model compounds of known structures may give information about the structure of an unknown compound, e.g. chemical analysis of cannabidiol, (a substance isolated from wild hemp), suggests that its structure could either be (I) or (II).

The UV spectra of this compound shows two bands around 276 and 282 nm. The shape and position of the bands resemble very closely with that of 5-amyl resorcinol rather than that of 4-amyl resorcinol which is quite different. Thus, the structure of cannabidiol corresponds to (I).

An aliphatic or alicyclic hydrocarbon, alcohol, ether, acid or a ketone does not show any absorption band in the 200–800 nm region. A weak band near 280 nm suggests an aldehyde or a ketone. A strictly substituted phenyl or triene can also give a band around 280 nm but its intensity is very strong.

The characteristic bands due to chromophores are an aid for determining the general structure of molecules. The conjugated double bonds in the molecule cause a red shift of absorption band of the parent molecule. These features when examined systematically provide many useful facts about structure. If a compound contains two, three or four conjugated double bonds, a band is observed in the 220–300 nm region and vice versa. This shows that a prior chemical information plays an important role in identification. It is to be noted that these group determinations are possible only in relatively simple but not for large chromophores like dyes. The procedure has been particularly useful in fields of carotenoids, unsaturated fatty acids, alkaloids, terpenes, steroids where the proposed structure contains double bonds, conjugated or unconjugated, cyclic (cis) or a cyclic (trans). We can only answer specific



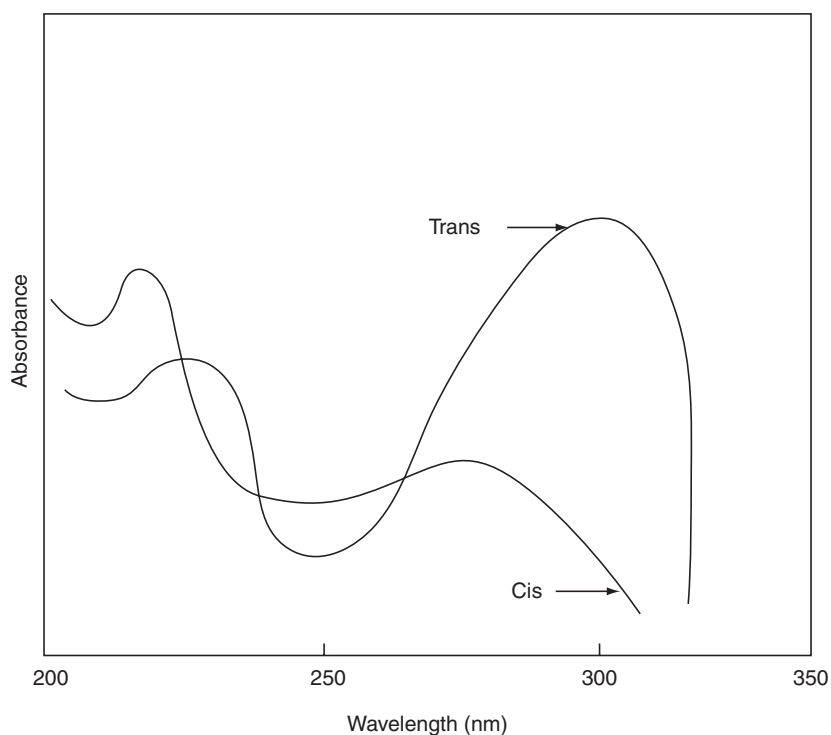


Fig. 5.63 Absorption spectra of *cis*- and *trans*-stilbenes.

questions on the basis of UV/V spectral data. This is demonstrated here with the aid of some typical examples. Chloralhydrate shows a band at 290 nm with $\epsilon_{\text{max}} = 33$. However, this band is absent in aqueous medium.

Thus, the structure of chloralhydrate is $(\text{CCl}_3 - \text{CHO}) \text{H}_2\text{O}$ but not structure (I) since the low intensity band at 290 nm is attributed to carbonyl group. Geometrical isomers with conjugation usually have different UV spectra. *Cis*-stilbene (1, 2-diphenyl ethylene) shows an absorption band at 280 nm with $\epsilon_{\text{max}} = 12300$ in ethanol while *trans*-isomer exhibits a corresponding band at 295 nm with $\epsilon_{\text{max}} = 25000$ in ethanol (Fig. 5.63). Delocalisation of the π -electrons, i.e. coplanarity, is destroyed by steric interference in *cis*-isomer. The molecule has to twist slightly out of plane to avoid clashing of the hydrogen atoms at the *o*-positions of the two benzene rings. Consequently, a low-intensity band is observed in the *cis*-form. A band in stilbene appears to be swamped by the intense band at 295 nm. The parent absorption bands of stilbene molecule shift to longer wavelengths and undergo increase in intensity also as ' n ' in $\text{C}_6\text{H}_5 - (\text{CH} = \text{CH})_n - \text{C}_6\text{H}_5$ increases. For $n = 7$, the molecule absorbs in the 400–465 nm region with $\epsilon_{\text{max}} = 135000$.

We can find whether the two double bonds in any unsaturated system are conjugated or not, e.g. mesityloxide an α - β unsaturated ketone, absorbs at 230.6 nm with $\epsilon_{\text{max}} = 12000$ in isooctane and 237.6 nm in chloroform. So it must be $-\text{C} = \text{C} - \text{C} = \text{O}$. Further, we can also differentiate whether the two double bonds conjugated are alicyclic diene or exocyclic or aliphatic diene. The former absorbs at 250 nm with $\epsilon_{\text{max}} = 5000$ while the latter at 225 nm with $\epsilon_{\text{max}} = 10,000$.

Apart from these, specific empirical rules have been worked out, which enable us to deduce the position of substituents or double bonds in a particular class of compounds, e.g. various heterocyclic compounds and their derivatives, fused ring systems (naphthalene), many steroids, terpenes, flavone, anthraquinone, etc.

5.20.2 Woodward–Fieser Rules for Predicting the Wavelength of Absorption Maximum in Conjugated Dienes

According to these rules, each type of diene has a certain fixed value. The wavelength of the absorption maximum λ_{max} depends upon (i) the number of alkyl substituents or ring residues on the double bond, (ii) the number of double bonds which extends conjugation, and (iii) the presence of polar groups such as $-\text{Cl}$, $-\text{Br}$, $-\text{OR}$, $-\text{SR}$, $-\text{NR}$, etc. These rules are summarised in Table 5.23.

These rules are obeyed by conjugated systems of four double bonds or less. For conjugated polyenes having more than four double bonds, the Fieser–Kuhn rules hold good.

Table 5.23 Woodward–Fieser rules for diene and triene (π – π^* transition) absorption (contribution of various structural units towards $\lambda_{\max}$).

	(nm)
Parent value for:	
Butadiene system or cyclic conjugated system	217
Heteroannular or open chain diene	214
Homoannular diene	253
Increments for:	
Alkyl substituent or ring residue	5
Exocyclic double bond	5
Double bond extending conjugation	30
Polar groups:	
– O alkyl	6
– O acyl	0
– S alkyl	30
– Cl, –Br,	5
– N (alkyl) ₂	60

Solvents have negligible contribution to $\lambda_{\max}$ of these π – π^* transitions, i.e. solvent correction is zero. In addition when both homo- and hetero-annular conjugated diene systems are present in the same compound, the base value corresponding to homo-annular diene, i.e. 253 nm, is used. When a diene system is present in bicyclic compound, then a correction factor of 15 nm due to strain in the bicyclic compound is added to the calculated value of absorption maximum.

Factors Affecting the Woodward–Fieser Rules The discrepancy between the observed and calculated values of absorption maximum (i.e. $\lambda_{\max}$) may be due to the following parameters:

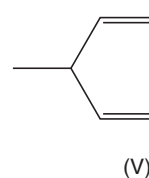
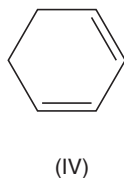
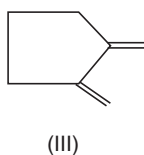
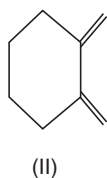


(i) Strain in the Molecule Strain in the molecule may cause a blue shift from the calculated value, e.g. verbenene (I) shows an absorption maximum at 245.5 nm while Woodward–Fieser rules yield a value of 229 nm, i.e. the blue shift deviation is 16.5 nm.

(ii) Distortion of Chromophore Distortion of chromophore in dienes may cause blue or red shifts depending upon the nature of distortion from the expected theoretical value. When distortion of chromophore affects the coplanarity of the structure, loss of conjugation takes place, and consequently, a blue shift results, e.g. the expected value for the diene (II) is 273 nm while the observed value is 220 nm ($\epsilon_{\max} = 5500$ nm). On the other hand, even when the coplanarity is not likely to be affected, still a red shift from the expected value results, e.g. the expected value for the diene (III) is 238.5 nm while the observed value is 248 nm ($\epsilon_{\max} = 15800$), i.e. a red shift of 9.5 nm.

(iii) Ring Size The change of ring size in case of simple homo-annular dienes exhibits a blue shift from the expected theoretical value, e.g. the expected value for diene (IV) is 263 nm while the observed value for cyclopentadiene is 238.5 nm ($\epsilon_{\max} = 3400$); cycloheptadiene is 248 nm ($\epsilon_{\max} = 7500$) and cyclohexadiene is 256 nm ($\epsilon_{\max} = 8000$)

(iv) Cross Conjugation Cross conjugation such as (V) in conjugated polyenes also affects the expected $\lambda_{\max}$ value.



In view of the foregoing discussion, one should be very careful while comparing the UV spectra of an unknown compound with the model compound. Corrections regarding the shape of the molecule, strain in the molecule, steric hindrance, distortion of chromophore, etc., must be taken into consideration before jumping to any conclusion about the structure of the unknown compound.

5.20.3 Fieser-Kuhn Rules

According to these rules, both the $\lambda_{\max}$ and $\epsilon_{\max}$ is related to the number of conjugated double bonds as well as other structural units by the following equations:

$$\lambda_{\max} = 114 + 5M + n(48.0 - 1.7n) - 16.5R_{\text{endo}} - 10R_{\text{exo}} \quad (5.79)$$

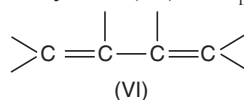
$$\epsilon_{\max} = (1.74 \times 10^4)n \quad (5.80)$$

where n is the number of conjugated double bonds, M is the numbers of alkyl or alkyl-like substituents on the conjugated system, R_{endo} is the number of rings with endocyclic double bonds in the conjugated system and R_{exo} is the number of rings with exocyclic double bonds in the conjugated system.

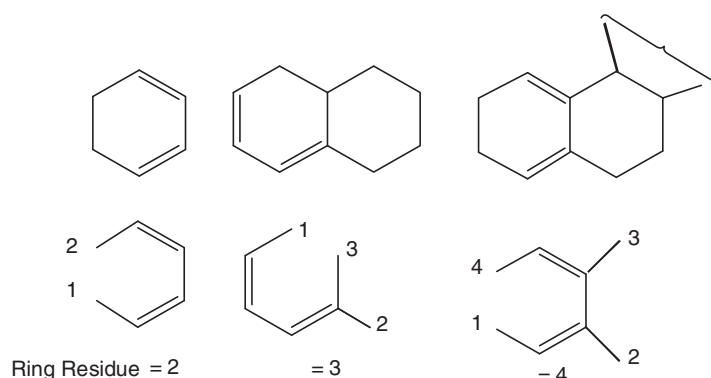
These rules hold good for polyenes with more than four conjugated double bonds, e.g. lycopene, α - and β -carotenes, etc.

Before applying these rules, let us describe the general structure and electronic spectra of various types of conjugated dienes. The four types of conjugated dienes are the following:

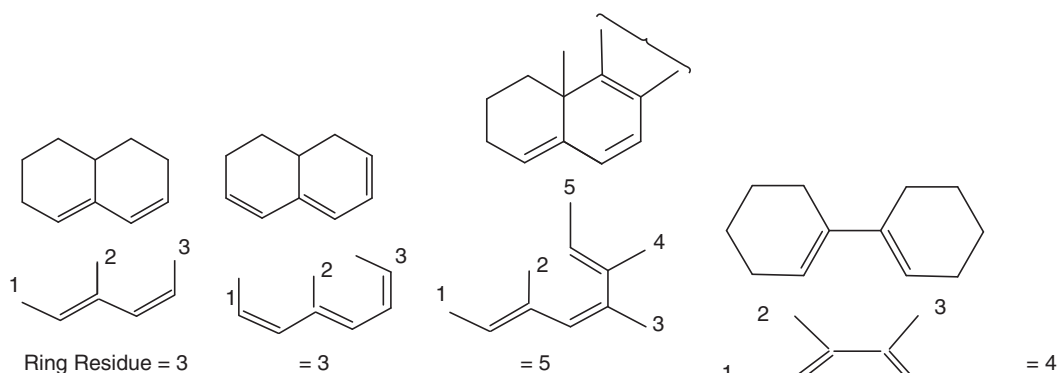
(a) Alicyclic Dienes or Dienes They are open-chain dienes and exist normally in the *s-trans* (transoid) conformation. The basic unit in them is the butadiene system (VI) i.e. $\epsilon_{\max}$ in these dienes lies in the 8000–20000 range.



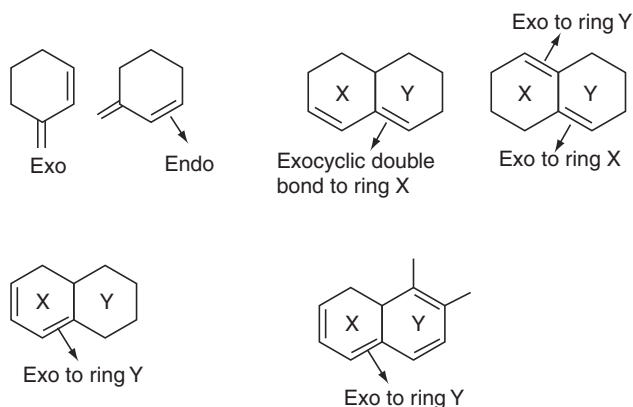
(b) Homo-annular Dienes They have conjugated double bonds in the same ring and exist in the *s-cis* (cisoid) conformation. Since the transition moment in homodienes is small as compared to those of hetero-annular and alicyclic dienes, the $\epsilon_{\max}$ is of the order of ~10,000. Typical examples of homo-annular dienes are shown below.



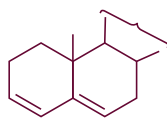
(c) Hetero-annular Dienes They have conjugated double bonds in different rings. $\epsilon_{\max}$ in these dienes is comparable to that of alicyclic dienes, i.e. $\epsilon_{\max} = 8000$ –20000. Typical examples of these systems are shown here.



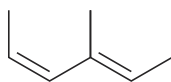
(d) Exocyclic and Endocyclic Dienes They contain exo- and endocyclic conjugated double bonds as shown in the systems.



Problem 5.22: Calculate the absorption maximum for cholesta-3, 5,-diene in ethanol,



Solution It is a heteroannular diene and its spectroscopic conjugated skeleton is



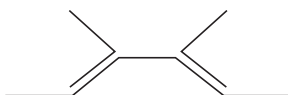
Thus, from Table 5.23 we write

Structural unit	Absorption (in nm)
Base value	214
Ring residues (= 3)	15
Exocyclic double bond (= 1)	5
	$\lambda_{\max} = 234 \text{ nm}$
	$\lambda_{\max} (\text{obs}) = 235 \text{ nm} (\epsilon_{\max} = 19000)$
Obs $\lambda_{\max}$ for cholesta-2, 4,-diene = 275 nm ($\epsilon_{\max} = 10000$)	

Problem 5.23: Calculate the absorption maximum for



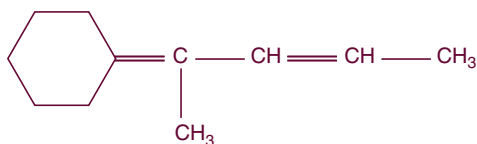
Solution It is heteroannular diene. Its spectroscopic conjugated skeleton is



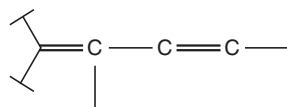
Thus, from Table 5.23 we write

Structural unit	Absorption (in nm)
Base value	214
Ring residues (= 4)	20
	$\lambda_{\max} = 234 \text{ nm} (\text{obs: } 234 \text{ nm})$

Problem 5.24: Calculate the absorption maximum for 4-cyclohexenyl-2-pentene.



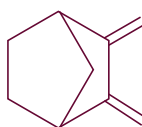
Solution It belongs to a butadiene system and its spectroscopic conjugated skeleton is



Thus, from Table 5.23 we write

Structural unit	Absorption (in nm)
Base value	217
Alkyl substituent (= 2)	10
Ring residues (= 2)	10
Exocyclic double bond (= 1)	5
	$\lambda_{\max} = 242 \text{ nm}$
	$\lambda_{\max} (\text{obs}) = 242 \text{ nm}$

Problem 5.25: Calculate the absorption maximum for 2, 3-dimethylene bicyclo [2, 2,] haptane;

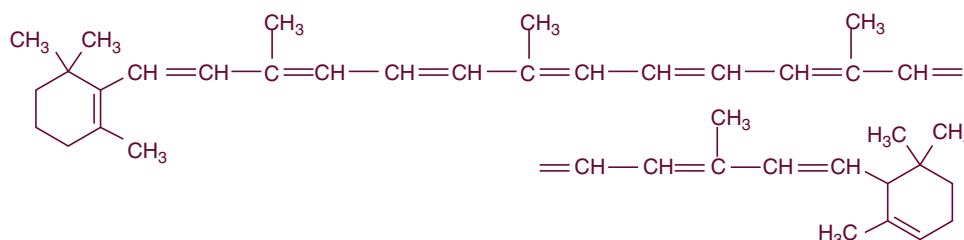


Solution From Table 5.23 we write

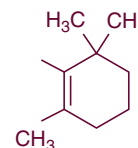
Structural unit	Absorption (in nm)
Base value	217
Ring residues (= 2)	10
Exocyclic double bonds (= 2)	10
Bicyclic system (= 1) cause strain	15
	$\lambda_{\max} = 252 \text{ nm}$ (obs: 254 nm)

Problem 5.26: Yellow plant pigments α -, β - and γ -carotene (e.g. carrots contain 15 per cent α , 85 per cent β , 0.1 per cent γ) and the red pigment of tomatoes, i.e. lycopene, are converted into vitamin A in the liver, the lack of which in the diet causes hardening of the conjunctiva, corneal softening and to complete blindness, weight loss and poor general physical condition; and a deficiency of vitamin A causes night blindness. All the four pigments have the same molecular formula ($\text{C}_{40} \text{H}_{56}$) but different structures given below:

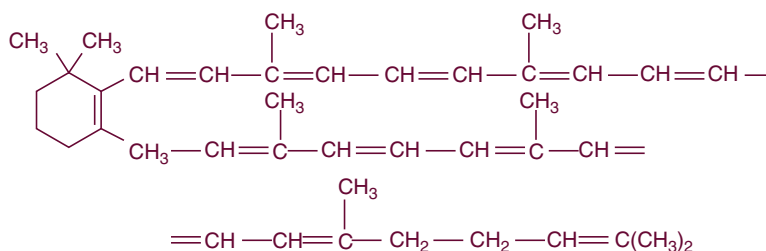
(a) α -carotene

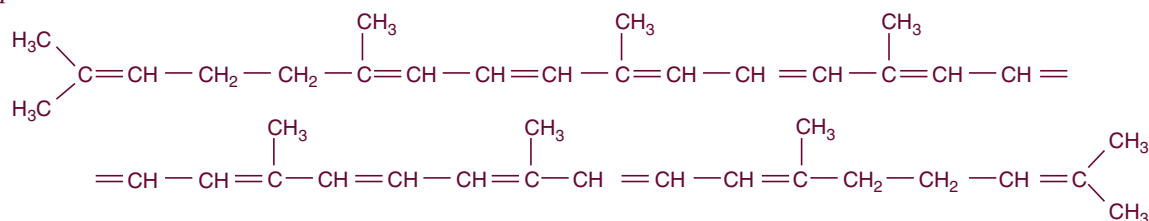


(b) β -carotene The ring on the right-hand side is



(c) γ -carotene



(d) *Lycopene*

Calculate the absorption maximum for the given systems.

Solution (a) In α -carotene, there are ten conjugated double bonds, i.e. $n = 10$; and five methyl groups on the conjugated system, i.e. $M = 5$. There are two rings with endocyclic double bonds in α -carotene. Thus from Eq. (5.79), we obtain

$$\lambda_{\max} = 114 + 5 \times 10 + 10(48.0 - 1.7 \times 10) - 16.5 \times 2$$

$$= 114 + 50 + 480 - 170 - 33.0 = 441 \text{ nm}$$

$$\lambda_{\max} (\text{obs}) = 445 \text{ nm.}$$

and from Eq. (5.80), we get

$$\epsilon_{\max} = (1.74 \times 10^4) 10 = 1.74 \times 10^5; \epsilon_{\max} (\text{obs})$$

$$= 1.45 \times 10^5$$

(b) In β -carotene, $n = 11$; $M = 10$, there are two rings with endocyclic double bond in the molecule.

Thus

$$R_{\text{endo}} = 2$$

From Eqs (5.79) and (5.80), we get

$$\lambda_{\max} = 114 + 5 \times 10 + 11(48.0 - 1.7 \times 11) - 2 \times 16.5 = 114 + 50 + 528 - 205.7 - 33$$

$$= 453.3 \text{ nm}; \lambda_{\max} (\text{obs}) = 452 \text{ nm (in hexane)}$$

$$\epsilon_{\max} = (1.74 \times 10^4) \times 11 = 1.91 \times 10^5; \epsilon_{\max} (\text{obs}) = 1.52 \times 10^5 (\text{in hexane})$$

(c) In γ -carotene, $n = 11$, $M = 9$ and $R_{\text{endo}} = 1$. With the aid of Eq. (5.79), we get

$$\lambda_{\max} = 114 + 9 \times 5 + 11(48.0 - 1.7 \times 11) - 16.5 \times 1 = 114 + 45 + 528 - 205.7 - 16.5$$

$$= 687 - 222.2 = 464.8 \text{ nm}$$

and from Eq. (5.80), we obtain

$$\epsilon_{\max} = (1.74 \times 10^4) \times 11 = 1.91 \times 10^5$$

(d) In lycopene, $n = 11$, $M = 8$ (six methyl groups and two chain residues). There is no ring system in lycopene, i.e. $R_{\text{endo}} = 0$ and $R_{\text{exo}} = 0$.

Thus, from Eq. (5.79), we obtain

$$\lambda_{\max} = 114 + 5 \times 8 + 11(48.0 - 1.7 \times 11) = 114 + 40 + 528 - 205.7 = 682 - 205.7 = 476 \text{ nm}$$

$$\lambda_{\max} (\text{obs}) = 474 \text{ nm (in hexane)}$$

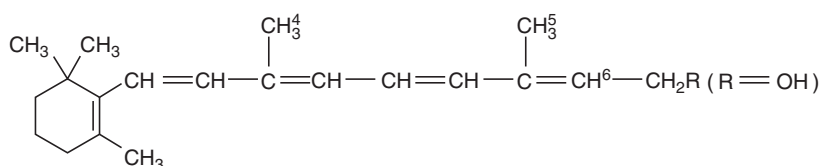
and Eq. (5.80) yields

$$\epsilon_{\max} = (1.74 \times 10^4) \times 11 = 1.91 \times 10^5.$$

$$\epsilon_{\max} (\text{obs}) = 1.86 \times 10^5 (\text{in hexane})$$

Problem 5.27: Calculate the absorption maximum for (a) Vitamin A_1 , and (b) Vitamin A_2 .

Solution (a) The molecular formula of vitamin A_1 is $C_{20}H_{30}O$ and its structural formula is



Here $n = 5$, $M = 6$. There is one ring with endocyclic double bond in the conjugated system. Thus $R_{\text{endo}} = 1$. Substituting these values into Eq. (5.79), we get

$$\begin{aligned}\lambda_{\text{max}} &= 114 + 6 \times 5 + 5(48 - 1.7 \times 5) - 16.5 = 114 + 30 + 240 - 42.5 - 16.5 \\ &= 384 - 59 = 325 \text{ nm.}\end{aligned}$$

$$\lambda_{\text{max}}(\text{obs}) = 326 \text{ nm (in ethanol)}$$

From Eq. (5.80), we obtain

$$\epsilon_{\text{max}} = (1.74 \times 10^4)5 = 87000 \text{ or } \log \epsilon_{\text{max}} = 4.94$$

$$\log \epsilon_{\text{max}}(\text{obs}) = 4.66 \text{ (in ethanol)}$$

or $\epsilon_{\text{max}} = 45709$

(b) The molecular formula of vitamin A₂ is C₂₀H₂₈O.

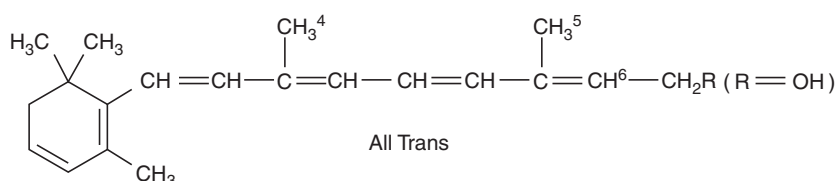
It differs from vitamin A₁, in that it has one extra ethylenic bond in it.

In vitamin A₂, $n = 6$, $M = 6$ and $R_{\text{endo}} = 1$

Substitution of these values in Eq. (5.79) yields

$$\begin{aligned}\lambda_{\text{max}} &= 114 + 6 \times 5 + 6(48 - 1.7 \times 6) - 16.5 = 114 + 30 + 288 - 77.7 \\ &= 432 - 77.7 = 354.3 \text{ nm}\end{aligned}$$

$$\lambda_{\text{max}}(\text{obs}) = 351 \text{ nm}$$



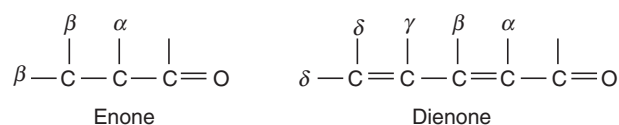
From Eq. (5.80), we get

$$\epsilon_{\text{max}} = (1.74 \times 10^4) \times 6 = 10200$$

or $\log \epsilon_{\text{max}} = 5.01$

5.20.4 Woodward–Fieser–Scott Rules for Predicting the Position of Absorption Maximum (π - π^* transitions) in Enones and Dienones

α , β -unsaturated aldehydes and ketones are called enones. The carbonyl group is conjugated with a ethylenic group in these systems, e.g. cyclopentenone, mesityloxide, retinene, etc. The basic structural units in these compounds are



Transitions in α , β -unsaturated carbonyl compounds are shown in Fig. 5.24.

Enones exhibit a strong absorption K -band (215–250 nm, $\epsilon_{\text{max}} = 10000$ –20000) and a poorly defined weak absorption R -band (310–330 nm). The rules to estimate absorption maximum in these compounds are summarised in Table 5.24.

Table 5.24 Woodward–Fieser–Scott rules to estimate absorption maximum (π - π^* transitions) in α , β -unsaturated ketones and aldehydes.

Parent values			(nm)
Acyclic α , β -unsaturated ketones			215
Six-membered cyclic α , β -unsaturated ketones			215
Five membered cyclic α , β -unsaturated ketones			202
* When carbonyl group is in five membered ring and doubled bond is exocyclic to five member ring.			215
α , β -unsaturated aldehydes			210
α , β -unsaturated acids and esters			195
Increments for:			
Double-bond extending conjugation			30
Alkyl group, ring residue:			
		α	10
		β	12
		γ and higher	18
*Ring strain (as in verbenone)			14
Auxochromes:			
	– OH	α	35
		β	30
		δ	50
	– OAc	α , β , δ	6
	– OMe	α	35
		β	30
		γ	17
		δ	31
	– Salk	β	85
	– Cl	α	15
		β	12
	– Br	α	25
		β	30
	– NR ₂	β	95
Exocyclic double bond			5
Homodiene component			
(Two conjugated double bonds, both in the same ring)			39
	$\lambda_{\max}^{\text{EtOH}}$		–

$\lambda_{\max}(\text{obs}) - \lambda_{\max}(\text{calc}) = \pm 3\text{nm}$, $\epsilon_{\max}$ for cisoid enones < 10,000 and for transoid enones > 10,000. The solvent correction must be applied to the predicted values (in ethanol). The solvent correction should be subtracted from the calculated values. The solvent corrections (in nm) for α , β -unsaturated ketones are: methanol (0), dioxane (+5), chloroform (+1), ether (+7), water (–8), hexane (+11), cyclohexane (+11). *Corrections for departure from the rules.

Problem 5.28: Calculate the absorption maximum for mesityloxide $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$ in (a) chloroform, and (b) water.

Solution Mesityloxide is an enone: $(\text{H}_3\text{C})_2\overset{\beta}{\text{C}}=\overset{\alpha}{\text{CHCOCH}_3}$

Applying the Woodward–Fieser–Scott rules, we write

$$\begin{aligned}\text{Base value} &= 215 \text{ nm} \\ 2 \beta\text{-alkyl group} &= 24 \text{ nm} \\ (2 \times 12) \\ \lambda_{\text{max}}^{\text{EtOH}} &= 239 \text{ nm} \\ \lambda_{\text{max}}^{\text{obs}} &= 237 \text{ nm} (\epsilon_{\text{max}} = 12600)\end{aligned}$$

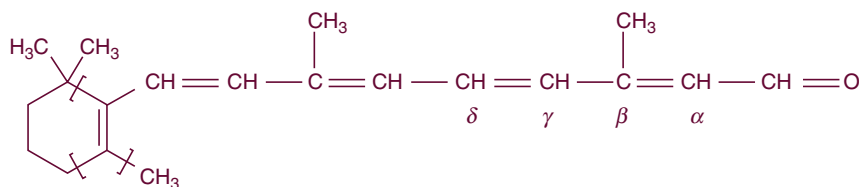
Applying the solvent-correction, we get

(a) $\lambda_{\text{max}}^{\text{CHCl}_3} = 239 - 1 = 238 \text{ nm}$ (obs : 237.6 nm)

and

(b) $\lambda_{\text{max}}^{\text{Water}} = 239 + 8 = 247 \text{ nm}$ (obs : 242.6 nm)

Problem 5.29: Rhodospin is the protein opsin linked to retinene (or retinal) which is the vitamin A₁ aldehyde. The chain of retinal has an all *trans*-configuration. Rhodospin absorbs light and retinal bound by rhodospin isomerises to 11-*cis* retinene. The structural formula of retinal is



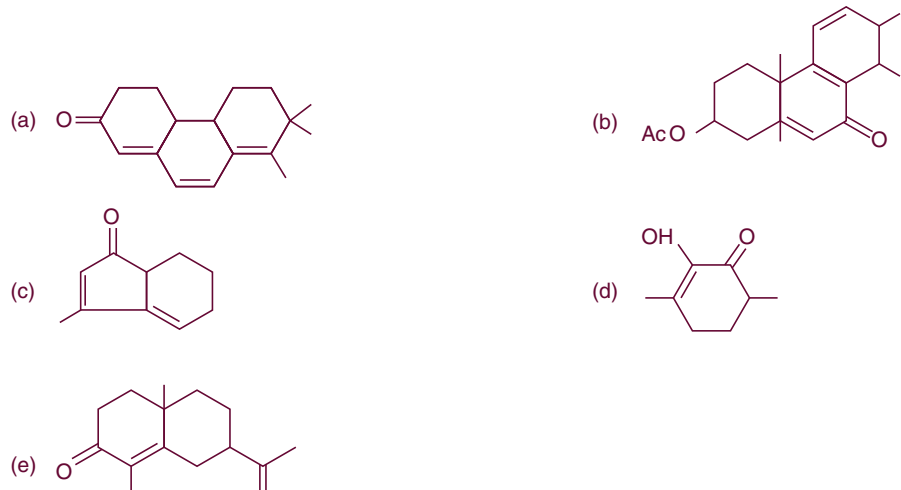
Calculate the absorption maximum for retinal.

Solution It is a α, β -unsaturated aldehyde.

Thus, from Table 5.24, we write

Retinene (structural units)	Absorption (in nm)
Parent value	= 210
α -substituent (=0)	= 0
β -substituent (=1)	= 12
γ and higher substituents (= 4)	= 72 (= 4 $\times$ 18)
Double bonds extending conjugation (= 4)	= 120 (= 4 $\times$ 30)
λ_{max} (calc)	= 414

Problem 5.30: Calculate the absorption maximum for the following compounds:



Solution

(a) The principal spectroscopic conjugated skeleton in the basic molecular structure is

Thus,

$\lambda_{\max} = 215 \text{ nm}$ (base value) + 60 nm (two double bonds extending conjugation) + 10 (Two exocyclic double bonds) + 12 nm (one β -ring residue) + 18 nm (one $\delta + 1$ ring residue) + 18 nm (one $\delta + 2$ ring residues) + 18 nm (one $\delta + 2$ alkyl groups) + 0 nm (one heteroannular conjugated diene) = 351 nm (obs: 354 nm).

(b) The principal spectroscopic conjugated skeleton in the molecular structure is

Thus,

$\lambda_{\max} = 215 \text{ nm}$ (base value) + 30 nm (one double bonds extending conjugation) + 10 (one α -ring residue) + 12 nm (one β ring residue) + 18 nm (one δ ring residue) + 39 nm (one homo conjugated diene) = 324 nm (obs: 327 nm).

(c) The main spectroscopic conjugated skeleton in the molecular structure is

Thus,

$\lambda_{\max} = 202 \text{ nm}$ (base value for cyclopentanone) + 30 nm (one double bond extending conjugation) + 12 nm (one β -alkyl group) + 18 nm (one γ -ring residue) + 18 nm (one δ -ring residue) + 39 nm (one homo conjugated diene) + 5 nm (one exo double bond) = 324 nm

(d) The basic spectroscopic conjugated skeleton in the molecular structure is

Thus,

$\lambda_{\max} = 215 \text{ nm}$ (base value) + 35 nm (one α -OH) + 12 nm (one β -alkyl group) + 12 nm (one β -ring residue) = 274 nm.

(e) The principal spectroscopic conjugated skeleton in the molecular structure is

Thus,

$\lambda_{\max} = 215 \text{ nm}$ (base value) + 10 nm (one α -alkyl group) + 24 nm (two β -ring residues) + 5 nm (one exocyclic double bond) = 254 nm (obs: 254 nm)

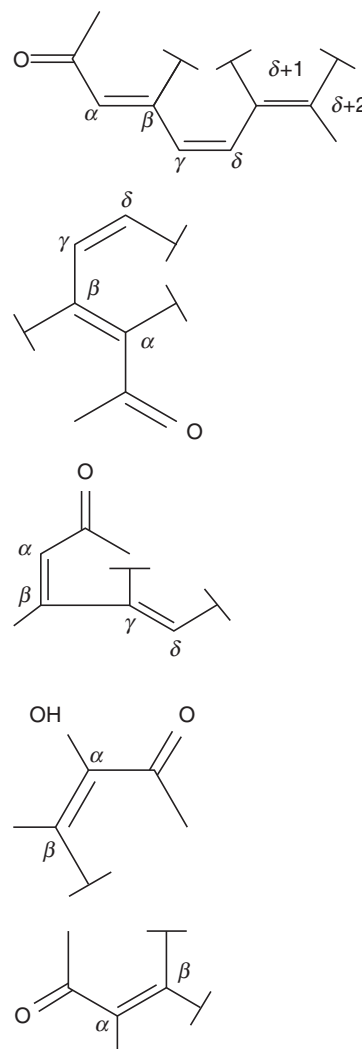
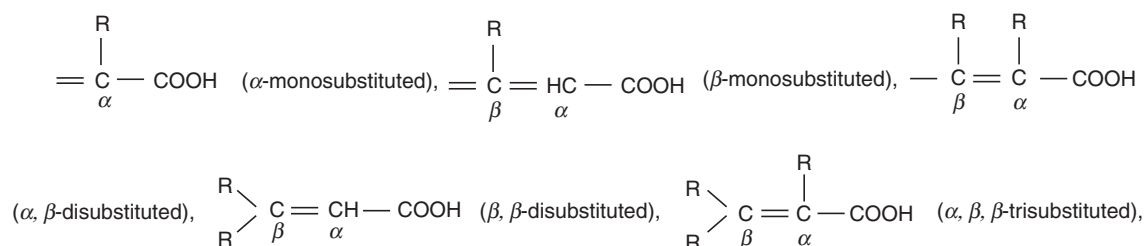


Table 5.25 Nielsen rules to predict the absorption maximum for α β -unsaturated acids, and esters ($\epsilon_{\max} > 10,000$).

Base value	(nm)
α or β -monosubstituted	208
α , β or β , β -disubstituted	217
α , β or β , β -trisubstituted	225
Increment for	
exocyclic α , β -double bond	5
exocyclic α , β -double bond-in five or seven membered ring	5

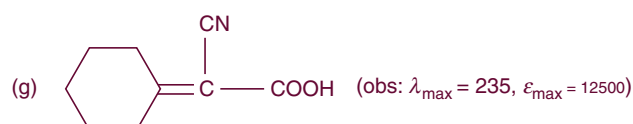
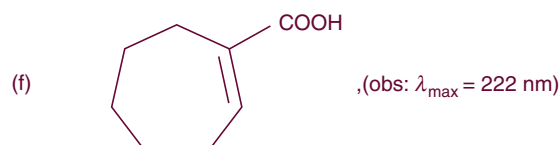
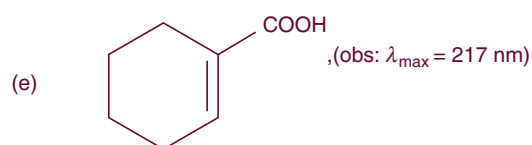
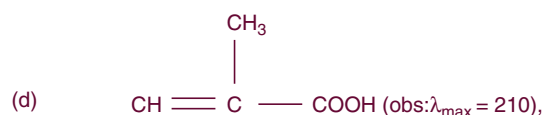
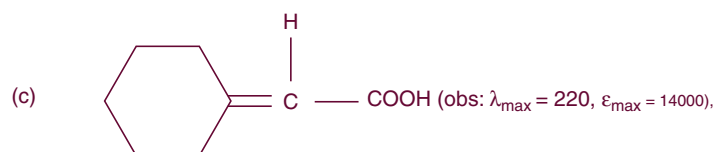
$\lambda_{\max}^{\text{calc}} - \lambda_{\max}^{\text{obs}} = \pm 5 \text{ nm}$. Data of Table 5.24 may be used here. The values are for ethanol as solvent. The change in $\lambda_{\max}$ in going from acid to ester is not more than 2 nm. When the number of double bonds extending conjugation is more than one, the contribution due to each bond extending conjugation should be taken as 36. The structure of the basic units in these compounds are



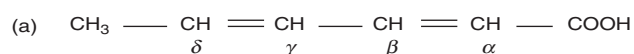
Problem 5.31: Calculate $\lambda_{\max}$ for the following acids:

(a) $\text{CH}_3-(\text{CH}=\text{CH})_2\text{COOH}$ (obs $\lambda_{\max} = 254\text{ nm}$, $\epsilon_{\max} = 25000$),

(b) $\text{CH}_3-(\text{CH}=\text{CH})_4\text{COOH}$ (obs: $\lambda_{\max} = 332\text{ nm}$, $\epsilon_{\max} = 49000$),



Solution

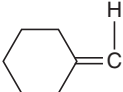


is a α, β -unsaturated acid. From Tables 5.25 and 5.24, we write.

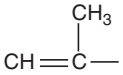
Structural units	Absorption (in nm)
Parent value	208
Double bonds extending conjugation (=1)	30
γ or higher alkyl group (= 1)	18
	$\lambda_{\max} = 256\text{ nm}$

(b) $\text{CH}_3-(\text{CH}=\text{CH})_4\text{COOH}$ is a α, β -unsaturated acid. From Tables 5.25 and 5.24, we write.

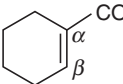
Structural units	Absorption (in nm)
Base value	208
Double bonds extending conjugation (= 3)	108
γ or higher alkyl group (= 1)	18
	$\lambda_{\max} = 334\text{ nm}$

(c)  is a α, β -unsaturated acid. From Tables 5.25 and 5.24, we write

Structural units	Absorption (in nm)
Base value (β, β -disubstituted)	217
Exocyclic α, β -double bonds (= 1)	5
	$\lambda_{\max} = 222 \text{ nm}$

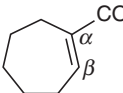
(d)  is a α -monosubstituted unsaturated acid.

Thus $\lambda_{\max} = 208 \text{ nm}$ (Base value) + 5 nm (α -methyl group) = 213 nm.

(e)  is a α, β -unsaturated acid.

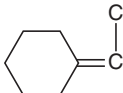
From Tables 5.25 and 5.24, we get

Structural units	Absorption (in nm)
Base value (α, β -disubstituted)	217
Exocyclic α, β -double bond in six membered ring (= 1)	0
	$\lambda_{\max} = 217 \text{ nm}$

(f)  is a α, β -unsaturated acid.

From Tables 5.24 and 5.25, we get

Structural units	Absorption (in nm)
Base value (α, β -disubstituted)	217
Exocyclic α, β -double bonds in seven membered ring	5
	$\lambda_{\max} = 222 \text{ nm}$

(g)  is a α, β -unsaturated acid

From Tables 5.25 and 5.24, we write

Structural units	Absorption (in nm)
Base value (α, β, β -trisubstituted)	225
α -substituent (= 1)	0
Exocyclic double bonds (= 1)	5
	$\lambda_{\max} = 230 \text{ nm}$

The absorption maximum for the derivatives of acylbenzenes, aromatic ketones, aromatic aldehydes, aromatic acids and aromatic esters can be calculated with the aid of rules devised by AI Scott. The rules are given in Table 5.26. Note that in polysubstituted benzene rings, when the substitution leads to steric hindrance preventing coplanarity of the carbonyl group and the ring, the contribution due to the substituent may be decreased markedly by steric hindrance to coplanarity.

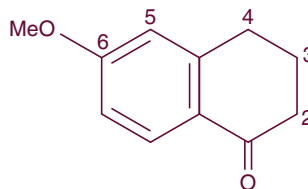
Table 5.26 Scott's rules for calculating the principal band (π - π^* transition) of substituted benzene derivative. R - C_6H_4 -COX in ethanol.

System	Orientation	$\lambda_{calc} (nm)$
Parent chromophore: C_6H_5		
X = alkyl or ring residue (e.g. C_6H_5COR)		246
X = $H(C_6H_5CHO)$		250
X = OH or O alkyl		230
Increment for each substituent on parent chromophore, i.e. C_6H_5		
R = alkyl or ring residue	$\begin{bmatrix} o-, m- \\ p- \end{bmatrix}$	3
		10
= OH, OMe, O alkyl	$\begin{bmatrix} o-, m- \\ p- \end{bmatrix}$	7
		25
$R = O^-$	$\begin{bmatrix} o- \\ m- \\ p- \end{bmatrix}$	11
		20
		78*
$R = Cl$	$\begin{bmatrix} o-, m- \\ p- \end{bmatrix}$	0
		10
$R = Br$	$\begin{bmatrix} o-, m- \\ p- \end{bmatrix}$	2
		15
$R = NH_2$	$\begin{bmatrix} o-, m- \\ p- \end{bmatrix}$	13
		58
$R = NHAc$	$\begin{bmatrix} o-, m- \\ p- \end{bmatrix}$	20
		45
$R = NHMe$	$p-$	73
$R = NMe_2$	$\begin{bmatrix} o-, m- \\ p- \end{bmatrix}$	20
		85

*This value may be decreased markedly by steric hindrance to coplanarity.

Problem 5.32: Calculate the values of absorption maximum for

- 4-aminobenzoic acid
- 3-aminobenzoic acid
- 2-hydroxy-4-methoxy acetophenone
- 2-hydroxy-5-methoxy acetophenone in ethanol.
- 6-methoxytetralone
- 4-dimethylamino benzaldehyde.



Solution From Table 5.26, we get

$$\begin{aligned} \text{(a) } \lambda_{\max} &= 230 \text{ nm (Parent chromophore)} + 58 \text{ nm (} p\text{-NH}_2\text{)} \\ &= 288 \text{ nm (obs: 289 nm; } \log \epsilon = 4.27\text{)} \end{aligned}$$

$$\begin{aligned} \text{(b) } \lambda_{\max} &= 230 \text{ nm (Base value)} + 13 \text{ nm (} m\text{-NH}_2\text{)} \\ &= 243 \text{ nm (obs: 241 nm, } \log \epsilon = 3.85\text{)} \end{aligned}$$

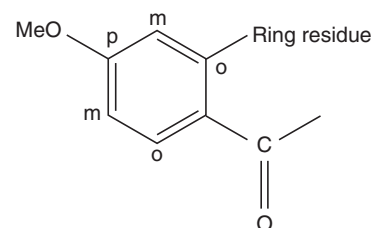
$$\begin{aligned} \text{(c) } \lambda_{\max} &= 246 \text{ nm (Base chromophore)} + 7 \text{ nm (} o\text{-OH)} + 25 \text{ nm (} p\text{-OCH}_3\text{)} \\ &= 278 \text{ nm (obs: 273.5 nm; } \log \epsilon = 4.2\text{)} \end{aligned}$$

$$\text{(d) } \lambda_{\max} = 246 \text{ nm (Parent chromophore)} + 7 \text{ nm (} o\text{-OH)} + 7 \text{ nm (} m\text{-OCH}_3\text{)} = 260 \text{ nm (obs: 255.5 nm, } \log \epsilon = 3.95\text{)}$$

(e) The principal spectroscopic skeleton in the basic molecular structure is

$$\text{Thus, } \lambda_{\max} = 246 \text{ nm (parent value)} + 3 \text{ nm (} o\text{-ring residue)} + 25 \text{ nm (} p\text{-OMe)} = 274 \text{ nm (obs: 276 nm, } \log \epsilon = 4.21\text{)}$$

$$\text{(f) } \lambda_{\max} = 250 \text{ nm (Base value)} + 85 \text{ nm (} p\text{-N(CH}_3\text{)}_2\text{)} = 335 \text{ nm (obs: 340 nm, } \log \epsilon = 4.5\text{)}$$



5.20.5 Quantitative Applications

The quantitative applications of UV-visible spectroscopy are based on intensity of the absorption band. Based on this quantity, a number of direct and indirect methods have been developed to expand the quantitative application field of this technique in other fields such as applied and biological sciences.

Concentration Determination Volumetric analysis as an analytical tool considered as one of the classical methods of chemical analysis. Volumetric titrations of all kinds are still being performed today in many industrial, hospital and research laboratories because of their simplicity, reliability and cheapness. These days, the spectrophotometric analysis has in many cases replaced volumetric analysis as an analytical tool especially in cases where it is cumbersome or impossible to analyse the samples volumetrically. Moreover, the methods of spectrophotometric analysis are less time consuming as compared to volumetry, and requires a small amount of the analyte (concentration of the solution as low as 10^{-6} – 10^{-7} g/mL can be determined). These methods of analysis are used extensively not only in chemistry but also in many other fields of study including biology, biochemistry, medicine, agriculture, etc. The quantitative analysis of samples by UV/V spectrophotometric technique is based on Beer–Lambert's law, i.e. $A = \epsilon cl$. Note that (i) when an impurity present in the sample absorbs at the absorption maximum of the sought for substance, the wavelength other than the absorption maximum is chosen for analytical work, and (ii) when the substance is present in two forms and amount of each is concentration dependent, e.g. acid–base indicator or cis-trans isomer, etc, then total concentration of both the forms is determined at the isosbestic point, i.e. the point at which both the forms have equal value of ϵ .

The sensitivity for analysis is enhanced on complexation of analyte with some suitable complexing agent. Even substances with little absorption often will form complexes with other molecules that absorb very strongly, thereby improving their sensitivity for analysis. Many important analytical procedures are based on this approach: analysis of phosphates in water; detergents and steels; calcium and magnesium in hard water; iron, nickel and copper; pH-measurements; food additives; acetone in blood and urine and detection of drugs, etc. The following steps are involved in the analysis of multicomponent systems: (i) Determine the absorption curves for each component in the same solvent. (ii) Determine the suitable wavelengths that show maximum difference in absorbance and overlap to some extent. (iii) Draw the Beer–Lambert's law plot for each component. (iv) Calculate the molar extinction coefficient for each component at selected wavelengths. (v) Prepare known mixtures and calculate

absorbances and check whether the absorbances are additive. (vi) Record the absorbance of unknown sample at selected wavelengths and solve the simultaneous equations for concentration of components of the system. Theory of Beer–Lambert's law and methods based on it has already been described in detail in Chapter 1 on introduction and in Chapter 3 on infrared spectroscopy. Some of the techniques of analysis are being described here.

(a) Method of Standard Addition This technique is useful when the absorbance of the sample at zero concentration of the sought-for substance in the sample is known or assumed to be negligible, say it is A_0 . In such a case, a known amount of the sought-for substance, say C_{en} is added to known portion of the sample and absorbance of the enriched sample is measured, say it is A_{en} . From the measured absorbance of the sample, say A_s , and the enriched reference, one can determine the concentration of the sought for substance in the sample, say C_s , under study from the expression:

$$\frac{A_s - A_0}{A_{en} - A_0} = \frac{C_s}{C_{en}} \quad (5.81)$$

or

$$C_s = \frac{C_{en}(A_s - A_0)}{(A_{en} - A_0)}$$

This procedure balances the influence of some undesired constituents in the sample and is used for some extracts of natural products.

(b) Method of Variable Reference Solution This technique is most suited to dyes which have similar absorptions, i.e. $\lambda_{\max}$ and $\epsilon_{\max}$, e.g. fluorescein and its derivatives, *m* dibromo and tetrabromo derivatives. Since they have similar spectra, they cannot be analysed very precisely by simultaneous analysis at three wavelengths. In such a case, the analysis is carried out by simple comparison of the spectral properties of the standard samples with the unknown. Let A_x , A_y and A_z be the absorbances of the three standard samples with compositions: $C_x + C_y + C_z$, $C'_x + C'_y + C'_z$ and $C''_x + C''_y + C''_z$ respectively, where C_s ' are the concentrations of the species *x*, *y* and *z* in the sample. If A_z is the absorbance of the unknown sample, then the composition of the unknown sample will be $C''_x + C''_y + C''_z$.

(c) Curvature Inversion Method This technique is especially useful in the assay of pharmaceuticals which may contain certain light scattering materials and other ingredients with unknown identity. In this method, different concentrations of pure analyte are kept in the reference cell and the concentration of the analyte is found at which the absorption inverts, i.e. goes below the baseline at the specific wavelength of interest.

(d) Method for Correction due to Colloidal Suspension or Turbidity in Photometric Methods This technique is used for protein precipitates or dispersed fats which are common causes of turbidity in biological samples. This method is based on the fact that the law of extinction and wavelength in colourless turbid media is of the form.

$$\epsilon = k \lambda^x$$

$$\text{or } \log \epsilon = \log k + x \log \lambda \quad (5.82)$$

where *k* and *x* are constants.

This gives a linear relationship between $\log \epsilon$ and $\log \lambda$ where λ_s are the wavelengths of the absorption maximum and of two minima on both sides of it.

Let the absorption curve of pure substances show two minima at wavelengths λ_1 and λ_3 on two sides of a maximum at wavelength λ_2 . The Beer–Lambert curve is plotted between $\log \epsilon$ or $\log A$ and concentration of pure substance at three wavelengths. The straight line through λ_1 and λ_3 crosses λ_2 at A_2^* . Then the correct absorbance of the substance will be $A_2 - A_2^*$.

(e) Absorbance Ratio Method The basic principle of this method has already been discussed in Chapter 3 on infrared spectroscopy. For a two-component system, we write:

At wavelength λ_1 ,

$$A' = a'_1 C_x + a'_2 C_y \quad (5.83)$$

and

At wavelength λ_2 ,

$$A'' = a''_1 C_x + a''_2 C_y \quad (5.84)$$

If one of the points, say λ_2 , is the isosbestic or isoabsorptive point then

$$A'' = a'' \quad (5.85.)$$

From Eqs (5.83) and (5.85), we get

$$R = \frac{A'}{A''} = \frac{a'_1 C_x + a'_2 C_y}{a''} \quad (5.86)$$

where a'' is the absorbance at the isosbestic point, i.e. the point of intersection of absorption curves at wavelengths λ_1 and λ_2 .

Thus a plot between R , the absorbance ratio, and C_x or C_y will be a straight line. If the isosbestic point is not taken then the plot between R and C_x or C_y will not be a straight but a curve joining 100 per cent of x to 100 per cent of y . The advantage of the slope ratio method is that it can be expanded to three-component analysis roughly resembling like a phase diagram.

(f) Method of Absorbance Difference This method is most suited when one of the constituents of the unknown mixtures is to be estimated. In this method, the difference of absorbance is determined at a selected wavelength, e.g. vitamin C has absorption maximum at 260 nm and disappears in its oxidised form. Thus, from the absorbance measurements of the unknown compounds containing vitamin C in the unoxidised and oxidised (ox) forms at absorption maximum of 260 nm, one can determine the amount of vitamin 'C' in the unknown sample from the expression:

$$\Delta A_{std} = A_{std} - A_{std}(ox) = \epsilon C_{std} l$$

$$\Delta A_{mix} = A_{mix} - A_{mix}(ox) = \epsilon C_{mix} l$$

or

$$\frac{\Delta A_{mix}}{\Delta A_{std}} = \frac{C_{mix}}{C_{std}}$$

$$C_{mix} = \frac{\Delta A_{mix}}{\Delta A_{std}} \times C_{std} \quad (5.87)$$

where ΔA_{std} represents the standard absorbance difference between the two forms of standard vitamin C and ΔA_{mix} for the vitamin C in the unknown sample. C_{std} and C_{mix} stand for the concentrations of vitamin 'C' in the standard sample and unknown mixture respectively. The same can be followed by changing one isomer to another as in arachidonic acid, i.e. 6, 10, 14, 18-Eico-satetraenoic acid $[\text{CH}_3(\text{CH}_2)_3(\text{CH}_2\text{CH}:\text{CH})_4(\text{CH}_2)_3\text{COOH}]$, $\lambda_{\max}$ (log ϵ) = 233 (4.24), 257 (4.09), 268 (4.21), 315 nm (3.82)] or by changing pH as in case of bromo thymol blue. The molar extinction coefficients in this case are markedly different at pH 5 and 11. Hence, the difference of absorbance values at these two pHs will be a measure of absorbance due to bromo thymol blue.

Problem 5.33: A sample of nonferrous alloy weighing 0.325 g is dissolved and treated with ammonia and 250 mL of a coloured solution is obtained. The absorbance of this coloured solution in a cell of 2 cm path length is 0.254. Determine the percentage content of copper in the alloy given that the molar extinction coefficient of copper ammoniate is 423.

Solution Here, $l = 2$ cm, $A = 0.254$, $\epsilon = 423$

Substituting these values in the Beer–Lambert's equation: $A = \epsilon Cl$, we get

$$\begin{aligned} C &= \frac{0.254}{423 \times 2} = 3.002 \times 10^{-4} \text{ mole lit}^{-1} \\ &= \frac{3.002 \times 10^{-4} \times 63.5}{4} \text{ g/250 mL} \\ &= 4.765 \times 10^{-3} \text{ g/250 mL} \end{aligned}$$

Hence, the percentage of copper in a given sample of nonferrous alloy is

$$= \frac{4.765 \times 10^{-3} \times 100}{0.325} = 1.46$$

Problem 5.34: Calculate the molar extinction coefficient of copper if the absorbance of a solution containing 0.48 mg of copper in 500 mL is 0.14 in a cell that is 2 cm in length.

Solution Atomic mass of copper = 63.5

$$\begin{aligned} C &= 0.48 \text{ mg/500 mL} \\ &= 0.96 \text{ mg/lit} = \frac{0.96 \times 10^{-3}}{63.5} \text{ mole/lit} \end{aligned}$$

$$l = 2 \text{ cm,}$$

$$A = 0.14$$

Substituting these values into the expression for Beer–Lambert law, i.e.

$$\begin{aligned} A &= \epsilon Cl, \text{ we get} \\ \epsilon &= \frac{0.14 \times 63.5 \times 10^3}{2 \times 0.96} (\text{mole/lit})^{-1} \text{ cm}^{-1} \\ &= 4630 (\text{mole/lit})^{-1} \text{ cm}^{-1} \end{aligned}$$

Problem 5.35: Both coffee and tea contain an alkaloid called caffeine with molecular formula $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{H}_2\text{O}$. This alkaloid is responsible for the mildly stimulating effect of beverages made from coffee beans, tea leaves, mate leaves, or cola nuts. Caffeine is also present in several common carbonated beverages (soft drinks), e.g. Coca-Cola. Caffeine shows an absorbance of 0.560 for a concentration of 5.17×10^{-5} mole lit^{-1} at 272 nm. A 2.00 g commercial sample of an instant soluble coffee is mixed with water to a volume of 500 mL. 20 mL of this solution is treated with 25 mL of 0.1 N sulphuric acid in a 500 mL flask for clarification by the prescribed procedure and the solution is then made up to 500 mL. This solution shows an absorbance of 0.402 at 272 nm. (a) Determine the molar decadic coefficient. (b) What is the percentage of caffeine in the given sample of instant coffee? Assume $l = 1$ cm.

Solution (a) $\lambda_{\text{max}} = 272$ nm,

$$A = 0.560,$$

$$C = 5.17 \times 10^{-5} \text{ mole lit}^{-1}$$

and

$$l = 1 \text{ cm.}$$

Substituting these values in the Beer–Lambert's equation: $A = \epsilon Cl$, we get

$$\begin{aligned} \epsilon &= \frac{0.560}{5.17 \times 10^{-5} (\text{mole lit}^{-1}) \times 1 (\text{cm})} \\ &= 1.083 \times 10^4 \text{ mole}^{-1} \text{ lit cm}^{-1} \end{aligned}$$

(b) For the unknown sample

$$A = 0.402$$

Therefore,

$$\begin{aligned} C &= \frac{0.402}{1.083 \times 10^{-4} (\text{mole}^{-1} \text{ lit}^1 \text{ cm}^{-1}) \times 1 (\text{cm})} \\ &= 3.71 \times 10^5 \text{ mole lit}^{-1} \\ &= 7.86 \times 10^{-3} \text{ g lit}^{-1} [\text{since molecular mass} = 212] \end{aligned}$$

or

$$\begin{aligned} C &= 3.93 \times 10^{-3} \text{ g/500 mL} \\ &= 1.965 \times 10^{-4} \text{ g/25 mL} \end{aligned}$$

Thus, the amount of caffeine in a 2 g commercial sample of instant coffee = $20 \times 1.965 \times 10^{-4} \text{ g}$
 $= 0.004 \text{ g}$ or 0.2 per cent

Problem 5.36: 100 mL of water from an industry is treated with o-phenanthroline and evaporated to 25 mL. The absorbance of this coloured solution has been found to be 0.460. Determine the iron content of industrial water (in mg lit⁻¹) if the molar extinction coefficient of this coloured compound is 1100 for a path length of 1 cm.

Solution We have $l = 1 \text{ cm}$, $\epsilon = 1100 \text{ mole}^{-1} \text{ lit cm}^{-1}$ and $A = 0.460$

Substituting these values into the expression for Beer–Lambert’s law, we get

$$C = \frac{0.460}{1 (\text{cm}) \times 1100 (\text{mole lit}^{-1} \text{ cm}^{-1})} = 4.181 \times 10^{-4} \text{ mole lit}^{-1}$$

or

$$\begin{aligned} C &= \frac{4.181 \times 10^{-4} \times 55.84 \times 25}{1000} \text{ g/25 mL} = 5.84 \times 10^{-4} \text{ g/25 mL} \\ &= 5.84 \times 10^{-1} \text{ mg/25 mL} = 5.84 \times 10^{-1} \text{ mg/100 mL of industrial water} \\ &= 5.84 \text{ mg/lit of industrial water [since 25 mL = 100 mL of industrial water]} \end{aligned}$$

Problem 5.37: To determine phosphorous in steel by dark-blue colour of a reduced phosphomolybdic complexes on absorbance scale, the following data are observed for standard samples of steel:

Amount of phosphorous in steel (per cent)	0.15	0.024	0.031	0.040	0.055
Absorbance	0.318	0.538	0.722	0.921	1.302

- (a) Determine the percentage content of phosphorous in the unknown sample whose reading on the absorbance scale is 0.619.
- (b) Determine also the percentage content of phosphorous from the straight-line expression derived from the standard data.

Solution (a) Draw a straight-line graph between absorbance and amount of phosphorous in the steel. From the graph, the amount of phosphorous in the unknown sample of steel corresponding to $A = 0.619$ has been found to be 0.028 per cent.

(b) The mathematical expression for the straight drawn in part (a) may be expressed as

$$A = mC + \text{Int}$$

where A stands for absorbance, m stands for slope and Int represents the intercept. In order to determine m and Int, select any two nonsuccessive values from the standard data and proceed as follows:

C per cent	0.024	0.040
A	0.538	0.921

Thus,
$$m = \frac{0.921 - 0.538}{0.040 - 0.024} = \frac{0.383}{0.016} = 23.9$$

and
$$A = 23.9 C + \text{Int}$$

In order to determine the value of intercept substitute any value of A and its corresponding value of C from the standard data into the above expression, i.e.

$$0.538 = 23.9 \times 0.024 + \text{Int}$$

$$\text{Int} = 0.538 - 23.9 \times 0.024 = -3.56 \times 10^{-2}$$

Hence, the expression of straight line for the standard data is $A = 23.9 C - 3.56 \times 10^{-2}$

Thus, for $A = 0.619$

$$C = \frac{0.619 + 3.56 \times 10^{-2}}{23.9} = 0.027 \text{ per cent}$$

Problem 5.38: A steel sample weighing 0.0532 g is dissolved in acid, the solution is treated with diethyl dithiocarbamate and its volume is made up to 100 ml. The solution is analysed spectrophotometrically at 328 and 368 nm in cell with a path length of 2 cm. The results obtained are $A_{328} = 0.67$ and $A_{368} = 0.45$. Determine the percentage contents of nickel and cobalt in the steel if $\epsilon_{\text{Ni}} = 35210$ and $\epsilon_{\text{Co}} = 3910$ at 328 nm and $\epsilon_{\text{Ni}} = 21820$ and $\epsilon_{\text{Co}} = 14340$ at 368 nm.

Solution The theory of the spectrophotometric method for the analysis of binary mixtures has been described in Chapter 3 on infrared spectroscopy. Based on the theory we write following expressions:

At wavelength λ_1 : $A_1 = \epsilon_1 C_1 l + \epsilon_2 C_2 l$ and

At wavelength λ_2 : $A_2 = \epsilon'_1 C_1 l + \epsilon'_2 C_2 l$

i.e. at λ_{328} : $0.67 = \epsilon_{\text{Ni}} l C_{\text{Ni}} + \epsilon_{\text{Co}} l C_{\text{Co}}$

i.e. at λ_{368} : $0.45 = \epsilon'_{\text{Ni}} l C_{\text{Ni}} + \epsilon'_{\text{Co}} l C_{\text{Co}}$

At λ_{328} : $\epsilon_{\text{Ni}} = 35210$ and $\epsilon_{\text{Co}} = 3910$

At λ_{368} : $\epsilon'_{\text{Ni}} = 21820$ and $\epsilon'_{\text{Co}} = 14340$

Substitute these values together with the value of l into the above expressions and solve for C_{Ni} and C_{Co} .

$$0.67 = 35210 \times 2 C_{\text{Ni}} + 3910 \times 2 C_{\text{Co}}$$

$$0.45 = 21820 \times 2 C_{\text{Ni}} + 14340 \times 2 C_{\text{Co}}$$

or

$$[0.67 = 70420 C_{\text{Ni}} + 7820 C_{\text{Co}}] \times 28680$$

$$[0.45 = 43640 C_{\text{Ni}} + 28680 C_{\text{Co}}] \times 7820$$

$$0.67 \times 28680 - 0.45 \times 7820 = (70420 \times 28680 - 43640 \times 7820) C_{\text{Ni}}$$

$$C_{\text{Ni}} = \frac{1.569 \times 10^4}{1.678 \times 10^9} \text{ mole lit}^{-1} = 9.350 \times 10^{-6} \text{ mole lit}^{-1}$$

$$= 9.350 \times 10^{-6} \times 58.7 \text{ g/lit} = 5.488 \times 10^{-4} \text{ g/lit}$$

or $C_{\text{Ni}} = 5.488 \times 10^{-5} \text{ g/100 mL}$

Hence, percentage of nickel in the steel sample is

$$\frac{5.488 \times 10^{-5} \times 100}{0.0532} = 0.10$$

Substituting the value of $C_{\text{Ni}} = 9.350 \times 10^{-6} \text{ mole lit}^{-1}$ into the equation in C_{Ni} and C_{Co} , we get

$$0.67 = 70420 \times 9.35 \times 10^{-6} + 7820 C_{\text{Co}}$$

or $C_{\text{Co}} = \frac{0.67 - 0.658}{7820} = 1.534 \text{ mole/lit}$

$$= 1.534 \times 10^{-6} \times 58.93 \text{ g/lit} = 9.04 \times 10^{-5} \text{ g/lit}$$

or $C_{\text{Co}} = 9.04 \times 10^{-6} \text{ g/100ml}$

Thus, the percentage of Co in the given steel sample is $\frac{9.04 \times 10^{-6} \times 100}{0.0532} = 0.017$

Problem 5.39: The solution in a dying vat after a hundredfold dilution yields the following absorbance data in a cell with path length of 5 cm at two wavelengths λ_1 and λ_2 : before dying, $A_{\lambda_1} = 2.2$ and $A_{\lambda_2} = 1.6$; after dying, $A_{\lambda_1} = 0.40$ and $A_{\lambda_2} = 0.25$. Determine the degree of extraction of dyes from the vat if $\epsilon_{\lambda_1} = 3400$ and $\epsilon_{\lambda_2} = 1500$ for the dye A and $\epsilon_{\lambda_1} = 1300$ and $\epsilon_{\lambda_2} = 2500$ for the dye B.

Solution Proceeding as in Problem (5.39), we write

Before dying,

$$2.2 = 17000 C_A + 7500 C_B$$

$$1.6 = 6500 C_A + 12500 C_B$$

Solving for C_A and C_B , we get

$$C_A = 9.465 \times 10^{-5} \text{ mole lit}^{-1}; C_B = 7.88 \times 10^{-5} \text{ mole lit}^{-1}$$

Similarly, after dying, we write

$$0.40 = 17000 C_A + 7500 C_B$$

$$0.25 = 6500 C_A + 12500 C_B$$

Solving for C_A and C_B we obtain

$$C_A = 1.908 \times 10^{-5} \text{ mole lit}^{-1}; C_B = 1.013 \times 10^{-5} \text{ mole lit}^{-1}$$

Hence, the degree of extraction of the dye A

$$\frac{(9.465 - 1.908) \times 10^{-5} \times 100}{9.465 \times 10^{-5}} = 79.84 \text{ per cent}$$

and of the dye B = $\frac{(7.88 - 1.013) \times 10^{-5} \times 100}{7.88 \times 10^{-5}} = 87.14 \text{ per cent}$

Problem 5.40: When incident light is passed through an empty cell placed in a single- beam photoelectric colourimeter, the galvanometer scale reading is observed at 100 divisions while it is at 80 divisions when the cell contains a solution having concentration C moles lit^{-1} . What will be the reading in the absorbance scale?

Solution (a) Here $I_o = 100$ divisions and $I_t = 80$ divisions. Thus

$$A = \log \frac{I_o}{I_t} = \log \frac{100}{80} = \log 100 - \log 80 \\ = 2 - 1.903 = 0.097$$

(g) Spectrophotometric Titrations A plot of absorbance at a specific wavelength against a volume of titrant is known as spectrophotometric titration curve and its nature depends upon the nature of titration. The change in absorbance of a solution is used to follow the change in concentration of a light-absorbing species during titration. The absorption varies linearly with concentration, i.e. Beer–Lambert’s law is obeyed. Thus, the titration curve consists of two straight lines with different slopes intersecting at a point called the *equivalence point* or *end point*. The curve may show a sharp angle or curvature near the end point. The curvature may be due to some equilibrium reactions, and the sharp end point in such a case is obtained by back extrapolation method.

The titration is performed at a wavelength which lies well apart from an absorption maximum to avoid interference by other absorbing species and the absorbance is adjusted initially by adjusting the sensitivity and slit width. The optimum concentration of the solution to be analysed depends upon the molar decadic coefficient of the analyte, i.e. titre. It is of the order of 10^{-4} – 10^{-5} mole lit^{-1} .

A measured volume of the reagent is added to the analyte placed in a cell, called titralyser, directly or by circulation-type arrangement. The solution is stirred and absorbance is measured. The reading is taken at several points before and after the end point and true end point is obtained graphically by the intersection of two straight line segments. Some of the typical titration curves are shown in Fig. 5.64. For accurate results, the absorbance ‘ A_{app} ’ must be corrected for dilution. It is to be multiplied by $\frac{V+v}{V}$ where V is the original volume of the solution and v is the added volume. Thus the true absorbance will be given by

$$A_{\text{true}} = A_{\text{app}} \left[\frac{V+v}{V} \right] \quad (5.88)$$

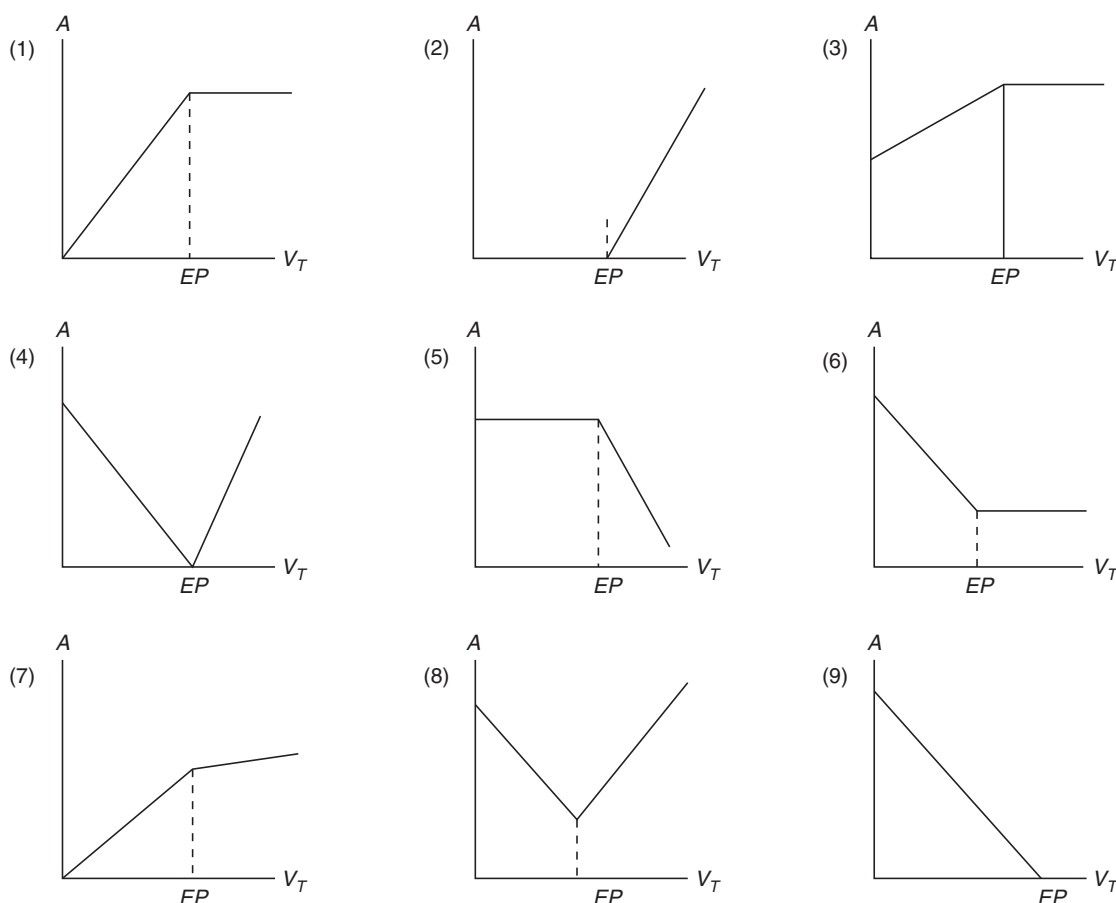


Fig. 5.64 Schematic diagram showing the shapes of some spectrophotometric titration curves: A-absorbance, V_T -volume of titrant; EP-end point. The volume correction improves the straight-line behaviour and hence the accuracy of the spectrophotometric titration.

This method is not used for only neutralisations, but also for redox and complex formation reactions. Weak acids which absorb at different wavelengths from its anion or if either acid or anion does not absorb, can be titrated by this method. Satisfactory results can be obtained provided the product of molar concentration and ionisation constant of the acid is greater than about 10^{-12} . Strong acids can't be titrated by this method because they are in the ionised state at all times. Some of the examples of spectrophotometric titrations are titration of *m*- and *p*-nitrophenol mixture with sodium hydroxide solution at $\lambda = 545$ nm; mixture of lead and bismuth with EDTA solution at $\lambda = 240$ nm; mixture of sodium acetate and *o*-chloroaniline in glacial acetic acid with HClO_4 solution at $\lambda = 312$ nm, etc.

Problem 5.41: A 25 mL volume of solution containing a mixture of Pb (II) and Bi (III) salts is titrated with a 0.01 M solution of complexon (III) at $\lambda = 240$ nm. The complexonate of Bi (III) is more stable than that of Pb(II) and, therefore, two inflexion points appear on the titration curve ($\epsilon_{\text{Pb,EDTA}} > \epsilon_{\text{Bi,EDTA}}$). Calculate the concentrations of Pb and Bi if the values of absorbances A_1 , and A_2 before the point of equivalence, corresponding to the volumes of added titrant, $V_1 = 1$ mL and $V_2 = 1.8$ mL, are known to be equal to 0.15 and 0.25, respectively. The absorbance of the solutions A' and A'' , after the first equivalence point corresponding to the volumes of the titrant $V_1 = 3.0$ and $V_2 = 3.5$ mL are equal to 0.75 and 1.00 respectively. The constant value of the absorbance reached at the end of titration is 1.20. Ignore the effect of dilution upon titration.

Solution Using the data given above we construct a titration curve of the absorbance against volume of the titrant added, (see Fig. 5.65).

From Fig. 5.65, we get two intersection points of the straight lines at EDTA volumes of 2.35 and 3.80 mL, respectively.

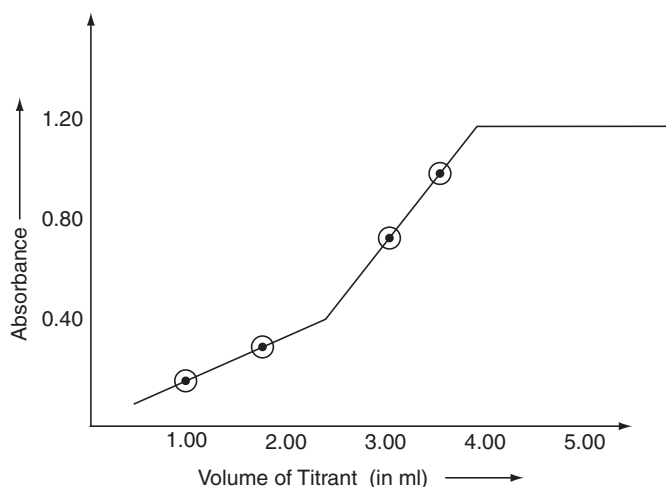


Fig. 5.65 A plot between absorbance and volume of titrant EDTA in the EDTA mixture of Pb (II) and Bi (III) system.

Concentration of EDTA = $0.01 \text{ mole lit}^{-1} = 0.01 \times 328 \times 10^{-3} \text{ g/mL} = 3.28 \times 10^{-3} \text{ g/mL}$

Volume of EDTA used for complexation with Pb = 2.40 mL

Volume of EDTA used for complexation with Bi = $3.80 - 2.40 = 1.40$ mL.

Thus, the amount of Pb in the mixture = $2.40 \text{ (mL)} \times 3.28 \times 10^{-3} \text{ (g/mL)} = 7.87 \times 10^{-3} \text{ g}$ and of Bi = $1.4 \text{ (mL)} \times 3.28 \times 10^{-3} \text{ (g/mL)} = 4.59 \text{ g}$

(h) Kinetic Method of Analysis This method is used to determine the concentration of catalyst in catalytic reactions. In this method, the variation of absorbance of a solution with time is measured in the presence of various amounts of the catalyst. A graph is then plotted between absorbance and time at different concentrations of the catalyst and the slopes of the resultant straight lines in the plot are then determined. A calibration graph is then obtained between slope ($\tan \alpha$) and concentration of the catalyst. Next, we plot a graph representing absorbance versus time for the solution with an unknown amount of catalyst and determine the slope, say $\tan \alpha'$, of the straight line so obtained. The concentration of the catalyst corresponding to this slope, i.e. $\tan \alpha'$, is then read off from the standard graph between slope against concentration of the catalyst.

Problem 5.42: Ruthenium catalyses the reaction of reduction of Fe^{3+} by tin chloride. For a solution containing different amounts of ruthenium, there have been obtained the following values of the absorbance of iron rhodanide as a function of time.

Time (in min)...	3	4	5	6	7
Absorbance without ruthenium...	0.55	0.50	0.46	0.43	0.40
2.4×10^{-6} g Ru...	0.48	0.42	0.36	0.31	0.26
4×10^{-6} g Ru...	0.42	0.35	0.28	0.21	0.15

Find the amount of ruthenium in the solution if under the same conditions the values of the absorbance of the solution vary with time as follows:

Time (in min)...	3	5	7
Absorbance...	0.39	0.32	0.23

Solution

- Draw a graph between absorbance and time at various concentrations of the solute and determine the slopes of the straight lines in the resultant graph.
- Draw a standard curve between slope and concentration of the catalyst.
- Draw a curve between absorbance and time for solution with unknown concentration of ruthenium and determine the slope of the curve.
- Determine the amount of ruthenium corresponding to the above slope from the standard graph. Our value has been found to be 1.60×10^{-6} g.

Problem 5.43: The oxidation of phenylenediamine by potassium iodate resulting in the formation of coloured products is catalysed by tungsten. In a determination by the fixed-time method, the following values of absorbance are obtained in 15 minutes at different concentrations of tungsten:

$C(\mu\text{g/mL})...$	0	0.25	0.60	0.75	1.00
Absorbance...	0.12	0.38	0.60	0.74	0.93

A 1.5 gram sample of the slags of tungsten production is dissolved in acid, the resulting solution is treated and diluted to 100 mL. In 15 minutes, the absorbance of 5 mL of this solution is 0.67. Determine the loss of tungsten in one ton ($= 10^{12}$ μg) of the slags. The volume of the coloured solution is 100 mL in all the cases.

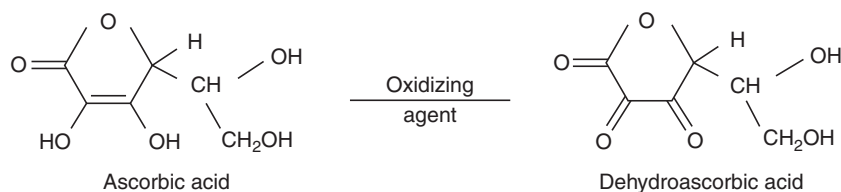
Solution From the straight line plot between C and absorbance, the value of C corresponding to absorbance = 0.67, has been found to be $0.635 \mu\text{g/mL} = 65.3 \mu\text{g}/100 \text{ mL}$. Thus, the loss of tungsten in 1 ton

$$(\text{= } 10^{12} \mu\text{g}) \text{ of slag} = \frac{10^2 (\mu\text{g}) \times 65.3 \mu\text{g}}{1.5 \times 10^6 \mu\text{g}} = 435 \times 10^6 \mu\text{g} = 435 \text{ g}$$

(i) Chemical Kinetics Studies Spectroscopy is one of the best methods of following the reaction and determining the rates when spectra of the products of reaction are different from any of the reactants. Spectra in visible and ultraviolet regions have an advantage in the case over infrared because here a wide variety of solvents in which reactions are normally carried out can be used in the visible and ultraviolet spectra. One can either follow the same procedure as in usual chemical methods of removing the samples periodically and stopping the reaction before estimation. This, however, does not work with very fast reactions. In such cases, intensity of a certain absorption peak—either of product, which goes on increasing with time or of the reactant which goes on decreasing with time—is monitored at different intervals of time. On a double-beam spectrophotometer, one can scan the spectrum repeatedly at a fast rate and get more information about the reaction mechanism. Kinetics of redox reactions where one of the species of reactants or the products is preferably coloured can easily be followed by spectrophotometric

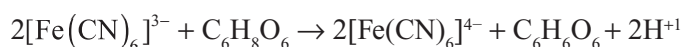
method. This is illustrated here by taking the example of oxidation of ascorbic acid by potassium ferricyanide, i.e. $\text{K}_3\text{Fe}(\text{CN})_6$ in an aqueous solution (100 mL of an $\sim 1.0 \times 10^{-3}$ mole lit^{-1} solution of $\text{K}_3\text{Fe}(\text{CN})_6 + \sim 4 \times 10^{-4}$ mole lit^{-1} ascorbic acid in ~ 0.01 mole lit^{-1} nitric acid).

Vitamin C ($\text{C}_6\text{H}_8\text{O}_6$) oxidises to dehydroascorbic acid ($\text{C}_6\text{H}_6\text{O}_6$) in an aqueous solution



Vitamin C plays a vital role in the regulation of biological oxidation–reduction processes (aiding cellular respiration by acting as hydrogen transporter). Man cannot exist without consuming vitamin C in our diet (the daily adult requirement is about 20 mg). It assists the body to withstand bacterial infection and toxins and is essential for the prevention of scurvy due to antiscorbutic activity. Vitamin C was the first vitamin isolated in the pure state in 1928 by A Szent-Gyorgyi from a number of natural resources. Later it was synthesised from glucose.

The stoichiometry of the oxidation reaction is



The overall reaction is of second order and is governed by the rate expression,

$$\frac{-d(a-x)}{dt} = \frac{dx}{dt} = \text{rate of exchange} = k(a-x) \left(b - \frac{x}{2} \right) \quad (5.89)$$

where k is the specific rate constant, a is the concentration of $[\text{Fe}(\text{CN})_6]^{3-}$, b is the initial concentration of ascorbic acid and x is the concentration of $[\text{Fe}(\text{CN})_6]^{3-}$ reacted at any time t . Thus, the concentration of ascorbic acid reacted at any time t is $\frac{x}{2}$.

Integrating the above expression and applying the condition $t = 0$ when $x = 0$ and $a \neq 2b$, we get

$$kt = \frac{2}{(a-2b)} \ln \frac{b(a-x)}{a\left(b - \frac{x}{2}\right)}$$

Rearranging the terms, we get

$$\ln \frac{(a-x)}{\left(b-\frac{x}{2}\right)} = \frac{k(a-2b)}{2}t + \ln \frac{a}{b} \quad (5.90)$$

Now the problem arises how to determine the value of $a - x$, the concentration of unreacted $[\text{Fe}(\text{CN})_6]^{3-}$ at any time by means of a spectrophotometer. Aqueous solutions of $[\text{Fe}(\text{CN})_6]^{3-}$ are yellow in colour and it has a λ_{max} at 418 nm. The other reactant and product species do not absorb at this wavelength and therefore do not interfere in the analysis. Assuming that the Beer–Lambert’s law is obeyed and if A_o is the absorbance (at $\lambda = 418$ nm) of $[\text{Fe}(\text{CN})_6]^{3-}$ solution having initial concentration ‘ a ’ mole lit^{-1} , then the concentration of unreacted $[\text{Fe}(\text{CN})_6]^{3-}$ at any time t , is

$$(a-x) = \frac{A_t}{A_\infty} \times a \text{ mole lit}^{-1} \quad (5.91)$$

where A_{λ} is the absorbance of the solution at 418 nm.

Thus,
$$\frac{x}{2} = \left(\frac{A_o - A_t}{A_o} \right) \frac{a}{2} \quad (5.92)$$

Substituting $(a - x)$ and $\frac{x}{2}$ from Eqs (5.91) and (5.92) into Eq. (5.90), we obtain

$$\ln \frac{2A_t}{A_o} \left[\frac{1}{2b - \left(\frac{A_o - A_t}{A_o} \right)} \right] = \frac{k(a - 2b)}{2} t + \ln \left(\frac{a}{b} \right) \quad (5.93)$$

The plot between $\ln \frac{A_t}{A_o} \left[\frac{1}{b - \left(\frac{A_o - A_t}{2A_o} \right)} \right]$ and t will be a straight line with slope $\frac{k(a - 2b)}{2}$ and intercept $= \ln \frac{a}{b}$. From the slope we can determine k , the second-order rate constant. Thus simply by monitoring intensity of a certain absorption peak (in UV/V region) at different intervals of time, the rate of chemical reactions can be followed.

Activation-energy parameters can be determined by carrying out the oxidation at three different temperatures. The value of energy of activation ($\Delta E^\ddagger$) can be calculated from the Arrhenius plot $\ln k$ against $\frac{1}{T}$. Entropy of activation ($\Delta S^\ddagger$), free-energy of activation ($\Delta G^\ddagger$), and heat of activation ($\Delta H^\ddagger$) can be computed by employing the Eyring equation from the absolute rate theory.

$$\begin{aligned} \Delta H^\ddagger &= \Delta E^\ddagger - RT \\ \ln k &= \ln (\kappa T/h) + \Delta S^\ddagger/R - \Delta H^\ddagger/RT \\ \Delta G^\ddagger &= \Delta H^\ddagger - T\Delta S^\ddagger \end{aligned} \quad (5.94)$$

It is to be noted that wherever possible, differential rate expressions for other ordered reactions can also be derived in a similar fashion.

(j) Stoichiometry of Complexes in Solution Phase The major advantage of spectrophotometric method to determine the composition of the complex formed between two components, say A and B , is that the equilibrium is not affected during the course of study.

In order to study equilibrium (i.e., $A + nB \rightleftharpoons AB_n$) involved in the formation of a complex, it is necessary to determine the concentration of at least one of the species present in the mixture containing known formal concentration of the reactants. The three well known methods which are routinely employed to measure the stoichiometry of the complexes in the solution phase are the following:

• **Mole-ratio Method (or Yoe and Jones Method)** Here, a series of solutions are prepared by mixing A and B as follows: The concentration of A is kept constant while that of B is varied. The absorbance of each solution is then measured at a designated wavelength, $\lambda_{\max}$, on a spectrophotometer either in the ultraviolet or visible region. A graph is then plotted between absorbance on the vertical axis and concentration of the variable component (B) added on the horizontal axis. The point of intersection of two straight lines in the resultant curves will determine the stoichiometry of the complex formed between components A and B in the solution phase, i.e. at the point of intersection $A:B :: \text{Moles of } A : \text{Moles of } B$.

• **Continuous Variation Method (or Job Method)** Here, equimolar stock solutions of components A and B are prepared and a series of solutions containing A and B are then prepared as follows. The molar ratio of two components is varied simultaneously and the total volume of the resultant solution is always kept constant. The absorbance of each solution is then measured at a designated wavelength $\lambda_{\max}$. A graph is then plotted between absorbance on the vertical axis and $V_B/(V_A + V_B)$, where V_B is the volume of the component B added to the volume V_A of the component A such that $V_A + V_B = \text{constant}$, on the horizontal axis. Generally, but not always, a parabolic-type curve results. The two linear segments of the curve are back-extrapolated to obtain a definite point of intersection which is a measure of the stoichiometry of the complex, i.e. $A : B :: \text{Moles of } A : \text{Moles of } B$.

It is to be noted that sharpness of the breaks in the curves of both these methods for the identification of a complex depends on the magnitude of stability constant of the complex.

• **Slope Ratio Method** The theory of this method has already been discussed in Chapter 3 on infrared spectroscopy. Two series of solutions are prepared in this method. In one of the series, varying amounts of the component A are added to a large excess of the component B and vice versa in the other series. In both the cases, a straight-line graph is drawn at designated wavelengths say $\lambda_{\max}(A)$ and $\lambda_{\max}(B)$. The ratio of the slopes of two resultant lines will correspond to the stoichiometric ratio of the components A and B in the solution, i.e. Slope A : Slope : Moles of A : Moles of B .

Problem 5.44 Determine the stoichiometry of the coloured compound of Pb^{2+} and pyridylazoresorcinol (PAR) by the mole-ratio method from the following data:

Concentration of PAR ($\times 10^5$) (mol lit $^{-1}$)	Absorbance
0.85	0.18
1.70	0.39
2.50	0.59
3.40	0.78
4.30	0.92
5.20	1.00
6.40	1.04
8.60	1.05
10.70	1.06
12.80	1.04

The constant concentration of lead ions in the solution is 4.4×10^{-5} g-ion lit $^{-1}$.

Solution Using the data given above, a graph is plotted between absorbance (on Y -axis) and concentration of PAR (on X -axis). From the break point of straight lines, we obtain Pb : PAR::1:1, i.e. the stoichiometry of the complex is 1:1.

Problem 5.45 Determine the stoichiometry of a complex of cobalt with nitroso- R -salt from the following spectrophotometric data obtained at pH = 4.12 and a wavelength of 570 nm.

Volume of cobalt solution (in mL); V_A	24.0	15.0	12.0	10.0	7.5	6.0
Volume of nitroso- R -salt (in mL); V_B	6.0	15.0	18.0	20.0	22.5	24.0
Absorbance	0.28	0.95	1.14	1.32	1.48	1.29

Equimolar stock solutions (10^{-3} mole lit $^{-1}$) of cobalt and nitroso- R salt have been prepared in a buffer of pH = 4.12 and used in spectrophotometric studies.

Solution

Concentration of cobalt solution = 10^{-3} mole lit $^{-1}$

Concentration of salt solution = 10^{-3} mole lit $^{-1}$

These solutions have been mixed in different proportions by volume and the total volume is made up to 30 mL.

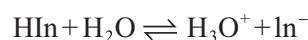
Applying the molality/normality formula, i.e. $M_1 V_1 = M_2 V_2$, we can calculate the molality of cobalt and nitroso- R -salt in the final solutions.

Thus,

Concentration of cobalt $\times 10^4$ (in mole lit $^{-1}$), C_A	8.00	5.00	4.00	3.33	2.50	2.0
Concentration of nitroso- R -salt $\times 10^4$ (in mole lit $^{-1}$), C_B	2.0	5.0	6.00	6.66	7.50	8.00
or $\frac{V_B}{V_A + V_B} \left \frac{C_B}{C_A + C_B} \right.$	0.2	0.5	0.6	0.66	0.75	0.8
Absorbance	0.28	0.95	1.14	1.32	1.48	1.29

Solution Using the data given above, plot a graph between absorbance (on vertical axis) and molar concentration ratio of cobalt and salt or $V_B/(V_A + V_B)$ (on horizontal axis) and find the breaking point in the resultant curve. This breaking point in the resultant curve will correspond to the stoichiometry of the complex formed between cobalt and nitroso-*R*-salt in a buffer solution of pH = 4.2. Our composition of the complex is [Co]:[Salt] = 1:3

(k) Determination of Dissociation Constant of a Reagent Organic reagents can be considered to be weak acids, HIn, which dissociate to give H_3O^+ and In^- ions:



As weak acids, HIn must satisfy the condition

$$K = \frac{[H_3O^+][In^-]}{[HIn]} \text{ or } \frac{[In^-]}{[HIn]} = \frac{K}{[H_3O^+]} \quad (5.95)$$

and
$$pK = pH + \log \frac{[HIn]}{[In^-]} \quad (5.96)$$

It follows that the reagent may exist in more than one form in the solution and the ratio $\frac{[In^-]}{[HIn]}$ is governed by the pH of the solution. At very low pH, HIn form of the reagent will be predominant, while at very high pH, In^- form will be predominant. Thus at intermediate pH values, both the forms will exist in solution. Accordingly, the visible or ultraviolet spectral absorption peaks of the reagent will be shifted when the reagent loses or gains a proton. This affords an interesting method of determining the dissociation constants of such reagents. The usual method is to measure absorbance (at the best wavelength, i.e. isosbestic wavelength, selected by measuring the absorbances of solutions at different pH values) as a function of pH. A graph is then plotted between absorbance and pH as shown in Fig. 5.66. The pH value midway between the maximum and minimum values of absorbances is equal to the dissociation constant since according to Eq. (5.96) when $[In^-] = [HIn]$, $pK = pH$.

The numerical method to determine pK from Eq. (5.95) is to calculate the concentrations of In^- and HIn. This is done by measuring the absorbances at the maximum values of λ_{In^-} and λ_{HIn} respectively.

Thus at λ_{In^-} ;

$$A = \epsilon_{In^-} C_{In^-} l + \epsilon_{HIn} C_{HIn} l$$

At λ_{HIn} :

$$A' = \epsilon'_{In^-} C'_{In^-} l + \epsilon'_{HIn} C_{HIn} l$$

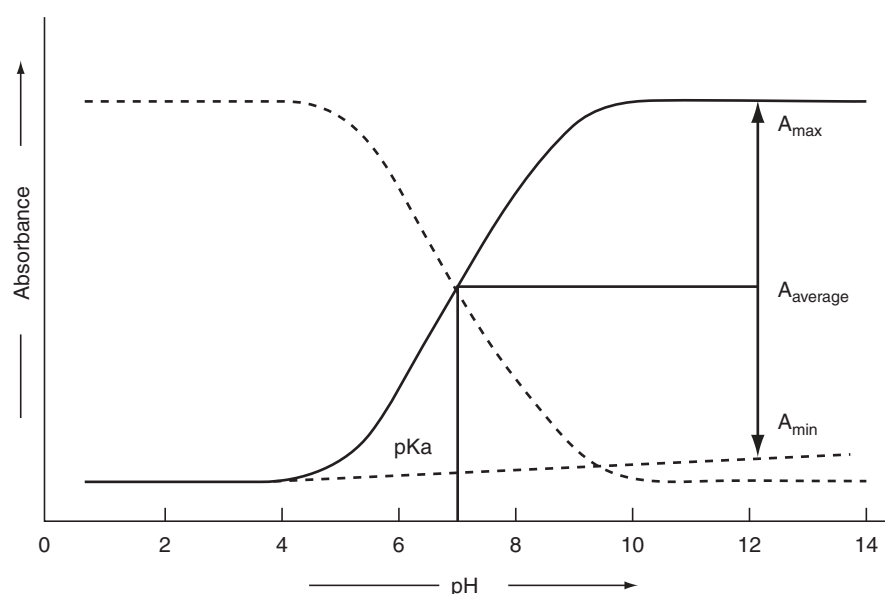


Fig. 5.66 A plot between absorbance and pH.

where ϵ_{In^-} , ϵ_{HIn} and ϵ'_{In^-} , ϵ'_{HIn} can be obtained from Beer–Lambert's plot at λ_{In^-} and λ_{HIn} respectively. The solution of these simultaneous equations will give the values of C_{In^-} and C_{HIn} . These values on substitution into Eq. (5.95) will give the value of pK.

The other nongraphical method to determine pK is to measure the absorbances at very low pH (i.e. A_{HIn}), at very high pH (i.e. A_{In^-}) and at intermediate pH (i.e. A_{mix}) values.

These values when substituted in the formula (5.95) yield the value of K and hence pK since

$$pK = -\log K$$

$$K = \frac{[In^-][H_3O^+]}{[HIn]} = \left[\frac{A_{mix} - A_{HIn}}{A_{In^-} - A_{mix}} \right] [H_3O^+] \quad (\text{Eq. 5.96})$$

Problem 5.46 Determine the dissociation constant of a reagent HR if at pH = 6.35 its absorbance is 0.360 and at pH = 3.0 and 11.8 its absorbances are respectively, equal to 0.890 and 0.025.

Solution To solve the problem we make use of the equation

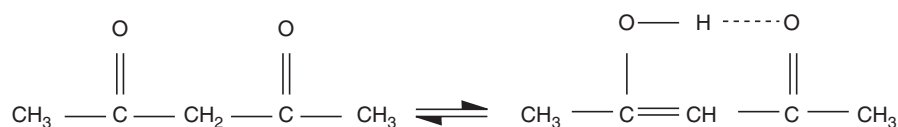
$$K_{HR} = \left[\frac{A_{mix} - A_{HR}}{A_{R^-} - A_{mix}} \right] [H^+] \quad (5.97)$$

Substituting the values given in the problem into Eq. (5.97) we get

$$pH = 6.35; [H^+] = 10^{-6.35} = 4.46 \times 10^{-7}$$

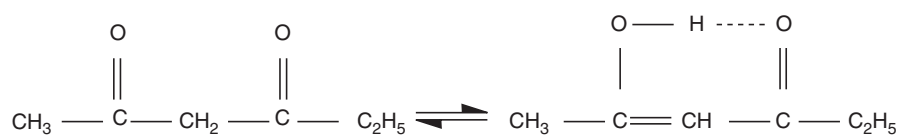
$$K_{HR} = \frac{0.360 - 0.890}{0.025 - 0.360} [4.46 \times 10^{-7}] = \frac{0.53 \times 4.46 \times 10^{-7}}{0.335} = 7.06 \times 10^{-7}$$

(I) Study of Keto-enol Tautomeric Equilibria Keto-enol tautomeric equilibria are shown by β -diketones. The enolic form is stabilised by H-bonding. Acetyl acetone and ethyl acetoacetate are the classic examples of keto-enol tautomerism. The tautomeric equilibria are temperature and solvent dependent.



$$\lambda_{\max} (\text{H}_2\text{O}) = 274 \text{ nm}, (\epsilon_{\max} = 2050)$$

$$\lambda_{\max} (\text{iso-octane}) = 272 \text{ nm}, (\epsilon_{\max} = 12000)$$



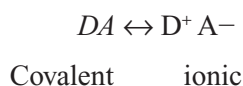
$$\lambda_{\max} = 275 \text{ nm}, (\epsilon_{\max} = 16)$$

$$\lambda_{\max} = 244 \text{ nm}, (\epsilon_{\max} = 16000)$$

The percentage content of the keto-enol forms in an equilibrium mixture can be deduced from the physical properties of the mixture since the keto and enol forms (enol form is conjugated) show different light absorption in the ultraviolet region and have different refractive indices. They will also exhibit different NMR signals. Since absorbance is directly dependent on the concentration (i.e. $A = \epsilon C l$), the amount of tautomers in various solvents and at different temperatures is determined from the intensity measurements at the absorption maximum of the respective tautomer.

In acetyl acetone, enol tautomer is about 80 per cent in pure liquid, 15 per cent in an aqueous solution and 91–92 per cent in vapour phase and in solutions of nonpolar solvents. In ethylacetoacetate, enolic form is 8 per cent in pure liquid, 51 per cent in hexane, 32 per cent in ether and 12 per cent in alcohol. The percentage of enol tautomer in pure liquid ethylbenzoylacetate is 80 per cent.

(m) Study of Charge-Transfer Complexes The molecular complexes of charge transfer (CT) type are a restricted case of the broad class of Electron Donor Acceptor (EDA) complexes or adducts, where partial or complete transfer of negative charge occurs from an electron donor (*D*) to an electron acceptor (*A*). The complex can be described by the resonance states



The formation of these complexes is explained by the quantum mechanical theory of Robert S Mulliken. His contributions concerning chemical bonds and the electronic structure of molecules by molecular orbital method were rewarded with a Nobel prize in chemistry in 1966. According to him, if $\psi(DA)$ is the wave function of no-bond case and $\psi(D^+ A^-)$ is the wavefunction for ionic case involving transfer of charge, then a combination of these two forms yields two wave functions ψ_0 and ψ_1 , for the charge transfer complex, i.e.

$$\psi_0 = \psi(DA) + \lambda \psi(D^+ A^-)$$

$$\psi_1 = \psi(DA) + \lambda' \psi(D^+ A^-)$$

where λ^2 is a measure of the amount of charge transfer, $\lambda' > \lambda$. One of these functions, say ψ_0 , corresponds to an energy lower than that of $\psi(DA)$ or $\psi(D^+ A^-)$. The transition between ψ_0 and ψ_1 states gives rise to a charge-transfer band since charge is transferred from *D* to *A* in this process. Valence bond theory is favoured for weak complexes while molecular orbital theory is favoured for strong complexes. The tendency of charge-transfer complexation and energy change in the transition depend upon the ionisation potential of the donor and electron affinity of the acceptor. The smaller the ionisation potential of the donor and larger the electron affinity of the acceptor, the stronger will be the charge-transfer complex. Charge transfer occurs primarily in the excited state and is stabilised relative to the ground state by electrostatic interaction between the separated charges on the donor and the acceptor. In *H*-bonded adducts, the electrostatic contribution is predominantly to the ground state of the complex.

The formation of molecular complexes can occur in the liquid/solution, solid or vapour phase. The solid state CT complexes are also sometimes called organic metals, as these solids exhibit high electrical conductivity, comparable with those of metals, though most organic solids are insulators, e.g. Quinolinium-TCNQ is the best organic metal and MEM (TCNQ)₂; where MEM = *N*-methyl-*N*-ethylmorpholinium behaves as a metallic conductor at 335 K. It is to be noted that donor and acceptor molecules complexed in solid state consists of stacks of alternate donor and acceptor molecules so that each donor has two acceptor neighbours and vice versa. The formation of complexes may be proved and their composition established by study of spectral properties like absorption of UV and visible radiations, absorption of infrared radiations, absorption of radio-frequency radiations under the influence of applied magnetic field, absorption of microwave radiations under the influence of applied magnetic field, absorption of γ -radiations, diffraction and scattering of radiations, etc., and nonspectral properties like melting point (phase diagrams), dipole moment, conductance, etc.

The charge-transfer process is an instantaneous process and the formation of a CT complex is characterised by the appearance of a new absorption band in the UV or visible region of the spectrum, e.g. benzene–Iodine system shows a band at 37300 cm^{-1} ($\approx 268 \text{ nm}$) with $\epsilon_{\text{max}} = 1650$ in the vapour phase at 25°C while in CCl_4 solution at 33700 cm^{-1} ($\approx 297 \text{ nm}$) with $\epsilon_{\text{max}} = 15400$ at 25°C . Diethylether-iodine system exhibits a new band at 42700 cm^{-1} ($\approx 234 \text{ nm}$) with $\epsilon_{\text{max}} = 2100$ in the vapour phase at 25°C while in CCl_4 and *n*-heptane solutions at 40200 cm^{-1} ($\approx 249 \text{ nm}$) with $\epsilon_{\text{max}} = 4700$ at 20°C and at 39700 cm^{-1} ($\approx 252 \text{ nm}$) with $\epsilon_{\text{max}} = 5650$ at 25°C respectively. In intramolecular CT complexes, the intensities of transitions are independent of concentration, the absorption band in such complexes arises as a result of charge-transfer interactions across space, e.g. interaction, in nicotinamide adenine-dinucleotide (NAD^+) occurs between the pyridinium ring and the adenine moiety. The mere production of a colour when two reagents are mixed has often been taken as the sole evidence for CT complex formation, e.g. TCNE (Tetracyanoethylene) when mixed with benzene forms a bright orange CT complex, all the higher condensed aromatic hydrocarbons anthracene, phenanthrene and acenes (condensed hydrocarbons with 4-, 5-, 6- and 7- benzene rings) readily form intensely coloured charge transfer complexes with trinitrobenzene, picric acid, TCNE, tetranitromethane, etc. However more positive evidence, such as systematic variation of the energy of the absorption band for complexes of a series of related donors with a given acceptor compared with other series of complexes with other acceptors or with ionisation potential of the donors is desirable before attributing the production of colour to the formation of a CT complex. Sometimes the instant appearance of colour may be due to the decomposition of the CT complex instantaneously to give coloured products. In some cases the absorption bands develop slowly and it is attributed to CT complexation. There is no evidence that CT complexes are formed slowly. Most probably such absorptions arise from products of normal covalent chemical reactions.

(i) Multiple Charge Transfer Transitions The appearance of multiple charge-transfer band maxima is due to the participation of more than one energy level of the donor. The energy difference between the two charge-transfer transitions in the complex is expected to be equal to the energy difference between the two appropriate levels of the donor and the same has been observed indeed. The energy difference between two observed transitions in a crystalline 1, 3, 5-trinitrobenzene-anthracene complex is 8000 cm^{-1} . This conforms to the calculated frequency difference of the two highest filled orbitals of anthracene, i.e. 8210 cm^{-1} . The difference between the charge transfer bands of complexes of a given donor is independent of the particular acceptor, especially in cases where more than two maxima have been observed as is evident from Table 5.27. The double maxima may also result due to transition from the highest filled level of the donor to two vacant levels in the acceptor, e.g. the energy difference between two observed transitions in hexamethyl benzene-1, 2, 4, 5-tetracyanobenzene in $\text{CHCl}_2\text{CHCl}_2$ has been found to be 6400 cm^{-1} and it conforms to the calculated energy difference between the two lowest unfilled levels in 1, 2, 4, 5-tetracyanobenzene. It is to be noted that the multiplicity cannot arise due to transitions from two donor levels since the highest filled level of hexamethylbenzene is doubly degenerate. The energy difference between the two maxima in such cases is independent of the nature of the donor for a particular acceptor as is evident from Table 5.27.

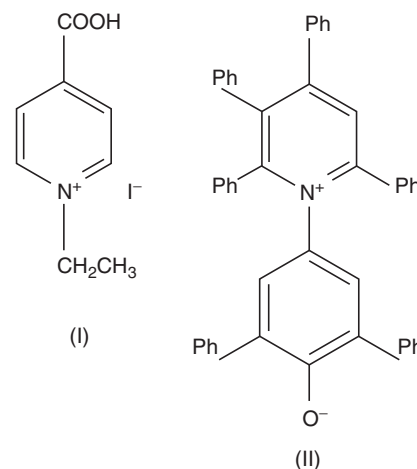
Table 5.27 Typical examples of multiple charge-transfer band maxima.

Donor	Acceptor	Solvent	$\bar{\nu}_1$ (in cm^{-1})	$\bar{\nu}_2$ (in cm^{-1})	$\bar{\nu}_3$ (in cm^{-1})	$\Delta\bar{\nu}_{1/2}$ (in cm^{-1})
Biphenyl	TCNE	CCl_4	20000	25700		5700
Biphenyl	CA	CCl_4	23000	28700		5700
Anthracene	TCNE	CCl_4	14500	17100	21900	2600
Anthracene	CA	CCl_4	17200	19800		2600
Chrysene	TCNE	CCl_4	15900	18800	22900	2900
Chrysene	CA	CCl_4	18500	21500		3000
Mesitylene	TCNB	Pure solid	28300	33700		5400
Hexamethyl benzene	TCNB	$\text{CHCl}_2\text{CHCl}_2$	23500	29900		6400
Naphthalene	TCNB	$\text{CHCl}_2\text{CHCl}_2$	25000	731300		> 6300
		Pure solid	24600	31500		6900
N, N'-dimethyl aniline	TCNB	$\text{CHCl}_2\text{CHCl}_2$	18300	25000		6700
N, N, N', N'-tetra methyl-p-phenylene- diamine	TCNB	$\text{CHCl}_2\text{CHCl}_2$	13900	20300		6400

TCNE-, Tetracyanoethylene; CA-Chloranil, TCNB-1, 2, 4, 5-Tetracyanobenzene.

• Estimation of Solvent Polarity or Effect of Solvent on the Energy of the Charge-Transfer Band

The energy of the charge-transfer band for the complex formed between the iodide ion and a pyridinium ion is very sensitive to solvents. The large dipole moment is perpendicular to the plane of the pyridinium ring in the ground state of the complex which is effectively an ion pair (I), which lies in the plane of the ring in the excited state of complex. Solvating molecules orient themselves about the complex (the so-called cybotactic region) to minimise the energy of the ground state. According to Franck–Condon principle, there will be no solvent reorientation at the instant of excitation. Thus the cybotactic region will tend to increase the energy of the excited state. The greater the solvating power of the solvent, the greater will be the decrease in energy of the ground state and greater the increase in the excited state compared with the ideal system of a single isolated complexed pair in vacuo, i.e. gas phase, and hence greater the hypsochromic shift. The solvent ionising power is expressed by, Kosower in terms of a parameter called 'Z-value' which is defined as the



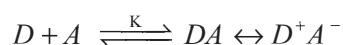
energy in kcal mole⁻¹ of the peak maximum of the charge-transfer band of 4-carbomethoxy-1-ethylpyridinium iodide in that solvent. This particular pyridinium iodide is chosen because of its greater solubility in the less solvating solvents. Some Z -values are compared with the energies E_T^* (in kcal mole⁻¹) of the peak maximum of the intramolecular charge transfer absorption band of the pyridinium- N -phenolbetaine (II) which is a solvent sensitive transition and is proposed as an alternative measure of polarity of the solvent in Table 5.28.

Table 5.28 E_T^* and Z values of some solvents at 298 K.

Solvent	E_T^* (kcal mole ⁻¹)	Z (kcal mole ⁻¹)
Water	63.1	94.6
Formamide	56.6	83.3
Ethanol	51.9	79.6
Acetonitrile	46.0	71.3
Dimethylformamide	43.8	68.5
Acetone	43.2	65.5
Dichloromethane	41.1	64.2
Pyridine	40.2	64.0
Chloroform	39.1	63.2
Chlorobenzene	37.5	58.0
Dioxane	36.0	
Hexane	30.9	
2, 2, 4-Trimethylpentane		60.1

E_T^* values are energies, in kcal mole⁻¹ of the peak maximum of the intramolecular charge transfer band of the phenolbetaine.

• **Determination of Equilibrium Constant** Let us Consider the charge-transfer equilibrium



The equilibrium constant of 1 : 1 CT complex formed between D and A is then given by.

$$K = \frac{[DA]}{[D][A]} = \frac{C_{DA}}{C_D C_A} \quad (5.98)$$

where C_{DA} , C_D and C_A are the concentration of complex, donor and acceptor respectively at equilibrium.

The general procedure is to measure the absorbance A of the complex (at $\lambda_{\max}^{DA}$) either as a function of concentration of donor or acceptor.

Thus,

$$A_{\text{abs}} = \epsilon_{DA} l C_{DA} \quad (5.99)$$

If C_D^0 and C_A^0 are the initial concentrations of D and A respectively such that $C_D^0 \gg C_A^0$ then Eq. (5.98) can be written as

$$K = \frac{C_{DA}}{(C_D^0 - C_{DA})(C_A^0 - C_{DA})} \quad (5.100)$$

Rearranging Eq. (5.100), we get

$$\frac{C_A^0}{C_{DA}} = \frac{1}{K} \frac{1}{C_D^0} + \frac{C_A^0}{C_D^0} + 1 - \frac{C_{DA}}{C_D^0} \quad (5.101)$$

Equating Eqs. (5.99) and (5.101), we get

$$\frac{C_A^0}{A_{\text{abs}}} = \frac{1}{K \epsilon_{DA} l} \frac{1}{C_D^0} + \frac{C_A^0}{C_D^0 \epsilon_{DA} l} - \frac{C_{DA}}{\epsilon_{DA} C_D^0 l} + \frac{1}{\epsilon_{DA} l} \quad (5.102)$$

Since $C_D^0 \gg C_A^0$ and C_D^0 and C_A^0 are very small, the second and third terms of Eq. (5.102) can be neglected so that

$$\frac{C_A^0}{A_{\text{abs}}} = \frac{1}{K \epsilon_{DA} l} \frac{1}{C_D^0} + \frac{1}{\epsilon_{DA} l} \quad (5.103)$$

Similarly, if $C_A^0 \gg C_D^0$, then Eq. (5.102) becomes

$$\frac{C_D^0}{A_{\text{abs}}} = \frac{1}{K \epsilon_{DA} l} \frac{1}{C_A^0} + \frac{1}{\epsilon_{DA} l} \quad (5.104)$$

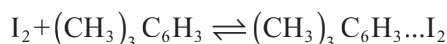
Both Eqs (5.103) and (5.104) are called Benesi–Hildebrand equations.

Thus, a plot between $\frac{C_A^0}{A_{\text{abs}}} / \frac{C_D^0}{A_{\text{abs}}}$ and $\frac{1}{C_D^0} / \frac{1}{C_A^0}$ should give a straight line with slope $= \frac{1}{K \epsilon_{DA} l}$ and intercept $= \frac{1}{\epsilon_{DA} l}$.

From the slope and intercept, both K and ϵ_{DA} can be obtained.

For example, the spectrum of iodine–mesitylene system in CCl_4 is shown in Fig. 5.67

The established equilibrium is given by



Mesitylene does not absorb in the visible region. The CT complex formed absorbs at the violet end (332 nm) of the visible spectrum while unreacted iodine absorbs at 500 nm. From the absorbance measurements at $\lambda_{\text{max}} = 332$ nm and employing Eq. (5.103), the value of equilibrium constant and ϵ_{max} has been found to be 0.82 (lit mole⁻¹) and $\epsilon_{\text{max}} = 8850$ lit mole⁻¹ cm⁻¹ respectively.

The equilibrium constants of some iodine-donor systems in CCl_4 at 25°C are given in Table 5.29 and of some metallocene donor-acceptor systems, in Table 5.30.

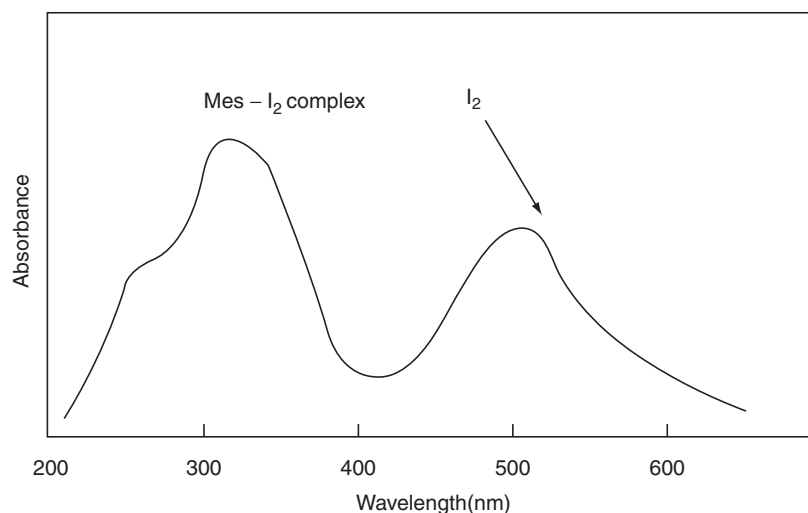


Fig. 5.67 The absorption spectrum of iodine-mesitylene system in CCl_4 at 25°C.

Table 5.29 Equilibrium constants of CT complexes of iodine with donors in CCl_4 at 25°C.

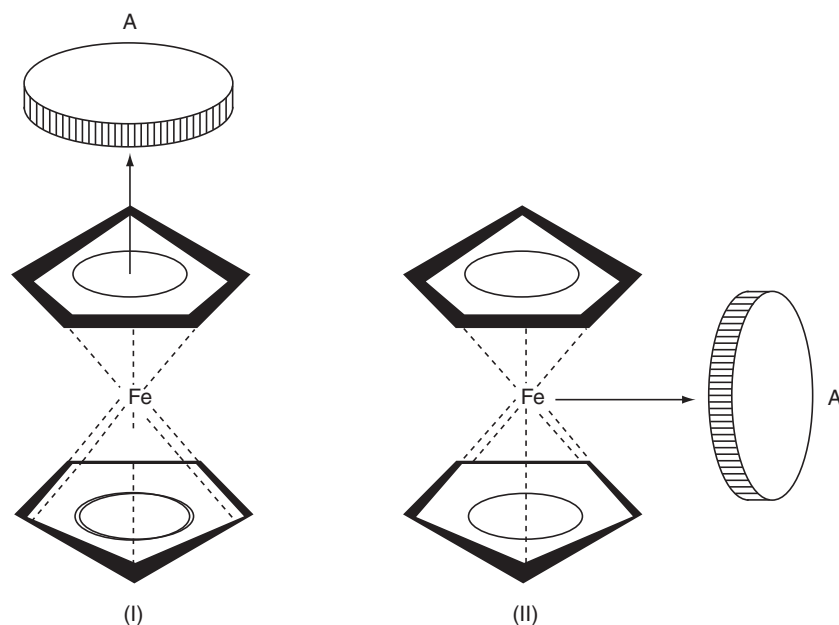
Donor	λ_{max} (in nm)	ϵ_{max} (lit mole ⁻¹ cm ⁻¹)	K (lit mole ⁻¹)
Benzene	292	16400	0.15
Toluene	302	16700	0.16
Mesitylene	332	8850	0.82
Hexamethylbenzene	375	8200	1.35
Trimethyleneoxide*	452, 248		26.1, 25.2
Tetrahydrofuran*	455, 249		17.2, 20.0
Diethylether*	462, 252		5.9, 6.6

*- in *n*-heptane

Table 5.30 Association constants of some selected metallocene CT complexes.

Donor	Acceptor	Solvent	Temp	$\bar{\nu}_{\text{CT}}$	K	ϵ_{max}	$-\Delta H$	$-\Delta S$
			(°C)	(cm ⁻¹)		(lit mole ⁻¹ cm ⁻¹)	(kcal mole ⁻¹)	(kcal mole ⁻¹ deg ⁻¹)
Ferrocene	TCNE	Cyclohexane	30	10000	30.0	474	3.8	5.5
Ferrocene	TNB	$\text{CH}_2\text{ClCH}_2\text{Cl}$	23	18700	2.8	630	1.8	4
Chloromer- curiferrocene	TNB	$\text{CH}_2\text{ClCH}_2\text{Cl}$	23	19400	.75			

TCNE-tetracyanoethylene, TNB-1, 3, 5-trinitrobenzene. Solid CT complexes are formed between ferrocene donor and acceptors such as *p*-benzoquinone, chloranil, tetracyanoethylene and DDQ. Cobaltocene forms solid complexes of ionic type with chloranil, tetracyanoethylene and DDQ: DDQ-2, 3-dichloro-5, 6-dicyano-*p*-benzoquinone. The latter being salts, are easily oxidisable.

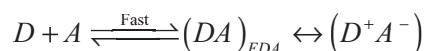
Fig. 5.68 (I) Filled *p*-orbital of a cyclopentadienyl ring (II) nonbonding electrons of metal.

The acceptor in metallocene complex may interact either with the filled *p*-orbital of a cyclopentadienyl ring (I) or with nonbonding electrons of the metal (II) as shown in Fig. 5.68. The *x*-ray diffraction of single crystal of ferrocene-tetracyanoethylene complex shows that the geometry corresponds to (I) and not (II), Mössbauer studies also conform to (I) and not (II).

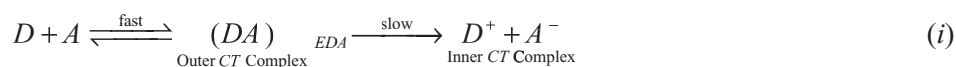
Ferrocene/Nickelocene/Ruthenocene/Osmocene-TCNE systems in more polar solvents such as acetonitrile show similar results, i.e. solvation in the first system causes ionisation into ferricinium ion and the radical ion of tetracyanoethylene.

(ii) **Chemical Reactions via Charge Transfer Complexes** The molecular interactions between electron donors and acceptors are generally classified into two types of reactions: The first type includes the formation of a weak charge-transfer complex (also known as outer complex or π -complex) and the second type includes the nucleophilic substitution reaction either via outer and inner complexes as intermediates or outer complexes and ionic species as intermediates. Either of the reaction paths listed above depend upon mostly on the electron donor characteristics, concentration of donor, temperature, permeativity of the solvent medium.

Accordingly, a CT band will appear due to 1: 1 CT complex formed between D and A in a nonpolar solvent. The intensity of the band will not change with time suggesting thereby that the CT complexation proceeds according to the scheme.



However, when donor is mixed with an acceptor in a solvent of high dielectric constant, the intensity of the CT band may decrease with time and simultaneously a new band with progressively increasing intensity may appear. Concurrently, the electrical conductivity of the solution will also increase rapidly and the solution will become paramagnetic and may give ESR signals corresponding to paramagnetic anionic and cationic species. This may be due to the formation of inner ionic CT complex as an intermediate according to the scheme.



The inner CT complex may further undergo reactions to yield isolatable or unisolatable products.

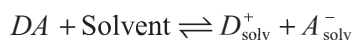


The outer CT complex may also yield products directly, i.e.



Some typical examples concerning reactions via charge-transfer complexes according to the above schemes are described here.

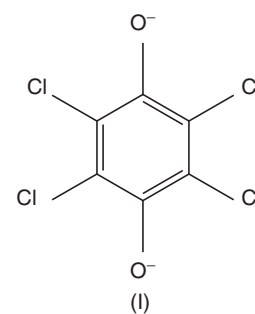
When a donor and acceptor are mixed in a highly polar solvent, ionisation of the nonionic CT complex will take place. The driving force is the energy of solvation of the ions formed. The chemical reaction



is analogous to the ionisation of HCl in a polar solvent, e.g. the CT complex of N, N, N', N'-tetramethyl-p-phenylenediamine (TMPD) and tetrachloro-p-benzoquinone (chloranil) when dissolved in cyclohexane shows a broad band due to CT complex at 870 nm. This band is absent in methanol solution. However, absorptions at 568 nm, 618 nm characteristic of the cation radical TMPD^+ are observed, together with absorptions at 426 nm, 452 nm due to semiquinone ion derived from chloranil. The assignments have been confirmed from the spectra of methanolic solution of TMPD^+ perchlorate salt which shows bands at 568 and

618 nm and methanolic solution of the product obtained by the action of sodium iodide on a solution of chloranil in acetone which shows bands at 426, 452 nm. It is pertinent to note that initially TMPD-CA complex ionises in solution to form D^+ and A^- , i.e. TMPD^+ and the dinegative ion of chloranil (I).

No ESR absorption is obtained for solution of TMPD-CA in solvents of low ionising power such as chloroform. However, a strong absorption is observed for acetonitrile solution immediately after mixing. This consists of singlet due to chloranil semiquinone ion, superimposed on a set of thirteen triplets attributed to TMPD^+ as shown in Fig. 5.69 (a). This absorption is characterised by ESR spectrum of $\text{TMPD}^+ \text{ClO}_4^-$. The relative instability of chloranil semiquinone ion compared to TMPD^+ is the collapse of singlet absorption in the aged solution as shown in Fig. 5.69 (b).



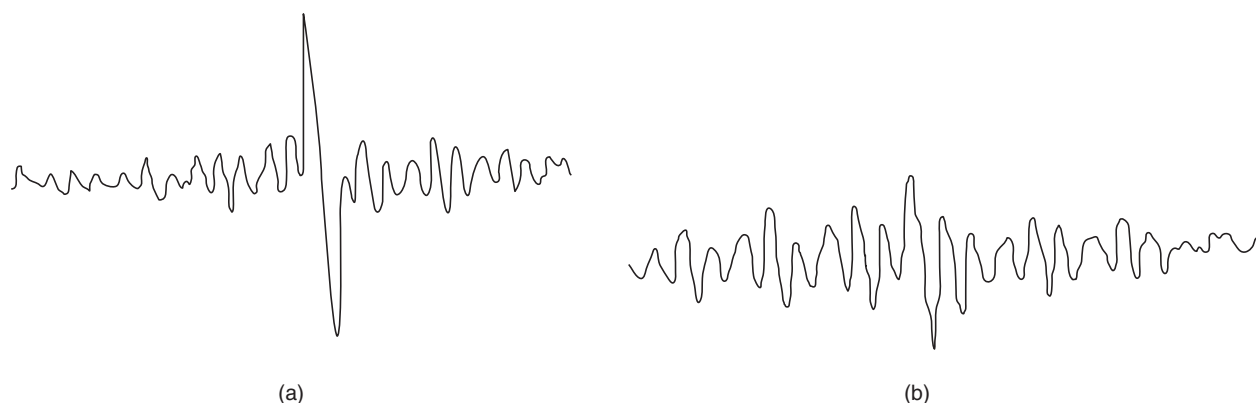
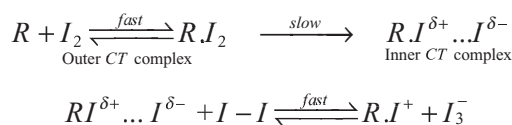


Fig. 5.69 ESR spectra of TMPD-CA system in acetonitrile (a) immediately after mixing, and (b) aged solution.

Ethanol and methanol form 1 : 1 CT complexes with iodine with $\lambda_{CT} \sim 225$ and 220 nm, respectively. The intensity of CT band decreases with time, and simultaneously progressive intensification of triiodide ion absorption at 297 and 363 nm is observed. Concurrently, the conductance of solution of iodine in ethanol/methanol also increases with time and ultimately becomes constant. The transformation of initially formed 1 : 1 outer CT complex of alcohol with iodine to inner CT complex followed by very fast reaction of inner CT complex with iodine to form triiodide ion takes place. according to the scheme:



where, $R = CH_3OH$ or C_2H_5OH .

The rate-determining step is monomolecular transformation of the outer CT complex to inner CT complex. The specific rate constant for the monomolecular transformation can be obtained by making use of the first-order rate constant equation.

$$k = \frac{2.303}{t} \log \frac{A_{\infty} - A_o}{A_{\infty} - A_t} \quad (5.105)$$

Here, A_o , A_t and A_{∞} are the absorbances measured immediately after mixing iodine in an alcohol, after time t and at the end of the reaction respectively.

Form the straight-line plot between $\log(A_{\infty} - A_t)$ and time, one can determine the value of k from the slope. Note that the absorption measurements as a function of time are either carried out at the absorption band of CT complex or at the product band. In case of ionic reactions, the specific rate constant can also be obtained from the expression

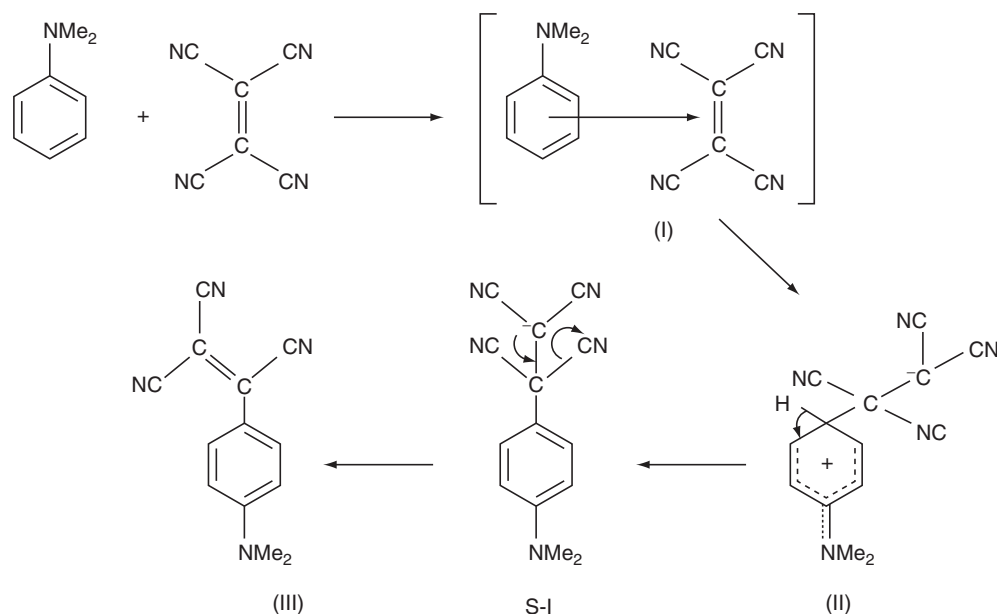
$$\ln \frac{\sigma_{\infty} - \sigma_{t_1}}{\sigma_{\infty} - \sigma_{t_2}} = kt + \phi \quad (5.106)$$

where, σ_{∞} , σ_{t_1} , σ_{t_2} are the conductances at time t_{∞} , t_1 , and t_2 respectively and ϕ is the intercept due to time lag.

TCNE with N, N-dimethylaniline in chloroform instantaneously forms a blue charge-transfer complex (I) with absorption maxima at 675 nm. The intensity of the band gradually decreases as an σ -intermediate (II) develops and the final product has been isolated as a solid and is identified as N, N-dimethyl-4-tricyanovinyl aniline (III). The kinetic data for the reaction is consistent with the bimolecular reaction of the CT complex with a molecule of the free aniline. The reaction proceeds according to the scheme.(S-I)

The reaction of N-methylaniline with TCNE in chloroform follows a sequence analogous to the reaction involving N, N-dimethyl aniline except that the decomposition of CT complex is fast and formation of final product is slower than in the reaction of N, N-dimethylaniline. A similar sequence is observed for the reaction of indole with TCNE in dichloromethane. The final product has been identified as 3-tricyanovinyl indole.

When chloranil is directly dissolved in excess of N, N-dimethylaniline, a broad band appears at 650 nm and is attributed to the formation of a neutral CT complex (I). The intensity declines with time and simultaneously a new band develops at 410 nm. Concurrently, the conductivity of the solution grows rapidly and an ESR absorption band corresponding to the chloranil semiquinone ion (II) is observed. This band assignment conforms to ESR band of solid sodium-chloranil compound as well as of electrolysed solutions of chloranil. The absence of



ESR signal due to N, N-dimethyl-aniline cation (III) at any stage of the reaction might be due to broadening of the signal through rapid electron exchange reaction between radical cation of N, -N dimethylaniline and the larger excess of neutral N, N-dimethylaniline molecules. After a number of days, the absorption at 410 nm decreases and somewhat later the intensity of ESR signal also decreases. The conductivity of the solution however does not change. The aged solution contains crystal violet as its cation (IV). Thus this reaction via CT complexation according to Kosower proceeds according the scheme (S-II).

Problem 5.47: When solutions of N-heterocyclics, i.e. pyridine (Py). α -picoline (α -P), β -picoline (β -P), γ -picoline (γ -P) and fluoranil (FA) in chloroform (concentration of N-heterocyclics being in far excess than that of fluoranil) are mixed, an absorption band appears around ~ 340 nm. The intensity of the band increases with time and concurrently the conductivity of the solution grows rapidly. The absorbance of N-heterocyclics-fluoranils systems at different time intervals in CHCl₃ solution at 298 K is given in Table 5.31, Assuming that 1 : 1 complex is formed in these systems and no products are isolated in the course of the reaction as well as from the final solutions,

- suggest the tentative mechanism in these systems, and
- calculate the rate constants for the reaction in these systems.

Solution

(a) We know that the formation of DA complex of CT type is an instantaneous process and band positions remain unaltered on changing the electron donor in these systems. The absence of absorption band characteristic of CT complex is due to very low concentration of DA complex left at any moment due to its immediate conversion to the final product according to the following scheme.



Since the position of the band does not change on changing the donor, the reaction species, i.e. product or a DA complex formed are structurally similar. The appearance of a band at around ~ 340 nm and concurrent increase in conductivity of the solution suggests the formation of ionic products.

- (b) The specific rate constants k at the products bands have been calculated using Eq (5.105)

$$k = \frac{2.303}{t} \log \frac{A_{\infty} - A_o}{A_{\infty} - A_t} \quad (\text{Eq. 5.105})$$

where the terms and symbols have their usual meanings. The straight-line plot between $\log (A_{\infty} - A_t)$ and t for various systems is shown in Fig. 5.70. The values of specific rate constants at 298K as determined from the slope of straight lines in Fig. 5.70 are

System	$k \times 10^3$
Py - FA	7.53
α - P - FA	10.60
β - P - FA	16.80
γ - P - FA	26.80

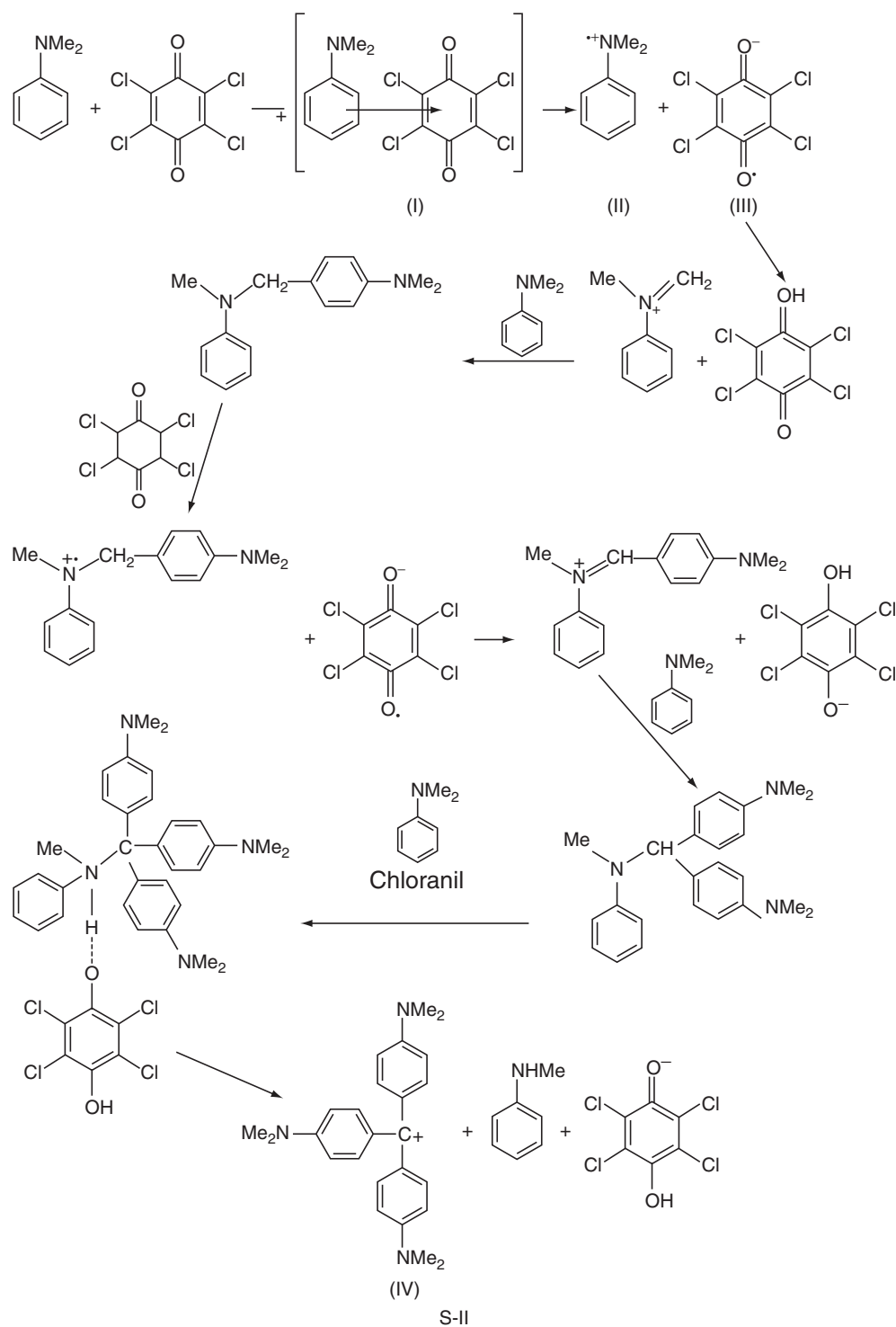


Table 5.31 The absorbance of *N*-heterocyclic – FA systems at different time intervals in CHCl_3 solution at 298 K.

Time (min)	Absorbance			
	$\frac{\text{Py} - \text{FA}}{348 \text{ nm}}$	$\frac{\alpha - \text{P} - \text{FA}}{341 \text{ nm}}$	$\frac{\beta - \text{P} - \text{FA}}{338 \text{ nm}}$	$\frac{\gamma - \text{P} - \text{FA}}{339 \text{ nm}}$
0.0	0.7661	0.6490	0.6440	0.6010
1.0	0.7676	0.6518	0.6485	0.6046
2.0	0.7706	0.6545	0.6539	0.6123
3.0	0.7718	0.6590	0.6578	0.6157
4.0	0.7739	0.6610	0.6626	0.6160
5.0	0.7765	0.6650	0.6654	0.6201

6.0	0.7776	0.6675	0.6707	0.6232
7.0	0.7787	0.6705	0.6758	0.6268
8.0	0.7822	0.6740	0.6804	0.6303
9.0	0.7837	0.6765	0.6833	0.6332
10.0	0.7844	0.6800	0.6877	0.6363
11.0	0.7871	0.6825	0.6918	0.6389
12.0	0.7891	0.6860	0.6959	0.6415
13.0	0.7904	0.6890	0.6992	0.6449
14.0	0.7916	0.6920	0.7029	0.6468
15.0	0.7916	0.6950	0.7052	0.6485
16.0	0.7940	0.6975	0.7094	0.6510
17.0	0.7968	0.7000	0.7123	0.6539
18.0	0.7983	0.7025	0.7159	0.6566
19.0	0.7999	0.7065	0.7186	0.6567
20.0	0.8027	0.7080	0.7226	0.6591
∞	1.0370	0.9490	0.9194	0.7480

5.20.6 Biological Applications

Biological applications of UV/V spectroscopy are centred around (i) quantitative analysis of biological samples from plant and animal systems in vivo and vitro carbohydrates, lipids, aminoacids and proteins, enzymes, nucleic acids, vitamins, pigments, phenolics, etc., and (ii) the study of inter- and intra-molecular interactions in biological systems. It has been suggested that intramolecular charge-transfer interactions across space may be involved in the structures of some biological macromolecules and various cellular systems and the intermolecular interactions are involved in biochemical reactions. Some of the typical biological applications of this tool are reported here.

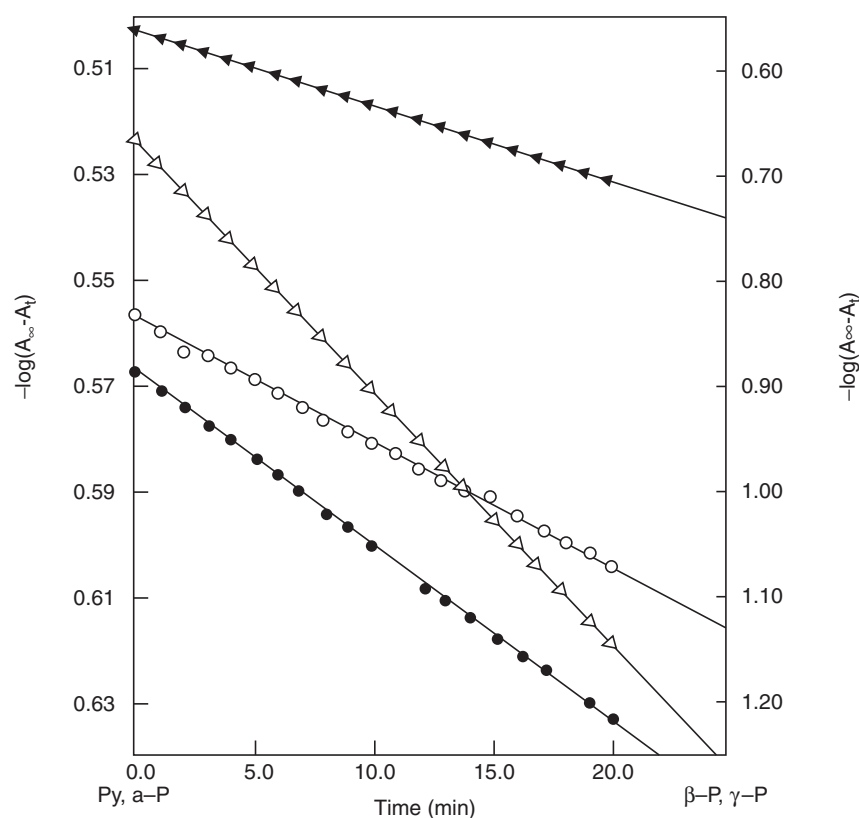
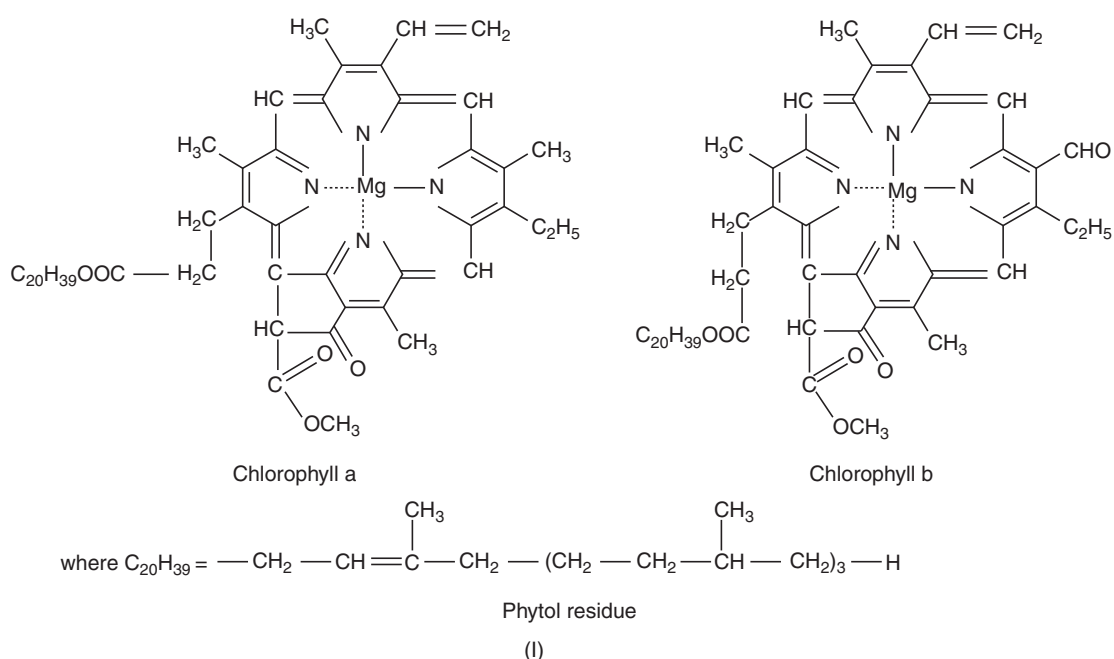


Fig. 5.70 Pseudo first-order rate plots for the N-heterocyclic-FA systems in CHCl_3 solution at 298 K • – Py, 340 nm; Δ – α -P, 341 nm, $\blacktriangle$ – β -P, 338 nm; $\circ$ – γ -P, 339 nm.

(a) Determination of Chlorophyll and Carotenoids in Plants All green vegetation contains the alcohol-soluble pigment chlorophyll. It is always associated with the carotenoids, carotene and lutein. The carotenoids act as photosensitisers in conjugation with chlorophyll. With the help of chlorophyll, plants assimilate carbon dioxide from the atmosphere converting it into water, oxygen and carbohydrates. Chlorophyll actually consists of two individual substances—chlorophyll ‘a’ and chlorophyll ‘b’ differing somewhat in colour. The only difference between them is that the chlorophyll ‘a’ contains methyl group while an aldehyde group is present in the chlorophyll ‘b’. Both chlorophylls are esters. A complete synthesis of chlorophyll was established in 1960 by Robert B Woodward and he was rewarded the Nobel prize in chemistry for his outstanding achievements in the art of organic synthesis. The chlorophyll content is estimated by the formula of Anderson and Boardman while total carotenoids are computed by the formula reported by Jenson and Jenson.

$$\text{Chlorophyll 'a' (in mg/g tissue)} = (12.7 A_{663} - 2.69 A_{645}) \times \frac{V}{1000w} \quad (5.107)$$

$$\text{Chlorophyll 'b' (in mg/g tissue)} = (22.9 A_{645} - 4.68 A_{663}) \times \frac{V}{1000w} \quad (5.108)$$



$$\text{Total chlorophyll (in mg/g tissue)} = (20.2 A_{645} + 8.02 A_{663}) \times \frac{V}{1000w} \quad (5.109)$$

where, V = Total volume of solution made (in mL)

w = Fresh mass of sample (in g)

$$\text{Carotenoids (in mg/g tissue)} = \frac{54A_{420} \times \text{chlorophyll 'a'} + 10.1 \times \text{chlorophyll 'b'}}{2185} \quad (5.110)$$

Problem 5.48: 50 mg of green leaves crushed in 2 mL of 80 per cent acetone was centrifuged. The supernatant was collected in a 5 mL flask. The residue was again treated with 2 mL of 80 per cent acetone and then centrifuged. The supernatant was again transferred to a 5 mL flask and the total volume was brought up to 5 mL with 80 per cent acetone. The absorbance of the above extract is measured at 663 nm, 645 nm, and 420 nm using 80 per cent acetone as blank and the following data are obtained.

$$A_{663} = 0.821, A_{645} = 0.345 \text{ and } A_{420} = 0.765$$

Calculate (a) the percentage of chlorophyll ‘a’, chlorophyll ‘b’, and (b) total carotenoids in the sample under study. Note that the amount of these species in infected leaves differs from that of healthy leaves. The amount of chlorophyll and carotenoids in leaves also differs from that of stem of plants.

Solution (a) Substituting the given values in the respective formulae, we obtain chlorophyll ‘a’ (in mg/g tissue)

$$= \frac{(12.7 \times 0.821 - 2.69 \times 0.345) \times 5}{50 \times 10^{-3} \times 1000} = \frac{(10.426 - 0.928)}{10} = 0.95$$

$$\text{Chlorophyll 'b' (in mg/g tissue)} = \frac{(22.9 \times 0.345 - 4.68 \times 0.821) \times 5}{50 \times 10^{-3} \times 1000} = \frac{(7.900 - 3.842)}{10} = 0.40$$

$$\text{Total chlorophyll (in mg/g tissue)} = \frac{(20.2 \times 0.345 + 8.02 \times 0.821) \times 5}{10} = \frac{(6.969 + 6.584)}{10} = 1.35$$

Thus,

$$\text{Chlorophyll 'a'} = \frac{0.95}{(0.95 + 0.40)} \times 100 = 70.4 \text{ per cent}$$

and

$$\text{Chlorophyll 'b'} = \frac{0.40}{(0.95 + 0.40)} \times 100 = 29.6 \text{ per cent}$$

(b) Substituting the given value of A_{420} together with the values of chlorophyll 'a' and chlorophyll 'b' from Part (a) into Eq. (5.110), we obtain

$$\begin{aligned} \text{Total carotenoids} &= \frac{54 \times 0.765 \times 0.95 + 10.1 \times 0.40}{2185} \\ &= \frac{39.244 + 4.040}{2185} = 1.980 \times 10^{-2} \text{ mg/g tissue.} \end{aligned}$$

(b) Estimation of Tyrosine and Tryptophan in Intact Protein We know that α -amino acids are of great biological importance and are the building blocks of proteins. They can be derived from natural materials by the hydrolysis of proteins present in meat, skin, gelatin, wool, hair, feather, and also the proteins of protoplasm and nuclei of plants and animal cells, casein from curds, a number of hormones such as insulin, enzymes (e.g. pepsin) etc. UV/V spectroscopy is used to determine the amount of tyrosine (tyr) and tryptophan (try) in intact proteins. Pure tyrosine shows band at $\lambda_{\text{max}} = 294 \text{ nm}$ while tryptophan exhibits maximum absorption at $\lambda_{\text{max}} = 280 \text{ nm}$ in 0.1 N NaOH or KOH. Both the bands overlap to some extent, i.e. both acids in solution will contribute to the absorption at $\lambda_{\text{max}} = 294 \text{ nm}$ as well as at $\lambda_{\text{max}} = 280 \text{ nm}$. From theory, we write

At $\lambda_{\text{max}} = 294 \text{ nm}$,

$$A_{\text{tyr}} = \epsilon_{\text{tyr}} C_{\text{tyr}} l + \epsilon_{\text{try}} C_{\text{try}} l$$

At $\lambda_{\text{max}} = 280 \text{ nm}$,

$$A_{\text{try}} = \epsilon'_{\text{tyr}} C_{\text{tyr}} l + \epsilon'_{\text{try}} C_{\text{try}} l$$

ϵ_{tyr} , ϵ'_{tyr} and ϵ_{try} , ϵ'_{try} are determined from the absorbances measurements on virgin acids in 0.1N KOH at the two wavelengths, i.e. at $\lambda_{\text{max}} = 294$ and 280 nm.

$$\lambda_{\text{max}} = 294 \text{ nm: } \epsilon_{\text{tyr}} = \frac{A_{\text{tyr}}}{C_{\text{tyr}} l}$$

$$\epsilon_{\text{try}} = \frac{A_{\text{try}}}{C_{\text{try}} l} \text{ and at}$$

$$\lambda_{\text{max}} = 280 \text{ nm.}$$

$$\epsilon'_{\text{tyr}} = \frac{A_{\text{tyr}}}{C_{\text{tyr}} l}$$

$$\epsilon'_{\text{try}} = \frac{A_{\text{try}}}{C_{\text{try}} l}$$

Thus, simply by measuring the absorbance of a protein solution in 0.1 N NaOH at $\lambda_{\text{max}} = 280$ and 294 nm and making use of the standard equations, we can determine the amounts of the two amino acids in a given protein.

UV absorption spectra of human and bovine erythrocyte in the wavelength region of 240 to 310 nm have been compared. Absorption spectrum of human erythrocyte shows bands at 254, 260, 266, 326 nm and shoulders at 270, 282 and 289 nm. The low intensity of the band in 280 nm region ($\epsilon_{265} = 17,000$) is attributed at the low content aromatic amino-acid residues, especially tyrosine and tryptophan. The absorption spectra in the visible region show a broad absorption band at 675 nm ($\epsilon_{675} = 275$) and shoulder at 440 nm. Thus erythrocyte is classified as nonblue copper protein. The ratio of absorbances $\frac{A_{259}}{A_{680}} = 31.4$ (5.111) in case of bovine erythrocyte since $\epsilon_{259} = 9840$ and $\epsilon_{680} = 313$. This ratio in case of human erythrocyte has been found to be $\frac{A_{265}}{A_{675}} = 61.8$.

This suggests the absence of tryptophan in bovine erythrocyte provided it is clear whether or not the human protein really contains two tryptophan residues.

Problem 5.49: Total sugars, i.e. pentoses and hexoses, when treated with concentrated H_2SO_4 and phenol (5%) yield a green-blue coloured condensate of furfural or hydroxymethylfurfural from pentose/hexose and phenol. The blue-coloured condensation product has a maximum absorption at 490 nm. To plot a calibration curve for the determination of total sugars colourimetrically, 10 mg of glucose was dissolved in 100 mL of H_2O . Five standard solutions of varying concentrations (10–90 μg) were prepared. The appropriate amounts of reagents were added to these standard samples, the final volume was made up to 7 mL with water indicated below. After these, the absorbances of all the solutions were measured with respect to the blank, i.e. 1 mL H_2O + 1 mL phenol (5 per cent) + 5 mL H_2SO_4 .

Volume of standard glucose solution(10 mg/100 mL)	0.1	0.3	0.5	0.7	0.9
Concentration of glucose (in μg)	10.0	30.0	50.0	70.0	90.0
Water (in mL)	0.9	0.7	0.5	0.3	0.1
Volume of phenol (5 per cent) added	1.0	1.0	1.0	1.0	1.0
Volume of concentrated H_2SO_4 added (in mL)	5.0	5.0	5.0	5.0	5.0
Absorbance at $\lambda_{\text{max}} = 490 \text{ nm}$	0.08	0.24	0.40	0.56	0.72

(a) Free sugars were extracted from 0.5 g of finely ground grains (or leaves) with 80 per cent ethanol. The extracted sugars were dissolved in 50 mL of H_2O . The absorbance of 0.2 mL of the extracted sugars in water measured under the same conditions has been found to be 0.48. What will be the percentage of total sugars in the given sample of grains?

(b) 0.5 g of sample starch obtained from 100 g of gram seeds was hydrolysed with 52 per cent perchloric acid to obtain 50 mL extract containing glucose. The absorbance of 0.2 mL of extract measured under the same conditions was 0.54. Calculate the amount of starch in 100 g of seeds.

Solution (a) Form the standard plot between absorbance and concentration of glucose, the amount of sugars in the unknown sample corresponding to the given absorbance, i.e. 0.48 is 60 μg , i.e. 60 μg of sugars is present in 0.2 mL of the extract.

The amount of total sugars in 50 mL of extract $\frac{50 \times 60}{0.2} = 15000 \mu\text{g} = 0.015 \text{ g}$

Thus, the amount of total sugars in 100 g of grains = $\frac{0.015 \times 100}{0.5} = 3 \text{ per cent}$

(b) From the standard graph, the amount of glucose corresponding to the given value of absorbance, i.e. 0.54, comes out to be 67.5 mg.

So the amount of glucose in 50 mL of extract or 0.5 g of starch sample

$$= \frac{50 \times 67.5}{0.2} = 168.75 \times 10^2 \mu\text{g} = 0.0168 \text{ g}$$

Therefore, the amount glucose in 100 g of starch sample = $\frac{100 \times 0.0168}{0.5} = 3.36 \text{ g}$

Thus, the amount of starch equivalent to 3.36 g of glucose = $3.36 \times 0.9 = 3.02$, i.e. 100 g of seeds, contain 3.02 g of starch.

Problem 5.50: Deoxyribonucleic Acid (DNA) is present in all living cells and is the substance of heredity. DNA when treated with diphenyl amine reagent, the 2-deoxy-D-ribose of DNA reacts to yield a blue-coloured product ($\text{CH}_3\text{COCHOHCH}_2\text{CH N}(\text{C}_6\text{H}_5)_2 \text{OH}$ i.e. $\text{C}_{17} \text{H}_{19} \text{O}_3\text{N}$) which shows a sharp absorption maximum at 595 nm. To plot a calibration curve for the determination of DNA colourimetrically, 15 mg of DNA was dissolved in 100 mL of ethanol. Four standard solutions of varying concentrations (45–90 μg) were prepared. The appropriate amounts of reagents were added to these standard samples, the final volume was made up to 5 mL with ethanol, indicated below. All the solutions were kept in boiling water for more than 10 minutes. After these, the absorbances of all the solutions were measured with respect to the blank, i.e. 1 mL ethanol + 4 mL reagent.

Volume of standard solution of DNA (15 mg/100 mL)	0.3	0.4	0.5	0.6
Concentration of standard solution of DNA (in μg)	45	60	75	90
Volume of alcohol added (in mL)	0.7	0.6	0.5	0.4
Volume of diphenylamine reagent added (in mL)	4.0	4.0	4.0	4.0
Absorbance at $\lambda_{\text{max}} = 595 \text{ nm}$	0.03	0.04	0.05	0.06

From 3 g of plant material, 50 mL of DNA extract was obtained. The absorbance of 0.5 mL of DNA extract measured under the same conditions was 0.02. What is the percentage of DNA in the plant material?

Solution Form the calibration graph between absorbance and concentration of standard DNA (in μg), the amount of DNA corresponding to absorbance = 0.02, has been found to be $30 \mu\text{g}$, i.e. $30 \mu\text{g}$ of DNA is present in 0.5 mL of DNA extract. The amount of DNA present in 50 mL of DNA extract = $\frac{30 \times 50}{0.5} = 3000 \mu\text{g} = 3 \times 10^{-3} \text{ g}$.

Thus the amount of DNA present in 100 g sample of plant = $\frac{100 \times 3 \times 10^{-3}}{3} = 0.1 \text{ per cent}$.

Note that in DNA, only the deoxyribose of the purine nucleotides reacts, so the value obtained represents half of the total deoxyribose present. Moreover, the reaction is given by 2-deoxypentoses in general and is not specific for DNA.

Problem 5.51: Free fatty acids present in oils are responsible for keeping the quality of oils. Lipids or oils react with cupric acetate pyridine reagent to yield a greenish blue-coloured complex which shows an absorption maximum at 715 nm. To plot a calibration curve for the determination of free fatty acids colourimetrically, 20 mg of oleic acid was dissolved in 100 mL of benzene. Four standard solutions of varying concentrations were prepared. The appropriate amounts of reagents were added to these standard samples, and the final volume was made up to 7.2 mL with benzene, indicated below. All the solutions were warmed for two minutes and allowed to stand. After these, the absorbance of supernatants of all the solutions were measured with respect to the blank, i.e. 5.2 mL benzene + 2 mL cupric acetate pyridine reagent.

Volume of standard oleic acid solution (20 mg/100 mL)	0.2	0.4	0.6	0.8
Concentration of standard oleic acid (in μg)	40.0	80.0	120.0	160.0
Volume of benzene added (in mL)	5.0	4.8	4.6	4.4
Volume of cupric acetate pyridine reagent (in mL)	2.0	2.0	2.0	2.0
Absorbance at $\lambda_{\text{max}} = 715 \text{ nm}$	0.21	0.42	0.63	0.84

400 mg of ground seeds were treated with petroleum ether to extract oil. The amount of oil extracted was 50 mL. The absorbance of 0.2 mL of extracted oil measured under the same conditions was 0.04. What will be the percentage of free fatty acids in the given sample of seeds?

Solution Form the plot of absorbance against concentration of standard oleic acid (in μg), the value of concentration of free fatty acids in 0.2 mL of extract corresponding to the given value of absorbance, i.e. 0.04, comes out to be $7 \mu\text{g}$. So the amount of free fatty acids in 50 mL of extracted oil = $\frac{50 \times 7}{0.2} = 1750 \mu\text{g}$

$$= 1750 \times 10^{-6} \times 10^3 \text{ mg} = 1.75 \text{ mg}$$

Thus, the percentage of free fatty acids in the given sample of seeds

$$\frac{100 \times 1.75}{400} = 0.43$$

Problem 5.52: Creatinine (1-Methylglycocyamidine, $\text{C}_4\text{H}_7\text{N}_3\text{O}$) plays an important role in storage and transmission of phosphate bond energy. In the presence of picric acid in alkaline medium, it gives a red or light-red coloured tautomer of creatinine-picric acid which exhibits an absorption maximum at 530 nm. To plot a calibration curve for the determination of creatinine colourimetrically, 50 mg of creatinine was dissolved in 100 mL of water.

Five standard solutions of different concentrations (100–400 $\mu\text{g/mL}$) were prepared. These samples were mixed with reagents in appropriate amounts, and the final volume was made up to 10 mL with water, indicated below. The solutions were allowed to stand for 10 minutes. After these, the following readings were obtained on an absorption spectrophotometer with respect to blank, i.e. 7 mL H_2O + 1 mL 1 N.NaOH + 2 mL saturated picric acid.

Volume of standard creatinine solution (50 mg/100 mL)	0.2	0.4	0.5	0.6	0.8
Concentration of standard creatinine (in μg)	100	200	250	300	400
Volume of water added (in mL)	6.8	6.6	6.5	6.4	6.2
1 N NaOH added (in mL)	1	1	1	1	1
Saturated solution of picric acid added (in mL)	2	2	2	2	2
Absorbance at $\lambda_{\text{max}} = 530 \text{ nm}$	0.28	0.56	0.70	0.84	1.12

The absorbance of 0.6 mL of urine sample measured under the same conditions was 0.20. Determine (a) the amount of creatinine in mg per 100 mL of urine, and (b) the creatinine coefficient, assuming body weight to be 50 kg and urine collected in a single day is 1500 mL.

Solution

- (a) Plot a graph between absorbance and concentration of creatinine (in μg). From the graph, our value of urine sample corresponding to the absorbance, i.e. 0.2, is 70 μg .

$$\begin{aligned}\text{Thus, amount of creatinine in 100 mL of urine sample} &= \frac{100 \times 70}{0.6} = 1.166 \times 10^4 \mu\text{g} \\ &= 1.166 \times 10^4 \times 10^{-6} \times 10^3 \text{ mg} = 11.66 \text{ mg}\end{aligned}$$

- (b) Creatinine coefficient is defined as the amount of creatinine present in urine sample collected per day per kg body weight. The amount of creatinine present in

$$1500 \text{ ml urine} = \frac{1500 \times 11.66}{100} = 174.9 \text{ mg}$$

$$\begin{aligned}\text{Thus, the creatinine coefficient} &= \frac{174.9}{50} \text{ mg/day/kg body weight} \\ &= 3.5 \text{ mg/day/kg body weight}\end{aligned}$$

(c) Folding and Unfolding of Protein Molecules The folding of polypeptide chains into compact globular structures is often assumed to be responsible for their biological functions in the cell. The unfolding of globular proteins such as ribonuclease, myoglobin, chymotrypsinogen, lysozyme, trypsin, etc., can easily be accomplished from their optical melting curves. The optical equilibrium curves are obtained by plotting a graph of absorbance change per degree as a function of temperature (Fig. 5.71). The pronounced asymmetry of the resultant differentiated melting curve is due to the change of specific heat upon folding of the protein molecule. Such a presentation of melting curves is very convenient and helpful since details of the equilibrium data, like the pronounced asymmetry, are more easily recognisable than they are from the integrated melting curves.

The unfolding of the globular proteins is based on the following two hypothesis: (i) The transition takes place between two macroscopic states, the native state A and the unfolded state B, which means that in a melting region, a mixture of fully native molecules and unfolded molecules exist with negligible amounts of intermediate states. The Van't Hoff analysis, i.e. free energy change in a function of the temperature and of the pressure of unfolding of protein based on intramolecular conformational change between the two

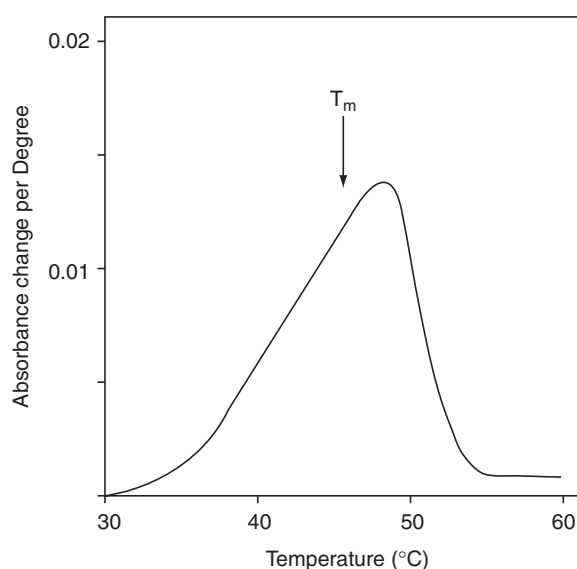


Fig. 5.71 Optical equilibrium melting point curve of chymotrypsinogen at acid pH (=2) and tryptophan absorbance at 293 nm.

Table 5.32 Comparison of specific heat (in $\text{kJ mol}^{-1} \text{K}^{-1}$) upon unfolding of globular proteins as determined by calorimetric and optical melting methods.

Protein	ΔC_p (calorimetric)	ΔC_p (Van't Hoff)
Chymotrypsinogen	16	14(16*)
α -chymotrypsin	12.5	14
Ribonuclease	5.5	8.5 (7.1*)
Myoglobin	11.3	10.5
Lysozyme	6.7	8.8

*Values within brackets are based on the pressure dependence of unfolding.

states, lends support to this hypothesis. (ii) There is a gradual unfolding of every protein molecule in the transition region with many different intermediate states, in such a way, for example, that at the melting temperature T_m , half of every molecule is unfolded, the rest being folded. Such behaviour is expected for the helical-coil transition of very long polypeptides.

The change of specific heat upon unfolding of globular proteins as deduced from calorimetric measurements and Van't Hoff analysis of optical melting curves are compared in Table 5.32.

(d) Molecular Interactions and Mechanism of Biological Systems Pyridine nucleotide and flavin nucleotide coenzymes are the oxidation–reduction coenzymes and play an important role in biological oxidation–reduction process.

Nicotinamideadenine dinucleotide (NAD^+) [I, R = H] nicotinamideadenine dinucleotide phosphate (NADP) [I, R = OP (OH)₂] are typical pyridine nucleotide coenzymes. They play a vital role in biochemical processes involving NAD^+ in oxidation–reduction in which the pyridinium ring of NAD^+ [II, R = ribosyl adenine phosphate residue] is reduced by hydride addition in the 4-position to give NADH [III, R = ribosyl adenine phosphate residue]. NADH has absorption maximum at 340 nm while NAD^+ has at 260 nm. The coenzyme NADP^+ may be reduced in a similar way to NADPH .

The two flavincoenzymes, flavinmononucleotide (FMN) [IV] and flavinadenine dinucleotide (FAD) [V], are derivatives of riboflavin [VI]. Just like pyridine coenzymes they are also involved in redox processes in which hydrogen is transferred at the isoalloxazine ring. The enzymitically reduced forms of FMN and FAD, i.e. FMNH_2 and FADH_2 , are represented by the structures [VII] in which R stands for the side chain of FMN and FAD respectively.

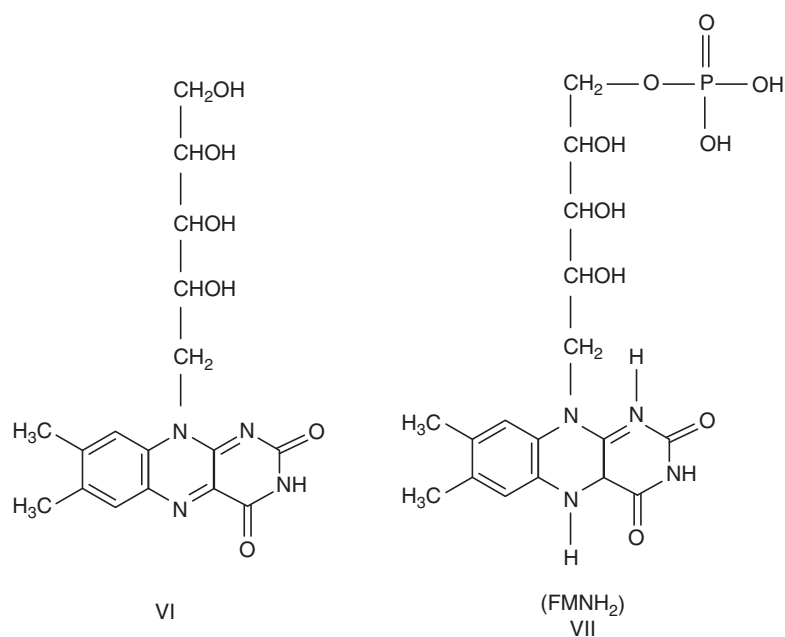
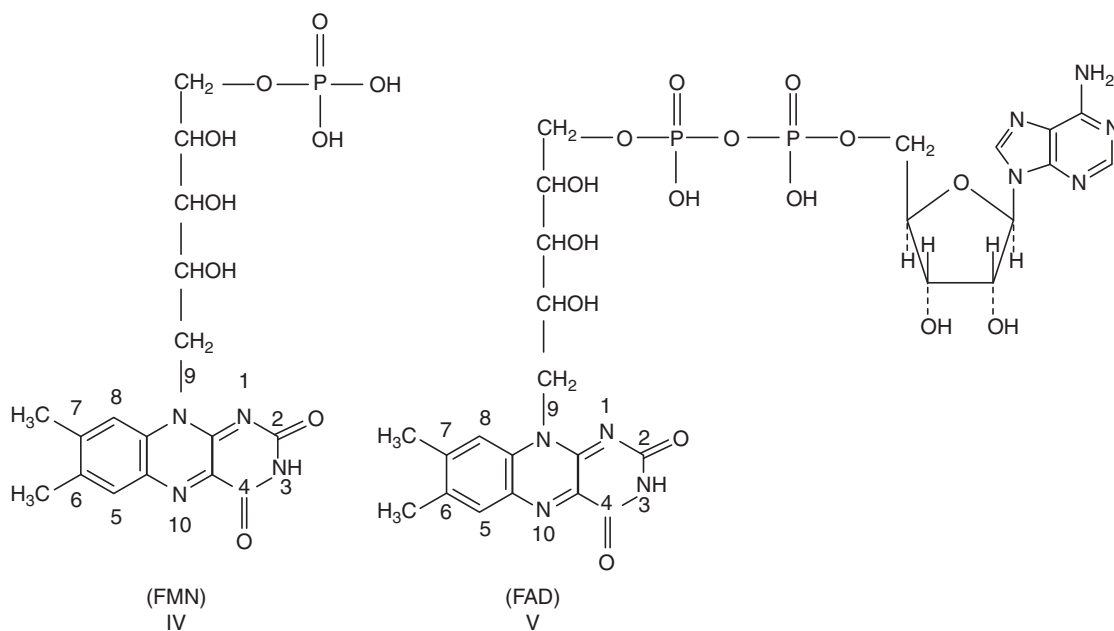
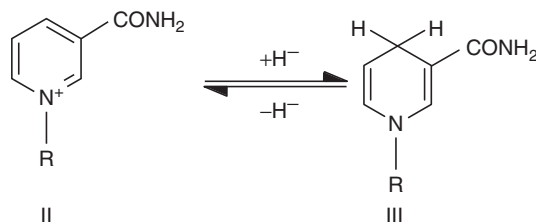
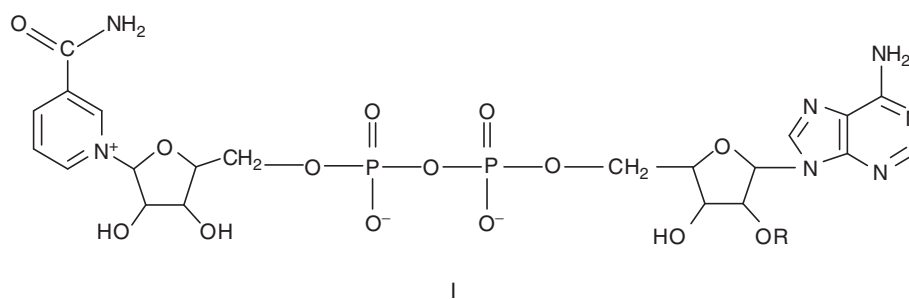
Mixtures of reduced flavin mononucleotide [VII] (FMNH_2) with NAD^+ (which has a absorption maximum at 260 nm) show a new absorption band at $\lambda_{\text{max}} = 21,000 \text{ cm}^{-1}$ (480 nm) and is attributed to an intermolecular charge transfer transition. The CT type interaction in such systems is substantiated by quantitative spectrophotometric measurements on solutions containing NAD^+ analogues, i.e. substituted methylpyridinium chlorides with FMNH_2 (Table 5.33). The values of association constant and optical characteristics of the complexes are consistent with charge-transfer complexation. The relatively high energy of the absorption band of the FMNH_2 – NAD^+ complex may be because of steric effects of the large group attached at the ring nitrogen atom in NAD^+ .

The reduced form of flavoprotein enzyme, lipoyl dehydrogenase, forms a green CT complex with either (i) NAD^+ with λ_{max} at 14000 cm^{-1} (700 nm); or (ii) the hypoxanthine derivative of NAD^+ with λ_{max} at 14000 cm^{-1} (700 nm), or (iii) oxidised thionicotinamide adenine dinucleotide with λ_{max} at 13500 cm^{-1} (740 nm). The intensities of the

Table 5.33 Association constants of the complexes FMNH_2 – NAD^+ analogues.

R in N-methyl pyridinium chloride	$\bar{\nu}_{CT} (\text{cm}^{-1})$	AD_{max}	$K (\text{l mole}^{-1})$
3- CONH_2	19000	830	4.3
4- CONH_2	15300	600	5.0
3- COOCH_3	18500	1000	7.7
4- COOCH_3	14100	1050	8.8
H	18500	600	1.1
ADPR*	22000	560	11.4

*ADPR—represents the adenine–phosphate–ribosyl moiety of NAD^+ .



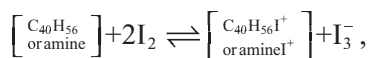
bands grow as the temperature is reduced and the effect is reversible.

NAD⁺ and NADP⁺ when mixed with indole and its derivatives, including tryptophan, show broad featureless absorptions extra to the absorptions of the component species. The extra band in these systems is attributed to CT type interaction between indole ring and pyridinium ring since absorption spectra of 1-(β -indolyethyl)-3-carbamidopyridinium chloride [VIII] in methanol solution and of an equimolar mixture of tryptamine hydrochloride and nicotinamide methochloride have been characterised by a broad band tailing into 22000 cm⁻¹ (450 nm) range of the visible spectrum, with an estimated maximum at 30,800 cm⁻¹ (325 nm). This low-energy absorption band in [VIII] is assigned to a charge-transfer transition across space between indole ring and pyridinium ring. The reluctance to undergo intermolecular association between NAD⁺ and NADH may be as a result of intramolecular charge-transfer interaction in NAD⁺ between the pyridinium ring and the adenine moiety. The broad absorption band shown by solutions of glyceraldehyde-3-phosphate dehydrogenase containing NAD⁺ may be the result of a charge transfer interaction again between the pyridinium ring acting as the acceptor site and an indole moiety as the donor site.

Mixtures of FMNH₂ and FMN show a new absorption band at $\lambda_{\max}$ 11000 cm⁻¹ (900 nm) and is attributed to charge-transfer complex formation.

The use of electronic spectroscopy to study the interaction of drugs with biological systems met with a limited success. A transient magenta colour develops when procaine hydrochloride is mixed with RNA. The band appears at 18200 cm⁻¹ (550 nm). The band is not due to CT type interaction since the colouration does not appear immediately.

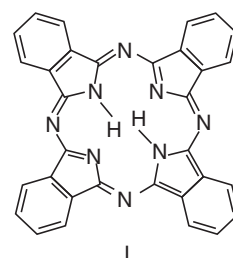
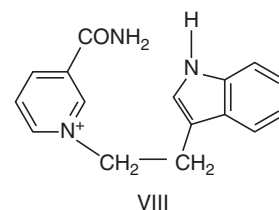
Proteins and amino acids *in vivo* are probably surrounded by very strong polarisation forces. Electronic absorption spectra of proteins or amino-acids-I₂ systems in water show a new band at 226 nm. When amino acid or protein is added to aqueous iodine, the intensity of the band at 455 nm due to solvated iodine decreases (iodine absorption in an inert solvent appears at 520 nm) while those of at 353 and 287 nm due to triiodide ion, I₃⁻ increases. A new band at 226 nm due to negative iodine ion, I⁻ appears. With passage of time the intensity of band at 226 nm increases while those of other, i.e. I₂ and I₃⁻ species decreases, the decrease may be due to slow iodination. The iodine presumably attaches itself to the amino group as the I⁻ ion. On the basis of CT complexation between beta-carotene (C₄₀H₅₆) and I₂ and amines and I₂ is according to the scheme.



it is suggested that CT complexes of the type $\left[\begin{array}{c} \text{aminoacid} \\ \text{or} \quad \text{I}^+ \\ \text{protiens} \end{array} \right]$ are initially present in the solutions of amino acids or proteins and iodine in water.

The most interesting and fascinating biological process where electronic spectroscopy provides an aid to understand its mechanism is photosynthesis. We have already discussed that chlorophyll in plants absorbs light, assimilates carbon dioxide from the atmosphere, convert it into water, oxygen and carbohydrates. The question arises how this absorbed light can be trapped and used in such processes without being dissipated as heat. The answer to this problem comes from the 'hopping model of electrical transport' which is applicable to lamellar phthalocyanine-electron acceptor systems. The conductivity of a pure donor or acceptor changes when a thin layer of a second component is deposited on the surface, e.g. the conductivity of film of phthalocyanine (I) is potentiated by 10⁷ when treated in this way with o-chloranil and vice versa. Similar large increases in conductivity have been observed when a matrix of violanthrene is coated with o-chloranil. According to the 'hopping model', an electron is transferred from a donor molecule to the neighbouring acceptor molecule to yield a dative structure D⁺ A⁻. The charges may separate subsequently via orbital overlap of D⁺ with another D molecule. Because of such successive interactions, the positive hole will become free of the negative charge and will cause hole conduction. The stronger the D-D⁺ interaction, the lower will be the activation energy for the charge separation and hence greater will be conductivity.

It is suggested that a similar process is taking place at the biological site of a photochemical energy transfer, called chloroplast, which also has lamellar structure. Chlorophyll (II) with its conjugated dihydroporphyrin ring structure acts a donor and forms a charge-transfer complex with plastoquinone, a quinone specific to chloroplasts. Absorption of light by chlorophyll causes the electron to move to the plastoquinone. This is followed by hole migration via neighbouring chlorophyll molecules so that back reaction is prevented. The migrating hole eventually reaches a cytochrome system at which electron-transfer from the



iron of the cytochrome or some other electron donor (cytochrome oxidase enzymes contain iron and copper), restores the chlorophyll to its initial state.

The charge-transfer process in photosynthesis is substantiated by the CT complexation between chlorophyll and other porphyrin-like molecules. Some of these porphyrins are involved in the related electron-transport chain in respiration. When an electron acceptor is added to a solution of a porphyrin, a broadening of the band structure with decrease in intensity of the porphyrin takes place. The appearance of isosbestic points is an evidence for the formation of 1 : 1 complex, e.g. aetioporphyrin I (III) -1, 3, 5-trinitrobenzene, and tetraphenylporphyrin-1, 3, 5-trinitrobenzene systems in nitrobenzene solvent show a charge-transfer band in the region $20,000\text{ cm}^{-1}$. The association constants for complexes of 2, 4, 7-trinitrofluorenone electron acceptors with some porphyrin type molecules are given in Table 5.34.

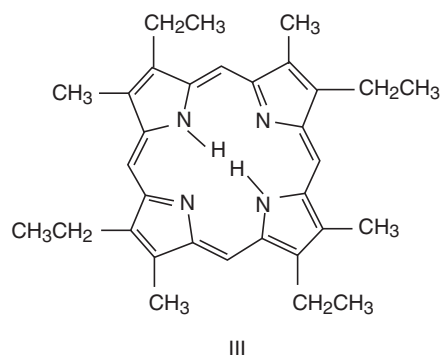


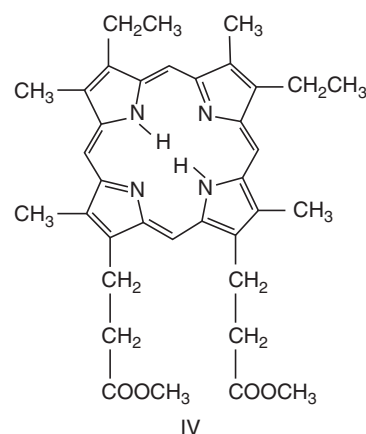
Table 5.34 Association constants of some complexes of porphyrin-type molecules with 2, 4, 7-trinitrofluorenone electron acceptors at 23°C.

Acceptor	Donor	Solvent	$\lambda^{\#}$ (in nm)	K (lit mole ⁻¹)
2, 4, 7-trinitrofluorenone	Meso p	CHCl ₃	497	2006
2, 4, 7-trinitrofluorenone	Aetio p	CHCl ₃	499	2356
2, 4, 7-trinitrofluorenone	Co (II) meso p	CHCl ₃	522	3038
2, 4, 7-trinitrofluorenone	Ag (II) meso p	CHCl ₃	561	2261

Meso p $\equiv$ mesoporphyrindimethylester (IV), aetio p $\equiv$ aetioporphyrin I; $\#$ wavelength at which optical measurements have been made.

The comparable values of association constants of metal-free porphyrins and metal porphyrins for the same acceptor show that electrons from the porphyrin ring but not from the metal are involved in the complexation.

It has been known for more than two decades that plants protect themselves from excess light, which can lead to oxidative damage to chlorophyll and other key photosynthetic pigments. But the biophysical mechanism of the protective process (known as feedback de-excitation) remained mysterious. Very recently, using femtosecond, i.e. ultrafast spectroscopic techniques and plant genetics, it was found that when spinach leaves are exposed to intense light triggers, zeaxanthin cation radicals are produced. These cation radicals result when zeaxanthin or zeaxanthol [$C_{40}H_{56}O_2$; $\lambda_{\text{max}}^{\text{alcohol}}$ (log ϵ): 275(4.34), 453(5.12), 480(5.07)], a carotenoid known to be produced by plants in response to bright sunlight, binds to photo-excited chlorophyll molecules. The zeaxanthin gives up an electron to the excited chlorophyll, yielding a chlorophyll anion radical and a zeaxanthin cation radical. These products subsequently undergo charge recombination, allowing the excited state energy of chlorophyll to be safely dissipated as heat. Thus, plants rely on a carotenoid to protect themselves from over-exposure to light. This feedback de-excitation mechanism might be manipulated for practical uses such as protecting artificial photosynthetic systems used for solar energy generations from light-induced damage.



(e) Study of Dye/Drug-Protein Interactions Coloured organic dyes are consumed by humans through food and medicine as they are present in the form of additives, preservatives, etc. When these coloured dyes, like other nutrients, enter the circulation in blood, they are bound specifically by a plasma protein in blood called serum albumin (having 580 amino-acid residues)—the transporting protein for various drugs, vitamins, hormones as well as for dyes in the blood. However, the dyes have no physiological role and have to be eliminated rapidly from the human system to avoid intoxication. When anionic substrates (organic small molecules) interact with serum albumin, the absorption spectra often show marked changes. Thus, the distribution and elimination of water-soluble anionic dyes such as eosine, metanil yellow, erythrosine, etc., can be judged from the strength of binding of dyes with plasma protein in the visible region of spectrum where albumin does not show absorbance. This enables to follow the absorbance of dye without interference from albumin. Bovine Serum Albumin (BSA) having molecular mass of 69000 DA being cheaper is an excellent model protein for studies. To a fixed [dye]

varying amounts of BSA (in phosphate buffer of pH = 7.4 and at 298 K) are added and absorbances are measured at the absorption maxima of the dye. The change in absorption indicates the dye-protein interaction. The binding of the dye to BSA can be quantified by the absorbance change method, i.e.

$$\frac{C_B}{C_T} = \frac{A_d - A_{pb}}{A_d - A_{cbd}} \quad (5.111)$$

where C_B is the bound and C_T is the total [dye], A_d is the absorbance of the dye alone; A_{pb} is the absorbance of the dye in the partially bound condition, A_{cbd} is the absorbance in the completely bound condition (at and above this [BSA], there is no change in absorbance of dye).

Further, the reversible binding of dyes to BSA can be represented by the equilibrium indicated below:



For 1:1 complex, i.e. one amino acid residue binding with one dye molecule,

$$C_B = [\text{Complex}] \quad (5.113)$$

Thus, the binding constant for dye-BSA complex formation is

$$K = \frac{C_B}{[\text{BSA}]_{\text{free}} C_f} \quad (5.114)$$

where C_f is the free [dye] and can be found as $C_f = C_T - C_B$. If $[\text{BSA}] \gg [\text{Dye}]$, $[\text{BSA}]_T \sim [\text{BSA}]_{\text{free}}$. Under these conditions, Eq. (5.114) modifies to

$$K = \frac{C_B}{[\text{BSA}]_T C_f} \quad (5.115)$$

From a set of K values, determined with the aid of Eq. (5.115), mean value of K can be determined.

According to theoretical model of Martin (Fig. 5.72) when dye bound has K of the order of 10^4 , then the fraction unbound is to the extent of 70 to 80 per cent and only least affected by the total dosage of the dye. If K is of the order of 10^7 , at low dosage the dye is mostly bound to albumin and unbound fraction is low. However, at high dosage, the bound fraction decreases, leading to increase in unbound concentration. Thus the binding constants ' K ' of the order of 10^3 to 10^4 can easily be eliminated from the system and are less toxic to the human system. In this respect, the binding constants of dye-albumin complex aids in discerning the careful selection of dye, and thus dyes having strong affinity towards albumin should be avoided in using them as additives, preservatives, flavouring or colouring agents. Many drug molecules have strong ultraviolet or visible absorption spectra. When such drugs interact with proteins, nucleic acids and other biological molecules, their absorption spectra show marked changes but many drugs, and most biological meromolecules absorb strongly at wavelengths below

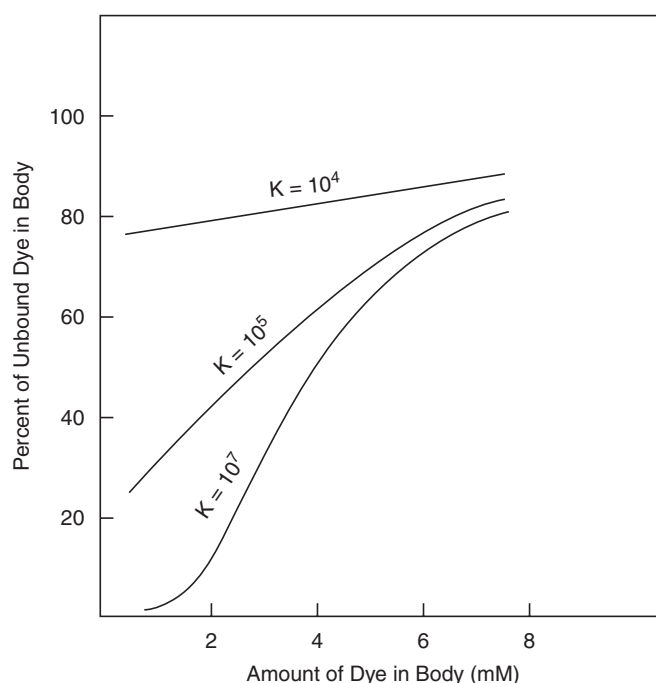


Fig. 5.72 Theoretical curves due to Martin showing the relationship between percentage of unbound dye in body and amount of dye in body at different values of K .

300 nm. Spectral changes in this wavelength region are often small and rather complex and are best observed by means of difference spectroscopy. When an interaction between a drug and a macromolecule alters the spectrum of one or both components then a difference spectrum will be generated. The observed spectrum of the phenylbutazone–human serum albumin (HSA) complex, for example, is not that which would be expected from an addition of the absorption spectra of the isolated drug and macromolecule (Fig. 5.73). These spectral changes give rise to a biphasic difference spectrum which characterises this particular interaction. The difference spectrum generated by dissolving phenylbutazone in the cationic detergent cetrimide (Fig. 5.74) is very similar to that observed when the drug binds to HSA. This suggests that the binding site for phenylbutazone is in a hydrophobic region of the protein.

5.21 PHOTOACOUSTIC UV/V SPECTROSCOPY (PAUVS/PAVS)

We have already introduced in Chapter 3 on infrared spectroscopy, the historical background and the basic principles of photoacoustic spectroscopy. It was Bell who in 1881 showed that PA effect is applicable to all matter and even visible light could produce PA effect. According to him, ‘the nature of the rays that produce PA effect on different substances depends upon the nature of the substances that are exposed to the beam and that the sound are in every case due to the rays of the spectrum that are absorbed of the body.

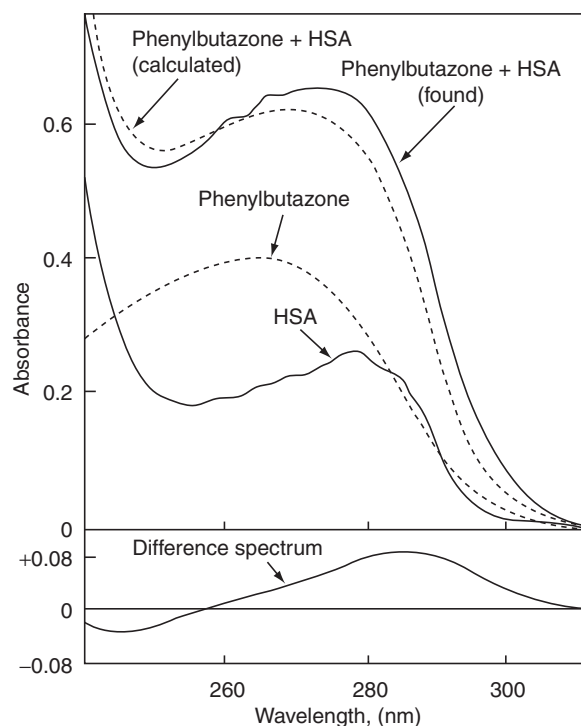


Fig. 5.73 The observed ultraviolet absorption spectrum of phenylbutazone, human serum albumin (HSA) and phenylbutazone–HSA mixture. The phenylbutazone + HSA (calculated) curve is obtained by adding the spectra of the individual components. The difference spectrum is obtained by combining the drug and protein in the sample beam and separating them in the reference beam. All the measurements have been made in sodium phosphate buffer of pH of 7.4.

5.21.1 Modern Photoacoustic Spectrophotometer

The self-explanatory block diagrams of single- and double-beam photoacoustic spectrophotometers have been shown in Fig. 5.75(a) and (b). The modern spectrophotometers resemble the spectrophone employed by Bell.

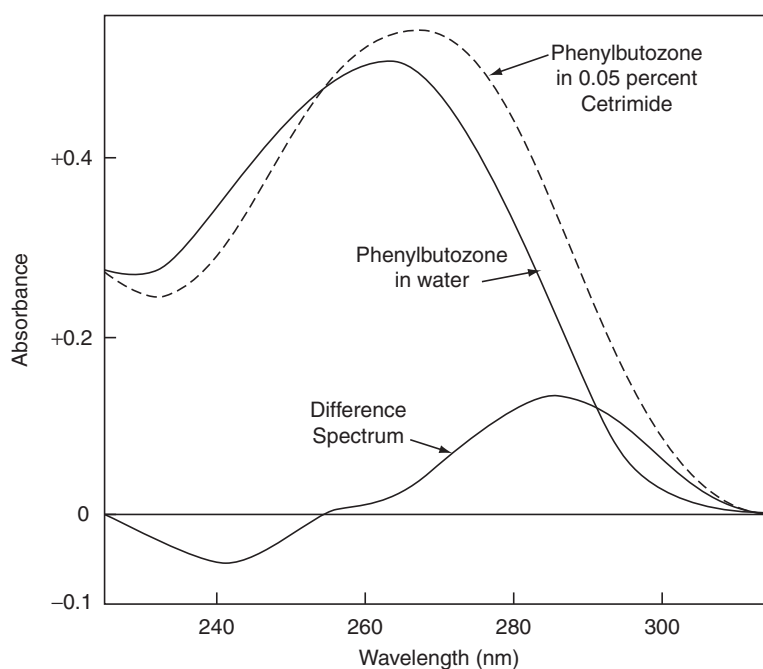


Fig. 5.74 The ultraviolet absorption spectrum of phenylbutazone measured in the presence and absence of cetrimide. Blank samples contain the same solvent but without the drug. The difference spectrum is obtained by placing the cetrimide solution of drug in the sample beam and an aqueous solution of drug in the reference beam. All the measurements are carried out in sodium phosphate buffer of pH 7.4.

Most of the improvements in Bell's spectrophone are only due to the improvement in technology. The reference cell in a double-beam spectrophotometer contains some strongly absorbent material like charcoal, sooty carbon black, etc., and the signal obtained reproduces the power spectrum of the lamp used. Usually, a high pressure 400 W xenon lamp is used. It gives all wavelengths between 210–1000 nm. The ratio of the sample signal to the reference signal gives the spectrum of the sample after some standardisation procedure. Since PA spectrum is a power spectrum so it depends not only on the photon flux but also on the energy of the photon. Thus, the signal at 200 nm would be twice as strong as that in the 400 nm region. The dependence of spectrum on the energy of the photon helps us in better spectra in the UV region, where the photon flux for most lamps is low. Factors affecting the signal intensity and precautions to be observed to minimise these factors have already been discussed in Chapter 3. The cell is the most important element of a photoacoustic spectrophotometer. Its self-explanatory block diagram is shown in Fig. 5.75 (c). The two removable plates of sapphire or suprasil for UV-visible, which act as windows, attenuate any external noise since their material is a good reflector of noise. Plates of NaCl or ZnSe are used for mid-IR. The total volume of the cell is of the order of 1 mL. The removable sample cup is loaded into the sample block from the top, with the window sealed over it. Typically, the cell is loaded with a sample layer 1.00 mm thick sample layer. Since the sample mounting is easy, it can be held in a cup by gravity so that even liquids can be studied. The gas atmosphere is controlled by attaching a gas line not shown in the figure to the cell. Note that the most PA effect is observed when the absorption is in a gas and that heated gas directly activates the microphone. Solids and liquids are studied indirectly, their surfaces are heated by absorption and this then heats a transparent gas in contact with it and activates the microphone.

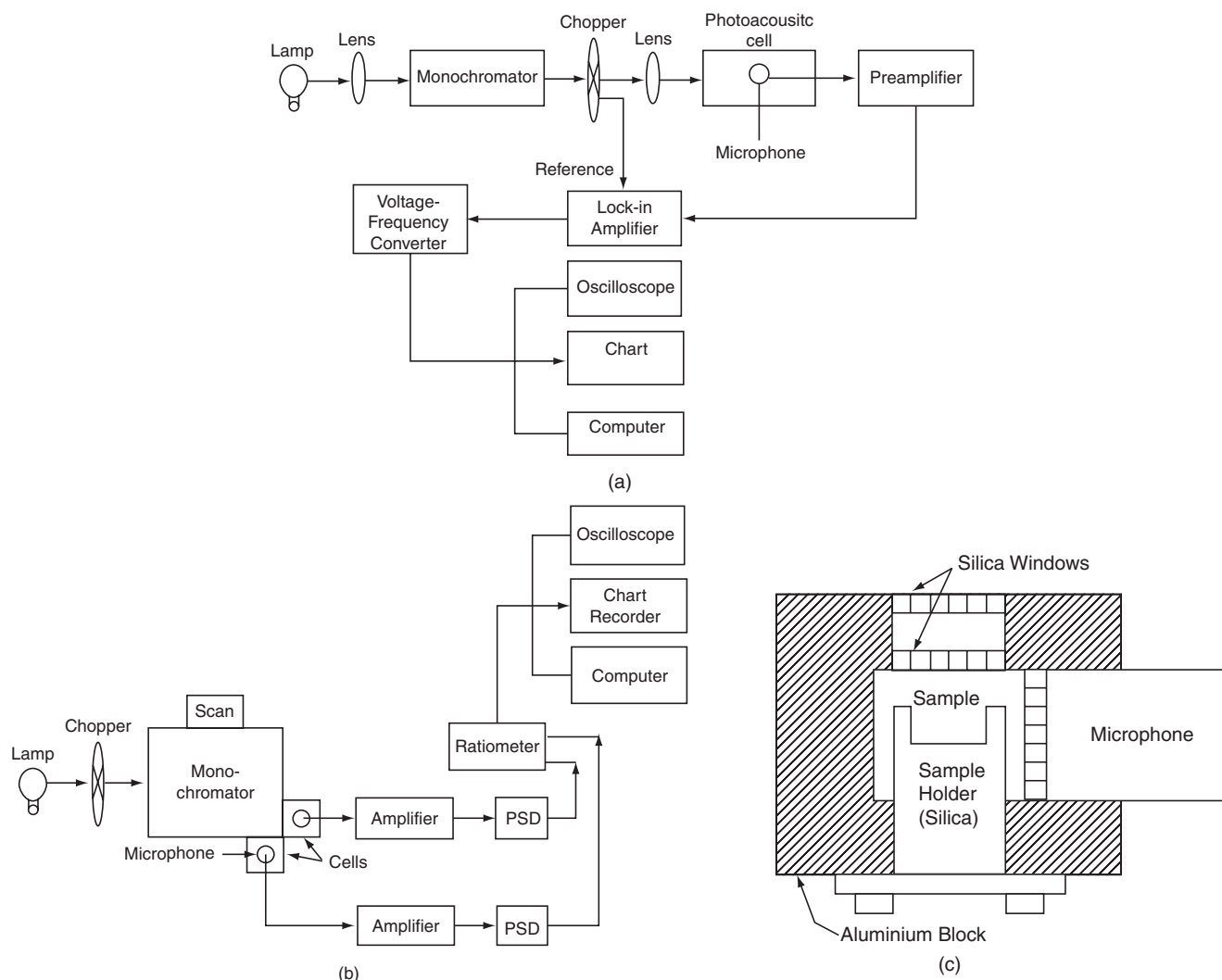


Fig. 5.75 Block diagram of (a) single-beam photoacoustic spectrophotometer, (b) double beam photoacoustic spectrophotometer, and (c) photoacoustic cell.

5.21.2 Applications of UV/V Photoacoustic Spectroscopy

The major advantage of PAS is that it enables us to obtain spectra similar to optical absorption spectra on any type of solid or semisolid material in the crystalline, powder, amorphous, smears, or gelatin, etc., forms. Moreover, since only light is converted to sound, light scattering which interferes in the study of solid materials by

conventional spectroscopic techniques presents no problem in PAS. A major advantage of PAS over conventional reflection spectroscopy, in studies of semiconductors and metals, is that highly reflecting, i.e. ultraclean surfaces, are not prerequisite for studies. Thus, the new classes of organic and glassy semiconductor and metallic systems, which are often in powder and amorphous forms, can be studied. Splendid effects from crystals of bichromate of potash, crystals of sulphate of copper, tobacco smoke and from a whole cigar have been observed. Plain water does not show the effect but when water is discoloured with ink, a feeble sound is produced. Biological substances *in vivo* and *in vitro* such as blood smears, membranes, gels, etc., and even whole leaves, flowers and grass can be studied by this technique. Some of the typical applications of UV-visible PAS are discussed here.

(a) Study of Organic and Inorganic Compounds

Absorption spectra of organic and inorganic substances in the liquid, solid and gaseous phase can be studied by PAS. Absorption spectra of powder and amorphous materials are much better resolved by PAS than by diffuse reflectance spectroscopy. Spectra of Cr_2O_3 obtained by various methods are shown in Fig. 5.76. It is seen that the two crystal field bands of the Cr^{3+} ion at 460 and 600 nm are clearly resolved in PAS spectrum than in the diffuse reflectance spectrum and compares favourably with absorption spectrum of the Cr_2O_3 crystal.

The conventional absorption spectrum of free iodine shows an absorption maximum at 520 nm. The PAS of iodine vapours matches with this description very nicely.

In ultramarine blue (synthetic lapis lazuli), the blue ion S_2^{2-} is entrapped in the cavities of the colourless sodium aluminium silicate matrix. The reflection spectra of this compound in the 400–800 nm region exhibits a broad maximum at 590–600 nm and a minimum at 450 nm. The PAS spectrum of this compound matches this description very nicely.

(b) Charge-Transfer Studies PA spectroscopy can also be used to study charge-transfer complexes. The PA spectrum of iodine vapours shows an absorption band at 520 nm and of ethyl sulphide vapours at ~235 nm. When ethyl sulphide vapours are added to a cell containing iodine vapours, the iodine absorption band disappears altogether and a charge-transfer band appears at 314 nm along with the absorption band due to ethyl sulphide at ~235 nm.

(c) Surface Studies The tool of PAS can be used in the study of adsorbed and chemisorbed molecular species and compounds on the surfaces of metals, semiconductors and insulators. This tool is sensitive enough to detect and identify a monolayer of adsorbed or chemisorbed compound. Fig. 5.77 shows the sensitivity of PAS in studying the spectra of benzylidene acetone directly on TLC plates. We note that even when a spot is developed from a starting drop containing $<0.1 \mu\text{g}$ of benzylidene acetone, the main broad absorption band of the benzylidene acetone at 250–300 nm is visible. From the area of TLC spot ($\sim 0.3 \text{ cm}^2$), the amount of material present in the TLC spot ($\sim 0.095 \mu\text{g}$) and the molecular weight of the compound, it can easily be shown that there is only one monolayer of the compound in the spot. The monolayer has been also detected on

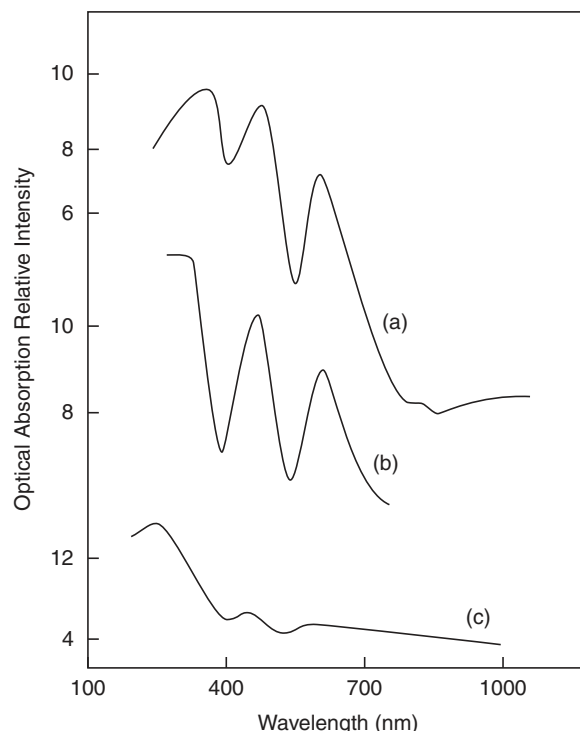


Fig. 5.76 Spectra of Cr_2O_3 (a) PAS of powder, (b) optical absorbance for single crystal, and (c) reflectance spectra of powder.

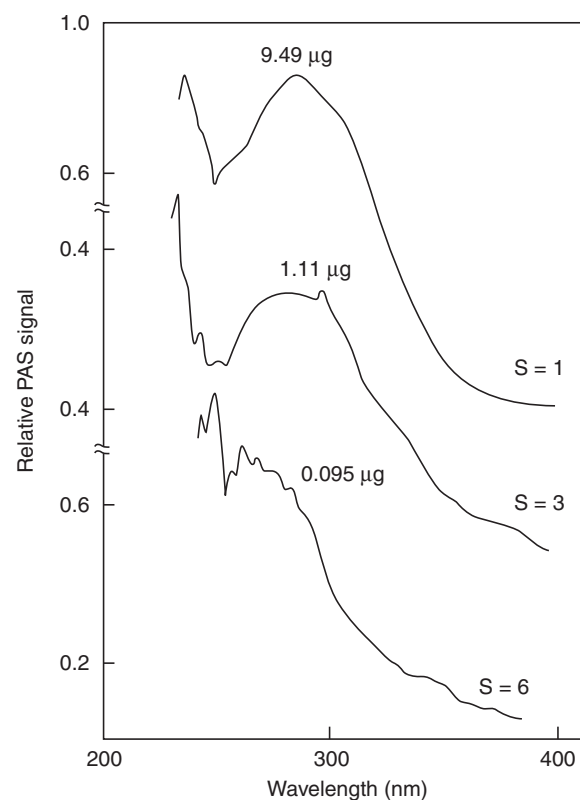


Fig. 5.77 Photoacoustic spectra of benzylidene acetone spots direct from TLC plates.

both the metallic and nonmetallic surfaces. Such studies provide information regarding the structure, valence, complexing, etc., of the deposited compound, e.g. the PA difference spectrum of the chemisorbed monolayer of benzotriazole on Cu surface in the 250–450 nm region obtained by subtracting the PA spectrum of untreated Cu surface from the spectrum of Cu surface treated with benzotriazole, a known passivating agent is different from the PA spectrum of benzotriazole powder. This difference has been attributed to some structural changes in benzotriazole due to chemisorption into Cu surface. Such structural changes may help us understand the mechanism of passivation of metal surfaces by passivating agents.

(d) Biological Studies Light scattering causes a major problem while obtaining the absorption spectra of biological systems, i.e. plant, animal, or microorganism *in vivo* and *vitro* by conventional spectroscopic techniques, but PAS is free from such a problem since in PAS, light is converted to sound. The range and usefulness of PAS in dealing with biochemical compounds in their solid or smear form and in solution is demonstrated here with the aid of some typical biological examples. The PAS spectrum of smear of whole blood is compared with those of oxyhaemoglobin freed from plasma and haemoglobin extracted from red blood cells in Fig. 5.78A. The comparison of spectra shows that the presence of other protein and lipid material in the whole blood, which poses problems in conventional spectroscopy from light scattering, does not create any difficulty in PAS. The PAS spectra of blood smears and some haemoproteins in the solid form and in solution have also been shown in Fig. 5.78 B.

The optical characteristics of chloroplasts in the leaf matter are Soret band at 420 nm, the carotenoid band structure between 450 and 550 nm and chlorophyll band between 600 and 700 nm. Thus, PAS can be used to study intact plant matter *in vivo* and *vitro* to gather information regarding the normal and abnormal plant processes and pathology. The spectra of spinach leaf by various methods or treatments are shown in [Fig. 5.79]. The PAS spectrum of intact spinach leaf [Fig. 5.79 (b)] does not show the characteristic chlorophyll band between 600 and 700 nm. However, the spectrum of a crushed leaf exhibits a band between 600 and 700 nm characteristics

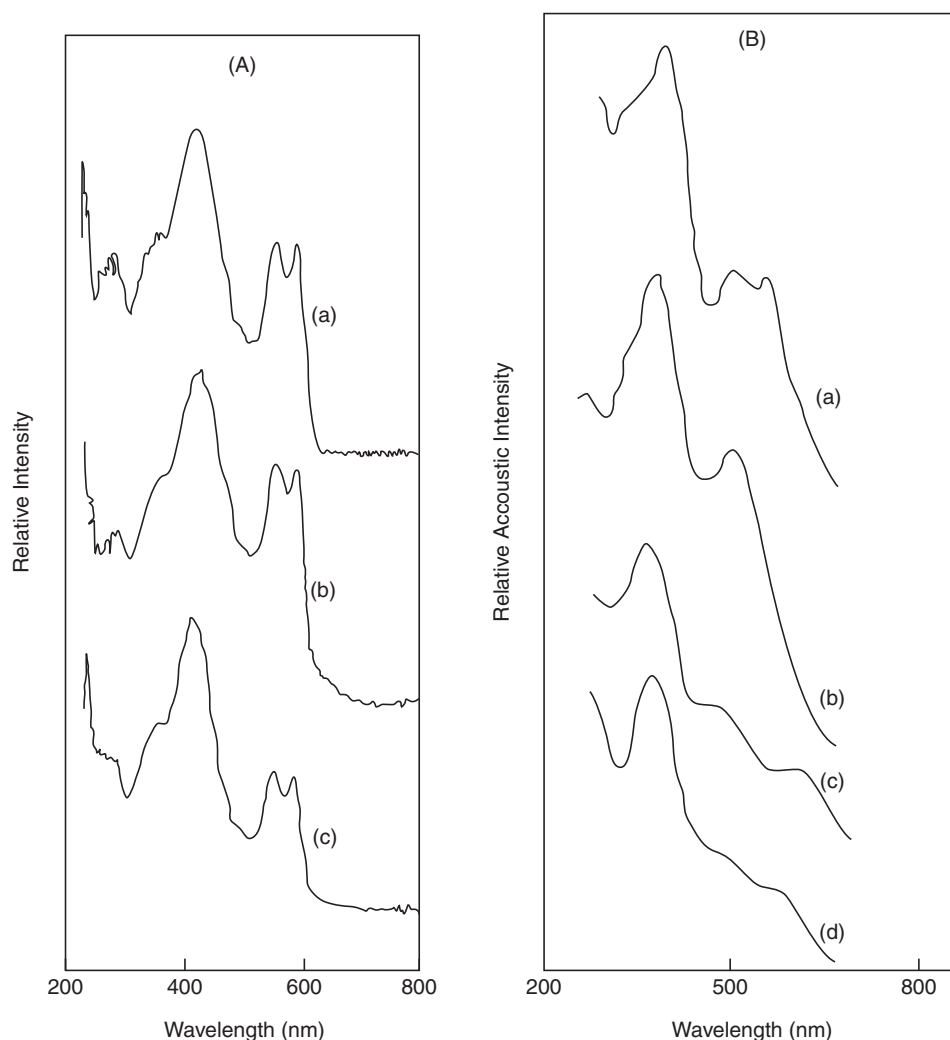


Fig. 5.78 (A) Photoacoustic spectra of (a) whole blood, (b) red blood cells freed from plasma, (c) haemoglobin extracted from red blood cells, and B: (a) whole blood smear, (b) cytochrome (20μ), (c) peroxidase (20μ), and (d) catalase (20 μ of 2% suspension in ammonium sulphate solution).

of Chlorophyll [Fig. 5.79 (c)]. The difference spectrum [Fig. 5.79 (d)] obtained from the difference of the spectra (c) and (b) matches with the description of the absorption spectrum shown in Fig. [5.79 (a)]. The difference between the crushed and the intact leaf is attributed to the difference in the thermal diffusivity of the surface wax layer and chlorophyll part below. Mathematically, thermal diffusivity is related to the phase lag and in the presence of the wax layer the acoustic signal becomes out of phase with the chopping frequency to which the detector is locked in. A 90° phase-shifted signal from the intact spinach leaf matches closely with the spectrum of the crushed leaf. Thus, this method can be used to study the spectra from two different layers. Unlike apex extract, the base extract of black-eyed susan flower petals is rich in ultra-violet absorbing flavanol glucosides, which serve as nectar guides to pollinating insects with ultraviolet vision. The absorption spectra of basal and apical extracted with methanol in the 200–800 nm region exhibit a carotenoid absorption band structure in the 400–500 nm region (i.e. a triplet: ≈416, 444 and 472 nm has been observed). The basal extract also exhibits a strong band at 350 nm and is attributed to the presence of nectar guide in this part of the petal. The PA spectrum of the whole petal shows that the carotenoid region becomes more pronounced, especially the central band, and shifts to some degree to a longer wavelength, i.e. 416, 463 and 491 nm. This spectrum of the whole petals corresponds to average of the apical and basal extract solution spectra.

The solution spectrum of cyanine extract from red rose petals shows a strong absorption band at 530 nm and a very weak band at 275 nm. PA spectrum of whole red rose petals shows two strong absorption bands at 530 and 340 nm. The former is attributed to cyanine, whereas the latter 340 nm is due to some other ultraviolet absorbing compound in the red rose petals. We can say that the band at 340 nm is functioning as a nectar guide in the red rose petals just like the 350 nm band in the black-eyed susan petals.

Substances secreted by female butterflies for attracting males by their smell can also be studied by UV/visible PA spectroscopy. Bombykol, an unsaturated alcohol extracted from the female silkworm has the formula: Butterflies feel its odour at an enormous distance.

UV/V photoacoustic spectroscopy has also been used for the study of photochemical processes in solids, e.g. Cooper blue (2, 2-di-methyl-4-phenyl-6-p-nitrophenyl-1, 3-diazobicyclo [3.1.0] hex-ene), and in medicine in the study of animal and human tissues, both hard tissues such as teeth and bone and soft tissues such as skin, muscle, etc, for example the difference PAS of tetrachlorosalicylanilide, i.e. TCSA (a most effective antibacterial agent but causes photosensitivity and other skin problems, the cause of which is unknown so far) bound within the epidermis in 250–650 nm region, have been reported. The spectrum shows a strong absorption band at 295 nm and a shoulder at 350 nm. The difference spectrum is obtained by subtracting the spectrum of guinea-pig epidermis from that of epidermis treated with 2 per cent ethanol solution of TCSA.

A new field of calorimetry known as photoacoustic calorimetry (PAC) has also emerged. Bond dissociation enthalpies of organic and organo metallic compounds have been determined in different solvents with great success, e.g. the average of bond dissociation energy of O–H bond in phenol in different solvents at 298 K and duly corrected for H-bonding to the solvent is 87.4 kcal mole⁻¹, while in the gas phase this value is 87 kcal mole⁻¹.

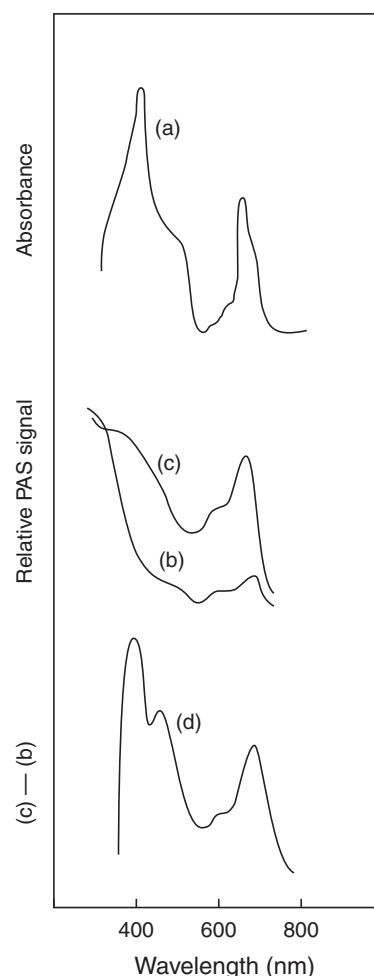
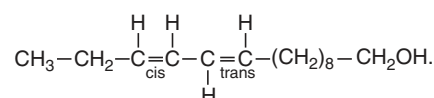


Fig. 5.79 (a) Solution absorption spectrum of acetone extract of fresh spinach leaf, (b) intact spinach leaf sample, (c) crushed spinach leaf, and (d) difference spectrum (c)–(b).



5.22 OPTICAL ROTATORY DISPERSION (ORD) AND CIRCULAR DICHROISM (CD)

The refractive index of a medium is not a constant but depends on the wavelength. Mathematically, $n = 1 + \frac{k_m \lambda^2}{\lambda^2 - \lambda_0^2}$,

where k_m and λ_0 are constants for the medium. Recall from Chapter 1 on introduction that plane polarised light is imagined to consist of left and right circularly polarised components (Fig 5.80). When a plane polarised light is passed through a medium containing asymmetric molecules then the left and right circularly polarised components

are transmitted at different speeds, i.e. they have different refractive indices. This phenomenon results in a rotation of the plane of polarised light and the compound concerned is said to be optically active. When optical rotation is measured as a function of wavelength then the resultant dispersion curve is generally plain, i.e. there is no maxima and minima in the curve and the phenomenon is called *optical rotatory dispersion*. However, in the wavelength region where the optically active compound absorbs light, the optical rotatory dispersion curve becomes anomalous, often changing sign, i.e. the rotatory power at first increases strongly, then falls off and changes sign. This anomalous behaviour is known as the *Cotton effect* and is shown in Fig. 5.81A.

In the wavelength region, where the optically active chromophore absorbs, there is also an unequal absorption of the right and left circularly polarised components of plane polarised light, i.e. $a_L(\epsilon_L) \neq a_R(\epsilon_R)$, where a_L and a_R have their usual meanings. This effect changes linearly polarised light into elliptically polarised light and is termed *circular dichroism*. CD is usually expressed as a differential dichroic absorption, $\epsilon_L - \epsilon_R$, usually written as $\Delta\epsilon$. When the differential dichroic absorption of a simple Cotton effect is plotted as a function of wavelength, it will have the form as shown in Fig. 5.81B. The CD maximum and the absorption maximum will occur at the same wavelength. Since CD results from a difference between ϵ_L and ϵ_R , it follows that this phenomenon is not observed outside the wavelength region where the optically active chromophore absorbs light. Contrary to this, optical rotation does extend into other wavelength regions, which explains why it is possible to measure optical activity, with the Na_D line (D line of sodium), of compounds having no visible absorption.

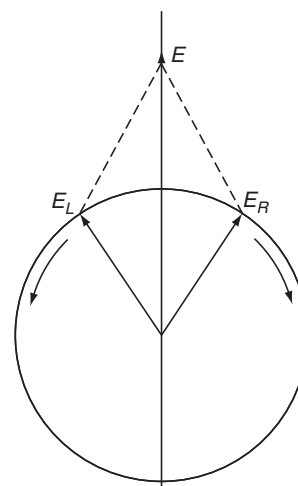


Fig. 5.80 Influence of an optically active absorbance sample on linearly polarised light (incident beam linearly polarised).

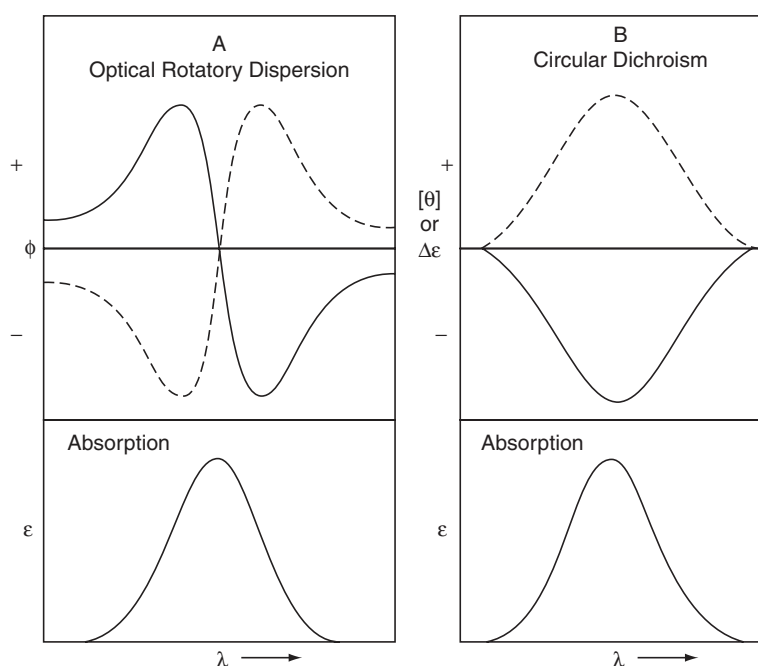


Fig. 5.81 Optical rotatory dispersion (A), circular dichroism (B) and ultraviolet absorption (lower) curves associated with an optically active chromophore. Dark line-Positive Cotton Effect; Dotted line-Negative Cotton effect.

If one assumes $\epsilon_L > \epsilon_R$ then amplitude of the R component will be greater than the L while the reverse will be true if $\epsilon_L < \epsilon_R$. The resulting elliptically polarised light has been represented in Fig. 5.82.

The angle between the major axis of the ellipse and the plane of the original radiation is the angle of rotation, α . The ellipticity, i.e. the angle whose tangent is the ratio of the minor axis of the plane, OB , to the major axis, OA , is known as θ and is expressed as

$$\theta = \frac{1}{2}(\epsilon_L - \epsilon_R) \quad (5.116)$$

The molecular, or molar, ellipticity, $[\theta]$, is given by the relationship

$$[\theta] = \frac{\theta \times 100}{l \times C} \quad (5.117)$$

where, $[\theta]$ = observed ellipticity (deg),

l = cell path length (cm) and C = concentration (mole lit^{-1})

$$\text{and} \quad [\theta] = 3305 \text{ or } 3300 (\epsilon_L - \epsilon_R) \quad (5.118)$$

$$= 3305 \text{ or } 3300 \Delta\epsilon$$

Here, $[\theta]$ is in $\text{deg cm}^2 \text{decimole}^{-1}$.

When comparisons have to be made between CD of optically active absorption bands with different absorptivities then it is often convenient to use the corresponding 'dissymmetry factors' g , calculated from the relationship

$$g = \frac{\Delta\epsilon}{\epsilon} \quad (5.119)$$

where $\Delta\epsilon$ = differential dichroic absorption and ϵ = extinction coefficient (using ordinary light) at the same wavelength. The specific rotation, $[\alpha]$ defined by Drude, below changes with wavelength, and as already stated, change of specific rotation with wavelength is known as the ORD.

$$[\alpha] = \sum_i \frac{k_i}{\lambda^2 - \lambda_i^2}, \quad i = 1, 2, 3 \dots \quad (5.120)$$

where λ is the wavelength of measurement and k_i s are the constants that can be identified with the wavelengths of maximum absorption of the optically active absorptions.

In the wavelength region far away from an optically active absorption band, the dispersion is normal and Eq. (5.120) can be written as

$$[\alpha] = \frac{k}{\lambda^2 - \lambda_0^2} \quad (5.121)$$

where λ_0 is a constant representing the wavelength of the nearest optically active absorption band. When $\lambda \gg \lambda_0$, Eq. (5.121) further reduces to

$$[\alpha] = \frac{k}{\lambda^2} = \frac{\pi}{\lambda} (n_L - n_R) \quad (5.122)$$

where,

$$n_L - n_R = \frac{\alpha(\text{deg})\lambda_0(nm)}{\pi(=180^\circ)l(dm)} \times 10^{-8} \quad (5.123)$$

The value of α can be measured directly with a polarimeter, but θ can only be determined indirectly through CD.

$$\text{Specific rotation} = [\alpha] = \frac{\alpha}{C} = \frac{1800}{\pi(180^\circ)} \quad (5.124)$$

The change of temperature has several effects upon the rotation of a solution or liquid. The length of the tube increases while, the density of liquid decreases with the growth of temperature. It causes changes in the rotatory power, of the molecules themselves due to association or dissociation, increased mobility of the atoms and affects other properties. In general, the effect of temperature may be defined as

$$[\alpha]^T = [\alpha]^{20} + z(T - 20) \quad (5.125)$$

where z = temperature coefficient of rotation (substances vary widely in their values of z), T = temperature in degree Celsius.

$$\text{Molecular rotation} = \Phi = \frac{[\alpha]M}{100} \quad (5.126)$$

where α is optical rotation (deg dm^{-1}), C = concentration (g mL^{-1}) and M = molar mass. Note that both molecular ellipticity and molecular rotation may be either positive or negative depending on the relationships between ϵ_R and ϵ_L or n_R and ϵ_L .

A plot of molecular rotation ϕ , versus wavelength for an organic and a hypothetical compound with single and double chromophore(s) has been displayed in Figs 5.83 and 5.84. The midpoint between peak and trough of the ORD curve corresponds to the CD maximum, and the ORD trough coincides in wavelength with the absorption maximum. The CD curves often aids in locating the hidden absorption maxima, and do so with less

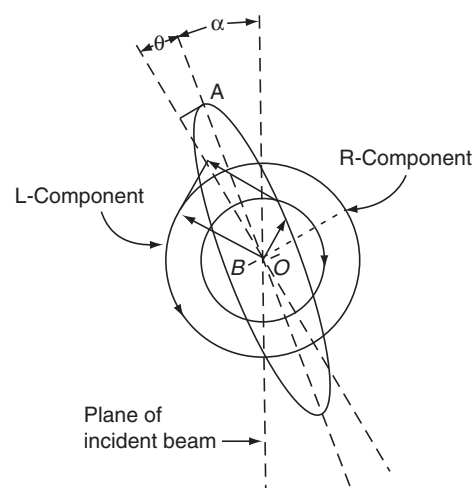


Fig. 5.82 Influence of an optically absorbance sample on linearly polarised light; transmitted light elliptically polarised when $n_R > n_L$ and $\epsilon_L > \epsilon_R$.

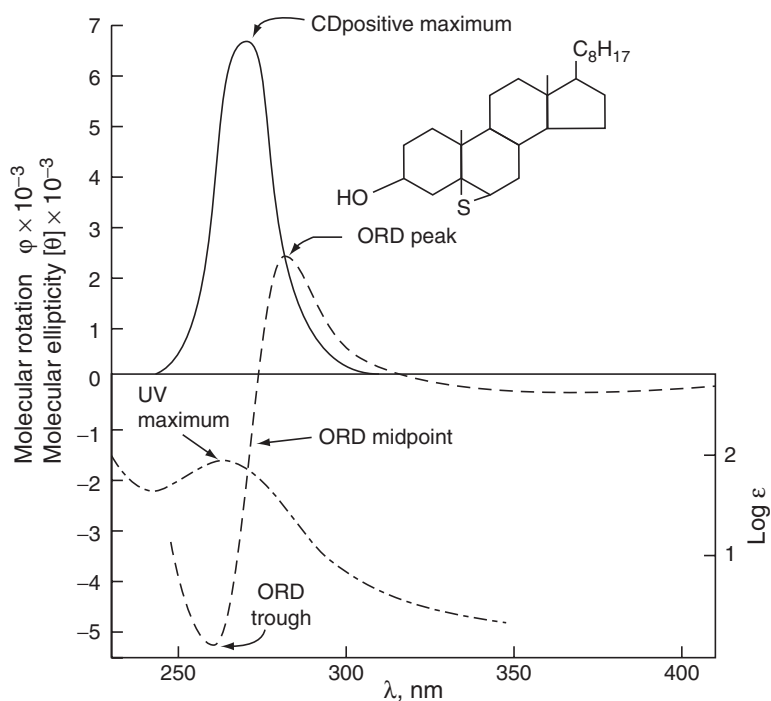


Fig. 5.83 Optical rotatory dispersion, circular dichroism, and ultraviolet absorption curves of 3β-hydroxycholestan-5α, 6α-episulphide.

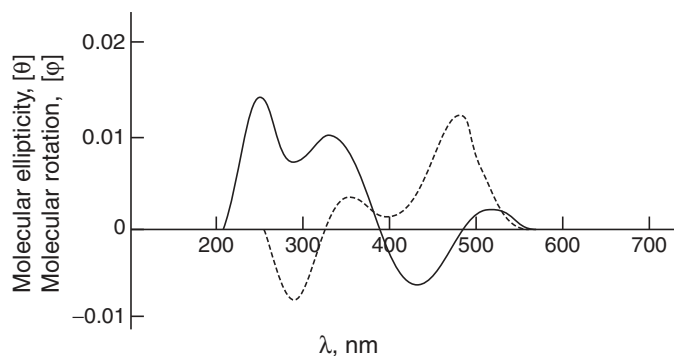


Fig. 5.84 Circular dichroism (...) and optical rotatory dispersion (-) for a hypothetical substance with absorption bands in the region 200–600 nm.

ambiguity than will the corresponding ORD curve. On the other hand, ORD curves are affected by more distant chromophoric bands and hence are more characteristic of specific compounds than CD. Both ORD and CD can give essential information about the stereochemical features of optically active materials.

Also we know that when any liquid or solution is placed in an external magnetic field, it rotates the plane of polarised light. This effect is called *Faraday effect* and has already been explained in Chapter 1. This effect results because of the effect of the applied field upon the motion of electrons in the molecules.

The angle of rotation is given by

$$\phi_F = VHl$$

where H is the magnetic induction, l is the path length and V is a constant (for the medium) called the *Verdict constant*.

The mathematical expression for the Kerr electric-optic effect discussed in Chapter 1 is

$$n_{\parallel} - n_{\perp} = KE^2\lambda$$

The quantity K is called the *Kerr constant*.

5.22.1 Origin of Absorption and Circular Dichroism

Both the phenomena have their origin in the charge displacements caused by the interaction of a molecule with the electromagnetic radiation which produces induced electric and magnetic dipoles. The rotational strength R_k of a chromophore for k electronic transition is expressed as

$$R_k = M_e M_m \cos \theta_{em}$$

where M_e and M_m are the electric and magnetic transition moments and θ_{em} is the angle between the directions of these two moments. If the molecule has either a centre of inversion or a reflection plane of symmetry then we may come across any one of the following three situations:

- (i) $M_e \neq 0, M_m = 0$; Electric dipole transition permissible but magnetic dipole transition forbidden
- (ii) $M_e = 0, M_m \neq 0$; Magnetic dipole transition permissible but electric dipole transition forbidden.
- (iii) $M_e \perp M_m; \cos\theta_{em} = 0$

In all cases, $R_k = 0$ and the molecule is optically inactive.

Problem 5.53: Assume that the initial beam intensity, I_0 , for R radiation equals I_R for I_L radiation. Develop the equation for molar ellipticity using a spectrophotometer.

Solution We know that

$$[\theta] = 3300 [\epsilon_L - \epsilon_R] \quad (\text{Eq. 5.118})$$

In order to develop an expression for use in a spectrophotometer, ϵ_L and ϵ_R must be expressed in terms of A_L and A_R respectively. Applying Beer–Lambert law to R and L radiations, we obtain

$$\log \frac{I_0}{I_L} = \epsilon_L \ell C$$

and

$$\log \frac{I_0}{I_R} = \epsilon_R \ell C$$

Lumping together these expressions, we write

$$\log \frac{I_R}{I_L} = (\epsilon_L - \epsilon_R) \ell C$$

or

$$(\epsilon_L - \epsilon_R) = \frac{1}{\ell C} \log \frac{I_R}{I_L}$$

Substituting $(\epsilon_L - \epsilon_R)$ into Eq. (5.118), we arrive at the desired expression, i.e.

$$[\theta] = \frac{3300}{\ell C} \log \frac{I_R}{I_L}$$

Problem 5.54: Calculate the circular birefringence for a substance giving a rotation of -12° for light of 500 nm wavelength in 15 g /150 mL solution. The polarimeter tube length is 2 dm.

Solution Substituting the data from the problem into Eq. (5.123), we get

$$n_L - n_R = \frac{-12^\circ \times 500 \times 10^{-9} \text{ m}}{180^\circ \times 0.2 \text{ m}} = -166 \times 10^{-7}$$

Problem 5.55: Calculate the molar ellipticity if the solution placed in a 2 dm tube showed spectrophotometer readings of 20 per cent transmittance for R -circularly polarised light and 21 per cent for L -circularly polarised light. The incident beams are equal in intensity. The concentration of the stock solution (in water) is 1 g/10 mL.

Solution Substituting the data in question into the expression deduced in Problem 5.54, we have

$$[\theta] = \frac{3300}{1(\text{g/mL}) \times 2\text{dm}} \log \frac{20}{21} = -0.70 \text{ g}^{-1} (\text{mL dm}^{-1})$$

5.22.2 Types of Optically Active Chromophores

They may be classified into two extreme types: (i) the inherently asymmetric chromophore, and (ii) the inherently symmetric chromophore which is asymmetrically perturbed. The former includes such compounds as hexahelicene and certain substituted biphenyls and allenes in which the chromophore itself is asymmetric. These structures are seldom encountered in biological systems. By far, the large majority of chromophores is symmetrical and can only become optically active when perturbed by an asymmetric centre. When an asymmetric centre induces optically activity in a chromophore which is a part of the same molecule then the molecule is said to be intrinsically optically

active. Intrinsic optical activity can also occur if the chromophore has an asymmetric arrangement in space, e.g. carbonyl group in the α -helical regions of proteins. Extrinsic optical activity may be observed when a symmetric molecule binds to a macromolecule, e.g. interaction between the ligand and an asymmetric binding site. But the interaction may also occur when binding results in an asymmetric spatial arrangement, e.g. the helical arrangement of basic dye molecules bound to poly-L- glutarnic acid.

The sign and magnitude of an induced Cotton effect (extrinsic or intrinsic) depends on the spatial relationship between the asymmetric centre and the perturbed chromophore. The space around a chromophore is divided into regions of positive and negative contribution to a Cotton effect according to well-defined symmetry rules. A given asymmetric centre may therefore generate either a positive or a negative Cotton effect, depending on its spatial relationship to the perturbed chromophore. The magnitude of a Cotton effect will increase as the distance between the asymmetric centre and the perturbed chromophore decreases. Theoretically, the sign of contribution can be depicted by the so-called 'octant rule'. *The rule states that the sign of the contribution that a given atom at the point P (x, y, z) makes to anomalous rotatory dispersion will vary as the simple product, $x \cdot y \cdot z$, of its coordinates.* For example, let us look at the carbonyl chromophore group in the chair form of cyclohexanone molecule in which the coordinates are defined by the X–Y, X–Z, and Y–Z planes as shown in Fig. 5.85.

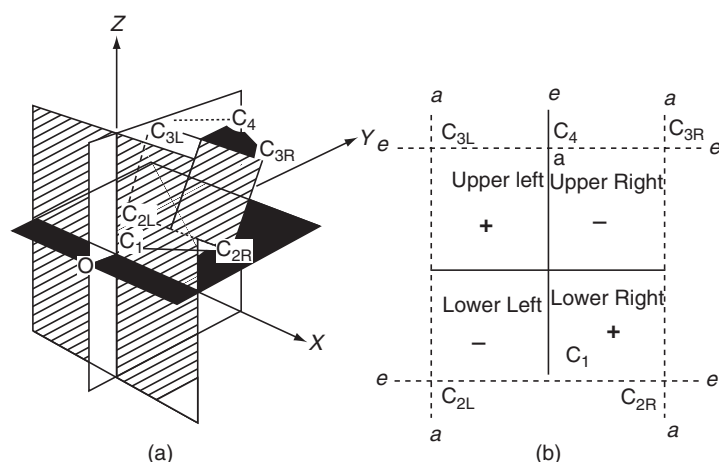


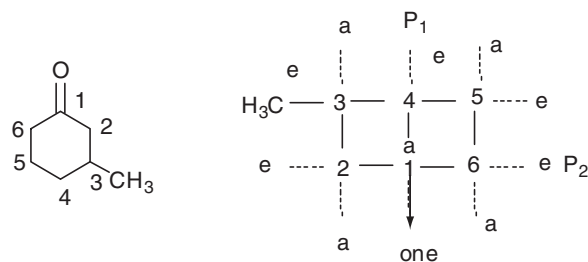
Fig. 5.85 Illustration of the octant rule for cyclohexanone (a) the octants, and (b) contributions of groups in the far octants.

The carbonyl group lies in the X–Y plane and is bisected by the Y–Z plane. Atoms or substituent atoms can now be located in one of the eight octants defined by $\pm x$, $\pm y$, and $\pm z$. Atoms or substituents in the $+x$, $+y$, $+z$; $+x$, $-y$, $-z$; $-x$, $+y$, $-z$; or $-x$, $-y$, $+z$ octants have positive contributions to the Cotton effect. Atoms or substituents in the other four octants, viz., $-x$, $-y$, $-z$; $-x$, $+y$, $+z$; $+x$, $-y$, $+z$; or $+x$, $+y$, $-z$ have negative contributions to the Cotton effect. Atoms or substituents which lie on or near the plane have little or no effect. The rule may further be elaborated as follows. Carbon atoms C_1 and C_4 lie in one plane. Carbon atoms C_1 , C_{2L} and C_{2R} lie in another plane from the observer viewpoint. The substituents in the equatorial positions at C_{2L} and C_{2R} are in this plane. The third plane bisecting the carbonyl group is perpendicular to the above-said two planes. Thus, the first two planes produce four octants and the third produces four more octants. The four octants defined by the third plane are usually vacant and are not considered. Only the four octants defined by the first two planes are considered. The midpoint of $C=O$ is taken as the origin of coordinate system. This rule is illustrated here by taking the example of 3-methylcyclohexanone molecule for conformation studies. The structure of the compounds must be known in such studies.

When the ketone group is oriented in order to apply the octant rule there are two alternatives: (i) Equatorial representation with the methyl group on the upper left (at C_{3L}) or (ii) axial representation with the methyl group on the upper right (at C_{3R}). The fact that a positive Cotton effect is observed confirms that (i) represents the correct conformation. There is no contribution from other groups since carbon atoms 2, 4, and 6 lie in or near the planes P_1 and P_2 and the contribution of the carbon atom 3 is cancelled by that of 5.

5.23 APPLICATIONS OF ORD AND CD

Both these techniques are used for the structure determination of optically active substances such as amino acids, polypeptides and proteins, steroids, antibiotics, terpenes and metal-ligand complexes. Some general rules are available for some classes of compounds and are the following:



The sign of Cotton effect in amino acids reflects the stereochemistry at the asymmetric centre. *L*- α - amino acids show a positive Cotton effect around 215 nm whereas their dextroenantiomers show a negative Cotton effect. In polypeptides, the percent of α -helix structure can be determined from measurements of ORD.

In steroids, different types of ORD curves corresponding to *cis* and *trans* forms have been observed. In one form, the specific rotation increases with decreasing wavelength until it reaches a peak and reverses (a positive curve) and in the other; the specific rotation decreases with decreasing wavelength until it reaches a trough and reverses (a negative curve). The sign of the Cotton-effect curve and the wavelength and specific rotation of the peak or trough also aids in locating the carbonyl groups in steroids.

Further, the large variety of optically active molecules present in biological systems makes ORD and CD two of the most widely applicable methods available for studying drug interactions. While either techniques may be employed, CD is probably easier to interpret, since ellipticity bands at any given wavelength are not complicated by contributions from optically active transitions occurring at other wavelengths. Optical rotation can be employed to monitor the interaction of small molecules with a macromolecule. For example, the examination of the effect of anesthetics procaine and procaine amide on intrinsic optical activity of adenosinetriphosphate (ATP) reveals that both these local anesthetics decrease the negative optical rotation of ATP over the range 350–600 nm suggesting that binding of procaine or procaine amide to ATP causes changes in the orientation of the adenine ring system of the nucleotide relative to its neighbouring sugar groups. The optically inactive acridine orange dye becomes optically active on interacting with poly-L-glutamic acid. The vanishing of optical activity of poly-L-glutamic acid as a result of such interaction is due to the destruction of its helical structure by a helical array of dye molecules. It has been found that many small symmetric molecules become optically active on binding to proteins and other macromolecules. In a majority of such cases, optical activity arises not from a special spatial arrangement of the ligand but from a perturbation of the ligand chromophore by an asymmetric locus at the binding site. Since extrinsic Cotton effects reflect the three-dimensional characteristics of specific sites on a macromolecule, the binding of anionic drugs to serum albumin can be examined by measuring their extrinsic Cotton effects.

The CD spectrum of Human Serum Albumin (HSA) in sodium phosphate buffer (pH 7.4) has a small negative ellipticity band at wavelengths below 320 nm (Fig. 5.86). The addition of flufenamic acid to HSA gives rise to a large positive ellipticity band at 296 nm and a smaller negative band at 345 nm (Fig. 5.86). Since ultraviolet absorption spectrum of flufenamic acid has a strong absorption band at 288 nm with a shoulder at 322 nm, the observed optical activity is extrinsic in origin. Thus, the acid takes up a preferred spatial relationship to its serum albumin binding site, so that an asymmetric locus at or near that site is in a region of positive contribution to a Cotton effect for the electronic transition occurring at 296 nm but in a region of negative contribution for the transition of 345 nm. The binding of structurally related drugs, mefenamic acid and meclofenamic acid, to HSA also generates biphasic extrinsic Cotton effects. The spectral data on the interaction of fenamic acids with HSA is listed in Table 5.35.

The dissymmetry factors for the three drugs (Table 5.35) indicate that meclofenamic acid is much less influenced by the asymmetry of the binding site as compared to mefenamic acid or flufenamic acid. However, an examination of molecular models shows that the bulky chlorine atoms of meclofenamic acid forced the N-phenyl ring out of coplanarity with the rest of the molecule. If the binding site for the fenamic acids on human serum albumin is a narrow crevice, meclofenamic acid may have difficulty in entering and hence will be less affected by the associated asymmetric locus.

The titration of a fixed amount of HSA with flufenamic acid at 295 nm in a sodium phosphate buffer (pH 7.4) indicates that each mole of protein is bound to 3 moles of drug. (Fig. 5.87).

The molar ellipticities of flufenamic acids bound to different serum albumins are recorded in Table 5.36. Just like HSA, some of the albumins exhibit biphasic Cotton effects while the others generate a single positive Cotton effect. This suggests that the serum albumins generating single positive Cotton effect have different drug-binding

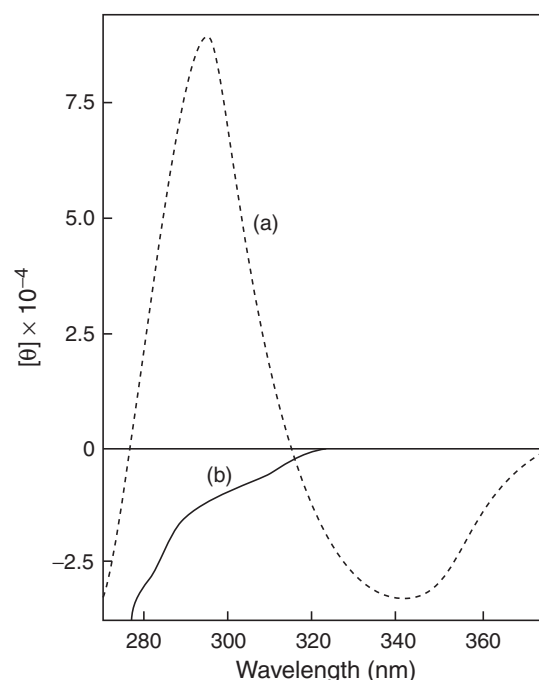
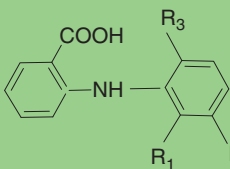


Fig. 5.86 Extrinsic circular dichroism of (a) flufenamic acid bound to human serum albumin, and (b) human serum albumin alone. All measurements are made in a sodium phosphate buffer of pH 7.4.

Table 5.35 Molar ellipticities of complexes between fenamic acids and human serum albumin.

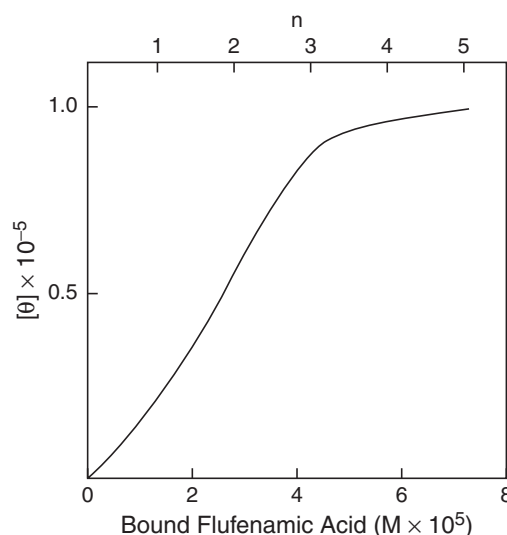
Drug				UV-absorption maximum		CD maximum		$g \times 10^4$
	R_1	R_2	R_3	λ_{max} (nm)	$\epsilon \times 10^{-4}$ (mole ⁻¹ cm ⁻¹)	λ (nm)	$[\theta] \times 10^{-4}$ (deg cm ² dmole ⁻¹)	
Flufenamic acid	H	CF ₃	H	288	1.24	296	+2.01	+5.70
				322	0.54	345	-0.69	-7.04
Mefenamic acid	CH ₃	CH ₃	H	284	1.40	292	+2.24	+4.70
				332	0.64	340	-1.44	-6.54
Meclofenamic acid	Cl	CH ₃	Cl	277	0.88	302	+0.44	+2.40
				315	0.56	332	-0.30	-2.80

sites on these proteins than those on human serum albumin, serum albumin, and (b) human serum alone. All measurements are made in a sodium phosphate buffer of pH 7.4.

The binding of phenylbutazone to HSA produces a positively ellipticity bandwith, a maximum at 287 nm. The UV spectrum of the drug exhibits an absorption maximum at 265 nm and is attributed to $\pi-\pi^*$ transitions in the phenyl group. The $n-\pi^*$ transitions of the carbonyl group are observed around 280 nm while $\pi-\pi^*$ transitions are observed around 185 nm. Thus, it is the $n-\pi^*$ transitions of the pyrazolidinedione ring carbonyl groups which are being perturbed by the asymmetric locus at the drug-binding site. The $n-\pi^*$ transitions give rise to relatively weak absorption bands which are hidden under the much stronger $\pi-\pi^*$ bands.

The substitution of Zn by Co in human carbonic anhydrase is accompanied by multiple absorption maxima in the region 500–600 nm. They may be attributed to $d-d$ electronic transitions of the cobalt ion. The cobalt enzyme is optically inactive in this wavelength region. However, the interaction of sulfonamide inhibitor acetazolamide, produces an asymmetrical anomalous rotatory dispersion with a peak at 590 nm, a crossover point at 554 nm and a trough at 525 nm. These results suggest that the binding of acetazolamide to human carbonic anhydrase is accompanied by protein conformational changes at the active site. Such studies will help to elucidate the mechanism of sulfonamide inhibition of carbonic anhydrase.

Extrinsic Cotton effects are often generated when drugs bind to nucleic acids, for example, when proflavine and acridine complexes with calf thymus DNA optical activity is observed. The dependence of the magnitude of

**Fig. 5.87** Relationship between molar ellipticity $[\theta]$ (deg cm² dmole⁻¹) measured at 295 nm and the concentration of flufenamic acid bound to human serum albumin. n = number of acid molecules bound per molecule of HSA; pH = 7.4 (sodium phosphate).**Table 5.36** Molar ellipticities of the complexes of flufenamic acid with different serum albumins.

Serum albumin	Wavelength (nm)	$\theta \times 10^{-1}$ (deg cm ² mole ⁻¹)	$g \times 10^4$	Remarks
Human	296	+2.01	+5.70	Biphasic Cotton Effects
	345	-0.61	-7.04	
Porcine	292	+1.90	+4.43	
	352	-0.31	-3.92	
Bovine	305	+0.77	+2.65	Single positive
	348	-0.26	-2.63	
Canine	295	+1.08	+2.84	Cotton effect
Ovine	302	+0.90	+3.22	

the extrinsic Cotton effect on the DNA/proflavine ratio suggests that a nearest-neighbour interaction between bound dye molecules is necessary for optical activity.

Quinacrine produces an extrinsic Cotton effect at 345 nm when bound to single-stranded DNA or *t*-RNA. On the other hand, binding of quinacrine to double helical DNA produces Cotton effect at 333 nm. These differences are related to the bimodal binding of acridine to DNA. A weak positive Cotton effect also appears at 350 nm when the antimalarial drug berberine binds to yeast RNA or calf thymus DNA.

When optically active chromophore participates in a reaction, the extent of that reaction can be followed by observing the reduction of the Cotton effect (if there is one). Thus when hydrochloric acid is added to a solution of (+) 3-methoxy cyclohexanone in methanol, a Cotton effect is reduced by 93 per cent as a result of the dimethyl ketal formation. In ethanol, the reduction is 33 per cent and in isopropanol there is no reduction.



5.24 FLUORESCENCE AND PHOSPHORESCENCE

The molecule from the lowest vibrational level ($V' = 0$) of a ground electronic state on absorption of light in the ultraviolet and visible region of the spectrum (200–800 nm) crosses over to one or more of the subvibrational levels of the first excited singlet state. The time taken for this process is 10^{-15} second. For any given molecule, the strong absorption bands which lie at the lowest wavelengths usually correspond to electronic transitions from the ground state to one or more of the vibrational sublevels of the first excited singlet state (Fig. 5.88). In liquids/solutions, vibration energy is dissipated as heat energy to the surroundings so that the excited molecule rapidly (within 10^{-13} – 10^{-12} second) reaches the lowest vibrational level ($V'' = 0$) of the first excited state via ladder mechanism. This dissipation of energy is due to collision between the solute molecules or between the solute and solvent molecules. The molecule from $V'' = 0$ vibrational level may then return directly to the ground state either by radiationless transition (in which excitation energy is transformed into the thermal energy) called internal conversion (ic); or by emission of light. Both the transitions occur between electronic states of same spin multiplicity, i.e. $S_1 \rightarrow S_0$. The light emitted by a $V'' = 0$ of the S_1 state when electron crosses over directly to one or more of the vibrational sublevels of the ground electronic state is called *fluorescence* (f). The time of fluorescence is approximately 10^{-8} second while that of internal conversion is 10^{-11} – 10^{-13} second. In the gas phase, when a molecule from the vibrational sublevels of the excited singlet state directly crosses over to the ground electronic state, the energy of emitted radiation is equal to the energy of the initial excitation energy. This process is called *resonance fluorescence*. Since atoms do not possess vibrational energy, they show resonance fluorescence. For example mercury vapours in the normal state when exposed to ultraviolet light of 253.7 nm wavelength, emit fluorescent light of 253.7 nm wavelength, corresponding to the transition $^3P_1 \rightarrow ^1S_0 + h\nu_f$. Further, fluorescence can be classified as either prompt or delayed depending on the time of fluorescence and the mechanism by which the fluorescence results. Prompt radiation is emitted within 10^{-8} second after the excitation radiation is switched off and results from the direct radiative $S_1 \rightarrow S_0$ transition. Radiation emission in this process occurs either from (a) an S_1 state molecule, or from (b) an excimer formed by the interaction of an

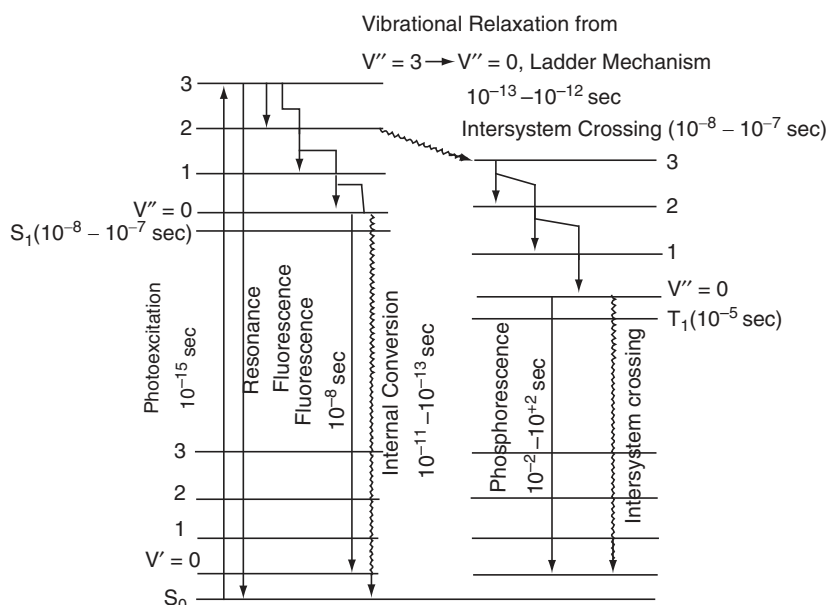
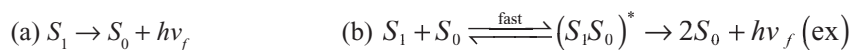


Fig. 5.88 Sematic diagram showing radiative, viz., fluorescence, phosphorescence and nonradiative intramolecular processes. The wavy arrows stand for radiationless transitions.

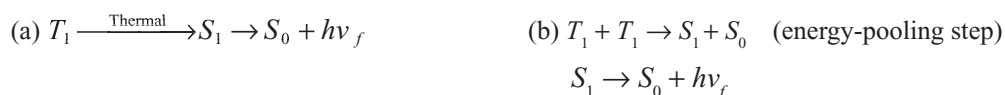
S_1 state molecule with an S_0 state molecule. By excimer we mean an excited-state dimeric species. The two processes resulting in prompt fluorescence are shown below:



The excimer fluorescence emission may or may not be similar to that of the free S_1 state molecule. The efficiency of either of these processes depends on the concentration of solute molecules. As the concentration of solute molecules is increased, the probability of $S_0 \rightarrow S_1$ transition increases and hence the probability of formation of $(S_1 S_0)^*$ excimer also increases. Thus, if there is a difference between the fluorescence spectrum of a molecule at two different concentrations, it is likely that excimers are formed in the system, e.g. dilute solutions of pyrene ($\sim 10^{-6}$ mole lit^{-1}) show violet fluorescence and have a structured spectrum, while concentrated solutions of it ($\sim 10^{-3}$ mole lit^{-1}) exhibit blue fluorescence and have a structureless spectrum.

The emission time of delayed fluorescence is longer ($>10^{-3}$ second) than that of prompt fluorescence (10^{-8} second) and this fluorescence arises as a result of transformation of S_1 state molecules formed from the corresponding low-energy T_1 state molecules to the S_0 state molecules. This type of fluorescence is emitted throughout the lifetime of the T_1 state of the molecule.

The S_1 state molecules giving rise to delayed fluorescence are formed either by (a) thermal excitation of a low-energy T_1 state molecules or by (b) collision of two T_1 state molecules. The processes resulting in delayed fluorescence are shown below:



The first step in the scheme (b) is called energy-pooling step or triplet-triplet annihilation since two low-energy states combine their energy to form a third state of higher energy than either of the initial two states, i.e. $2T_1$.

The fluorescence emission by the scheme (a) is temperature dependent while that by the scheme (b) is temperature independent. Normally, the form of prompt fluorescence arising from the free S_1 state molecule is similar to that of delayed fluorescence. The intensity of delayed fluorescence rarely exceeds a few per cent of that of prompt fluorescence.

Further, the molecule in the excited state can emit radiation by another process called *phosphorescence* (p). The molecules in the lowest vibrational level ($V'' = 0$) of the S_1 state could cross over to one or more of the vibrational sublevels of the first triplet state T_1 corresponding to the singlet state S_1 of the molecule. *This radiationless process occurring between states of different multiplicities is called intersystem crossing (ISC)*. The time for such a process is approximately 10^{-8} to 10^{-7} second which is the same order of magnitude of the lifetime of the singlet excited state. Hence, this ISC process and fluorescence are mutually competitive. The lifetime of the triplet state being longer ($\sim 10^{-5}$ second), the chances of losing energy along radiationless processes are great. The molecules in the vibrational sublevels ($V'' = 1, 2, 3$) of T_1 state lose energy to the surroundings as thermal energy and moves to the lowest vibrational level ($V'' = 0$) of the T_1 state via ladder mechanism.

The molecules in the vibrational level $V'' = 0$ of the T_1 state can now directly return to the ground state S_0 with the emission of radiation. This process is called *phosphorescence* (or sometimes β -phosphorescence) and is *independent of temperature*. The time of phosphorescence is 10^{-2} – 10^{+2} second. The other process by which the molecules can move from T_1 ($V'' = 0$) state to the S_0 state is the *intersystem crossing*. Phosphorescence occurs at longer wavelengths compared to fluorescence because triplet state has lower energy relative to the corresponding singlet state. Further, since phosphorescence is exhibited mainly by solids (i.e. in a rigid solvent), the extent of fluorescence ($S_1 \rightarrow S_0$) decreases and under certain conditions, the molecule moves from T_1 state to the S_1 state. The activation energy is small (i.e. 7–9 kcal which is almost identical with the calculated energy difference for blue and yellow phosphorescent radiations for the fluorescein) and corresponds to radiation in the far infrared region of the spectrum. The molecule may now directly cross over to the ground state (S_0) from the S_1 state with emission of radiation. Such a process is called α -phosphorescence and is temperature dependent. The frequency of α -phosphorescence will of course be the same as that of fluorescence. In phosphorescence, the emission can occur provided the energy is taken by the molecule in the T_1 state from the surroundings. This is confirmed by the fact that lowering of temperature as in the case of freezing of liquids, is helpful in producing phosphorescence. However, excessive cooling slows down the emission and at liquid air temperature, the emission may be completely cut off. The two processes giving rise to α and β phosphorescence are shown below:



Phosphorescence spectra of dyes exhibit two distinct bands. As an example, fluorescein in boric acid shows phosphorescence in the blue (~ 570 nm) and yellow (~ 480 nm) regions. The former is known as α -phosphorescence

and is identical with fluorescence and becomes less marked as the temperature is lowered and disappears completely at 0°C. The yellow or β -phosphorescence is independent of temperature and has been observed at 23 K.

5.24.1 Quantum Yield or Quantum Efficiency of Photophysical Processes

Note that all the activated molecules convert rapidly to the $V'' = 0$ vibrational levels of the S_1 and T_1 states via radiationless ladder transitions and intersystem crossing-ladder mechanisms respectively. When the molecules in the excited state do not take part in any chemical reaction, they return back unchanged from $V'' = 0$ levels of the S_1 and T_1 states to the initial ground state of the molecule. The efficiency for the reformation of the ground state via this mechanism is expressed in terms of a parameter called *quantum yield or quantum efficiency*, and is defined as

$$\phi = \frac{\text{number of ground state molecules reformed}}{\text{number of ground state molecules initially excited}} \quad (5.127)$$

The value of ϕ for the reformation of the ground state from the excited states by the above mechanism will thus be equal to unity. But on the other hand, the molecules in the $V'' = 0$ level of the activated singlet molecules may cross over to the initial ground state via number of processes such as radiative (phosphorescence, $T_1 \rightarrow S_0$; and fluorescence, $S_1 \rightarrow S_0$) and non-radiative (interconversion (ic), $S_1 \rightleftharpoons S_0$ and intersystem crossing (isc), $S_1 \rightleftharpoons T_1 \rightleftharpoons S_0$); Fig. 5.89.

The quantum efficiency of each of these processes is defined as

$$\phi = \frac{\text{number of molecules deactivated by the process}}{\text{number of ground state molecules initially activated}} \quad (5.128)$$

or
$$\phi_{\text{process}} = \frac{\text{rate of process}}{\text{rate of absorption of radiation}} \quad (5.129)$$

Thus, for fluorescence

$$\phi_f(S_1 \rightarrow S_0) + \phi_{ic}(S_1 \rightleftharpoons S_0) + \phi_{isc}(S_1 \rightleftharpoons T_1) = 1.00 \quad (5.130)$$

provided there is no photochemical reaction or there is no loss of energy from excited states by intermolecular quenching.

Similarly, we can write for phosphorescence

$$\phi_p(T_1 \rightarrow S_0) + \phi_{ic}(T_1 \rightleftharpoons S_0) + \phi_{isc}(S_1 \rightleftharpoons T_1) = 1.00 \quad (5.131)$$

The quantum efficiency increases in proportion to the wavelength (λ) of the absorbed radiation. After attaining a maximum value in a certain interval of λ_{max} , the quantum efficiency drops rapidly to zero on further increase in wavelength.

Further, if k_f , k_{ic} , k_{isc} , ($S_1 \rightleftharpoons T_1$), k_p and k_{isc} ($T_1 \rightleftharpoons S_0$) represent the unimolecular rate constants for each of the processes shown in Fig. 5.89 then the quantum yield for each of these processes is related to their respective rate constants by the expression

$$\phi_{\text{process}} = \frac{k_{\text{process}}}{\sum k_i} \quad (5.132)$$

where $\sum k_i$ is the sum of the rate constants for each of the processes. The observed radiative lifetimes of the S_1 and T_1 states are determined from the rates of the deactivation processes originating from the respective states, and are given by the expression

$$\tau = \frac{1}{\sum k_i} \quad (5.133)$$

Factors Affecting Rate Constants of Photophysical Processes The energy gap ΔE ($S_1 - T_1$) determines the relative magnitudes of k_{isc} , k_f , k_p and k_{ic} . It is found that as ΔE decreases, the ratio of ϕ_p/ϕ_f increases. The rate of internal conversion and hence rate constant k_{ic} ($S_1 \rightleftharpoons S_0$)/intersystem crossing and hence k_{isc} ($T_1 \rightleftharpoons S_0$) decreases as the energy gap ΔE ($S_1 - S_0$)/ ΔE ($T_1 - S_0$) decreases.

Fluorescence is very sensitive to temperature, so that rate of fluorescence can be increased relative to other processes by deactivating the S_1 state by lowering the temperature of the system. The fluorescence quantum yield ϕ_f varies with temperature according to the following equation:

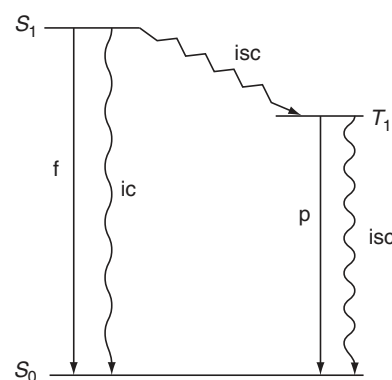


Fig. 5.89 Flowsheet diagram representing the radiative and nonradiative intramolecular transitions in an excited molecule.

$$\frac{1}{\phi_f} = \alpha + e^{\beta/T} \quad (5.134a)$$

or

$$\ln \left[\frac{1}{\phi_f} - \alpha \right] = \frac{\beta}{T} \quad (5.134b)$$

where, β is a constant, $\alpha = (1 + \Sigma k'_i \tau)$, τ is the observed radiative lifetime of the S_1 state and $\Sigma k'_i$ is the sum of the rate constants for deactivation of the S_1 state by processes other than fluorescence. The rate of isc ($S_1 \rightsquigarrow T_1$) can be enhanced relative to the rate of fluorescence ($S_1 \rightarrow S_0$) and ic ($S_1 \rightsquigarrow S_0$) by substituting a heavy atom in the molecule or by using solvents containing a heavy atom. This results in higher value of ϕ_p and the lower values of ϕ_f in the system with a heavy atom present. The heavy atom causes spin-orbit decoupling due to which two electrons are present in two orbits. The presence of heavy atoms also increases the rate of ($T_1 \rightsquigarrow S_0$) intersystem crossing and reduces phosphorescence lifetime of the T_1 state.

Relative rates of various deactivation processes also depend on the nature of S_1 and T_1 states. The relative rates depend on whether the excited state is ($n - \pi^*$) or ($\pi - \pi^*$). Some of the criteria fixed for identifying S_1 and T_1 states of the (n, π^*) and (π, π^*) type are summarised in Table 5.37.

Table 5.37 Some of the criteria used for identifying the S_1 and T_1 states of the ($n-\pi^*$) and ($\pi-\pi^*$) type.

Spectra	$n-\pi^*$	$\pi-\pi^*$
Absorption spectra		
$\epsilon_{\max}$ values	$S_0 \rightarrow S_1, \epsilon_{\max} < 10$	$S_0 \rightarrow S_1, \epsilon_{\max} > 100$
O ₂ perturbation	$S_0 \rightarrow T_1$, not normally enhanced	$S_0 \rightarrow T_1$, normally enhanced
$\Delta E (S_1 - T_1)$ range	1500–15,000 cm ⁻¹	10,000–20,000 cm ⁻¹
Solvent polarity	Blue shift of $n-\pi^*$ bands, vibrational fine structure broadens on increasing solvent polarity.	Red shift of $\pi-\pi^*$ transitions, vibrational fine structure remains unchanged on increasing solvent polarity.
Emission spectra		
Fluorescence	$\tau_f > 10^{-6}$ second	$\tau_f \sim 10^{-9} - 10^{-7}$ second
	$\phi_f < 0.01$	$\phi_f \sim 0.5 - 0.05$
Phosphorescence	$\tau_p \sim 10^{-3} - 10^{-2}$ second	$\tau_p \sim 0.1 - 100$ second
	$\phi_p \sim 0.5 - 0.05$	$\phi_p \sim 0.5 - 0.05$

5.24.2 Relationship Between Luminescence (Fluorescence/Phosphorescence) Intensity and Concentration

If I_0 is the intensity of the incident radiation and I_t that of the transmitted radiation then the intensity of the radiation absorbed by the sample will be ($I_0 - I_t$).

Fluorescence intensity is related to the absorbed radiation intensity by

$$I_f = \phi(I_0 - I_t) \quad (5.135)$$

According to Beer–Lambert's law

$$I_t = I_0 e^{-\epsilon C l} \quad (5.136)$$

Lumping together Eqs (5.135) and (5.136),

$$I_f = \phi I_0 (1 - e^{-\epsilon C l}) \quad (5.137)$$

For dilute solutions, i.e. when C (absorbance, A) is small, we can write Eq. (5.137) as

$$\begin{aligned} I_f &= \phi I_0 [1 - (1 - \epsilon C l)] \\ &= \phi I_0 \epsilon C l \end{aligned} \quad (5.138)$$

Thus, the fluorescence intensity linearly varies with the concentration provided only a single absorbing and fluorescing species is present in a solution.

At higher concentration, i.e. until quenching starts, even if intensity may not be linearly varying with concentration, we can plot a graph of intensity against concentration and use it as a calibration curve for unknown

concentrations. At higher concentrations, I_f drops off resulting in a curve, which resembles negative deviation from Beer's law. The decrease in value of I_f at higher concentrations is governed by the expression

$$I_f = \phi I_0 \left[\epsilon C l - \frac{(\epsilon C l)^2}{2} + \frac{(\epsilon C l)^3}{3} - \dots \right] \quad (5.139)$$

The disadvantage of fluorescence is that it is highly temperature dependent and the intensity of fluorescence depends on the excitation intensity. Neither of these is true for spectrophotometry.

The fluorescence efficiency of the substances under study can be found by comparing the fluorescence intensity with that of the standard. Some of the standard materials whose fluorescence efficiencies are known are quinine sulphate, fluorescein, and 2-aminopyridine.

The total fluorescence yield ϕ_i arises from contribution of light polarised parallel and perpendicular to the direction of the excitation light vector.

$$I_f = I_{\parallel}^f + 2I_{\perp}^f \quad (5.140)$$

Further, information on the flexibility of the fluorescent chromophore and rotational movement of its carrier is obtained from measurements of the fluorescence anisotropy, r_i which is defined as

$$r_i = \frac{I_{\parallel}^f - I_{\perp}^f}{I_{\parallel}^f + 2I_{\perp}^f} = \frac{\sum \epsilon_i C_i \phi_i r_i}{\sum \epsilon_i C_i \phi_i} \quad (5.141)$$

where (ϵ_i) denotes the molar decadic coefficients of species i at the excitation wavelength, ϕ_i is the integrated quantum yield of the emission spectrum, which is observed at a space angle θ_f (Fig. 5.90), and r_i denotes the anisotropy of the i^{th} species.

Problem 5.56: The calibration graph for luminescence determination of uranium in a solution of tributylphosphate is expressed by the equation

$$C = 2 \times 10^{-5} + 5 \times 10^{-4} \log I$$

where C is the concentration (in g/mL) and I , the luminescent intensity expressed in arbitrary units. Determine the concentration of uranium (in g/mL) if its luminescent intensity is 50 arbitrary units.

Solution Substituting the value of $I = 50$ into the equation of the problem, we get

$$C = 2 \times 10^{-5} + 5 \times 10^{-4} \log 50$$

$$\text{or } C = 2 \times 10^{-5} + 5 \times 1.698$$

$$\text{or } C = 10^{-4} [0.2 + 8.490]$$

$$\text{or finally } C = 8.690 \times 10^{-4} \text{ g/mL}$$

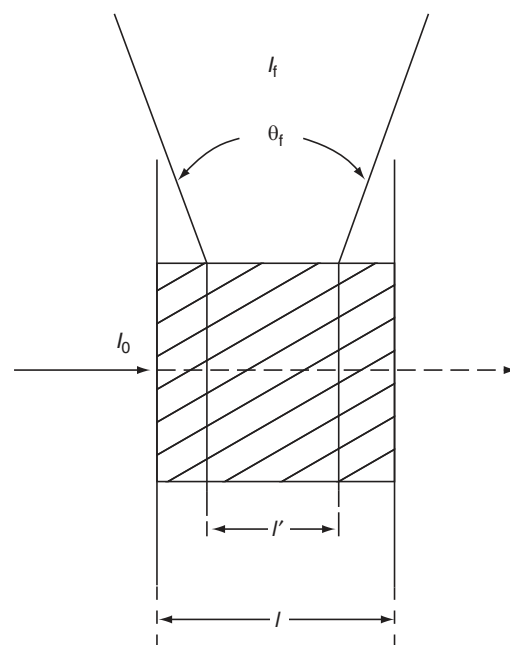


Fig. 5.90 Schematic diagram of optical path for the measurement of fluorescence observed at space angle θ_f .

Problem 5.57: The luminescence (or fluorescence) of triazinyl stilbexone is quenched by Cr^{3+} ion and the results of observations are as follows.

Concentration of Cr^{3+} ($C \times 10^7$); g ion lit^{-1}	0.0	0.4	1.2	2.3	4.4	8.3	12.0	16.0
Luminescence intensity arbitrary units	100	95	87	79	68	56	49	44

By using the method of least squares, derive an equation for the calibration curve; assuming the following linear relation:

$$\frac{1}{I^2} - \frac{1}{I_0^2} = kC$$

where I is the luminescence intensity of the solution and I_0 is the luminescence intensity of the blank sample.

Determine the concentration of Cr^{3+} (in g-ion lit^{-1}) from this equation if the luminescence intensity is equal to 75 arbitrary units.

Solution Applying the method of least squares (as discussed in Chapter 1), on the data deduced from the equation

$$\left(\frac{1}{I^2} - \frac{1}{I_0^2} \right) = k C, \text{ the value of 'k' comes out to be } 2.6 \times 10^2.$$

Thus the equation for the calibration curve is

$$\frac{1}{I^2} - \frac{1}{I_0^2} = 2.6 \times 10^2 C$$

In order to obtain 'C', put the values of I ($= 75$ units) and I_0 ($= 100$ units) into the above equation

$$\frac{1}{(75)^2} - \frac{1}{(100)^2} = 2.6 \times 10^2 C$$

or
$$C = \frac{1}{2.6 \times 10^2} [1.777 \times 10^{-4} - 10^{-4}]$$

or
$$C = \frac{0.777 \times 10^{-4}}{2.6 \times 10^2} = 2.98 \times 10^{-7} \text{ g ion lit}^{-1}$$

Problem 5.58: The luminescence (fluorescence) intensity of an unknown solution of aluminium in 8-hydroxyquinoline is 0.99 arbitrary units. Determine the concentration of aluminium in this solution in ($\mu\text{g/mL}$) if the luminescence intensity of the standard solution containing $5 \mu\text{g}$ of aluminium in 1 mL is 0.45 arbitrary units under the same circumstances. The luminescence under the conditions of determination is proportional to the concentration of aluminium.

Solution Since $I \propto C$, therefore

$$\frac{I_{un}}{I_{std}} = \frac{C_{un}}{C_{std}}$$

or
$$C_{un} = \frac{C_{std} \times I_{un}}{I_{std}} = \frac{0.99 \times 5 (\mu\text{g/mL})}{0.45} = 11 \mu\text{g/mL}$$

5.24.3 Apparatus for Detecting Fluorescence (Fluoremeter)

The schematic diagram for the three possible geometries of an instrument for detecting fluorescence is shown in Fig. 5.91. The apparatus consists of a source of light giving radiation in the ultraviolet and visible regions of the spectrum, a primary monochromator to select the required wavelength for excitation, a sample cell, a secondary monochromator to remove the unwanted fluorescence due to impurities, luminescence from the cell and surroundings, etc., photomultiplier and the recorder (Fig. 5.92).

Mercury and xenon arc lamps are the most commonly used sources of radiation in fluoremetry. Mercury arcs of low and high pressures have energy outputs varying from 100 watts to 2 or 3 watts. Low-pressure Hg arcs are strong line sources at specific wavelengths, but high-pressure arcs give a continuum due to overlapping of lines. Xe arcs provide a strong continuum with an intensity maximum between 400–600 nm. These days, strong radiation

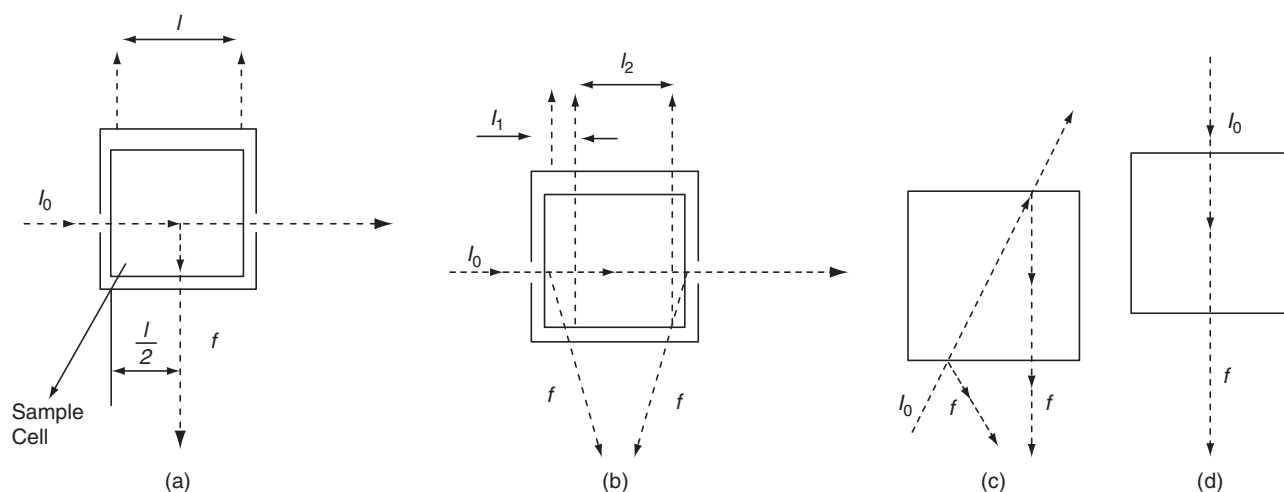


Fig. 5.91 Possible illumination and viewing geometries in a fluoremeter. Observation (a) and (b) at right angles, (c) at a small angle (frontal method), and (d) in a straight line (in-line method).

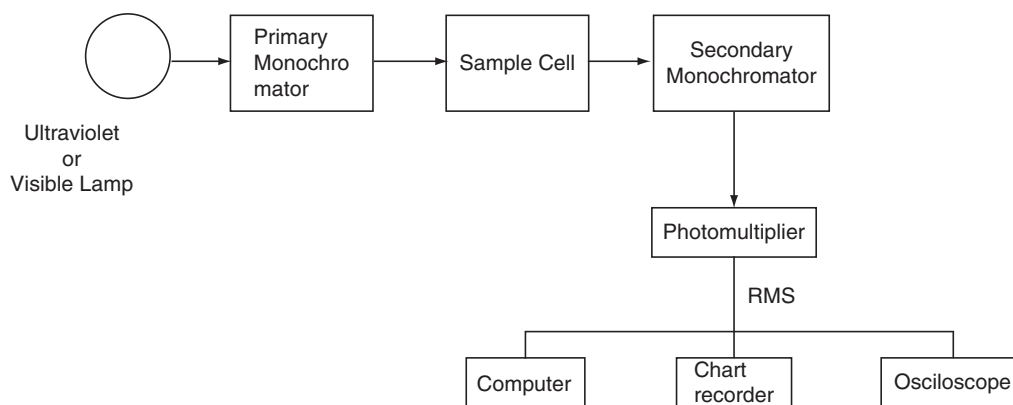
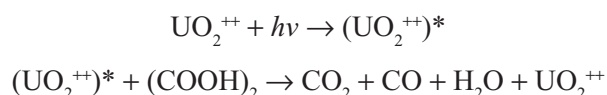


Fig. 5.92 Schematic diagram of a fluorometer.

sources up to a few j watts are available. The output of the source is often found with the help of a ferrioxalate/uranyl oxalate actinometer and is often counted in quanta/second. In a chemical actinometer, the intensity is measured by the amount of reaction produced by the radiation. A uranyl oxalate actinometer consists of a $0.05 \text{ mole lit}^{-1}$ solution of oxalic acid mixed with an equal volume of $0.01 \text{ mole lit}^{-1}$ of uranyl nitrate or sulphate as sensitiser. The actinometer, when exposed to violet or ultraviolet light within a wavelength range of 254 to 435 nm, decomposes oxalic acid. The extent of decomposition during a given period of time is determined by titration with standard KMnO_4 at the beginning and at the end of the exposure.

Sensitiser



Quantum yield in the said wavelength range lies in the range 0.49–0.60. In the ferrioxalate actinometer, a trace of FeCl_3 is used as a sensitiser.



Choice of the geometry of the apparatus depends on inner filter effect and the possibility of scattering and fluorescence of the cell walls. When monochromatic radiation passes through a solution over a certain distance, it is absorbed and consequently cannot excite fluorescence over subsequent layers of the solution. *This is called inner filter effect.* This effect does not cause any serious problem in dilute solutions but in concentrated solutions, this effect cannot be ignored. On the other hand, the major culprit in dilute solutions is *fluorescence blank*, which is due to scattering and fluorescence by the walls of the sample cell. In such a case, right-angle geometry is used. In case of concentrated solutions, one has to choose between the frontal method or the inline method. The frontal method is the obvious choice if the solution is turbid or if it absorbs appreciably at the wavelengths of the emitted light possibly due to other substances present and for solids. The fluorescence emission will occur from the surface of the sample where the absorption of the incident ultraviolet radiation will be greatest and will have penetrated through a minimum thickness of the sample.

The inline method is useful if the theoretical parameters such as quantum yield are to be estimated from the experimental observations because the theoretical equations correlating the experimental data with the theoretical parameters are not based on a fewer number of assumptions. The other most important parameter that needs be stated is the sensitivity. The term sensitivity in fluorescence and phosphorescence spectroscopy is used in three distinct ways:

(a) Instrumental Sensitivity It is the minimum detectable signal-to-noise ratio in terms of the corresponding concentration of some standard substance observed under certain precisely specified conditions. The instrumental sensitivity is governed by the light gathering power of monochromators, sensitivity of photomultiplier–amplifier–recorder combination, efficiency of various entrance- and exit-slit optics (not shown in figure), etc.

(b) Absolute Sensitivity It is the luminescence sensitivity of a particular substance in a stated solvent and is independent of the instrument used to measure it. It depends on molar decadic coefficient and the fluorescence efficiency.

(c) Method Sensitivity This is the overall sensitivity of a particular method of analysis. This type of sensitivity is determined by one or more of the following factors: Raman emission from the solvent; luminescence of the sample cell and surroundings, scattered light, luminescent impurities in solvent and in reagents, luminescence of other components of the specimen.

Problem 5.59(a): An uranyl oxalate actinometer is exposed to light of 435 nm wavelength for 10 minutes. At the end of 10 minutes, it is found that 0.001 mole of oxalic acid has been decomposed by light. At this wavelength, the quantum efficiency of the actinometer is 0.5. (a) What might be the average intensity of the light used? (b) An uranyl oxalate actinometer is exposed to light of 435 nm wavelength for 15 minutes. At the end of 15 minutes, it is found that oxalic acid equivalent to 12 mL of 0.001 molar KMnO_4 has undergone photochemical decomposition. At this wavelength, the quantum efficiency of the actinometer is 0.58. Find the average intensity of the light used. (c) The fluorescence and phosphorescence of naphthalene (at 77 K) has been excited by radiation of wavelengths 274 and 310 nm respectively. The peaks in the former have been observed at 310, 320, 335, 355 nm while in the latter at 475, 490, 515, 565 nm. Draw the energy-level diagram for the fluorescence and phosphorescence transitions to the vibrational levels in the ground electronic state.

Solution (a) Number of molecules of oxalic acid decomposed = $0.001 \times 6.023 \times 10^{23}$
 $= 6.023 \times 10^{20}$

$$\begin{aligned}\text{Energy of one quantum of radiation} &= \frac{6.62 \times 10^{-34} (\text{J s}) \times 3 \times 10^8 (\text{m/s})}{435 \times 10^{-9} \text{ m}} \\ &= 4.56 \times 10^{-19} \text{ J}\end{aligned}$$

$$\text{Quantum efficiency} = \frac{\text{Number of molecules decomposing}}{\text{Number of quanta absorbed}}$$

$$\text{Number of quanta absorbed} = \frac{6.023 \times 10^{20}}{0.5} = 1.20 \times 10^{21}$$

We know that

$$\frac{\text{Total energy of radiation absorbed}}{\text{Number of quanta absorbed}} = \text{Energy of one quantum of radiation}$$

Therefore, total energy of radiation absorbed = Number of quanta absorbed $\times$ Energy of one quantum of radiation

$$= 1.20 \times 10^{21} \times 4.56 \times 10^{-19} \text{ J} = 5.47 \times 10^2 \text{ J}$$

$$\begin{aligned}\text{Intensity of radiation} &= \frac{5.47 \times 10^2}{10 \times 60 (\text{s})} \text{ J} = 0.91 \text{ J/s} = \frac{0.91}{4.56} \times 10^{19} \text{ quanta/s} \\ &= 2 \times 10^{18} \text{ quanta/s}\end{aligned}$$

$$\text{(b) Amount of } \text{KMnO}_4 \text{ in 12 mL of solution} = \frac{12 \times 0.001}{1000} = 12 \times 10^{-6} \text{ mole}$$

Oxidation of oxalic acid by KMnO_4 in presence of sulphuric acid shows that 2 moles of $\text{KMnO}_4 = 5$ moles of $(\text{COOH})_2$

Thus, the amount of oxalic acid that undergoes decomposition in light

$$= 12 \times 10^{-6} \times 5/2 = 30 \times 10^{-6} = 0.30 \times 10^{-4} \text{ mole.}$$

Number of molecules of oxalic acid that have undergone decomposition

$$= 0.30 \times 10^{-4} \times 6.023 \times 10^{23} = 1.806 \times 10^{19}$$

Now, proceeding as in the above problem, we obtain

$$\text{Number of quanta absorbed} = \frac{1.806 \times 10^{19}}{0.58} = 3 \times 10^{19}$$

$$\text{Therefore, total energy of radiation absorbed} = 3 \times 10^{19} \times 4.56 \times 10^{-19} \text{ J} = 13.68 \text{ J}$$

$$\text{The intensity of radiation absorbed} = \frac{13.68 \text{ J}}{15 \times 60 (\text{s})} = 1.52 \times 10^{-2} \text{ J/s}$$

$$= \frac{1.52 \times 10^{-2} \times 10^{19}}{4.56} \text{ quanta/s} = 3.33 \times 10^{16} \text{ quanta/s}$$

5.24.4 Measurements of Radiative Lifetimes of Excited States from the Absorption Spectra

The luminescence (phosphorescence/fluorescence) decay of a molecule is accompanied by the depopulation of the excited state. If the depopulation of the excited state occurs by emission process only, i.e. *no radiationless processes contribute to its depopulation, then the emission lifetime of that state is called the natural radiative lifetime* τ_0 of the excited state.

The natural radiative lifetimes of S_1 and T_1 states can sometimes be determined from absorption spectra by making use of the relationship

$$\tau_0 = \frac{3.47 \times 10^8}{\bar{\nu}^2 \int_{\bar{\nu}_1}^{\bar{\nu}_2} \epsilon d\bar{\nu}} \cdot \frac{g_u}{g_l} \quad (5.142)$$

where g_u and g_l are respectively the degeneracies of the upper and lower electron states involved in the transition. The degeneracy terms are equal to one for a singlet state and three for a triplet state; $\bar{\nu}$ is the mean frequency (in cm^{-1}) of the $S_0 \rightarrow S_1$ or $S_0 \rightarrow T_1$ absorption band and $\int \epsilon d\bar{\nu}$ is the integrated intensity of the absorption band; $\int \epsilon d\bar{\nu} = \Delta\bar{\nu}_{1/2} \times \epsilon_{\text{max}}$, $\Delta\bar{\nu}_{1/2}$ is in cm^{-1} .

The numerical values of τ_0 as determined from absorption spectra of anthracene are $\tau_0(S_1) = 13.5 \text{ ns}$ (16.7 ns) and $\tau_0(T_1) = 90.0 \text{ ms}$ (0.1 ms). The quantities within bras are from radiative emission.

The natural radiative lifetimes τ_f^0 and τ_p^0 , may be determined from the relationships

$$\tau_f^0 = \frac{\tau_f}{\phi_f}; \quad \tau_p^0 = \frac{\tau_p}{\phi_p} \quad (5.143)$$

where τ 's and ϕ 's are the observed lifetimes and quantum yields respectively.

But it is not always true. The other deactivation processes also compete with the emission process and the lifetime of a state is then determined by the sum of all the processes depopulating the state. Consequently, the observed radiative lifetime τ will be less than the natural radiative lifetime of the excited state, i.e. $\tau < \tau_0$. Since the states which are populated readily are also depopulated readily, the radiative lifetime of a state will be inversely proportional to the probability of populating that state. Thus, for states which are depopulated by allowed transitions, the radiative lifetime will be short. The relationship between the radiative lifetime of an excited state and the allowedness of a transition is approximated by the equation

$$\tau \cong \frac{10^{-5}}{\epsilon_{\text{max}}} \quad (5.144)$$

where ϵ_{max} is the molar extinction absorption coefficient at the absorption band maximum. In general, ϵ_{max} values for $S_0 \rightarrow S_1$ transitions in organic molecules are much greater than for $S_0 \rightarrow T_1$ transitions. The lifetimes of the allowed and spin-forbidden transitions approximated by this equation are listed here:

Transition	$\epsilon_{\text{max}}, \text{m}^2 \text{mole}^{-1}$	Lifetime of excited state; τ, s
$S_0 \rightarrow S_1$	10^3	$10^{-8}(S_1)$
$S_0 \rightarrow T_1$	10^{-3}	$10^{-2}(T_1)$

The data indicate that the triplet-state molecules will decay slowly as compared to the excited singlet-state molecules and, therefore, the triplet-state molecules will reside in the system for longer periods than the excited singlet-state. Consequently, the probability of collision of triplet-state molecules with other solute species will be high and hence, the chances of participation of triplet-state molecules in photochemical reactions with other molecules will be high as compared to singlet-state molecules.

5.24.5 Measurements of Lifetimes of Excited States from Fluorescence or Phosphorescence Intensity

Measurements of the lifetimes of S_1 and T_1 states will give information on the rates of the photophysical processes undergone by excited-state molecules. When the molecules emit fluorescence or phosphorescence, the

lifetimes can be determined from the measurement of decay of luminescence as a function of time. The decay of luminescence is normally first order and follows the rate law:

$$I_t = I_0 e^{-t/\tau} \quad (5.145a)$$

or

$$\ln I_t = \ln I_0 - \frac{t}{\tau} \quad (5.145b)$$

Thus, from the slope of the plot of $\ln I_t$ against t , we can determine the lifetime of the excited state. Since compounds which show phosphorescence are likely to show fluorescence also, a phosphoremeter must be able to differentiate between the two. This is achieved by using a rotating shutter or cylinder such that definite time lag is introduced between times during which the sample is excited and observed.

The schematic diagram of a single-beam phosphoremeter used to monitor I_p as a function of time is shown in Fig. 5.93. Monochromatic radiation is made to fall on a sample through a slit in a rotating shutter. The incident radiation is cut off from the sample as the cylinder rotates and there is a preset time lag during which fluorescence is emitted before the slit in the cylinder arrives in front of the photomultiplier. The output from the photomultiplier is fed to an oscilloscope or computer or pen recorder and a curve of phosphorescence intensity versus time is recorded.

Since fluorescence lifetimes are much shorter than phosphorescence lifetimes, mechanical devices shown in Fig. 5.93 can't be operated rapidly enough to record the fluorescence decay. A pulse of short duration ($\sim 10^{-9}$ second) from the discharge lamp is used to populate the S_1 state. The exciting flash is switched off before the emission of fluorescence is over and the fluorescence decay is monitored using a photomultiplier and oscilloscope or computer or a pen recorder.

In case of photo-excited molecules which do not emit fluorescence or phosphorescence, the lifetimes of excited states of such molecules are measured using the technique of flash photolysis. The sample is subjected to a high-intensity flash of short duration ($\sim 10^{-9}$ – 10^{-6} second) to populate the S_1 state. If $\phi_{S_1} - \phi_{T_1}$ for intersystem crossing is nonzero then within a period of $\sim 10^{-12}$ – 10^{-14} second the T_1 state of the molecule will be populated.

Typical flash photolysis apparatus and the electronic excitation processes occurring in a flash photolysis experiments are shown in Fig. 5.94.

Light pulses as short as 1×10^{-14} second are routinely generated these days in the laboratories. The laser output is split into two parts by a beam splitter. Consider the path travelled by each beam from the beam splitter to the sample. The path lengths are made different so that the two pulses arrive at the sample at different times. In a time-resolved laser experiment, some property of the sample is measured as a function of delay time between these two laser pulses. The laser pulse that initiates the photochemistry is called the *pump pulse*. The laser pulse that is used to record changes in the sample since the pump pulse arrived is called the *probe pulse*. Depending on the nature of studies under consideration, the pump and probe pulses can be at the same or different wavelengths. For example, in case of ICN, $\lambda_{\text{probe}} = 388 \text{ nm}$ and $\lambda_{\text{pump}} = 360 \text{ nm}$. If the probe laser pulse travels a pathlength that

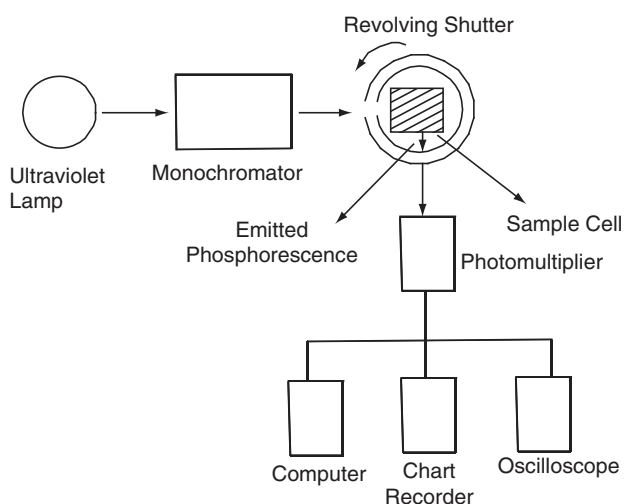


Fig. 5.93 Flow sheet diagram of single-beam phosphoremeter.

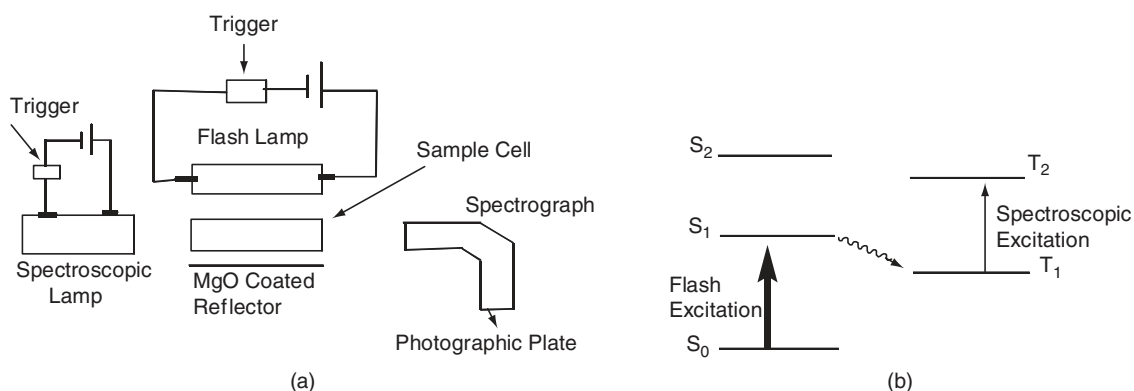


Fig. 5.94 (a) Schematic diagram of a typical flash photolysis apparatus (b) Excitation processes taking place in a flash photolysis experiment.

is 20 cm longer than that travelled by the pump laser pulse, the difference in arrival times of the two pulses of light at the sample will be

$$\frac{(20 \text{ cm})}{3 \times 10^{10} \text{ cm/s}} = 6.666 \times 10^{-10} \text{ s}$$

The potential-energy curve depicting the time-resolved laser photochemical reaction for the ground and first excited state of $AB(g)$ molecule is shown in Fig. 5.95

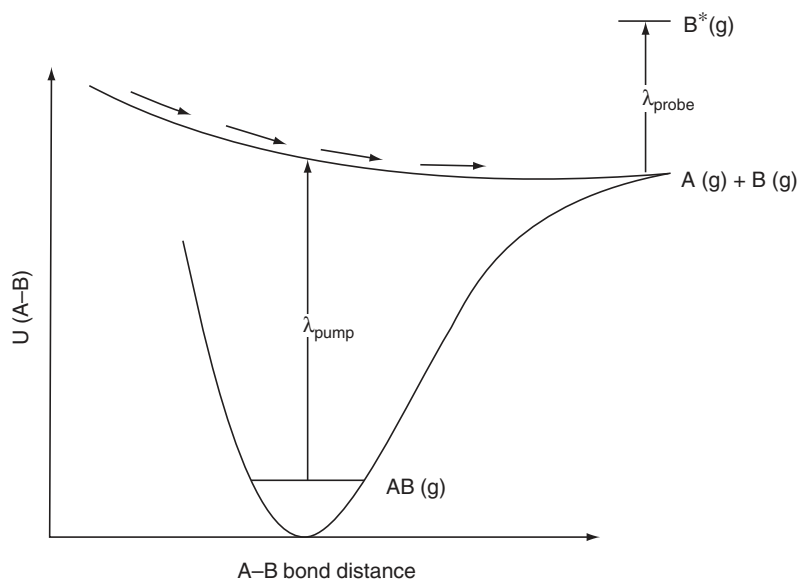


Fig. 5.95 Potential energy curve depicting the time resolved laser photochemical reaction.

The intensity of fluorescence caused by the probe pulse is a measure of the concentration of $B^*(g)$ free radical present in the sample. The plot between I_f and delay time ' t ' fits into the equation $I_f = 1 - \exp(t/\tau_{1/2})$ where $\tau_{1/2}$ is the half-life of the reaction.

Since the triplet state has a relatively long lifespan ($\sim 10^{-5}$ – 10^7 second), so during its lifetime, radiation from a low-intensity flash from the spectroscopic lamp is passed through the sample in order to measure the absorption spectra of the triplet–triplet (i.e. $T_1 \rightarrow T_2$, $T_1 \rightarrow T_3$, etc.) transitions. Thus, from the absorption transition spectra of $S_0 \rightarrow S_1$ and $T_1 \rightarrow T_2$ transitions, we can determine the lifetimes of the S_1 and T_2 states respectively. Moreover, from the absorption spectra of triplet–triplet transitions, the wavelength positions of such transitions can be accomplished. The lifetime of the T_1 state can then be determined by measuring the decay in intensity of absorption with time. In order to do this, a flash of monochromatic radiation corresponding to the wavelength of maximum absorption of $T_1 \rightarrow T_2$ band from the xenon or tungsten lamp is used to excite the molecule and the immediate decrease in intensity of radiation of the xenon or tungsten lamp is monitored as a function of time. Lifetimes of excited states of pyrene and phenanthrene as measured by flash photolysis and by emission methods are listed below:

Compound	S_1 state ^a (ns)		T_1 state ^b (ns)	
	Emission	FP	Emission	FP
Pyrene	261	296	0.2	0.7
Phenanthrene	67.2 ^c	65.0 ^c	3.3	3.3

^a -measurements made in cyclohexane solution; ^b -in ether - isopentane ethanol at 77 K and ^c - in rigid polymethyl methacrylate

5.24.6 Rate Constants of Fluorescence and Phosphorescence

The fluorescence emission or phosphorescence emission from an excited-state molecule follows first-order rate law, i.e.

$$\text{rate of fluorescence} = k_f[S_1] \quad (5.146)$$

$$\text{rate of phosphorescence} = k_p[T_1] \quad (5.147)$$

where k_f and k_p are respectively, the specific rate constants for the fluorescence and phosphorescence processes and $[S_1]$ and $[T_1]$ are the concentrations of the excited-state molecules giving rise to the radiative emission.

The rate constants for the fluorescence and phosphorescence emissions can be derived from the experimental values of τ_f , ϕ_f and τ_p , ϕ_p respectively from the following relationships.

$$k_f = \frac{1}{\tau_f^0} = \frac{\phi_f}{\tau_f} \quad (5.148)$$

$$k_p = \frac{1}{\tau_p^0} = \frac{\phi_p}{\tau_p} \quad (5.149)$$

The values of k_f and k_p (in s^{-1}) for benzene and naphthalene have been found to be 1×10^6 and $1.6 \times 10^{+2}$; and 1×10^6 and 1.6×10^{-2} respectively. For a given molecule $k_f \gg k_p$ or $\tau_f \ll \tau_p$.

Rate Constants for Intersystem Crossing The rate constants for the $S_1 \rightsquigarrow T_1$ and $T_1 \rightsquigarrow S_0$ intersystem crossings can be determined from the experimentally observed values of the rate constants and quantum yields of fluorescence and phosphorescence emissions.

Applying the steady-state hypothesis respectively to the S_1 and T_1 states, we write:

Rate of formation of S_1 = Rate of removal of S_1

$$k_{abs} = k_{ic}[S_1] + k_f[S_1] + k_{isc}[S_1] \quad (5.150)$$

Rate of formation of T_1 = Rate of removal of T_1

$$k_{isc}[S_1] = k'_{isc}[T_1] + k_p[T_1] \quad (5.151)$$

Equations (5.150) and (5.151) respectively yield

$$[S_1] = \frac{k_{abs}}{k_{ic} + k_f + k_{isc}} \quad (5.152)$$

and

$$[T_1] = \frac{k_{isc}[S_1]}{k'_{isc} + k_p} \quad (5.153)$$

Substituting the value of $[S_1]$ from Eq. (5.152) into Eq. (5.153), we write

$$[T_1] = \frac{k_{isc}k_{abs}}{(k'_{isc} + k_p)(k_{ic} + k_f + k_{isc})} \quad (5.154)$$

The quantum yields for fluorescence and phosphorescence are given by the expressions:

$$\phi_f = \frac{\text{rate of fluorescence emission}}{\text{rate of absorption of radiation}} = \frac{k_f[S_1]}{k_{abs}} \quad (5.155)$$

$$\phi_p = \frac{\text{rate of phosphorescence emission}}{\text{rate of absorption of radiation}} = \frac{k_p[T_1]}{k_{abs}} \quad (5.156)$$

Thus,

$$\frac{\phi_p}{\phi_f} = \frac{k_p[T_1]}{k_f[S_1]} \quad (5.157)$$

Elimination of $[T_1]/[S_1]$ from Eq. (5.157) yields

$$\frac{\phi_p}{\phi_f} = \frac{k_p}{k_f} \left[\frac{k_{isc}}{k'_{isc} + k_p} \right] \quad (5.158)$$

If total emission yield is high, i.e. $\phi_f + \phi_p \rightarrow 1$, then $T_1 \rightsquigarrow S_0$ intersystem crossing will be minimal. As a consequence thereof,

$$k_p \gg k'_{isc}$$

In such a situation, Eq. (5.158) reduces to

$$\frac{\phi_p}{\phi_f} = \frac{k_{isc}}{k_f} \quad (5.159)$$

Thus, the rate constant k_{isc} for the $S_1 \rightsquigarrow T_1$ intersystem crossing process can be determined from Eq. (5.159) provided the measured values of the parameters ϕ_p , ϕ_f and k_f are known for the molecule under study.

Now, in order to determine the rate constant k'_{isc} for the $T_1 \rightsquigarrow S_0$ intersystem crossing, we proceed mathematically as follows:

$$\phi_f + \phi_p + \phi_{isc}(T_1 \rightsquigarrow S_0) = 1 \quad (5.160)$$

The quantum yield for the $T_1 \rightsquigarrow S_0$ intersystem crossing process is given by

$$\phi_{isc}(T_1 \rightsquigarrow S_0) = \frac{\text{rate of } T_1 \rightsquigarrow S_0 \text{ intersystem crossing}}{\text{rate of absorption of radiation}} = \frac{k'_{isc}[T_1]}{k_{abs}} \quad (5.161)$$

Lumping together Eqs (5.156) and (5.161), we get

$$\phi_p / [\phi_{isc}(T_1 \rightsquigarrow S_0)] = \frac{k_p}{k'_{isc}} \quad (5.162a)$$

or
$$\phi_{isc}(T_1 \rightsquigarrow S_0) = \frac{\phi_p k'_{isc}}{k_p} \quad (5.162b)$$

Now combining Eqs (5.160) and (5.162b), we write

$$\phi_f + \phi_p + \frac{\phi_p k'_{isc}}{k_p} = 1 \quad (5.163a)$$

$$k'_{isc} = k_p \frac{1 - (\phi_f + \phi_p)}{\phi_p} \quad (5.163b)$$

Thus, one can calculate the value of k'_{isc} from Eq. (5.163b) provided the observed values of quantities k_p , ϕ_p and ϕ_f are known. Once the value of k'_{isc} is determined, the value of k_{isc} can be determined by making use of Eq. (5.158) for those molecules which do not have a high emission yield. Rate constants for $S_1 \rightsquigarrow T_1$ (i.e. k_{isc}) and $T_1 \rightsquigarrow S_0$ (i.e. k'_{isc}) intersystem crossings processes in case of benzene have been found to be $8 \times 10^6 \text{ s}^{-1}$ and 0.10 s^{-1} respectively. In case of acetophenone, $k_{isc}(S_1 \rightsquigarrow T_1) = 5 \times 10^9 \text{ s}^{-1}$ and $k'_{isc} = 50.0 \text{ s}^{-1}$.

For aromatic compounds, the range of magnitude of rate constants for each of the intramolecular processes originating from S_1 and T_1 states are given in the self-explanatory Fig. 5.96

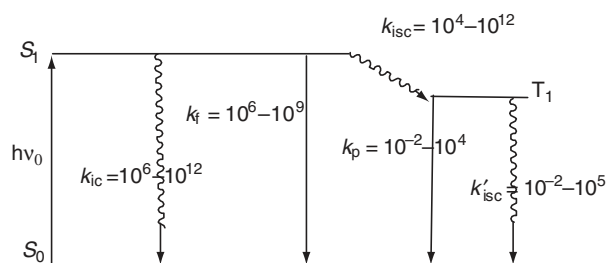


Fig. 5.96 The range of magnitude of rate constants (in s^{-1}) for each of the intramolecular processes originating from S_1 and T_1 states for aromatic molecules.

5.24.7 Comparison of Absorption, Fluorescence and Phosphorescence Spectra

Absorption is shown by solids, gases and liquids. Fluorescence is also known for gases, liquids and solids but gases will show fluorescence only at low pressure. Different substances fluoresce with light of different wavelengths, e.g. fluorspar fluoresces with blue light, chlorophyll with red light, oranges and greens of fluorescent dyes absorb in the ultraviolet and blue, and fluoresce in the visible, fluorescence which is very marked with NO_2 in blue light (492–455 nm) becomes weaker in violet light (455–365 nm) and practically vanishes at or beyond 365 nm, acetone absorbs at 270 nm (corresponding to C=O group) but fluoresces in blue, etc. Phosphorescence is exhibited by solids but is virtually unknown for dissolved substances and is only observed when phosphor is frozen into glasses at liquid nitrogen temperature (rather than freezing to a crystalline state) so that collisional deactivation is prevented or at least severely restricted, i.e. the reduction in temperature enhances the probability of $S_1 \rightsquigarrow T_1$ transition, the required condition for phosphorescence and also to diminish competing processes for nonradiative return to the ground state. When fluorescent substances are mixed by fusion with boric acid and are cooled, the resultant mass so produced exhibits phosphorescence, e.g. alkaline earth sulphides and a trace of

heavy metal enhances phosphorescence. A mixture of ethylether, isopentane and ethanol (5:3:2 by volume) called EPA is the best solvent. The Franck–Condon principle is valid both for the emission and absorption processes, whereas the absorption spectrum results when the molecule moves from the lowest vibrational level ($V' = 0$) of the ground electronic state (S_0) to one or more of the vibrational sublevels (V'') of the excited singlet state (S_1). The fluorescence and phosphorescence results respectively from the lowest vibrational level ($V'' = 0$) of the excited singlet (S_1) and triplet (T_1) states to one or more of the vibrational sublevels (V') of the molecule (Fig. 5.97).

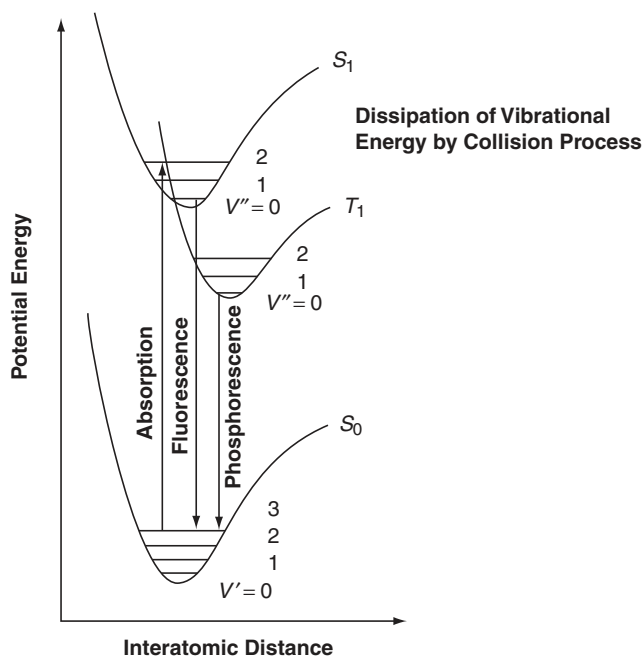


Fig. 5.97 Schematic diagram showing Franck–Condon principle in absorption, fluorescence and phosphorescence processes.

The relative spectral positions of absorption, fluorescence and phosphorescence follow the wavelength order:

$$-\lambda_{abs}^{\max} < -\lambda_f^{\max} < -\lambda_p^{\max}, \text{ and that of wave number}$$

$$-\bar{\nu}_{abs} > -\bar{\nu}_f > -\bar{\nu}_p.$$

The intensities of vibrational bands in fluorescence spectra of diatomics follow the order:

$$I(V = 0 \rightarrow 0) < I(0 \rightarrow 1) > I(0 \rightarrow 2) > I(0 \rightarrow 3) > I(0 \rightarrow 4).$$

Further, at a fixed value of wavelength (i.e., $\lambda_{abs}^{\max}$), the linear relationship between the absorption intensity and concentration of the absorbing substance holds good over a fairly wide range of concentrations. The same is not true for fluorescence intensity since it is dependent on other competitive processes, viz. internal conversion and intrasystem crossing available. Thus, as we increase the concentration, collision among solute molecules will result in quenching of fluorescence intensity. Only in very dilute solutions a linear relationship between the concentration and the fluorescence intensity is found.

Furthermore, the fluorescence and phosphorescence spectra vary in a similar manner to bands in absorption spectra, i.e. fluorescence and phosphorescence spectra generally consist of many lines, mostly in the visible region. In the solution phase, lines are broadened and fuse together to give a structured spectrum having an appearance more or less similar to that of an ultraviolet or visible absorption spectrum. The short-wavelength end of a fluorescence spectrum usually overlaps slightly with the long-wavelength end of the absorption spectrum which gives rise to the excitation, but this overlap may not occur in phosphorescence (Fig. 5.98).

5.24.8 Factors Affecting Fluorescence and Phosphorescence

All molecules can't show fluorescence and phosphorescence. Only those molecules which absorb ultraviolet or visible radiation fluoresce. In general, greater the absorption of radiation, greater the luminescence. Some of the factors which influence fluorescence are the following:

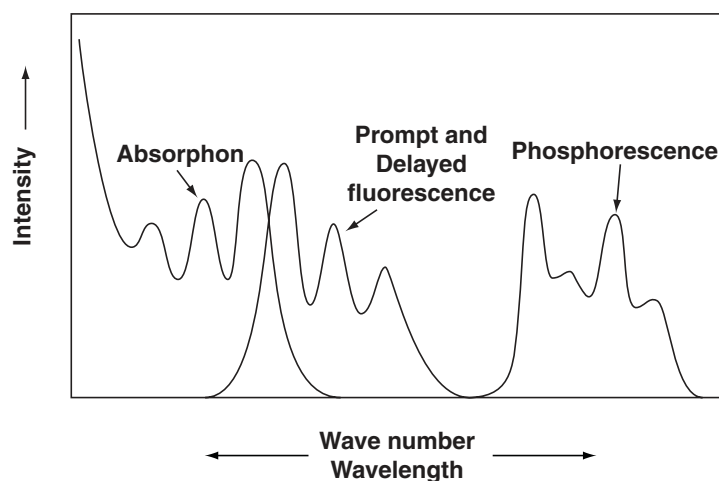


Fig. 5.98 Comparison of absorption, fluorescence and phosphorescence spectra.

(a) Effect of Substituent Only those organic molecules will behave as fluorescers that contain multiple conjugated double bonds with high degree of resonance stability, e.g. benzene and polycyclic aromatics, etc. Moreover, substituents often affect fluorescence. Though there are no unique set of rules which can predict the effect of substituent on the fluorescence of the parent fluorescer, some generalities have been made:

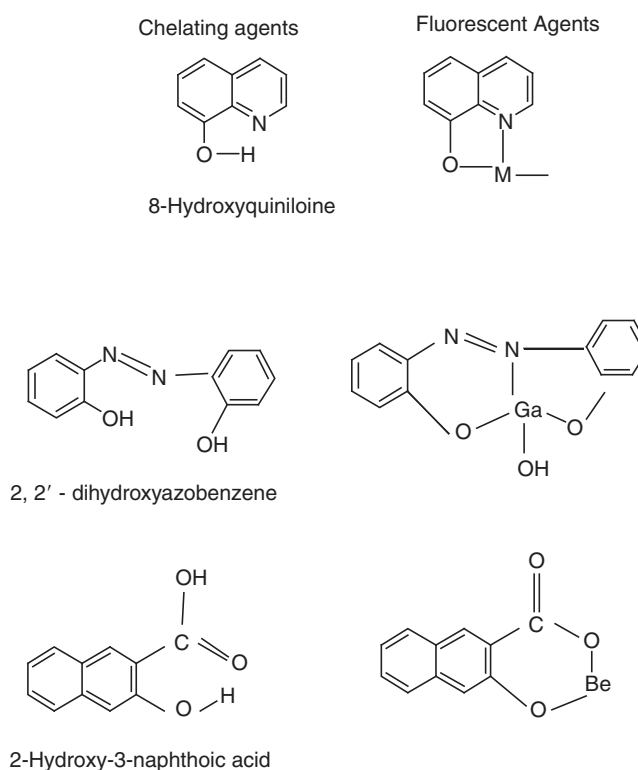
- Substituents that cause delocalisation of electrons enhance fluorescence of the parent fluorescer, e.g. NH_2 , OH , F , OCH_3 , NHCH_3 and $\text{N}(\text{CH}_3)_2$.
- Substituents that promote localisation of electrons decrease or quench fluorescence completely, e.g. Cl , Br , I , NHCOCH_3 or COOH .
- In heterocyclics, pyridine is nonfluorescent but 3-hydroxypyridine behaves as a fluorescer because of the electron-delocalising substituent, i.e. OH .
- Ring closure in aromatics also enhances fluorescence, e.g. phenolphthalein is nonfluorescent but fluorescein is fluorescent. The bridging oxygen in the latter induces rigidity and hence fluorescence. The higher the rigidity, the higher will be the fluorescence. In general, we can say that fluorescence in multicyclic aromatics is due to rigidity.
- Effect of geometry of the fluorescer—when the fluorescer structure is coplanar relative to the chromophore, the fluorescence will be enhanced. The higher the degree of coplanarity, the higher will be the fluorescence. On the other hand, nonfluorescent structures interfere with coplanarity.

(b) Effect of Chelation Metal-chelate formation often promotes fluorescence. The fluorescence in such complexes is due to certain structural features such as rigidity and coplanarity. Minor modification of the ligand structure may markedly affect the intensity of fluorescence as this may offer alternative paths for energy transfer. The fluorescence is stronger in an inert solvent than in a polar solvent. As examples, some chelating agents and fluorescent chelates are shown below.

Generally, only those cations which are diamagnetic when coordinated and are nonreducible will form fluorescent metal-chelate compounds, e.g. magnesium and zinc compounds behave as strong fluorescers but are nonphosphorescers. The transition metals with unfilled outer d -orbitals quench fluorescence completely. On the other hand, paramagnetic metal ions such as $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$ on complexation, though quench fluorescence, promote intersystem crossing. Consequently, such complexes are strong phosphorescers but are nonfluorescers.

(c) Effect of Substituents on Phosphorescence

The parent cyclic and polycyclic hydrocarbons and their CH_3 , NH_2 , OH , COOH and OCH_3 substituent derivatives



have lifetimes in the range of 5 to 10 seconds and 1 to 4 seconds for many naphthalene derivatives. The nitro group decreases phosphorescence intensity and shortens the lifetime of the triplet state to about 0.2 second. Carbonyl groups in ketones and aldehydes shorten the lifetime of the triplet state to about 0.01 second. Bulky substituents introduce nonplanarity in the parent molecule and hence profoundly decrease the lifetime of the excited triplet state; consequently the phosphorescence intensity will also decrease markedly.

(d) Effect of Solvent The effect of solvent on fluorescence and phosphorescence is quite different from that on absorption since in the former, the electron moves from the excited state to the ground state while in the latter, quite the opposite takes place. Accordingly in solutions, the interaction takes place between solute in the excited state and solvent both in fluorescence and phosphorescence.

Fluorescence intensity and wavelength often vary with solvent. For nonpolar solutes and solvents, the weak Van der Waal's type interaction (i.e. electrostatic interaction) between the solute and solvent does not produce significant variations in fluorescent yields; whereas for polar solute or solvent, polar solvent or solute and polar solute and solvent, the Van der Waal's type binding (i.e. solute-dipoles-induced-dipoles in the solvent or solvent dipoles-induced dipoles in the solute and dipole-dipole), the solvent promotes the lifetime of a collisional encounter and favours deactivation. Consequently, the intensity variations are significant but small compared to those produced in H-bonding. For excitation wavelength of 285 nm in each solvent, the λ_{max}^f for indole = 297 nm in cyclohexane, 305 nm in benzene, 310 in dioxane, 330 in ethanol and 350 nm in water. Fluorescence of chlorophyll is markedly influenced upon addition of a polar solvent to dry nonpolar solvent. Moreover, the presence of heavy substituents such as thiocyanate, Cl, Br, I (i.e. iodine, in ethyliodide), NO_2 , or $-\text{N}=\text{N}-$ in solvent cause an increase in efficiency of $S_1 \rightsquigarrow T_1$ intersystem crossing due to spin-orbit decoupling. Consequently, the efficiency of fluorescence decreases while that of phosphorescence increases. The dissolved impurities in solution may also influence fluorescence and phosphorescence. For instance, dissolved oxygen quenches excited triplet and singlet states of many molecules, especially of aromatic hydrocarbons, by diffusion controlled process. So, the solutions should be degassed and freeze-dried before use, since the freezing of a solution reduces quenching. It is to be noted that the shift in the fluorescence spectrum of a substance in solution compared to that in the gas phase is because of solute-solvent interactions involved in the former.

(e) Effect of Viscosity The fluorescence increases as the viscosity of the medium increases and this increase is due to the decrease in the number of deactivating collisions in the viscous medium. For example, the sodium salt of phenolphthalein which does not show visible fluorescence in aqueous solution, fluoresces when dissolved in solid gelatin, sucrose, succinic acid or benzamide.

(f) Effect of pH The effect of pH on the fluorescence of an organic compound containing acidic or basic group is often quite different from that observed for its absorption spectrum. pH changes in the system if it affects the charge on the chromophore will influence fluorescence: Neutral (pH = 7) or alkaline (pH = 12) aqueous solution of aniline fluoresces in the visible but in acidic solution (pH = 2) the visible fluorescence vanishes due to the formation of anilinium ion (Fig. 5.99). Aniline also fluoresces in ultraviolet, but this fluorescence is temperature independent. Both phenol and anisole show fluorescence at 300 and 310 nm at pH 7 but at pH 12 phenol becomes nonfluorescent due to the formation of phenoxide ion whereas anisole remains fluorescent. Thus, pH sensitive fluorescent substances can be used as indicators in acidbase titrations. A few are cited below.

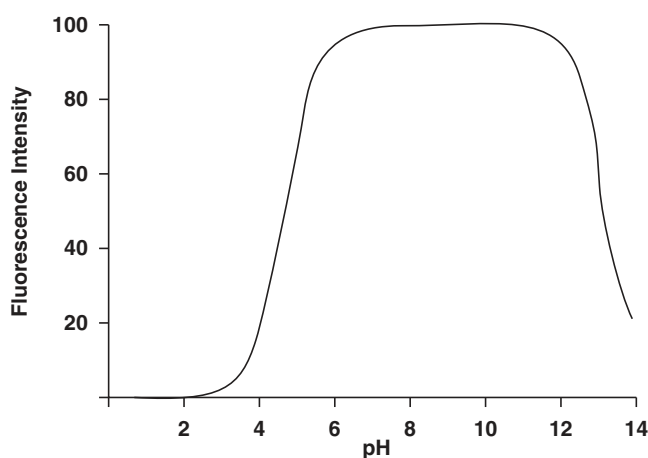


Fig. 5.99 Behaviour of pH with fluorescence intensity of aniline in aqueous solution.

System	pH range	Colour change
Erythrosin	2.5–4.0	Colourless to green
β -naphthoquinoline	4.4–6.3	Blue to colourless
o-coumaric acid	7.2–9.0	Colourless to green

(g) Hydrogen Bonding Hydrogen bonding may bring about changes in the position of excited states, $n-\pi^*$ states which are normally low-energy states as compared to $\pi-\pi^*$ states, are raised in energy due to intermolecular H-bonding. Consequently, the nonfluorescent substances become fluorescent in strong polar solvents. Intramolecular H-bonding may inhibit fluorescence because they offer alternative paths for the loss of energy.

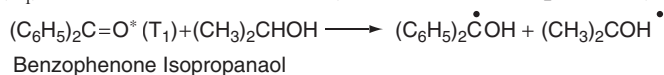
(h) Effect of Temperature Temperature and viscosity of a solvent has a marked effect on fluorescence. The lowering of temperature will prolong the lifetime of a collisional encounter between the solute and solvent molecule and favour deactivation of the S_1 state. Thus, substances fluoresce more brightly in rigid state or in viscous solutions. The probability of intermolecular energy transfer between fluorescent molecules and other molecules reduces at low temperature and in a medium of high viscosity in which rotational relaxation time of the fluorescent substance is much longer than the lifetime of the excited state.

All these environmental factors must be kept in mind while devising a fluoremetric method of analysis.

5.24.9 Intermolecular Deactivation (or Quenching) of Excited States

The deactivation of excited-state molecules by other molecular species present in the system occurs via biomolecular processes. The loss of excess energy of the excited-state molecules by such processes depromotes the activated molecules to the original ground state. Such intermolecular processes are additional to the intramolecular processes described earlier by which the decay of the excited state occurs. Thus, the overall decay of the state is the sum total of the decay rates for the intermolecular and intramolecular paths. As an example, the bimolecular processes involving in the decay of triplet-state molecule are

- (a) Chemical reaction: $D^* (T_1) + \text{Reactant} \rightarrow \text{Products (radicals or stable products)}$



- (b) Collision deactivation: $D^* (T_1) + \text{substrate molecule} \rightarrow D (S_0) + \text{substrate molecule}$

The collision process results in the transfer of energy as heat energy from the triplet-state molecule to the surroundings. The rate of such collision processes can't be greater than the rate of diffusion of triplet-state molecules into the solvent molecules. The rate of diffusion is given by the modified Debye equation:

$$k_{\text{diff}} = \frac{8RT}{2\eta} \times 10^3 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1} \quad (5.164)$$

provided the temperature T is expressed in K, the viscosity η of the solvent is expressed in N s m^{-2} and R , the gas constant, is expressed in $\text{J K}^{-1} \text{ mole}^{-1}$, $R = 8.3 \text{ J K}^{-1} \text{ mole}^{-1}$. For organic solvents at room temperature, the value of k_{diff} lies in the range $1 \times 10^{10} - 4 \times 10^{10} \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$.

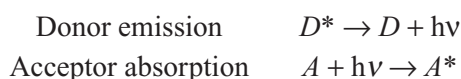
Since the lifetime of the excited triplet state is long, so such collisions often occur. However, when such collisions take place, they result in the emission of delayed fluorescence.

- (c) Energy transfer $D^*(T_1) + A \cdots \rightarrow D (S_0) + A^*$

Such type of collisional processes are very common in photochemical systems and provide an efficient method for the deactivation of excited-state molecules even by very minute quantity of the quencher. O_2 is an effective quencher for triplet-state molecules. So the system must be degassed in order to remove dissolved oxygen from the system. On the other hand, the decay of the triplet state in different concentrations of dissolved oxygen can be used to determine the amount of dissolved oxygen in unknown samples. The details of the method are deferred here but will be described in detail later on under the title *fluorescence quenching*.

The various mechanisms by which the donor triplet-state molecule transfers energy to the acceptor molecule are the following:

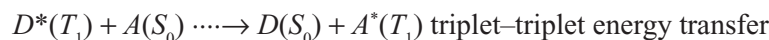
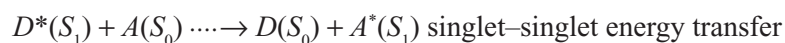
Radiative Transfer The general mechanism for radiative transfer can be written as



The efficiency of the mechanism increases provided the $\lambda_{\max}$ and intensity of the emission band of the donor is similar to that of the absorption band. The larger the degree of similarity, the greater will be the absorption of emitted radiation by the acceptor.

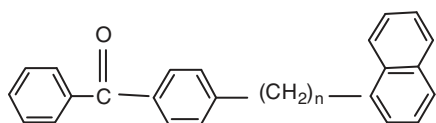
(i) Short-Range Radiative Transfer Such type of radiative transfer occurs provided the intermolecular separation between the donor and acceptor molecules approaches the collision diameter. Energy transfer can take place even without the collision process since energy transfer can take place at distances slightly greater than the collision diameter.

Short-range energy processes are possible provided the Wigner spin-conservation rule is obeyed, i.e. S – S and T – T energy transfer are possible



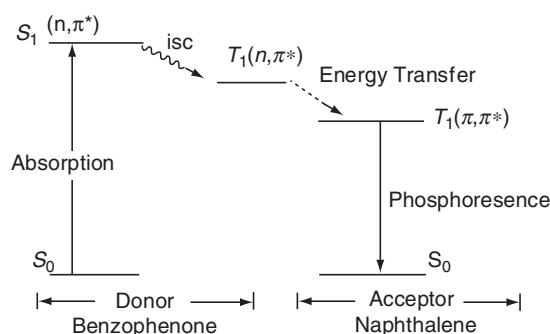
As an example, short-range energy transfer occurs in the benzophenone (D) –naphthalene (A) system by the following process:

Short-range intramolecular energy transfer can also take place between the benzophenone moiety and the naphthalene moiety when two groups are present in the same molecule, e.g.



where $n = 1, 2, 3, \dots$

The absorption spectrum of such a molecule is composite absorption spectra of 4-methyl-benzophenone (D) and 1-methyl-naphthalene (A). Phosphorescence emission characteristic of a π – π^* state will be emitted from the naphthalene triplet state.



(ii) Long-Range Radiative Transfer Such type of radiative transfer occurs even if the distance between donor and acceptor molecules is much greater than the donor-acceptor collision diameter, provided the energy differences between the vibrational levels of the ground and first excited states of the donor correspond to the energy differences between the vibrational levels of the ground and first excited states of the acceptor, e.g. in anthracene (S_1)–perylene (S_0) system $r = 5.4$ (3.1) nm, $k \times 10^{-10} = 12(2.3)$ dm³ mole⁻¹ s⁻¹; perylene (S_1)–rubrene (S_0) system, $r = 6.5$ (3.8) nm; $k \times 10^{-10} = 13(2.8)$ dm³ mole⁻¹ s⁻¹. The quantities within bras are the calculated values.

5.24.10 Kinetics of Intermolecular Processes

Deactivation of the photo-excited molecular species via intermolecular interactions takes place with the loss of energy through the following two pathways: (a) energy transfer from excited donor (D^*) to the acceptor (A) molecule, and (b) chemical reaction with a suitable reactant. Since inter- and intramolecular interactions go side by side, the deactivation steps involved in intramolecular processes must be taken into account while deducing the rate constant expressions for the intermolecular processes. The possible inter and intramolecular pathways which contribute to the deactivation of the excited-state molecules are shown in Fig. 5.100.

The rate constants for the deactivation of photo-excited state via intramolecular processes are evaluated under experimental conditions such that the intermolecular processes are eliminated but the reverse is not possible. In this section, we shall be dealing with the kinetics of the deactivation of the excited state by the energy-transfer process. The energy-transfer process is called quenching if the rate of deactivation by the energy transfer process is so high that deactivation by fluorescence or phosphorescence process is quenched.

Energy transfer from the photo-excited D^* to the ground state of an acceptor A takes place from either the S_1 or the T_1 state of the donor with the formation of an S_1 or a T_1 state of the acceptor, i.e. the energy transfer may take place via $S_1 - S_1$, $S_1 - T_1$ and $T_1 - T_1$ transitions. Here, we shall be mainly treating with the kinetics of deactivation via both spin and energy allowed $S_1 - S_1$ and $T_1 - T_1$ energy-transfer transitions. It is assumed that the photo-excited donor D^* does not participate in any chemical reaction.

(a) Kinetics of Triplet-Triplet Energy Transfer The various intramolecular processes which compete with the deactivation of photo excited donor molecule via triplet-triplet energy transfer process are shown in Fig. 5.101.

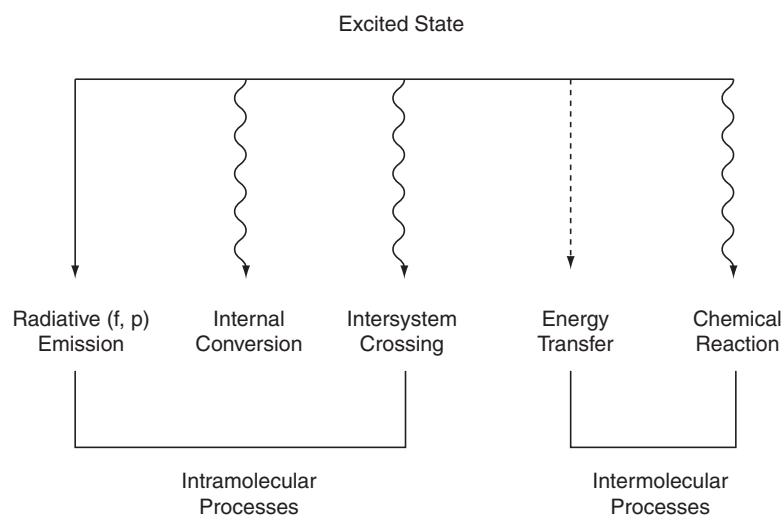


Fig. 5.100 Possible pathways for the deactivation of an excited state. Energy transfer from donor to acceptor also occurs via radiationless process and but is shown by a dotted arrow.

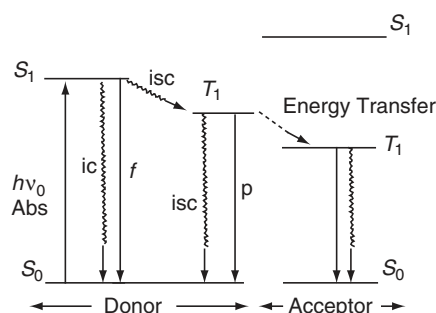


Fig. 5.101 Energy level diagram representing triplet-triplet energy transfer in donor-acceptor system.

The reaction scheme showing the inter and intramolecular processes involved in the deactivation of excited donor D^* indicated in Fig. 5.101 can be written as follows:

Process	Representation	Rate
Excitation	$S_0(D) + h\nu_0 \rightarrow S_1(D)$	k_{abs}
Internal conversion	$S_1(D) \rightsquigarrow S_0(D)$	$k_{ic}[S_1]$
Fluorescence	$S_1(D) \rightarrow S_0(D) + h\nu_f$	$k_f[S_1]$
Intersystem crossing	$S_1(D) \rightsquigarrow T_1(D)$	$k_{isc}[S_1]$
Phosphorescence	$T_1(D) \rightarrow S_0(D) + h\nu_p$	$k_p[T_1]$
Intersystem crossing	$T_1(D) \rightsquigarrow S_0(D)$	$k'_{isc}[T_1]$
Energy transfer (quenching)	$T_1(D) + S_0(A) \cdots \rightarrow S_0(D) + T_1(A)$	$k_e[T_1][A]$

where k_e is the rate constant for triplet-triplet energy transfer and k_{abs} is the rate constant for the absorption of incident radiation.

Applying the steady-state hypothesis respectively to the intermediate states S_1 and T_1 of the donor we get

$$k_{abs} = k_{ic}[S_1] + k_f[S_1] + k_{isc}[S_1] \quad (5.165)$$

$$k_{isc}[S_1] = k_p[T_1] + k'_{isc}[T_1] + k_e[T_1][A] \quad (5.166)$$

Rearrangement of Eq. (5.165) and Eq. (5.166) respectively yields

$$[S_1] = \frac{k_{abs}}{k_{ic} + k_f + k_{isc}} \quad (5.167)$$

and

$$[T_1] = \frac{k_{isc}[S_1]}{k_p + k_e[A] + k'_{isc}} \quad (5.168)$$

The expressions for the quantum yields of phosphorescence in the presence and absence of the energy acceptor A can be written as

$$\phi_p = \frac{k_p[T_1]}{k_{abs}} \quad (5.169)$$

$$\phi_p^0 = \frac{k_p[T_1]'}{k_{abs}} \quad (5.170)$$

where $[T_1]'$ is the steady-state concentration of the donor in its triplet-state in the absence of the energy acceptor A . The combination of Eq. (5.169) and Eq. (5.170) yields

$$\frac{\phi_p^0}{\phi_p} = \frac{[T_1]'}{[T_1]} \quad (5.171)$$

Now, substituting the value of $[T_1]$ from Eq. (5.153) and $[T_1]'$ from Eq. (5.168) respectively into Eq. (5.171), we get

$$\frac{\phi_p^0}{\phi_p} = \frac{k_p + k'_{isc} + k_e[A]}{k_p + k'_{isc}} \quad (5.172a)$$

or

$$\frac{\phi_p^0}{\phi_p} = 1 + \frac{k_e[A]}{k_p + k'_{isc}} \quad (5.172b)$$

If the ratio of the intensities of phosphorescence emission in the absence and presence of the energy acceptor A is measured instead of the ratio of $\frac{\phi_p^0}{\phi_p}$ then Eq. (5.172b) can be written as

$$\frac{I_p^0}{I_p} = 1 + \frac{k_e[A]}{k_p + k'_{isc}} \quad (5.173)$$

Equations (5.172 b) and (5.173) are known as Stern–Volmer equations (See also Eq. 5.197). According to Eq. (5.173), the plot of $\frac{I_p^0}{I_p}$ against $[A]$ will be a straight line with slope $\frac{k_e}{k_p + k'_{isc}}$. From the slope, the value of k_e can be determined provided the values of k_p and k'_{isc} are known for the donor.

Let us now examine the case in which the deactivation of the donor T_1 state proceeds solely via the intramolecular processes of phosphorescence ($T_1 \rightarrow S_0$) and $T_1 \rightsquigarrow S_0$ intersystem crossing. The lifetime of the T_1 state in such a case is given by

$$\tau = \frac{1}{k_p + k'_{isc}} \quad (5.174)$$

If deactivation of the T_1 state of the donor $T_1 \rightarrow T_1$ via energy-transfer process is also considered in addition to the $T_1 \rightsquigarrow S_0$ and $T_1 \rightsquigarrow S_0$ intramolecular processes, then the lifetime of the T_1 state will be given by

$$\tau^e = \frac{1}{k_p + k'_{isc} + k_e[A]} \quad (5.175)$$

Lumping together Eqs. (5.174) and (5.175), we obtain

$$\frac{1}{\tau^e} = \frac{1}{\tau} + k_e[A] \quad (5.176)$$

Equation (5.176) indicates that the plot between the reciprocal of the lifetime τ^e of the T_1 state and the concentration $[A]$ of the acceptor will be a straight line of slope equal to k_e and intercept = $1/\tau$. Biacetyl acts both as a donor and an acceptor. In the biacetyl–naphthalene system, the rate constants for the triplet–triplet energy transfer to and from the T_1 state of biacetyl ($E_T = 234 \text{ kJ mole}^{-1}$) in benzene solution at 293 K as determined from Eq. (5.175) have

been found to be 1×10^{10} and $2 \times 10^6 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ respectively. The value of E_T for naphthalene is 255 kJ mole^{-1} .

The rate constants for triplet–triplet energy transfer between donors and acceptors determined by the above method depend upon the observation and measurement of emitted phosphorescence. Since most of substances do not show phosphorescence in fluid solution, the rate constants for the triplet–triplet energy transfer in such D–A systems is determined by flash photolysis technique.

(b) Singlet-Singlet Energy Transfer Rate constants for singlet–singlet energy transfer can be determined from the fluorescence emitted by the donor or acceptor species. The energy-level diagram showing the relative energies of the lowest excited states of donor and acceptor is shown in Fig. 5.102.

The reaction scheme corresponding to the inter and intramolecular processes shown in Fig. 5.102 is as follows:

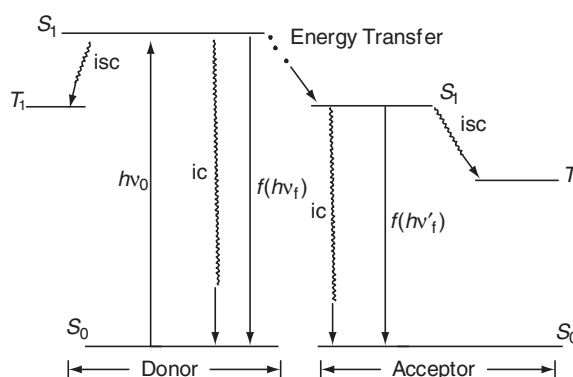


Fig. 5.102 Energy-level diagram showing the singlet–singlet energy transfer in donor–acceptor systems. $h\nu_0 > h\nu_f > h\nu'_f$.

Process	Representation	Rate
Excitation	$S_0(D) + h\nu_0 \rightarrow S_1(D)$	k_{abs}
Internal conversion	$S_1(D) \rightsquigarrow S_0(D)$	$k_{ic}[S_1]_D$
Fluorescence	$S_1(D) \rightarrow S_0(D) + h\nu_f$	$k_f[S_1]_D$
Intersystem crossing	$S_1(D) \rightsquigarrow T_1(D)$	$k_{isc}[S_1]_D$
Energy transfer (quenching)	$S_1(D) + S_0(A) \rightarrow S_0(D) + S_1(A)$	$k_e[S_1]_D [A]$
Internal conversion	$S_1(A) \rightsquigarrow S_0(A)$	$k'_{ic}[S_1]_A$
Phosphorescence	$S_1(A) \rightarrow S_0(A) + h\nu'_f$	$k'_f[S_1]_A$
Intersystem crossing	$S_1(A) \rightsquigarrow T_1(A)$	$k'_{isc}[S_1]_A$

Applying the steady-state hypothesis to the S_1 state of the donor.

$$k_{abs} = k_{ic}[S_1]_D + k_f[S_1]_D + k_{isc}[S_1]_D + k_e[S_1]_D [A] \quad (5.177)$$

Rearrangement of Eq. (5.177) yields

$$[S_1]_D = \frac{k_{abs}}{k_{ic} + k_f + k_{isc} + k_e [A]} \quad (5.178)$$

The quantum yield of fluorescence in the presence of an energy acceptor A is given by

$$\phi_f(D) = \frac{k_f [S_1]_D}{k_{abs}} \quad (5.179)$$

From Eqs (5.178) and (5.179), we get

$$\phi_f(D) = \frac{k_f}{k_{ic} + k_f + k_{isc} + k_e [A]} \quad (5.180)$$

In the absence of an acceptor, Eq. (5.180) reduces to

$$\phi_f^0(D) = \frac{k_f}{k_{ic} + k_f + k_{isc}} \quad (5.181)$$

Thus, the ratio of fluorescence quantum yields in the absence and presence of energy transfer acceptor is given by

$$\frac{\phi_f^0(D)}{\phi_f(D)} = \frac{k_{ic} + k_f + k_{isc} + k_e [A]}{k_{ic} + k_f + k_{isc}} \quad (5.182a)$$

or

$$\frac{\phi_f^0(D)}{\phi_f(D)} = 1 + \frac{k_e [A]}{k_{ic} + k_f + k_{isc}} \quad (5.182b)$$

Equation (5.182b) shows that the plot of fluorescence quantum yield ratio $\frac{\phi_f^0(D)}{\phi_f(D)}$ against the concentration of acceptor A will give a straight line of slope equal to $\frac{k_e}{k_{ic} + k_f + k_{isc}}$.

From the slope one can determine the value of k_e , the rate constant for the energy transfer from the donor singlet state to the acceptor provided the values of the rate constants k_{ic} , k_f and k_{isc} are known for the donor. The rate constants for singlet–singlet energy transfer from aromatic hydrocarbons to biacetyl have been determined by this procedure. For biphenyl ($E_{S_1} = 400 \text{ kJ mole}^{-1}$) – biacetyl ($E_{S_1} = 277 \text{ kJ mole}^{-1}$) system in aerated hexane solution at 298 K, the value of k_e is equal to $2.2 \times 10^{10} \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$. The high value for the measured rate constant is because of the large energy gap, i.e. 123 kJ mole^{-1} between the S_1 state of the donor biphenyl and the S_1 state of the acceptor biacetyl.

The experimental values for the rate constants of singlet–singlet and triplet–triplet energy transfer helps in deciding whether the transfer takes place via the short range or long-range mechanism.

In long-range interactions, the value of rate constant k_e should be independent of the viscosity of the solvent or the temperature of the system. The rate constants for a diffusion controlled process should change when the viscosity of the solvent or the temperature of the system is changed. The diffusion controlled rate constants indicate that the mechanism involves collision or near collision of the donor and acceptor molecules, i.e. short-range interaction.

5.24.11 Chemical Reaction

Till now we have discussed the kinetics of triplet–triplet and singlet–singlet energy transfer processes in the D - A systems on the assumption that there is no chemical reaction between photo-excited molecules and the reactant. Let us now consider the case in which the photo-excited molecule gets deactivated by a chemical reaction with some suitable reactant. It is assumed that (a) the photo-excited molecule M^* reacts with a reactant R in a single bimolecular step to give radicals or stable products $M^* + R \rightarrow$ radicals or stable products; (b) the products of bimolecular reaction do not react with either M or M^* , and (c) only the triplet state of the photo-excited molecule participates in the reaction though the reaction via singlet state is also possible.

The deactivation of the photo-excited molecules via photophysical and photochemical processes on the above assumptions involve the following steps:

Process	Representation	Rate
Rate excitation	$S_0(M) + h\nu_0 \rightarrow S_1(M^*)$	k_{abs}
Internal conversion	$S_1 \rightsquigarrow S_0$	$k_{ic}[S_1]$
Fluorescence	$S_1 \rightarrow S_0 + h\nu_f$	$k_f[S_1]$
Intersystem crossing	$S_1 \rightsquigarrow T_1$	$k_{isc}[S_1]$
Phosphorescence	$T_1 \rightarrow S_0 + h\nu_p$	$k_p[T_1]$
Intersystem crossing	$T_1 \rightsquigarrow S_0$	$k'_{isc}[T_1]$
Chemical reaction	$T_1(M^*) + R \rightsquigarrow$ radical or Stable products	$k_r[T_1][R]$
Energy transfer (quenching)	$T_1(M^*) + S_0(A) \cdots \rightarrow S_0(M) + T_1(A)$	$k_e[T_1][A]$

where k_r denotes the rate constant for the chemical-reaction steps.

The last step in the above scheme is due to the impurities present in the system or added energy-transfer acceptor A ; the acceptor quenches the T_1 state of M . The energy state T_1 of the acceptor should be below that of the T_1 state of the photoexcited reactant. Consequently, the rate constant k_e for the triplet–triplet energy transfer will be equal to the diffusion- controlled rate constant, whose value can be calculated from Eq. (5.176).

Applying the steady-state hypothesis to the T_1 state of M , we obtain

$$k_{isc}[S_1] = k_p[T_1] + k'_{isc}[T_1] + k_r[R][T_1] + k_e[A][T_1] \quad (5.183)$$

Rearrangement of Eq. (5.183) yields:

$$[T_1] = \frac{k_{isc}[S_1]}{k_p + k'_{isc} + k_r[R] + k_e[A]} \quad (5.184)$$

The expression for the quantum yield of the chemical reaction of M^* in the triplet state with the reactant R is

$$\varphi = \frac{k_r [T_1] [R]}{k_{\text{abs}}} \quad (5.185)$$

Eliminating $[T_1]$ from Eqs (5.184) and (5.185) and rearranging the resultant equation, we get

$$\frac{1}{\varphi} = \frac{k_{\text{abs}}}{k_{\text{isc}} [S_1]} \left[1 + \frac{k_d}{k_r [R]} + \frac{k_e [A]}{k_r [R]} \right] \quad (5.186)$$

where, $k_d = k_p + k'_{\text{isc}}$

In the absence of acceptor A , Eq. (5.186) reduces to

$$\frac{1}{\varphi^0} = \frac{k_{\text{abs}}}{k_{\text{isc}} [S_1]} \left[1 + \frac{k_d}{k_r [R]} \right] \quad (5.187)$$

Combining Eqs (5.186) and (5.187), we get

$$\frac{\varphi^0}{\varphi} = 1 + \frac{k_e [A]}{k_d + k_r [R]} \quad (5.188)$$

Now, the lifetime of the T_1 state of M is equal to the reciprocal of the sum of the rates of the processes involved in the deactivation of T_1 state. In the absence of a quencher, the lifetime of the triplet state, i.e. T_1 , is given by

$$\tau = \frac{1}{k_d + k_r [R]} \quad (5.189a)$$

or

$$\frac{1}{\tau} = k_d + k_r [R] \quad (5.189b)$$

Combining Eqs (5.188) and (5.189b), we get

$$\frac{\varphi^0}{\varphi} = 1 + k_e \tau [A] \quad (5.190)$$

Equation (5.190) shows that the plot of measured ratio of quantum yields $\frac{\varphi^0}{\varphi}$ of the reaction in the absence and presence of a quencher against concentration of the quencher and a fixed concentration of R should be a straight line with a slope equal to $k_e \tau$. The value of τ at different concentrations of acceptor can be obtained provided k_e is known. Similarly, we can calculate the value of τ at various fixed concentrations of R . Now, once the values of τ are obtained at different concentrations of the reactant R , we can obtain the value of rate constants k_r and k_d by making use of Eq. (5.189 b). The slope of the plot between the reciprocal of the lifetime τ of the T_1 state and the concentration of the reactant will be equal to k_r and the intercept of the plot will give the value of k_d . The rate constants for the photoreaction of thymine using cis-1,3-pentadiene as an acceptor are $k_e (T_1 - S_0) = 1.1 \times 10^{10} \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$, $k_d (T_1 - S_0) = 2.2 \times 10^5 \text{ s}^{-1}$, and $k_r (T_1)$ reaction with thymine (S_0) to give dimeric product = $7 \times 10^8 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$.

Further, the kinetic of photochemical reactions aids in determining the concentration of substances using the method of chemical/kinetic method of analysis. In this method, a pseudo first-order condition is accomplished by adding excess amount of all reactants except the one to be assayed. The rate of the reaction is measured as a function of the concentration of the substance under examination. Fluorescence is one of the most sensitive indicators of reaction rates of photochemical reactions. One can measure the initial rate of change of fluorescence of the reactant or product or the time taken to reach a particular fluorescence level or the fluorescence after a preset time interval. Any one of these can be used in the assay of the reactant.

5.24.12 Fluorescence Quenching

The decrease in the intensity of fluorescence due to specific effects of constituents of the solution under study is called *quenching*. Quenching occurs due to the partial absorption of the fluorescence light by some component of the solution. When the fluorescent substance itself absorbs the fluorescent light, the phenomenon is called

self-quenching. Quenching results due to the transfer of energy from the activated molecules of the fluorescent substance to the solvent or other solutes present in the solution by the collision process and subsequently, the activated molecules relax to the ground state simultaneously, both by the nonradiative mechanism and emission process. Temperature affects quenching. The higher the temperature, the larger will be the number of collisions between the fluorescent and quenching molecules and hence larger will be quenching. The fluorescence is also quenched when the wavelength of the exciting light exceeds a certain value. The study of the effect of quencher concentration provides valuable information regarding the rates of photochemical processes in solution.

The intensity of fluorescence from an excited state is proportional to the population, i.e. concentration of the molecules in that excited state.

$$I_f = k_f[A^*] \quad (5.191)$$

where k_f the specific rate constant for fluorescence decay from an excited state and A^* is the concentration of the activated molecules in that excited state.

Rate of formation of the excited state

$$A^* = k_{abs} \quad (5.192)$$

The excited state relaxes to the ground state simultaneously by both the radiative decay and transfer of energy to the quencher. Therefore,

$$\text{Rate of loss of } A^* = k_f[A^*] + k_q[A^*][Q] \quad (5.193)$$

where k_q is the specific rate constant for the decay of A^* by the quenching process. In the steady state,

$$k_{abs} = k_f[A^*] + k_q[A^*][Q] \quad (5.194)$$

Rearrangement of this equation yields

$$[A^*] = \frac{k_{abs}}{k_f + k_q[Q]} \quad (5.195)$$

The fluorescence intensity I_f , is then expressed as

$$I_f = k_f[A^*] = \frac{k_f k_{abs}}{k_f + k_q[Q]} \quad (5.196)$$

The inverse form of this equation is called the Stern–Volmer equation, i.e.

$$\frac{1}{I_f} = \frac{1}{k_{abs}} + \left[\frac{k_q}{k_{abs}k_f} \right][Q] \quad (5.197)$$

The inverse form is useful to determine the constants involved in the equation and is similar to Eq. (5.173).

The plot of $\frac{1}{I_f}$ versus $[Q]$ will yield a straight line with slope $= \frac{k_q}{k_{abs}k_f}$ and intercept $= \frac{1}{k_{abs}}$. From the slope and intercept, we can obtain the values of (k_q/k_f) and k_{abs} . In order to determine the values of k_q and k_f rather than their ratio, a second set of experiments is performed. The excitation source is switched off and the fluorescence decay to zero is measured as a function of Q . The fluorescence decay is exponential and is governed by Eq. (5.145a).

$$I_f = I_{f_0} e^{-t/\tau}$$

where I_f and I_{f_0} are the fluorescence intensities at times $t = t$ and $t = 0$, respectively and τ is the time constant of fluorescence.

Rate of loss of

$$A^* = k_f[A^*] + k_q[A^*][Q]$$

or

$$\frac{[A^*]}{\tau} = k_f[A^*] + k_q[A^*][Q]$$

or finally,

$$\frac{1}{\tau} = k_f + k_q[Q] \quad (5.198)$$

Thus, the fluorescence lifetime τ of the process depends on concentration of quencher. From the slope and intercept of the graph of $1/\tau$ against $[Q]$, we can determine the values of k_q and k_f respectively.

Note that unlike fluorescence, the general expression of an exponential form for the decay of phosphorescence is a complicated one. However, the phosphorescence decay of ZnS phosphor is governed by the hyperbolic law in its simplest form $I_p = At^{-\alpha}$ (5.199). The value of α varies from 1.0 to 1.7 and t is the time of decay, I_p is the intensity of phosphorescence and A is a constant. The values of α and A are determined from the plot of $\ln I_p$ against $\ln t$. Slope of the line will be equal to α while its intercept will be equal to $\ln A$.

Problem 5.60: The luminescence (fluorescence) of a solution of a plant pigment activated by 330 nm has been studied in the presence of a quencher, and the following results are obtained.

$[Q], (\text{mmole lit}^{-1})$	0.5	1.0	1.5	2.0
$\frac{I_f}{I_{\text{abs}}}$	0.15	0.09	0.06	0.05

In the second series of experiments, the excitation source is switched off, and the data pertaining to the fluorescence decay is indicated below:

$[Q] (\text{mmole lit}^{-1})$	0.5	1.0	1.5	2.0
$\tau, (\text{n s})$	38	22.5	16	12.5

Determine the quenching rate constant and the half-life of the fluorescence.

Solution Draw a graph between (I/I_f) and Q . The intercept of the graph will give the value of I/k_{abs} whereas the slope will be equal to $k_q/k_{\text{abs}}k_f$. From the slope and intercept, the value of k_q/k_f can be determined. The value of k_q/k_f can also be determined from the plot of k_{abs}/I_f versus $[Q]$. Here slope of the graph equals to k_q/k_f .

In order to determine k_q , draw a graph between $1/\tau$ and Q . The slope of the resultant curve equals k_q and the intercept equals $k_f \tau_{1/2}$ will then be equal to $\ln 2/k_f$. The value of k_f comes out to be equal to $9.2 \times 10^9 \text{ lit mole}^{-1} \text{ s}^{-1}$ and that of $\tau_{1/2}$ comes out to be equal to $1.9 \times 10^{-7} \text{ s}$.

Problem 5.61: The decay of fluorescence of a dye activated by radiation of wavelength 350 nm fits well into the equation $1/\tau = 2.1 \times 10^6 + 8.9 \times 10^6 [Q]$ provided Q is expressed in mmole lit^{-1} and τ in s. What might be the value of τ and $\tau_{1/2}$ for $Q = 3.5 \text{ mmole lit}^{-1}$?

Solution Substituting the value of $Q = 3.5 \text{ mmole lit}^{-1}$ into the equation given in the problem, we obtain

$$\frac{1}{\tau} = (2.1 \times 10^6 + 8.9 \times 10^6 \times 3.5) \text{ s}^{-1}$$

$$= 10^6 (2.1 + 31.1) \text{ s}^{-1} = 33.2 \times 10^6 \text{ s}^{-1}.$$

or
$$\tau = \frac{1}{33.2 \times 10^6 \text{ s}^{-1}} = 30 \times 10^{-9} \text{ s} = 30 \text{ ns}.$$

and
$$\tau_{1/2} = \frac{\ln 2}{2.1 \times 10^6 (\text{s}^{-1})} = \frac{0.693}{2.1 \times 10^6 (\text{s}^{-1})} = 3.3 \times 10^{-7} \text{ s}$$

Problem 5.62: Which of the answers given characterises correctly the phenomenon of fluorescence quenching?

- Quenching in the presence of a foreign substance is attributed to the fact that a foreign substance emits fluorescence, the fluorescence of the unknown substance becomes increasingly weak.
- The fluorescence is quenched when the wavelength of the exciting light exceeds a certain value.
- The fluorescence is always quenched as pH of the solution increases.
- The quenching of fluorescence by foreign substances (particularly by oxygen of air) is associated with the interaction of these substances with a fluorescing substance, which results in the formation of a nonfluorescing product.
- The fluorescence is quenched when the temperature falls abruptly.
- The fluorescence is quenched by foreign substances because they change the ionic strength of the solution.

- (g) The presence of impurities results in the fluorescence being quenched and therefore, they must be removed from the solution.
- (h) The fluorescence is quenched as the concentration of the fluorescent substance exceeds a certain value.
[Ans: (b), (d), (h)]

Problem 5.63: The slow reaction of oxidation of lucigenin by hydrogen peroxide is accompanied by a decrease in the luminescence of lucigenin and is catalysed by osmium. The luminescence of standard solution amounts to 25 arbitrary units after the following time intervals.

C_{os} $\mu\text{g/mL}$	0.5	1.0	1.5	2.0	2.5	3.0
t , min	11.2	6.25	3.55	2.7	2.17	1.83

Determine the concentration of osmium in the solution if the value of 25 arbitrary units is reached for 4.416 minutes.

Solution The equation for slow reactions is

$$\frac{1}{t} = \left(\frac{k}{C} \right) C_{os} \quad (5.199)$$

Calculate the value of $1/t$ from the above data and plot a graph of $1/t$ versus C_{os} . From the resultant graph, the value of C_{os} corresponding to $t = 4.416$ min, $1/t = 0.226$ comes out to be equal to $1.20 \mu\text{g/mL}$.

5.24.13 Applications of Fluorescence and Phosphorescence

Fluorescence and phosphorescence spectrometry is used for the analysis of agrochemicals, biochemicals, pharmaceuticals, petrochemicals, air pollutants, etc., *in vivo* and *in vitro*. Keeping in view the various factors affecting fluorescence and phosphorescence, one can devise fluoremetric and phosphoremetric methods of analysis. The shift in the spectrum is important for analytical work since one measures the intensity at one particular wavelength corresponding to the peak of the spectrum. Depending on the solvent, this wavelength will differ. Some of the methods are described below.

• **Direct Method of Analysis** This method is applied when the natural luminescent varies linearly with the concentration of the analyte. The concentration of the analyte in the unknown sample is read off from the standard graph between luminescent intensity and concentration of the analyte.

• **Fluorescence-Increment Method** This is just the extension of direct fluoremetric method. In this method, the fluorescence of a portion of the standard is measured in the same solution with the unknown. This method enables one to make sure that any impurities have the same effect upon the standard and the unknown. Moreover, this method is especially useful when minute quantities of the sample are to be assayed from the crude sample. For example, the amount of uranium in a uranium ore and riboflavin in foodstuff, etc., can be assayed by this method.

• **Quenching Method** The substances which quench the natural fluorescence/quench fluorescence and subsequently enhance phosphorescence can be analysed by measuring the intensity of fluorescence/ phosphorescence light as a function of concentration of the quencher. Quenching may or may not vary linearly with the concentration of the quencher.

• **Kinetic Method of Analysis** This method has been described in detail in section (5.20.4.h). In this method, the rate of fluorescent of reactant or of product of photochemical reaction as the case may be is measured as a function of the concentration of the analyte under examination.

Applications of fluorescence and phosphorescence are described here under two subtitles, viz. nonbiological and biological applications. However, there may be some ambiguity in applications under these subtitles.

(a) Nonbiological Applications Aromatic hydrocarbons, individually as well as in a mixture, and heterocyclics are analysed by direct method of fluoremetry. Perylene can be determined in a mixture containing 3,4-benzopyrene and tetracene as major components by using heavy atom. In methyl iodide, the fluorescence of the latter components is quenched. 3,4-benzopyrene has been analysed in smoked food, beer, cigarette smoke, etc. Usually, chromatography, in conjunction with fluoremetry, is used in such studies.

Direct fluoremetric analysis has been applied to optical brighteners, i.e. fluorescence dyes, paints and glasses. These absorb in the near ultraviolet at around 350 nm and fluoresce in the violet–blue region. To avoid photochemical degradation, freshly prepared solutions should be kept in dark until the actual analysis is to be made.

Biological important substances showing natural fluorescence, e.g. vitamin A, riboflavin (vitamin B₂), drugs such as quinine and porphyrin and plant pigments are analysed by the direct fluoremetric method. Riboflavin in foodstuff such as poultry feed can be estimated by dithionite method. These results are calculated according to the following scheme:

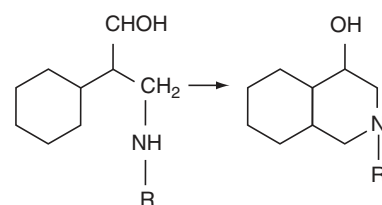
Solution	Designation
10 mL of oxidised sample + 1 mL water sample (acid extract is oxidised with KMnO ₄)	A
10 mL of oxidised sample + 1 mL water sample (acid extract is oxidised with KMnO ₄) + solid sodium dithionite (reducing agent).	B
10 mL of oxidised sample + 1 mL water sample (acid extract is oxidised with KMnO ₄) + 1 mL standard	C

Thus,

$$\frac{I_B^f - I_A^f}{I_C^f - I_A^f} = \frac{m_s}{m_s + m_{std}} \quad (5.200)$$

where m_s and m_{std} are the masses of riboflavin in the sample and standard in the cell.

Nonfluorescent biological substances, namely thiamine, can be assayed by converting to fluorescent product. Thiamine is commonly assayed by the blue fluorescence of its oxidation product, thiochrome. Even thiamine can be determined in pork and other food products. The sample is treated with phosphatase, an enzyme, which causes hydrolysis of the phosphate esters of thiamine which are frequently present in food materials.



Epinephrine, R=CH₃ (fluorescent)

(I) Norepinephrine, R = H

Amino acids containing aromatic systems are fluorescent, viz., tryptophan, tyrosine and phenylalanine. Even these absorb below 300 nm, the region which excites other compounds occurring in hydrolysates. A chemical method for tyrosine (reaction with α -nitroso β -naphthol in the presence of nitric acid and nitrous acid) gives a fluorescent product that can be excited in the visible region at 460 nm.

Simultaneous determination of epinephrine and norepinephrine can be carried out by converting to trihydroxy indole.

Epinephrine, R= CH₃ (fluorescent)

Norepinephrine, R = H (I)

Both amines react at pH 6.5 but only epinephrine reacts at pH 3.5. Thus, by carrying out the fluoremetric analysis at pH 3.5, one can determine the amount of epinephrine in the mixture.

Acetyl salicylic acid in the concentration range 0 to 50 mg lit⁻¹ can be determined by direct fluoremetric method using 280 nm excitation and emission at 335 nm.

Acrolein and related compounds are nonfluorescent but they react with m-aminophenol to give fluorescent 7-hydroxy quinoline derivative. The derivative, on excitation at 400 nm, emits fluorescence at 510 nm. Concentration of acrolein of the order of 10⁻⁵ mole/mL can be determined.

We know that a number of substances quench the fluorescence of the substances. Thus, the quenchers can be assayed by the quenching method, Some of the fluorescer-quencher systems are listed here:

Fluorescer	Quencher
Eosin	Iodide ion
Dyes	Oxygen
3,4-benzopyrene	Ozone
Rhodamine B	Flavanones
Anthranilic acid	Glucose
4, 4'-diamino-2,2'- disulphostilbene-N-N'-N' tetra acetic acid	Iron (of the order of 10 ⁻⁷ mg/mL)

Cyanide can be determined by the kinetic method of analysis. The quinones are nonfluorescent, but can be converted to highly fluorescent cyanohydroquinones upon reaction. The rate of production of fluorescence with time is measured and is proportional to the concentration of cyanide.

As has already been stated, compounds which show phosphorescence are also likely to show fluorescence. So, a phosphorescence meter must be able to differentiate between the two. This is achieved using a rotating shutter such that a definite time lag is introduced between the times during which the sample is excited and observed (See Fig. 5.93). Phosphorescence is invariably weak and it has to be observed at low temperature ($= 77\text{ K}$). Analytical curves are plotted between phosphorescence intensity and concentration of standard solution of analytes. The standard curves are linear over a 10^4 fold concentration range. Negative deviation from straight-line behaviour results in the 10^{-4} molar and higher concentration range due to self-absorption, molecular association and concentration quenching. Positive curvature near the minimum detectable concentration ($\sim 10^{-9}$ molar) is generally a result of contaminant luminescence. The contaminants could be detergents used for cleansing glassware, stopcock grease, filter paper, ion-exchange resins, chromatic materials and plastic containers. Phosphorescence being a long-lived phenomenon ($> 10^{-5}\text{ s}$), it can be used to analyse a mixture where components have varying decay times. By adjusting the phosphorescence, one can eliminate one or more components of the mixture.

(b) Biological Applications Spectrofluorimetry has made deep inroads into the fields of biochemistry, biology and medicine. Many biological molecules such as aromatic amino acids (i.e. acids containing tyrosine and tryptophan residues), proteins, vitamins, coenzymes, purines and oestrogens are fluorescent under normal physiological conditions. A wide variety of biologically important components sometimes fluoresce at shorter wavelengths, so the best methods for analyses of biological compounds are based on the natural fluorescence which generally occurs at longer wavelengths and is not interfered by many of the other compounds present in biological material. For example, natural methods are used for vitamin A, riboflavin, drugs such as quinine, and porphyrin and plant pigments. Nonfluorescent biological materials can be assayed by chemical method of analysis in which one has to choose a substance which fluoresces or yields a fluorescent product of reaction. The other methods used in the study of biological compounds are based on fluorescent probes, fluorescent quenchers, etc. Some of the typical biological applications of fluorescence are the following:

(i) Determination of Concentration of Nonfluorescent Enzymes Nonfluorescent enzymes also catalyse the photochemical reactions. So, they can be assayed by the kinetic method of analysis. One has to select a substance which fluoresces or gives a fluorescent product of reaction. The time taken to reach a particular level of fluorescence is then measured at different concentrations of the enzyme. Thus, based on the equation,

$$\frac{1}{t} = \left(\frac{k}{C} \right) C_{\text{enzyme}} \quad (5.201)$$

One can draw a standard curve between $1/t$ and concentration of the enzyme. Now, the time taken to reach a specified value of fluorescence in the presence of the enzyme sample to be assayed is measured and using the standard graph, one can determine the amount of enzyme in the unknown sample. For example, lipase can be assayed by this method, since it catalyses the hydrolysis of the esters of fluorescein.

(ii) Drug Interaction The native fluorescence of biological substances is often profoundly modified by drug molecules. The modification and degree of modification can thus, be fixed as criterion to accomplish binding and extent of binding respectively of drug to biological molecules. For example, the natural fluorescence of Bovine Serum Albumin (BSA) is quenched by androstane and other steroids. Since the absorption spectra of these steroids do not overlap the fluorescence emission spectrum of BSA, it is inferred that fluorescence quenching results from a change in protein conformation (but not because of energy transfer from BSA to steroid) due to BSA–steroid binding. The tryptophan fluorescence of Human Serum Albumin (HSA) excited by 290 nm (bandwidth = 12 nm) is observed at 335 nm (bandwidth = 12 nm). The tryptophan emission band overlaps extensively the absorption maximum ($\sim 365\text{ nm}$) of 4-butyl-1- (p-nitrophenyl) -2- phenyl-3,5-pyrazolidinedione, an analog of antiinflammatory drug phenylbutazone. This overlap permits the resonance transfer of energy from the excited tryptophan residue of HSA to the bound phenylbutazone analog and results in a quenching of native protein fluorescence. The point of inflexion in the titration curve of the intensity of fluorescence monitored at 335 nm while exciting at 290 nm against drug/HSA is observed at a molar ratio of one, indicating that energy transfer occurs at only one protein-binding site. The association constant for this interaction has been found to be $5 \times 10^5\text{ mole lit}^{-1}$.

The intrinsic fluorescence of certain drug molecules may be modified by binding to proteins, DNA, RNA. As an example, the fluorescent quantum yield of N, N, -dimethyl-1-naphthalene-5-sulphonamide (DNSA) increases

17-fold on binding to bovine erythrocyte carbonic anhydrase. At the same time, the drug fluorescence emission spectrum shows a large shift to shorter wavelengths. This suggests that DNSA is bound to a hydrophobic region of carbonic anhydrase.

The binding of nonfluorescent drugs to macromolecules can be studied by means of fluorescent probes such as dansylglycine (DSG). Note that DSG is weakly fluorescent in water but its fluorescence maximum shifts towards the blue and its quantum yield increases markedly in solvents of low dielectric constants, such as dioxane. Since similar changes have been observed when DSG binds to BSA, it is suggested that dansyl-amino acids can be used as probes for the hydrophobic regions of proteins. The interaction of nonfluorescent anionic drugs (phenylbutazone, dicumarol, flufenamic acid) to serum albumin has been established by measuring their ability to completely displace DSG. Similarly, the displacement of fluorescent drug warfarin by nonfluorescent dicumarol has been monitored by measuring the resultant decrease in warfarin fluorescence.

In addition, the technique of fluorescence polarisation can also be used to study protein–drug interaction. This technique is only applicable to drug molecules which are highly fluorescent before and after binding to the macromolecule, e.g. the interaction of chlorpromazine with horseshoe crab myosin B.

(iii) Conformational Equilibria in Biological Macromolecules The conformational equilibria in macromolecules can be studied by pulsed fluorescence measurements. The information regarding the conformational states can be deduced from the changes in the lifetime of excited states of the fluorescent probe placed at a strategic position in the structure of the carrier molecule. When the isomers T_1 and T_2 of the structure T affect the lifetime of the probe differently, one can detect the presence of these two conformations by a pulsed fluorescence relaxation spectrometer. The fluorescence emission of probe excited by a short pulse of light will decay exponentially to the ground state after the light pulse has vanished; for each conformation with a different time constant. For the equilibrium,

$T_1 \xrightleftharpoons{\text{fast}} T_2$, the observed total fluorescence intensity $I^m(t)$ will decay as

$$I^m(t) = \sum_{i=1}^2 a_i e^{-t/\tau_i} \quad (5.202)$$

In case T is labeled at a single site, the amplitude a_i is related to the concentration of the isomer T_i by

$$a_i = \text{Constant } [T_i] \varepsilon_i k_i^e \quad (i = 1, 2) \quad (5.203)$$

where ε_i is the absorption coefficient and k_i^e is the emission rate in the absence of a quenching process. When the ratio $(\varepsilon_2 k_2^e)/(\varepsilon_1 k_1^e)$ is known, the equilibrium constant $K = [T_2]/[T_1]$ can be calculated from the ratio of amplitudes a_2/a_1 .

When ethidium (ED) – labeled tRNA^{Phe} ($\text{tRNA}^{\text{Phe}} \equiv \text{Phenylalanine-tRNA}$ from yeast $\text{tRNA}_{\text{yeast}}^{\text{Phe}}$ (Fig. 5.103) the probe is inserted between nucleotide bases) is excited with short pulse of polarised light, the intensity decay of polarised component (I_{11}^f) and of the nonpolarised component I_f^m is monitored and analysed. tRNA^{Phe} is labeled at the position 16/17 or at the position 37 by replacing the corresponding nucleotides by ethidium bromide (EB).

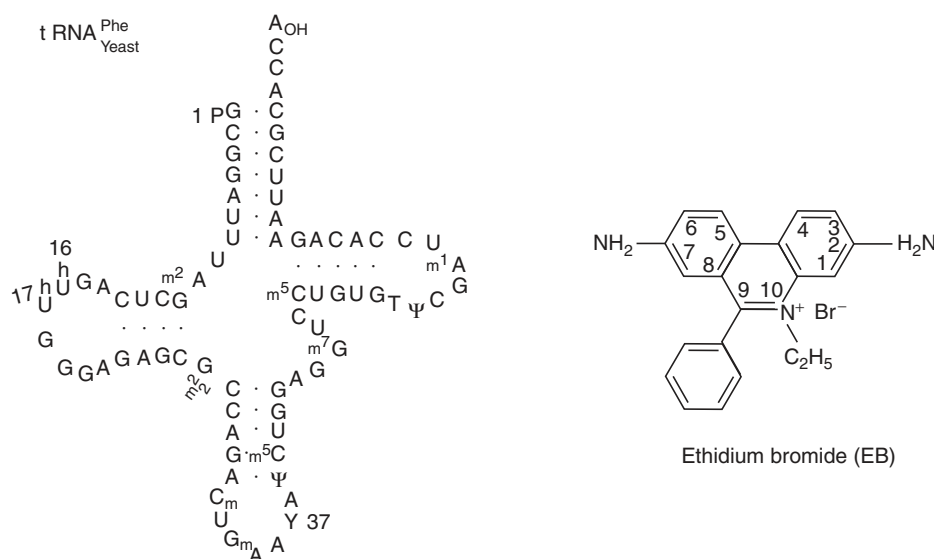


Fig. 5.103 Primary sequence of $\text{tRNA}^{\text{Phe}}_{\text{yeast}} \equiv \text{Phenylalanine-tRNA}$ from yeast.

From the derivative at the position 37 two fractions are separated by column chromatography. They are designated as tRNA^{Phe}_{EB37B} and tRNA^{Phe}_{EB37C} and most probably represent isomers with respect to the amino group of *EB* which has reacted with the ribose. Note that the natural fluorophore Y base at the position 37 is replaced by the probe *EB*. The advantage of *EB* over the Y-base as a probe is that it has a longer lifetime which facilitates the analysis of the rotational motion of tRNA.

For tRNA^{Phe}_{EB37C}, the decay of I_f^m is described by at least two exponential terms.

$$I_f^m(t) = a_1 e^{-\frac{t}{\tau_1}} + a_2 e^{-\frac{t}{\tau_2}} \quad (5.204)$$

Note that the sample is excited at 510 nm and fluorescence is measured at 590 nm. The parameters have been estimated as $\tau_1 = 34$ ns, $\tau_2 = 11$ ns, $a_1 = 4.64 \times 10^{-4}$, $a_2 = 4.18 \times 10^{-4}$.

Let us now examine the effect of MgCl_2 on the amplitudes a_1 and a_2 and on the amplitude ratio a_2/a_1 of tRNA^{Phe}_{EB37C}. For MgCl_2 (in the concentration range between 0–20 m mole lit^{-1}) at 10°C, at all concentrations, the same two lifetimes τ_1 and τ_2 are found while the amplitudes corresponding to τ_1 and τ_2 varies. The amplitude ratio a_2/a_1 increases from 0.17 to about 1 when MgCl_2 concentration is increased to about 16 mmole lit^{-1} . At higher temperatures (25 and 35°C), a third term τ_3 has to be introduced in order to describe the decay of $I_f^m(t)$. The analysis of data at 35 °C show that $\tau_3 = 20$ ns while the values of τ_1 and τ_2 are the same as that at 10°C. The variation of the amplitudes a_1 and a_2 with increasing concentration of MgCl_2 are similar to that found at 10°C, the third amplitude a_3 vanishes as the concentration of MgCl_2 is increased. If the spectroscopic parameters $\epsilon_i k_i^e$ ($i = 1, 2, 3$) are the same, the amplitudes a_1, a_2, a_3 are proportional to the concentration of the three excited states of ethidium. The ‘amplitudes ratios a_2/a_1 and a_3/a_1 thus, correspond directly to the constants describing the equilibrium between three conformational states reflected by the probe. Thus, it is inferred that tRNA^{Phe} exists in three conformational states, one of which is populated to a significant degree only at elevated temperature (> 10°C) and low Mg^{2+} concentrations (<1 m mole lit^{-1}). Further, note that the same results have been found for tRNA^{Phe} labeled at position 16/17.

The existence of two different configurations of tRNA^{Phe}_{yeast} is also indicated by the analysis of the polarised component $I_{\parallel}^f(t)$. To simplify the analysis, rotating spheres (each of which is described by one rotational relaxation time) are used as models for tRNA.

Thus, for fitting $I_{\parallel}^f(t)$ at least two rotational relaxation times are required.

$$I_{\parallel}^f(t) = a_1 e^{-t/\tau_1} (1 + r_1 e^{-t/\tau_{r1}}) + a_2 e^{-t/\tau_2} (1 + r_2 e^{-t/\tau_{r2}}) \quad (5.205)$$

In this model, τ_{r1} is the rotational relaxation time of the structure T_1 with lifetime τ_1 and rotational amplitude r_1 , and τ_{r2} is the rotational relaxation time of structure T_2 with a lifetime τ_2 and rotational amplitude r_2 . $\tau_{r1} = 29$ ns; $r_1 = 0.633$ and $\tau_{r2} = 14$ ns; $r_2 = 0.680$.

The presence of two significantly different rotational relaxation times supports the interpretation that tRNA exists in two conformational states at low temperature. The large difference in τ_{r1} and τ_{r2} suggests a substantial change in the conFiguration of tRNA.

PROBLEMS

1. Sketch the Fortrat diagram for (a) $B_{v''} > B_{v'}$ and a 20 percent difference between the two. Given $B_{v''} = 10 \text{ cm}^{-1}$, $B_{v'} = 8 \text{ cm}^{-1}$. Read off the position of the band head from the Fortrat diagram and compare it with that determined theoretically. (b) $B_{v''} > B_{v'}$ and a 15 per cent difference between the two. Take $B_{v''} = 10 \text{ cm}^{-1}$ and $B_{v'} = 11.5 \text{ cm}^{-1}$. Determine the value of J corresponding to the band head.
[Ans: (a) 5 (b) 7]
2. Prove that in isotopic molecules of the type $X^{m_1} Y^{m_2}$ and $X^{m_1^*} Y^{m_2}$ (e.g. HC1 and DC1), where $m_1^* - m_1 = \Delta m$ and Δm cannot be disregarded compared to m_1 , the quantity
3. The values of w_0 and $x_0 w_0$ for the two electronic states, i.e. $^2\pi_i$ and $^2\Sigma^+$ ($^2\pi_i \leftrightarrow ^2\Sigma^+$), of the CN molecule are 1814.43 cm^{-1} , 12.883 cm^{-1} ; and 2068.705 cm^{-1} , 13.144 cm^{-1} respectively. The energy difference between the two Morse curves is 9241.66 cm^{-1} . What is the energy corresponding to $V' = 0 \rightarrow V'' = 9$ transition in cm^{-1} ?
[Ans: 9114.59 cm^{-1}]
4. The analysis of the rotational fine structure in the electronic absorption spectrum of CN molecule corresponding to the transition $^2\pi_i \leftrightarrow ^2\Sigma^+$ yields $B_0(^2\pi_i) = 1.7165 \text{ cm}^{-1}$ and $B_0(^2\Sigma^+) = 1.8996 \text{ cm}^{-1}$. Using the required data from Problem 3 and from the given data, calculate (a) the force constants for the fundamental modes of vibration of CN in the two states, (b) the energy difference between band head and null line, (c) the CN bond distances in the two

$$\rho - 1 = \frac{m_2 \Delta m}{(m_1 + m_2) \left[\sqrt{m_1 m_1^*} + m_1 \right]}$$

states, and (d) zero point energies corresponding to the two states.

[Ans: (c) 1.2328 Å, 1.1719 Å]

5. The values of w_e and x_e for the two electron states, i.e. $^2\Pi_i$ and $^2\Sigma_i^+$, $^2\Pi_i \leftrightarrow ^2\Sigma_i^+$ of CO^+ are 1562.06 cm^{-1} , 8.661×10^{-3} ; and 2214.24 cm^{-1} ; 6.848×10^{-3} respectively. The energy difference between the two Morse curves is $247.926 \text{ kJ mole}^{-1}$. What is the energy of corresponding to the $0 \rightarrow 0$ band? [Ans 20407.5 cm^{-1}]
6. The energy levels of the rotational fine structure of CO^+ molecule fit well into the expression

$$\bar{\nu}_{\text{elec-rot}} = \bar{\nu}_{00} + 3.5666m - 0.3878m^2, \text{ cm}^{-1}$$

Calculate (a) the value of band head and its frequency, (b) the separation between band head and null line of the spectrum, (c) the CO^+ bond distances in the two states of the molecule, and (d) using the data from Problem 5, find the values of dissociation energies in the two states.

[Ans: (a) 5; 20415.64 cm^{-1}
(b) 8.14 cm^{-1} , Band is red shaded
(c) 1.1150 cm^{-1} , 1.2436 cm^{-1}
(d) 10.00 eV , 5.58 eV]

7. The molar extinction coefficient of beryllium-acetylacetonate complex in chloroform is 31,600 for a wavelength of 295 nm. What is the minimum percentage content of beryllium that can be measured in a 2 g sample dissolved in 100 mL, in a cell of 5 cm path length, assuming that the minimum reading on the absorbance scale of the instrument is 0.025? The coloured compound contains a molecule of acetylacetonate per beryllium atom.

[Ans: 7.15×10^{-6} percent]

8. Calculate the dissociation constant of a reagent HR if at $\text{pH} = 7.33$ the absorbance A_{mix} equals 0.442. In an acidic medium at $\text{pH} < 2$, the absorbance A_{HR} is 0.017, and in a basic medium at $\text{pH} > 11$, the absorbance A_{R^-} is 0.705. [Ans: 7.54×10^{-8}]

9. Calculate the contents of copper, cobalt and nickel in a mixture from the light absorption by their diethyldithiocarbamate complexes (DDC) in chloroform at 436, 367 and 328 nm. The absorbance of the chloroform solution of mixture of the ions to be determined as measured in a cell of 1 cm path length are as follows: $A_{436} = 0.45$, $A_{367} = 0.36$; and $A_{328} = 0.86$. The volume of solution analysed spectrophotometrically is 25 ml; the molar decadic coefficients of the complexes in chloroform are

λ (nm)	$\epsilon_{\text{Cu(DDC)}_2}$	$\epsilon_{\text{Co(DDC)}_2}$	$\epsilon_{\text{Ni(DDC)}_2}$
436	12850	2260	1720
367	1260	13340	3910
328	2230	21820	35210

[Ans: $C_{\text{Cu}} = 3.01 \times 10^{-5} \text{ mole lit}^{-1}$;
 $C_{\text{Co}} = 1.97 \times 10^{-5} \text{ mole lit}^{-1}$;
 $C_{\text{Ni}} = 1.02 \times 10^{-5} \text{ mole lit}^{-1}$]

10. The following vibrational bands have been observed in the near UV electronic absorption spectrum of isoamyl nitrite in the vapour phase: 26035, 27056, 28065, 30127, 29132,

32094, 31104 cm^{-1} . The intensity of the bands decreases as the wave number increases. Deduce and assign the frequencies corresponding to the fundamental vibration modes of isoamyl nitrite. On the basis of IR studies, the bands at 1600, 800 and 600 cm^{-1} have been assigned to N=O stretching, N—O stretching and ONO bending modes respectively.

[Ans: 0—0 band at 27056 cm^{-1}
 $\nu'(\text{C—O}) = 1021$; $\nu''(\text{C—O}) = 1009 \text{ cm}^{-1}$]

11. Fill the value of X in the following Table:

Ion or substance being determined	Reaction by which coloured compounds are formed	λ_{max} (nm)	ϵ	Path length (cm)	C	A
Al^{3+}	With oxyquinoline ArR_3	390	6700X		$2.5 \times 10^{-4} \text{ mole lit}^{-1}$	0.836
Quinoline	Intrinsic colour	275	45002.00	3	3 mg lit^{-1}	X
Azobenzene	Intrinsic colour	438	11005.00	X	X mg lit^{-1}	0.356

12. The galvanometer scale reading on a single-beam photoelectric colourimeter for a series of solutions having different concentrations are

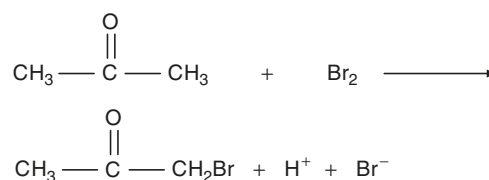
Concentration, C (mole lit^{-1})	0	C_1	C_2	C_3	C_4	C_5	C_6
Deflection	100	80	70	60	50	40	30

Calculate the absorbances corresponding to the galvanometer scale readings.

• Hint: $A = \log \frac{I_0}{I_t} = \log (\text{deflection})$

[Ans: For $C = C_1$,
 $A = 0.097$; For $C = C_6$
 $A = 0.523$]

13. Br_2 absorbs at 400 nm and it reacts with acetone. The overall reaction but not the actual molecular collisions in reaction is given by the following equation:



Only bromine molecule absorbs visible light which means that its concentration can be determined by measuring the intensity of Br_2 absorption at 400 nm. The amount of light absorbed decreases with time as Br_2 disappears. Derive the differential rate equation in terms of absorbance from which one can get information about the actual molecular processes involved.

14. When light is passed through a layer of solution of 2 cm thickness, its intensity decreases by 5 per cent. What will be the intensity of light when it is passed through a layer of the same solution having a thickness of 5 cm?

[Ans: 88 per cent of the initial value]

15. The absorbance data for various concentrations of acetone (in mg/100 mL) after applying the correction for reagent blank fits well into the equation $A = 2.285 \times 10^{-2} C$. (a) Calculate the molar extinction coefficient and specific absorptivity. (b) Calculate the concentration of acetone in the blood and urine of a normal person and a ketonic patient from the following absorption data: normal blood; $A = 0.065$, ketonic blood, $A = 0.192$, normal urine; $A = 0.095$, ketonic urine, $A = 0.200$ after $\frac{1}{40}$ dilution. The absorbance values are after the correction for the reagent blank.

Ans: (a) 1.325×10^{-2} ; $2.285 \times 10^{-2} (\text{mg}/100)^{-1} \text{ cm}^{-1}$
 (b) 2.84 and 8.40 mg/100 mL; 4.15 and 350 mg/100 mL

16. To determine the traces of copper, the reaction between H_2O_2 and ethoxyaniline is used which proceeds with the formation of coloured products and is catalysed with copper salts. The variation of absorbance of a solution with time in the presence of various amounts of copper is measured and the resultant data are given here.

Concentration of Cu (in $\mu\text{g}/\text{mL}$)	0	0.0015	0.0030	0.0050	0.0075
Absorbance after					
1 min...	0	0.05	0.09	0.11	0.17
2 min...	0.02	0.07	0.13	0.21	0.30
3 min...	0.03	0.12	0.21	0.34	0.43
4 min...	0.05	0.18	0.28	0.43	0.58
5 min...	0.04	0.19	0.36	0.53	0.76

The values of absorbance for a solution with unknown amount of copper under the same conditions are

Time (in min)	1	2	3	4	5
Absorbance	0.09	0.17	0.29	0.35	0.45

Determine the concentration of copper of the unknown solution. **[Ans: 0.0043 $\mu\text{g}/\text{mL}$]**

17. Vitamins D (D_2 —calciferol; D_3 —cholecalciferol) are fat-soluble substances which are essential constituents of human (animal) diet. They are present in fish-liver oil, butter, milk, eggs (yolk) and mushrooms. They control the assimilation of calcium and the growth of bones and teeth. Deficiency of vitamin D in a young organism causes 'rickets', i.e. softness and distortion of bones. The absorbance of 3.296×10^{-5} mole/lit calciferol in alcohol at 264 nm is 0.6. The molecular mass of calciferol is 396 ($\text{C}_{28}\text{H}_{44}\text{O}$) and $l = 1$ cm. (a) Calculate the molar extinction coefficient, and (b) determine the per cent content of calciferol in the commercial sample if 2 mg of the sample dissolved in 100 mL of alcohol shows an absorbance of 0.8 at $\lambda_{\text{max}} = 264$ nm. **[Ans: (a) $\epsilon_{\text{max}} = 18203$ (b) 87 per cent]**

18. Determine the pK_a of (a) p-nitrophenol, and (b) papaverine (cation form) from the following data.

p-nitrophenol $\epsilon_{\text{max}} \times 10^{-3}$			Papaverine $\epsilon_{\text{max}} \times 10^{-4}$		
pH	317 nm	407 nm	pH	239 nm	251 nm
4.0	9.72	0.33	2.0	3.36	5.90
7.0	5.55	9.16	6.4	4.86	3.71
10.0	1.39	18.33	12.0	6.44	1.56

[Ans: (a) $\text{pK}_a = 6.99$; (b) $\text{pK}_a = 6.44$]

19. From Fig. 5.64 given in the text, choose the correct graph of spectrophotometric titration for the cases listed below: The symbol X represents the unknown substance, T is the titrant, and P is the resultant product.

- X and P are coloured and T is colourless.
- T and P are coloured and X is colourless.
- X and T are coloured and P is colourless.
- T and P are colourless and X is coloured.
- X and P are colourless and T is coloured.
- T and X are colourless and P is coloured.

[Ans: (a) 3 (b) 7 (c) 4 (d) 9 (e) 2 (f) 1]

20. A certain volume of solution containing a mixture of amines having different absorption bands, i.e. aniline and 2-naphthylamine, is titrated with acetic anhydride at the absorption maximum of the latter which has a slower rate of acetylation. Calculate the volume of acetic anhydride consumed in reaching the each end point if the values of A_1 and A_2 after the first point of equivalence corresponding to the volumes of added titrant $V_1 = 1.20$ and $V_2 = 1.40$ mL are known to be equal to 0.36 and 0.275 respectively. The absorbances of the solution, A' and A'' , before the second end point corresponding to volumes of titrant $V_1 = 1.60$ and $V_2 = 3.0$ are equal to 0.19 and 0.04 respectively. The constant value of absorbance A_0 reached at the end of titration is 0.035 while it is 0.46 before the first end point.

[Ans: Aniline: 0.96 mL, 2-naphthylamine: 1.95 mL]

21. A mixture of sodium acetate and o-chloroaniline, 10 mL each in glacial acetic acid, is titrated with 0.1010 M HClO_4 solution at 312 nm. Sodium acetate does not absorb in UV region but is a stronger base than o-chloroaniline. Calculate the original aliquots of sodium acetate and of o-chloroaniline if the values of A_1 , A_2 and A_3 after the first end point corresponding to the volumes of added titrant $V_1 = 4.0$, $V_2 = 6.0$ and $V_3 = 7.0$ mL are known to be equal to 0.67, 0.63, and 0.56 respectively. The constant value of absorbance A_0 before this end point is 0.68.

The absorbances of solutions A' , A'' and A''' before the second end point corresponding to volumes of titrant $V_1 = 8.5$, $V_2 = 9.0$ and $V_3 = 9.5$ mL are equal to 0.32, 0.20 and 0.09 respectively. The value of A_0 reached at the end point of titration is 0.02.

[Ans: Sodium acetate = 0.0681 mole lit^{-1} ; o-chloroaniline = 0.0313 mole lit^{-1}]

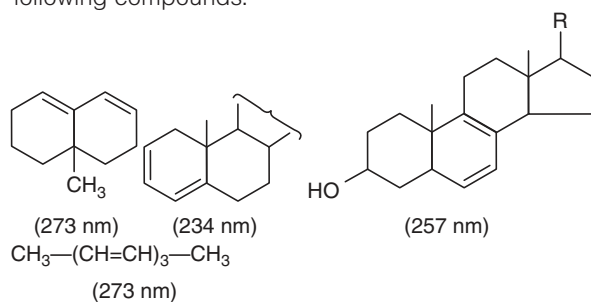
22. Cholesterol is a sterol ($\text{C}_{27}\text{H}_{46}\text{O}$; molecular mass = 386.67) found in animal tissues and brain tissue contains up to 7 per cent (on the dry basis) of cholesterol. The deposition of cholesterol in the blood vessels is considered to be responsible for atherosclerosis. Cholesterol or any related sterol solution in chloroform when treated with acetic anhydride: H_2SO_4 (30 : 1) yields the corresponding bluish green ester which shows an absorption maximum at 625 nm. To plot a calibration curve for the determination of cholesterol colourimetrically, 12.5 mg of cholesterol was dissolved in 100 mL of chloroform. Four standard solutions of different concentrations (60–250 μg per mL) were prepared. These samples were mixed with reagents in appropriate amounts; the final volume was made up to 4 mL with chloroform indicated below. The solutions were allowed to stand for 15 minutes. After these, the following readings were obtained on an absorption spectrophotometer with respect to the blank, i.e. 2 mL chloroform + 2 mL acetic anhydride: H_2SO_4 (30 : 1).

Volume of standard cholesterol solution (12.5 mg/10 mL)	0.5	1.0	1.5	2.0
Concentration of standard cholesterol (in μg)	62.5	125	187.5	250
Volume of chloroform added (in mL).	1.5	1.0	0.5	0.0
Volume of acetic anhydride: H_2SO_4 (30: 1)	2.0	2.0	2.0	2.0
Absorbance at 625 nm.	0.17	0.34	0.51	0.68

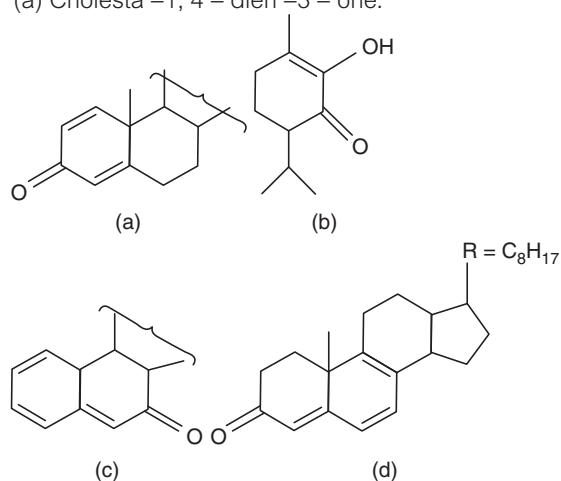
To 0.2 mL of blood serum sample was added 10 mL of alcohol: acetone (1 : 1) and the solution was boiled for 15 minutes. The solution was filtered and the residues were dissolved in 5 mL of chloroform. The absorbance of 1 mL of unknown solution measured under same conditions was 0.25. (a) Draw the calibration graph. (b) Determine the amount of cholesterol in mg per 100 mL of the serum sample.

[Ans: 202.5 mg per 100 mL. Literature value: 150–240 mg per 100 mL]

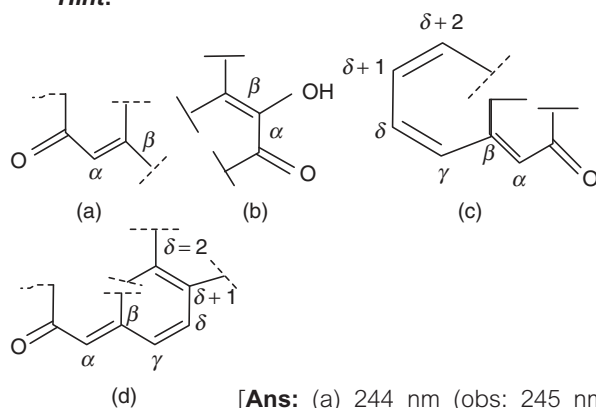
23. Identify theoretically the absorption maximum in the following compounds.



24. Calculate λ_{max} for the following compounds in ethanol
(a) Cholesta-1, 4 - dien -3 - one.



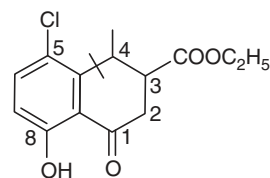
• Hint:



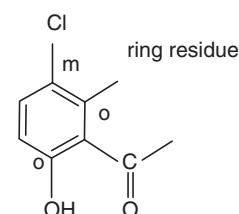
[Ans: (a) 244 nm (obs: 245 nm),
(b) 274 nm (obs: 270 nm)
(c) 349 nm (obs: 348 nm), (d) 385 nm]

25. By making use of the data reported in Table 5.28, determine the value of absorption maximum for

(a) 3-carbethoxy-4-methyl-5-chloro-8-hydroxytetralone,



• Hint:

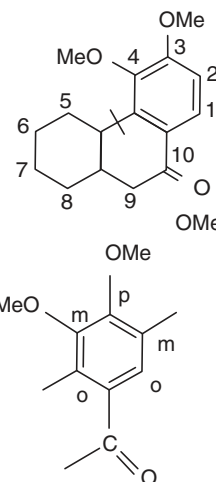


m-Cl, o-ring residue and o-OH,

[Ans: 256 nm (obs: 257 nm)]

(b) 3, 4-dimethoxy-4 b, 5, 6, 7, 8, 8 (a), 9, 10-octahydrophenanthren-10-one

• Hint:



p-OMe, m-OMe, o-ring residue,

[Ans: 281 nm (obs: 278 nm)]

(c) 4-hydroxy-3-methoxy benzaldehyde. [Ans: 282 nm, (obs: 279 nm; log ϵ = 4.01)]

26. Just like DNA, ribonucleic acid (RNA) is also present in animal and plant cell plasma. When RNA is treated with concentrated HCl, D-ribose, a pentose sugar present in it gets converted into furfural which reacts with orcinol reagent to give a blue-coloured complex. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the reagent acts as a catalyst. The blue-coloured complex shows an absorption maximum at 665 nm. To plot a calibration curve for the determination of RNA, 10 mg of RNA was dissolved in 100 mL of 98 per cent ethanol. Four standard solutions of varying concentrations (10–25 μg) were prepared. Appropriate amounts of reagents, i.e. orcinol reagent (3.5 mL of orcinol (6 per cent) in alcohol and 100 mL of 0.1 per cent ferric chloride in concentrated HCl) were added to these solutions, and the final volume was made up to 4 mL with ethanol indicated below. The solutions were heated in a water bath for 15–20 minutes. After these, the following readings were obtained on an

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absorption spectrophotometer with respect to blank, i.e. 1 mL ethanol + 3 mL orcinol reagent.

Volume of standard RNA solution (10 mg/100 mL)	0.2	0.3	0.4	0.5
Concentration of standard RNA (in μg)	10	15	20	25
Volume of alcohol added (in mL)	0.8	0.7	0.6	0.5
Volume of orcinol reagent added (in mL)	3.0	3.0	3.0	3.0
Heated the solutions for 15–20 minutes				
Absorbance at $\lambda_{\text{max}} = 665 \text{ nm}$	0.07	0.11	0.15	0.19

Total yeast RNA was obtained by extracting the whole cell with 90 per cent phenol. The turbid suspension was centrifuged and supernatant was taken in a separating funnel. The upper aqueous layer containing RNA was used for analysis while the lower layer containing DNA was disregarded. The absorbance of 0.5 mL of RNA extract measured under the same conditions was 0.37. What will be the amount of RNA in 100 mL of the extract?

[Ans: 10.6 mg/100 mL]

27. L-amino acid, when boiled with ninhydrin reagent solution, yields a bluish purple product which has an absorption maximum at 570 nm. In case of proline, a different product having yellow colour is formed. Asparagine, which has a free amide group, reacts with ninhydrin to give a brown-coloured product. The intensity of the bluish purple colour depends upon the amount of proline and asparagine in the system. To plot a calibration curve for the determination of amino acids, 10 mg of glycine in the present case (or leucine) was dissolved in 100 mL of H_2O . Four standard solutions of varying concentrations (20–160 μg) were prepared. Appropriate amounts of reagents were added to these solutions, and the final volume was made up to 5 mL with 0.5 M sodium citrate buffer (14.5 mL citric acid + 35.5 mL 0.5 M sodium citrate), indicated below. The solutions were heated in a boiling water bath for 10–15 minutes and allowed to cool. After these, the following readings were obtained on an absorption spectrophotometer with respect to blank, i.e. 3.8 mL ninhydrin + 1.2 mL buffer.

Volume of standard glycine solution (10 mg/100 mL)	0.1	0.2	0.4	0.6	0.8
Concentration of glycine (in μg)	20	40	80	120	160
Volume of ninhydrin (1 per cent ninhydrin in 0.5 M solution of sodium citrate buffer added in mL)	3.8	3.8	3.8	3.8	3.8
Volume of sodium citrate buffer added (mL)	1.1	1.0	0.8	0.6	0.4
Heated the solutions in a boiling water bath for 10–15 minutes and allowed to cool					
Absorbance at $\lambda_{\text{max}} = 570 \text{ nm}$	0.11	0.22	0.45	0.68	0.91

25 mL extract containing free amino acids was obtained by treating 0.5 g of gram flour with 80 per cent alcohol.

The absorbance of 1.0 mL of the extract when measured under the same conditions was found to be 0.28. Determine the amount of amino acids in 100 g of flour.

[Ans: 250 mg]

28. Peptide bonds of proteins react with copper sulphate in an alkaline medium to yield a blue-coloured complex. The intensity of the colour enhances when in addition, the tyrosine and tryptophan residues of proteins produce blue-coloured products with Folin's reagent. The resultant intensity of blue colour depends on the amount of these aromatic amino acids in proteins. The blue-coloured complexes show an absorption maximum at 570 nm. To plot a calibration curve for the determination of proteins, 10 mg of bovine serum albumin (BSA) was dissolved in 100 mL of water. Five standard solutions of varying concentrations (50–150 μg) were prepared. Appropriate amounts of reagents, i.e. C (A : B : :50 : 1). (A) 2 per cent sodium carbonate in 0.1 N NaOH and (B) 0.5 per cent $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ in 1 per cent sodium potassium tartarate in the ratio 50 : 1, and Folin's reagent (D) were added to these solutions, and the final volume was made up to 7.5 mL with 0.1 N NaOH, indicated below. The solutions were allowed to stand for 10–15 minutes with rigorous shaking. After these, the absorbances of the five solutions were measured with respect to blank, i.e. 2 mL 0.1 N NaOH + 5 mL C + 0.5 mL D.

Volume of standard BSA solution (10 mg/100 mL)	0.50	0.75	1.00	1.25	1.50
Concentration of standard RNA solutions (in μg)	50	75	100	125	150
Volume of 0.1 N NaOH added (in mL)	1.50	1.25	1.00	0.75	0.50
Volume of solution C added (in mL)	5.0	5.0	5.0	5.0	5.0
Volume of Folin's reagent i.e. solution D added (in mL)	0.5	0.5	0.5	0.5	0.5
Shake the solutions for 10–15 minutes at room temperature					
Absorbance at $\lambda_{\text{max}} = 520 \text{ nm}$	0.068	0.10	0.132	0.166	0.20

500 mg of grains were ground with 10 mL of sodium acetate buffer and supernatant was collected for analysis of proteins. If 0.5 mL of the supernatant showed an absorbance of 0.02, what will be the percentage of proteins in the given sample. (6.0 percent) [Ans: 6.0 percent]

29. Reducing sugars, i.e. glucose, lactose; galactose and maltose, etc., when treated with alkaline solution of copper tartarate reagent and arseno molybdate reagent, yields molybdenum blue which has an absorption maximum at 620 nm. To plot a calibration curve for determination of reducing sugars, colourimetrically 10 mg of glucose was dissolved in 100 mL of H_2O . Four standard solutions of varying concentrations (20–80 μg) were prepared. The appropriate amounts of reagents were added to these standard samples, the final volume was made up to 10 mL with

water indicated below. After these, the absorbances of all the blue-coloured solutions were measured with respect to blank, i.e. 1 mL H₂O + 1 mL alkaline copper tartarate reagent + 1 mL arsenomolybdate reagent + 7 mL water (for dilution).

Volume of standard glucose solution (10 mg/100 mL)	0.2	0.4	0.6	0.8
Concentration of glucose (in μg)	20	40	60	80
Water (in mL)	0.8	0.6	0.4	0.2
Volume of alkaline copper tartarate reagent added (in mL)	1.0	1.0	1.0	1.0
Volume of arseno molybdate added (in mL)	1.0	1.0	1.0	1.0
Volume of water added for dilution (in mL)	7.0	7.0	7.0	7.0
Heated the solutions in boiling water bath for 20 minutes and then allowed to cool;				
Absorbance at 620 nm	0.11	0.22	0.33	0.44

Using the data from the problem on the unknown sample, calculate the amount of reducing sugars if the absorbance of 0.2 mL of extracted sugars in water under the present set of conditions is 0.15.

[Ans: 1.4 per cent]

30. Fructose, a keto-hexose is usually accompanied by sucrose in fruits like apple. Honey is a rich source of fructose. When treated with concentrated HCl, it gives hydroxymethyl furfural which then reacts with 0.1 per cent resorcinol in 95 per cent ethanol to give a red-coloured product which has an absorption maximum at 520 nm. To plot a calibration curve for determination of fructose colourimetrically, 10 mg of fructose was dissolved in 100 mL of H₂O. Five standard solutions of varying concentrations (20–60 μg) were prepared. Appropriate amounts of reagents were added to the standard samples, the final volume was made up to 5 mL with water, indicated below. The solutions were then heated in a thermostat at 80°C for exactly ten minutes. After these, the absorbances of all the solutions cooled to room temperature were measured with respect to blank, i.e. 1 mL H₂O + 1 mL 0.1 per cent resorcinol + 3 mL 30 per cent HCl at λ_{max} = 440 nm.

Volume of standard fructose solution (10 mg/100 mL)	0.2	0.3	0.4	0.5	0.6
Concentration of fructose solutions (in μg)	20	30	40	50	60
Volume of water added (in mL)	0.80	0.70	0.60	0.50	0.40
Volume of 0.1 per cent resorcinol added (in mL)	1.0	1.0	1.0	1.0	1.0

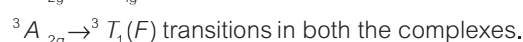
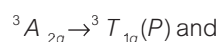
Volume of HCl (30 per cent) added (in mL)	3.0	3.0	3.0	3.0	3.0
Heated the solutions in a boiling water thermostat at 80°C for 10 minutes and allowed to cool.					
Absorbance at λ_{max} = 520 nm	0.15	0.22	0.30	0.38	0.45

Using the data from the problem on the unknown sample, calculate the amount of fructose if the absorbance of 0.2 mL of the extracted sugars in water under the present set of conditions is 0.30.

[Ans: 2 per cent]

Note that insulin is a polymer consisting of fructose units with β -2-1 linkage. It is present in onion, garlic and in many other plant parts. The amount of insulin is expressed in terms of fructose concentration. The extract for its estimation colourimetrically is prepared as follows. The ground sample is treated with 80 per cent ethanol for six hours to remove free sugars and the sample is dried. Take 500 mg of dried sample in a conical flask and add to it 20 mL of water. Heat the contents in the flask in a water bath at 90°C for 10 minutes. Collect the extract and add 70 mL of water to the remaining residues in the flask. Repeat the extraction process for 30 minutes and collect the extract again. Pool the extracts and filter the solution for clarification and make up to 100 mL.

31. Absorption spectra of $\text{Ni}[(\text{CH}_3)_2\text{SO}]_6^{2+}$ and $\text{Ni}[\text{CH}_3\text{C}(\text{O})\text{N}(\text{CH}_3)_2]_6^{2+}$ ions show absorption maxima at 7728, 12970, 24038 cm^{-1} and 7576, 12738 (14285), 23809 cm^{-1} respectively. The value of Racah parameter B for the Ni^{2+} gaseous ion is 1056 cm^{-1} . Using the given spectral data and energy level diagram for d^7 -configuration, calculate the values of Dq , B' , β and β° and the positions of the absorption maxima corresponding to the



[Ans: $\text{Ni}[(\text{CH}_3)_2\text{SO}]_6^{2+}$, 772.8 cm^{-1} , 921.5 cm^{-1} , 0.872, 12.73 per cent, 24028 cm^{-1} and 12970 cm^{-1} ; $\text{Ni}[\text{CH}_3\text{C}(\text{O})\text{N}(\text{CH}_3)_2]_6^{2+}$, 757.6 cm^{-1} , 921 cm^{-1} , 0.87, 12.78 per cent, 23808 cm^{-1} and 12734 cm^{-1}]

32. The electronic absorption spectrum of $[\text{Cr}(\text{F})_6]^{3-}$ exhibits three bands at 34400, 22700 and 14900 cm^{-1} . Calculate the values of Racah parameters and that of the bending constant. The value of B for bare Cr^{3+} ion is 918 cm^{-1} . [Ans: $B' = 826.6 \text{ cm}^{-1}$, $\beta = 0.90$; $\beta^\circ = 9.9$ per cent and $x = 4120 \text{ cm}^{-1}$]

33. The electronic absorption spectrum of $[\text{Co}(\text{F})_6]^{4-}$ shows three bands at 7150, 15200 and 19200 cm^{-1} . Calculate the values of Racah parameters as well as that of Dq and bending constant. $B(\text{Co}^{2+}) = 971 \text{ cm}^{-1}$.

[Ans: $Dq = 805 \text{ cm}^{-1}$, $x = 710 \text{ cm}^{-1}$, $B' = 863 \text{ cm}^{-1}$, $\beta = 0.89$; and $\beta^\circ = 11.09$ per cent]

34. The electronic absorption spectrum of tetrahedral $[\text{Co}(\text{TMG})_4]^{2+}$ where TMG is tetramethyl guanidine exhibits a doublet with maxima at 530 nm (18867 cm^{-1}), $\epsilon_{\text{max}} = 204$ and 590 nm (16949 cm^{-1}), $\epsilon_{\text{max}} = 269$ and is assigned to ${}^4A_2 \rightarrow {}^4T_1(P)$ transition. The near infrared spectrum shows

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a triplet: 1204 nm (8306 cm⁻¹), $\epsilon_{\max}$ = 91.5; 1320 nm (7576 cm⁻¹) $\epsilon_{\max}$ = 85.0 and 1540 nm (6494 cm⁻¹), $\epsilon_{\max}$ = 23.5 and is assigned to $^4A_2 \rightarrow ^4T_1(F)$ transition. The splitting of $T_1(F)$ states is because of spin orbit coupling and the weightage factors of the respective triplet peaks are $(-9/4)\lambda'$, $(+6/4)\lambda'$ and $(+15/4)\lambda'$, calculate the values of the Racah parameters as well as the energy in cm⁻¹ for the $^4A_2 \rightarrow ^4T_2(F)$ transition.

[Ans: $B' = 811$ cm⁻¹, $\beta = 0.83$, $\beta^\circ = 16.5$ per cent, $E [^4A_2 \rightarrow ^4T_2(F)] = 17908$ cm⁻¹]

Hint: The average energy corresponding to the $^4A_2 \rightarrow ^4T_2(F)$ transition

$$= \frac{(18867 + 16949)\text{cm}^{-1}}{2} = 17908\text{cm}^{-1} \quad \text{and to the}$$

$^4A_2 \rightarrow ^4T_1(F)$ transition

$$= \frac{4}{30} \left[\frac{9}{4} (6494\text{cm}^{-1}) \right] + \frac{6}{4} (7576\text{cm}^{-1}) + \frac{15}{4} (8306\text{cm}^{-1})$$

$$= \frac{4}{30} (14612\text{cm}^{-1} + 11612\text{cm}^{-1} + 31148\text{cm}^{-1})$$

$$= \frac{4}{30} (57124\text{cm}^{-1}) = 7616.5\text{cm}^{-1}$$

35. Calculate the value of $\lambda_{\max}$ for CH₃—(CH=CH)₃COOH. [Ans: 294 nm]

36. The specific rotation of the polarisation plane for ephedrine and pseudo-ephedrine in a 68 per cent water–ethanol solution at various wavelengths has the following values.

Wavelength, nm	313	334	365	405	436	546	589
Specific rotation, degrees							
Ephedrine	44.5	20.0	12.6	6.28	2.96	0 - 0.24	
Pseudo-ephedrine	108	173	138	107	86.7	54.2	46.1

Find the conditions for a polarimetric determination of ephedrine and pseudo-ephedrine in their mixture and set up the necessary equations for calculation.

[Ans: $C_{pe} = 1.64 [\alpha]_{546}/l$, $C_e = [[\alpha]_{334} - 3.18 [\alpha]_{546}]/0.05l$]

37. The specific rotation of the polarisation plane for glucose at various wavelengths has the following values:

Wave-length, nm	447	479	508	535	656
Specific rotation, degrees	+ 96.62	+ 83.88	+ 73.61	+ 65.35	+ 41.89

Determine the specific rotation of the polarisation plane for the characteristic hydrogen lines: yellow (589 nm), blue (486 nm), and violet (434 nm).

[Ans: $\alpha_{589} = 52^\circ$, $\alpha_{486} = 80^\circ$, $\alpha_{434} = 104^\circ$]

38. (+) Malic acid rotates the plane of polarisation to the right, and (–) malic acid rotates it to the left. The specific rotation of the polarisation plane for both acids is 2.3°. Determine the content of (+)– malic acid in a solution for which the angle of rotation of the polarisation plane is + 0.8° if the total concentration of the acids is taken to be equal to unity. [Ans: 0.67 g /100 mL]

39. The following data are reported on the CT band observed around 300 nm in the 2, 4-dinitrophenol (as an electron acceptor) – π systems.

Donor	$\epsilon_{\max}$ (dm ³ mole ⁻¹ cm ⁻¹)	$\Delta\bar{\nu}_{1/2}$ (cm ⁻¹)
chlorobenzene	2042.0	590
p-xylene	2491.0	827
Hexamethylbenzene	2777.0	967

Calculate the values of oscillator strengths and transition dipole moments for the CT band observed in the donor–acceptor systems.

[Ans : 5.2×10^{-3} , 0.57D; 8.9×10^{-3} , 0.75D; and 11.6×10^{-3} , 0.86D]

40. Calculate the concentrations of tyrosine and tryptophan in a sample obtained by hydrolysis of a protein from the absorption data indicated below.

$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (dm ³ mole ⁻¹ cm ⁻¹)	Absorbance (Hydrolysed protein sample)	
	Tryptophan	Tyrosine	
240	2.00×10^3	1.12×10^4	0.660
280	5.40×10^3	1.50×10^3	0.221

[Ans : 2.58×10^{-5} mole lit⁻¹; 5.43×10^{-5} mole lit⁻¹]

41. Calculate the Doppler half-intensity width of sodium line at 5893 Å in pm if the light source is at 500 K and $R = 8.3 \times 10^7$ ergs mole cm⁻¹ [Ans: 1.9 pm]

42. The fluorescence decay of a dye excited by light of 350 nm wavelength follows the equation $\frac{1}{\tau} = 1.15 \times 10^7 + 7.7 \times 10^7 [Q]$ provided τ is in second and Q is expressed in units of m mole lit⁻¹. Determine the value of τ and $\tau_{1/2}$ if $[Q] = 6.0$ m mole lit⁻¹.

[Ans : $\tau_{1/2} = 0.06 \mu\text{s}$; $\tau = 2.1$ ns.]

43. The relation between the luminescence intensity of a solution of a mixture of luminol, copper ammoniate and hydrogen peroxide and the concentration of fluoroglucine used as inhibitor is characterised by the following data.

Conc of inhibitor, mole $\times 10^3$	0	0.013	0.023	0.071	0.141	0.269	0.446	0.708
Luminescence intensity, arbitrary units.	180	143	90.4	53.3	38.5	27.3	20.2	14.3

Determine the concentration of fluoroglucine (in mg/mL) if its luminescence intensity equals 45 arbitrary units.

[Ans: 1.26×10^{-2} mg/mL]

44. The degree of quenching of the luminescence of rhodamine by zinc is characterised by the following data.

Conc. of zinc, $\mu\text{g}/5\text{mL}$	1	2	3	4	5	6	7
Luminescence intensity, Per cent of initial	63	50	45	39	32	29	25

A 0.5 g sample of indium sulphide containing traces of zinc is treated to prepare 100 mL of a solution. The addition of 5 mL of this solution to rhodamine under the conditions in which the calibration curve is plotted reduced its intensity to 42 per cent. Determine the percentage content of zinc in the sample.

[Ans: 0.013 per cent]

45. To determine iron in waste water by luminescence intensity of its compound with stilbexone, a standard solution is prepared by dissolving 0.586 g of chemically pure Fe_2O_3 containing 2.5 per cent of hygroscopic water, in 250 mL of water. Stilbexone is added to the following volumes of the standard solution, which are then made up to 100 mL. The following data are obtained.

Vol. of stan- dard solution; mL	0.5	1.0	1.5	2.0	2.5	3.0
Luminescence intensity, $\times 10^{+2}$, arbitrary units	18	31	42	51	58	64

To 5 mL of sample of waste water under analysis, stilbexone is added and the resultant solution is diluted with water to 25 mL. The luminescence intensity of the solution so obtained equals 0.25 arbitrary units. Determine the amount of iron in the waste water (in g/m^3).

[Ans: $30 \text{ g}/\text{m}^3$]

46. A 0.15 g sample of uranium ore is dissolved and after appropriate treatment, the solution is diluted with water to 100 mL. The luminescence intensity of the solution has been found to be 60 arbitrary units. When $5 \mu\text{g}$ of uranium is added to 20 mL of this solution, the luminescence intensity is raised to 110 arbitrary units. The luminescence intensity of a blank sample is equivalent to that of $1 \mu\text{g}$ of uranium.

What might be the content of uranium in the ore in kilogram per ton, if the luminescence intensity is proportional to the amount of uranium present?

47. Figure X shows schemes for transfer of electrons from various levels and sublevels of molecules. Which of the following answers explain correctly the energy processes taking place in these transitions?

- The transfer 'a' involves the evolution of energy as heat.
- The transition 'h' involves the liberation of an absorbed energy quantum in the form of a radiation of the same frequency. Such transitions are hardly probable.

- The transfer 'e' occurs in two stages. First, the heat energy is evolved and then the energy in the form of luminescent radiation.
- The transitions 'c', 'e', and 'f' take place in several stages, each of which involves the evolution of radiant energy in the form of luminescent radiation.
- The transitions 'c' and 'f' involve the evolution of heat energy when electrons are transferred within the confines of one level, and radiant energy in the form of luminescence when the electrons are transferred from one level to another.
- Of all the electron transfers given, only the transition 'e' involves luminescent emission, the magnitude of the quantum of absorbed energy being higher than that of the quantum of radiant energy.
- In 'c', 'e', and 'f', the transfer of electrons from one sublevel to another involves a weak luminescent emission, and in transitions from one level to another, heat energy is evolved.
- The transitions 'd' and 'g' are accompanied by the emission of a strong luminescence.

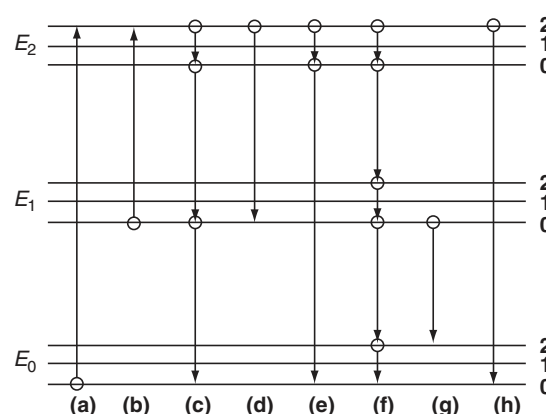


Fig. X

[Ans: (b),(c),(f)]

48. (a) The quantum yield of ICN into $\text{I}(\text{g})$ and $\text{CN}^*(\text{g})$, $X^2\Sigma^+$ by a 306 nm pump pulse is 1.00. If the energy of the pump pulse is 1.5×10^{-7} kJ, determine the number of $\text{CN}^*(\text{g})$ ($B^2\Sigma^+$) radicals produced per pulse if only 0.2 per cent of the incident light is absorbed by the ICN (g) sample.

- Hint: Energy of a 306 nm photon = 6.49×10^{-22} kJ.

Number of photons absorbed = $\frac{0.2}{100} \times \text{number of photons in a } 1.55 \times 10^{-7} \text{ kJ pulse.}$

[Ans: 4.78×10^{11}]

(b) Time resolved laser studies for the reaction in part (a) $\lambda_{\text{pump}} = 306 \text{ nm}$ and $\lambda_{\text{probe}} = 388 \text{ nm}$ yield the following data.

Intensity (I_t in arbitray units)	1	0.979	0.946	0.857
Time of delay (in f s)	1200	800	600	400
	205	100	10	-400

Plot a graph between I_t and delay time and fit the resultant curve into some suitable function. Determine also half-life of the reaction.

49. The upper level of the H_2 (g) laser is the lowest excited state of the molecule, the $B^1\Sigma_u^+$ state and the lower level

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is the $X \ ^1\Sigma_g^+$ ground state. The lasing occurs between the $V'' = 5$ level of the excited and $V' = 12$ level of the ground state. Determine the wavelength of the laser light from the H_2 (g) laser by using the spectroscopic data indicated below.

State	$\nu_{\text{elec}}(\text{cm}^{-1})$	$\omega_e(\text{cm}^{-1})$	$\omega_e x_e(\text{cm}^{-1})$
$B \ ^1\Sigma_u^+$	91689.9	1356.9	19.93
$X \ ^1\Sigma_g^+$	0	4401.2	121.34

A 1.0 ns pulse can be produced with a pulse radiant power of 100 kW. Calculate the radiant energy of such a laser pulse and the number of photons in this pulse.

[Ans: 160 nm, 1.0×10^{-4} J, 810×10^{11} photons]

50. The term symbols for some of the homonuclear diatomics are given below:

Molecule	Term symbol
H_2, C_2, Li_2, F_2	$^1\Sigma_g^+$
He_2^+	$^2\Sigma_u^+$
B_2, O_2	$^3\Sigma_g^-$
O_2^+	$^2\Pi_g$

Write the meanings of the notations involved in the term symbols.

51. (a) The force constants for the diatomic molecules B_2 through F_2 , are given below: (i) Is the order what you expect? Explain. (ii) Compute the vibrational frequencies of the diatomics.

Molecule	B_2	C_2	N_2	O_2	F_2
$k(\text{millidynes}/\text{\AA})$	3.50	9.30	22.60	11.40	4.50

(b) Compare the bond orders of O_2^+ , O_2 , O_2^- and O_2^{2-} ,

C_2 and C_2^- ; NO^+ and NO

- **Hint:** Write the electronic configuration and compute the bond orders.

Bond order = $\frac{1}{2}[(\text{number of electrons in the bonding orbitals}) - (\text{number of electrons in the antibonding orbitals})]$

The larger the bond order, the smaller the bond length.

[Ans: $\frac{5}{2}$, 2, $\frac{3}{2}$, 1; 2, $\frac{5}{2}$; 3, $\frac{5}{2}$]

CHAPTER 6

PHOTOELECTRON
SPECTROSCOPY

I have little patience with scientists, who take a board of wood, look for its thinnest part, and drill a great number of holes where drilling is easy.

—Albert Einstein

6.1 INTRODUCTION

Photoelectron Spectroscopy (PES) involves the measurement of parameters, namely kinetic energies, abundance's and angular distributions of photoelectrons emitted from the occupied atomic orbitals or molecular orbitals, i.e. bonding, nonbonding and antibonding of a sample irradiated by high-energy photons. The photoelectron parameters are a function of the element of the sample irradiated and its electronic environment. They are characteristic of the individual energy of the individual atomic/molecular orbitals from which they originate and binding energy of the individual electron in the element. It is presently the best available technique for directly measuring the ionisation energies (IE) or potentials (IP) or binding energy (BE) of electronic states of positive ions which are closely related to the energies of different atomic/molecular orbitals in neutral atoms/molecules. PES has a symbiotic relationship with atomic/molecular orbitals. The language of AO/MO proved itself to be the most suitable vehicle for understanding the photoelectron spectrum. According to Koopman's theorem, *the vertical ionisation energies, IE_j (or ionisation potentials, IP_j) of an atom or a molecule is equal in magnitude to the orbital energies E_j , determined by Self-Consistent Field (SCF) molecular orbital calculations;*

$$IP_j / IE_j = -E_j \quad (6.1)$$

where IE_j is taken as the difference in energy between an electron at an infinite distance from the atomic/ molecular ion and the same electron in the atom/molecule.

According to this theorem, one band is expected per orbital.

There are two types of ionisation energies encountered in PES, viz., vertical and adiabatic. The *vertical ionisation energy* (I_{vert}) refers to the most probable transition predicted by the Franck Condon principle and corresponds to the experimentally measured value (Fig. 6.1), while the *adiabatic ionisation energy* (I_{ad}) refers to $V' \rightarrow V'' = 0 \rightarrow 0$ transition, and corresponds to true ionisation potential of atom/molecule (Fig. 6.1). I_{vert} is always greater than I_{ad} .

6.2 TYPES OF PHOTOELECTRON SPECTROSCOPY

Traditionally, it has been subdivided according to the source of exciting radiation for ionisation into the following:

(i) Vacuum ultraviolet photoelectron spectroscopy (UPS or UV-PES) which uses vacuum UV (10 – 45 eV) radiation to examine the valence levels. In UPS, the outer-shell electrons are removed from an atom/molecule using He (I), 21.22 eV as UV radiation source and hence is also called PhotoElectron Spectroscopy for Outer Shells (PESOS). It was discovered independently by two groups, one led by F I Vilesve in Leningrad (Russia) and the other by D W Turner in London (England) in early 1960. (ii) *x*-ray Photoelectron Spectroscopy (XPS) uses soft *x*-ray (200 – 2000 eV) radiation to examine the core levels. XPS when used for analysis is termed Electron Spectroscopy for Chemical Analysis (ESCA). In XPS, the inner-shell electrons are removed from an atom/molecule using MgK_{α} 1253.6 eV or AlK_{α} 1486.6 eV as *x*-ray radiation source and

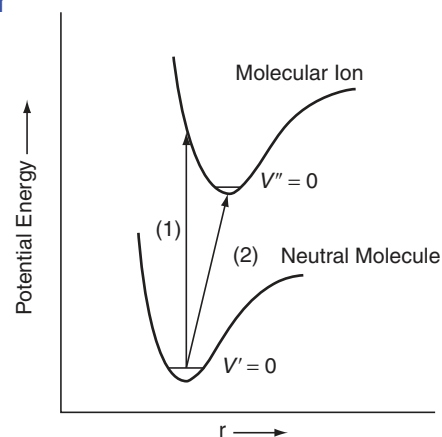


Fig. 6.1 Schematic diagram showing the difference between vertical and adiabatic ionisation energies.

hence is also called PhotoElectron Spectroscopy for Inner Shell (PESIS) emission. This technique was developed by K M Siegbahn and his group at Uppsala (Switzerland) in 1946. The studies were concentrated more on solids than on free molecules. The most important and interesting aspect of XPS is that the core electron-binding energy of an atom in a molecule is a significant factor of the chemical environment of the atom. In 1981, the Nobel prize was awarded to him for his contribution to the development of high-resolution electron spectroscopy, especially ESCA. Both the techniques are used to determine the structure of atoms/molecules and for analysis; the detection limit being of the order 10^{-5} mg.

6.3 PHOTOELECTRIC EFFECT

It is the very basis of photoelectron spectroscopy. Therefore, it is imperative to discuss in brief this phenomenon. When light of suitable wavelength strikes a metal surface, it acquires a positive charge with the emission of electrons. It was accidentally discovered by Hertz in 1887 as he was investigating the electromagnetic waves predicted by Maxwell's theory of the electromagnetic field. The interpretation of the photoelectric effect was proposed by Albert Einstein on the basis of quantum theory. According to him, when a photon of energy $h\nu$ falls on a surface, an electron is emitted with some velocity and the kinetic energy of the electron given by

$$\frac{1}{2}m_e v^2 = h\nu - \phi_e \quad (6.2)$$

where m_e is the mass of the electron and ϕ_e is a constant characteristic of the metal. This is also called the *electronic work function* of the metal which is defined as the minimum energy required to liberate an electron from the attractive forces of positive ions in a metal or a semiconductor at absolute zero temperature. The lower the work function, the greater the number of electrons that can break loose from the specimen. This relationship is called the *photoelectric law*. Further, it is to be noted that (i) the number of photoelectrons liberated is proportional to the intensity of the impinging radiations, and (ii) the minimum kinetic energy of photoelectrons depends on the energy, but not on the intensity of incident radiation. In 1921, Einstein was awarded the Nobel prize for theoretical physics and especially for correctly developing the theory of photoelectric effect.

The first direct experimental evidence to Einstein's law was produced by Robert Andrews Millikan in 1914 and in 1923, the Nobel prize was awarded to him for his work on elementary charge of electricity and on the photoelectric effect.

6.4 THEORY OF PHOTOELECTRON SPECTROSCOPY

Before describing the theory of photoelectron spectroscopy, it is useful to briefly review the electronic structure of isolated atoms and of solids, and the associated nomenclature with them. According to conventional chemical nomenclature, the electronic structure of isolated atoms and of solids along with their associated nomenclature has schematically been illustrated in Fig. 6.2 (a), (b) and Fig. 6.3. respectively. The core levels or shells *K*, *L*, *M*... of atoms are given on the left-hand side while the orbitals associated with the respective shells are given on the right-hand side. However, scientists working with x-rays use the 'alternative nomenclature' on the left. The shells or core levels designated as *K*, *L*, *M*... correspond to the principle quantum numbers 1, 2, 3... respectively. In Fig. 6.2. (b), the numerical component of *K*, *L*, *M*... style of nomenclature is usually written as a subscript immediately following the main-shell designation. Levels with nonzero value of the orbital angular momentum quantum number, i.e. azimuthal quantum number ($l > 0$), or *p*, *d*, *f*, levels, show spin-orbit splitting. When the magnitude of this splitting is too small, the double subscript for these levels represents both the levels, i.e. $L_{II,III}$ represents both the L_2 and L_3 levels.

Figure 6.3 shows that in the solid state, the core levels of atoms are little perturbed but remain as discrete, localised

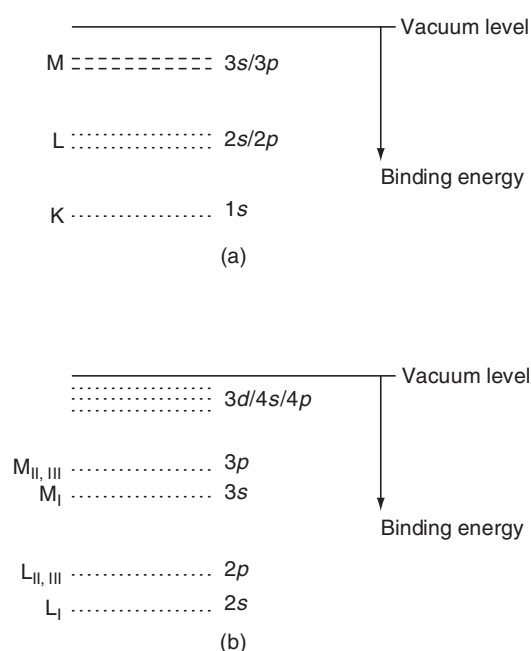


Fig. 6.2 (a) Schematic diagram showing the electronic structure of isolated atoms and the nomenclature associated with it (b) An expanded view of the part of the energy scale of Fig. 6.2 (a) close to the vacuum level.

(i.e. atomic-like) levels. The valence orbitals, however, overlap significantly with those of neighbouring atoms giving rise to bands of spatially delocalised energy levels. The energy-level diagram for the solid closely resembles that of the corresponding isolated atom, except for the levels closest to the vacuum level.

It is to be borne in mind that for gases, the reference level of zero binding energy is the zero energy of an electron at rest in a vacuum and the BE in gases is designated as BE^V while for solids, the Fermi level, which is the energy associated with the highest filled orbital/energy level at absolute zero, is taken as the reference level of zero binding energy and the BE is designated as BE^f . Both the scales have been shown in Fig. 6.4.

The Fermi level in the conduction band is named after the famous Italian physicist Enrico Fermi who got the 1938 Nobel prize for demonstration of the existence of new radioactive elements produced by neutron irradiation and for related discovery of nuclear reactions brought about by slow neutrons.

Figure 6.4 is drawn assuming the sample to be metallic. The results also hold true if the sample is an insulator or semiconductor. Further, it is to be noted that the energy difference between the Fermi level and the vacuum level just outside the surface in the case of both semiconductors and metals is a measure of the quantity ϕ_e . Thus, if ϕ_e of a reference solid is known, the ϕ_e of another solid surface can be determined from the contact potential difference. For metals, the photoelectric threshold is equal to ϕ_e . This is not true in general for semiconductors. For semiconductors, the photoelectric threshold is equal to the difference in energy between the vacuum level and the top of the valence band (i.e. BE / ionisation potential) when the bands are flat to the surface over the escape depth of emitted electrons and when the surface-state emission is negligible. The maximum kinetic energy, the Fermi energy of any electron is

$$E_f = \frac{h^2}{8m_e} \left(\frac{3N}{\pi V} \right)^{2/3} \quad (6.3)$$

where N is the total number of electrons, m_e (9.11×10^{-31} kg) is the electron rest mass and V is the volume. The volume of one kilomole of metal

$$V_m = \frac{\text{Molecular mass of metal (kg/kmole)}}{\text{Density of metal (kg/m}^3\text{)}} \quad (6.4)$$

Thus, the volume of each atom of metal (in m^3/atom),

$$V_{\text{atom}} = \frac{V_m (\text{m}^3/\text{k mole})}{N_A (\text{atoms/k mole})} = \frac{V_m}{N_A} \text{m}^3/\text{atom} \quad (6.5)$$

On the assumption that there is one free electron per atom, the number of electrons per unit volume $N_L = \frac{1}{V_{\text{atom}}}$ (electrons/ m^3). This number is called the *Loschmidt number*. Equation, (6.3) becomes

$$E_f = \frac{h^2}{8m_e} \left(\frac{3 N_A}{\pi V_m} \right)^{2/3} = \frac{h^2}{8m_e} \left(\frac{3}{\pi V_{\text{atom}}} \right)^{2/3} = \frac{h^2}{8m_e} \left(\frac{3 N_L}{\pi} \right)^{2/3} \quad (6.6)$$

or

$$E_f = \frac{[6.625 \times 10^{-34} (\text{J s})]^2}{8 \times 9.11 \times 10^{-31} (\text{kg})} \left[\frac{3 \times 7 \times 6.023 \times 10^{26} (\text{atoms})/\text{kmole}}{22 \times V_m (\text{m}^3) / \text{kmole}} \right]^{2/3}$$

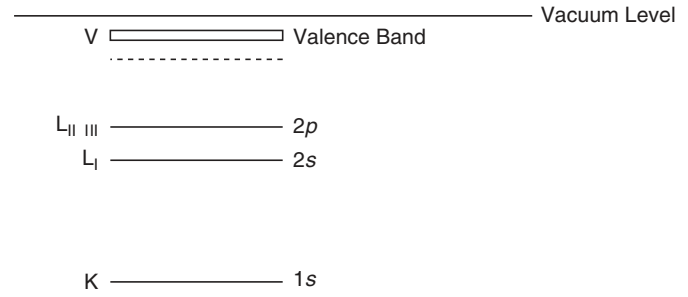


Fig. 6.3 Schematic diagram showing the electronic structure of atoms in solids and the nomenclature associated with it.

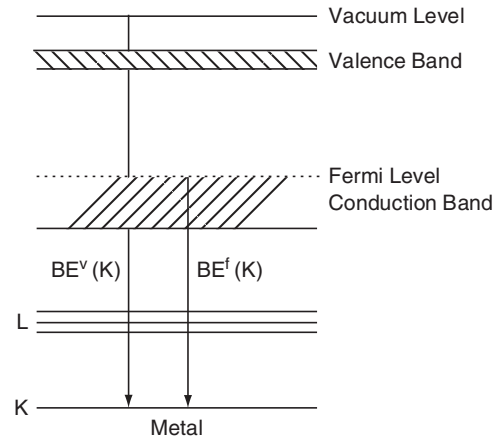


Fig. 6.4 Schematic diagram showing the reference levels of zero-point energy in gases and solids.

$$E_f = 6.022 \times 10^{-38} \left[\frac{5.749 \times 10^{26}}{V_m} \right]^{2/3} \text{ J}$$

$$E_f = 4.163 \times 10^{-20} \left[\frac{1}{V_m} \right]^{2/3} \text{ J} \quad (6.7)$$

Here, V_m is the volume in $\text{m}^3/\text{k mole}$, i.e. the volume of one kilomole of metal.

For sodium metal, $V_m = \frac{23 \text{ kg/k mole}}{970 \text{ kg/m}^3} = 0.0237 \text{ m}^3/\text{k mole}$

Hence,

$$E_f(\text{Na metal}) = 4.163 \times 10^{-20} \left[\frac{1}{0.0237} \right]^{2/3} \text{ J}$$

$$= 4.163 \times 10^{-20} \times 1.211 \times 10^1 \text{ J}$$

$$= 5.04 \times 10^{-19} \text{ J} = 3.15 \text{ eV}$$

The basic principle of UV-PES and XPS is the same except that in the former, the outer-shell electrons are involved whereas in the latter, the inner-shell electrons are involved in photo ionisation of neutral atom/molecule.

When a monochromatic beam of photons of short wavelength strikes a neutral atom/molecule, say A , it promotes an electron from the ground-energy state, i.e. low-energy orbital (say Ψ_0 with energy E_0) to a vacant lesser potential-energy state, i.e. high-energy orbital (say Ψ_j with energy E_j). This process of 'jump' of an electron from lower to higher energy state under the influence of radiation of short wavelength is identical with an electron transition and is represented as



When the incident photon imparts sufficient energy to the electron, the latter escapes from atom/molecule leaving behind a cation. The process of eviction of an electron from the chemical species under the influence of a photon of high energy occurs in a single step and is termed as direct photoionisation. It is represented as



Here, A^{+*} is a cation in a highly excited state. Furthermore, all of the absorbed energy which is in excess of the minimum needed to expel the electron from the neutral atom/molecule manifests itself as the discrete kinetic energy (E_{kin}) of the photoelectron.

The law of conservation of energy requires

$$h\nu = (E_j^+ - E_0) + E_{\text{kin}} \quad (6.10)$$

This relationship was first proposed by Albert Einstein in 1905 and is known as *photoelectric law*. Here, E_j^+ is the energy of the highly excited quantum state ψ_j^+ of A^{+*} . The difference $(E_j^+ - E_0)$ is termed as the electron-binding energy BE or the ionisation energy IE_j (or ionisation potential IP_j). It is defined as the energy difference between the ground state of the neutral atom/molecule and the final state of the cation. In general,

$$BE_j = (E_j^{N-1} - E_0^N) \quad (6.11)$$

where E_0^N and E_j^{N-1} are the total energies of the N electron initial state and the $N-1$, hole final state of the system. In a one-electron picture, each BE_j can be associated with an ion having a hole in the i^{th} orbital, including the possibility of multiplet splittings. The change in the energy of the final state E_j^{N-1} due to the relaxation of $N-1$ possible electrons towards the j^{th} hole is called *relaxation energy*. The relaxation energy or shift of BE with respect to the orbital energy is not a constant or a fixed fraction of the BE . For a given photon energy, various final states of the cation (A^{+*}) will be reached corresponding to the different binding energies.

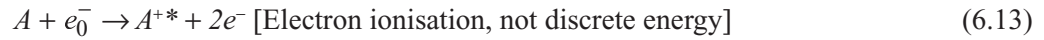
The photoelectrons with discrete kinetic energies liberated from the neutral atom/molecule by the direct photoionisation process, also called the *primary process*, using x-ray photons are called *ESCA electrons*.

The mechanism of removal of 1s ESCA electrons from neutral atom/molecule is shown in Fig. 6.5 (a). The kinetic energy of an ESCA electron is expressed as

$$E_{\text{kin}} = h\nu - BE(1s) = h\nu - BE(K) \quad (6.12)$$

In addition to the direct photoionisation process, the other primary process of ionisation is *electron ionisation*. Electron ionisation of an atom/molecule produces both an excited ion and a second electron.

However, because of electron–electron interactions, discrete electron energies are not observed. The process of electron ionisation is represented as



The electron ionisation can produce only Auger electrons but not ESCA electrons.

Further, the ion A^{+*} in the highly excited quantum state ψ_j^+ may relax to some stable excited state of A by the following two secondary processes.

Firstly, the excited state A^{+*} cation may relax to an excited state of cation A^+ by *x-ray fluorescence* with the emission of *x-ray* photon with energy $h\nu'$ such that $h\nu' < h\nu$. This process is represented as



The mechanism of *x-ray* fluorescence is shown in Fig. 6.5 (b). An electron drops from 2p electron to fill the 1s hole, and an *x-ray* photon is emitted. This result is $K\alpha$ *x-ray* emission. The energy of the emitted *x-ray* photon is expressed as

$$h\nu' = BE(1s) - BE(2p) = BE(K) - BE(L_{II}) \quad (6.15)$$

The second secondary process competing simultaneously with the *x-ray* fluorescence is the Auger electron emission. In this process, the highly excited cation A^{+*} relaxes to the excited state of doubly ionised atom A^{++} with the emission of a second electron having discrete energy. The electron emitted is called the *Auger electron*, and the process of electron emission is represented as



The latter process is more probable than the former for elements of atomic numbers less than about 32. Unlike photoelectrons, the energy of the Auger electrons is independent of the energy of the incident photons. The process of Auger-electron emission is shown in Fig. 6.5 (c). A 2s electron drops to fill the 1s hole, simultaneously liberating a 2p electron. This is known as KL_1L_{III} Auger process. The energy of the Auger electrons is independent of the initial core-hole formation. The kinetic energy of an Auger electron is given by

$$\begin{aligned} E_{\text{kin}} &= BE(1s) - BE(2s) - BE(2p) \\ &= BE(K) - BE(L_I) - BE(L_{III}) \end{aligned} \quad (6.17)$$

An Auger transition is thus characterised primarily by (i) the location of the initial hole, (ii) the location of the final two holes although the existence of different electronic states (terms) of the final doubly ionised atom may lead to a fine structure in the high-resolution spectrum. Note that when describing the transition, the initial hole

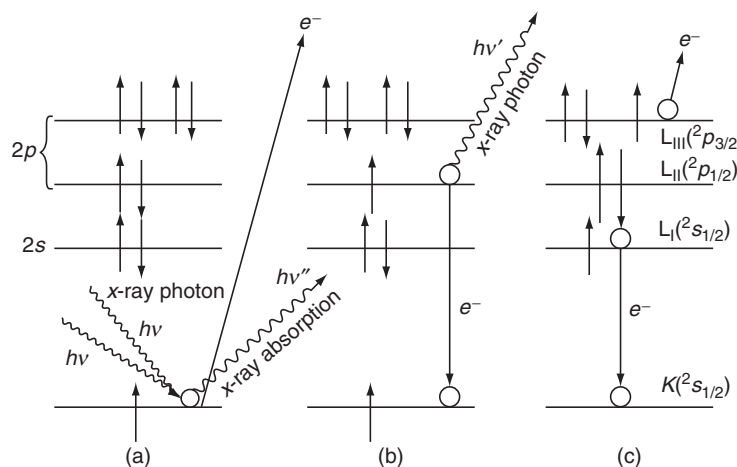


Fig. 6.5 Schematic diagram illustrating the mechanism of (a) liberation of an ESCA electron and the x-ray absorption; $E_{\text{kin}} = h\nu - BE(K)$; $h\nu'' = h\nu - E_{\text{kin}}$ (b) x-ray fluorescence; $h\nu' = BE(K) - BE(L_{II})$ (c) production of an Auger electron; $E_{\text{kin}} = BE(K) - BE(L_I) - BE(L_{III})$.

location is given first, followed by locations of the final two holes in order of decreasing binding energy, i.e. the transition illustrated is KL_1L_{IIIII} when the L_{II} and L_{III} shells are degenerate. The final state is a doubly ionised atom with core holes in the L_1 and L_{IIIII} shells. The inner shell vacancies created in either of the two secondary processes are filled within 10^{-17} to 10^{-12} second by electrons from outer shells.

For low-energy processes (1000 eV), the Auger effect will dominate while for higher energy processes (10,000 eV) x-ray emission will dominate. x-ray ionising sources are used for ESCA while electron guns are used for Auger Electron Spectroscopy (AES). The basis of AES is an effect discovered in 1932 by Auger in which electrons are liberated in an atom with energies characteristic for the emitting atom.

The general expression for the kinetic energy of an Auger electron in an atom is given by

$$E_{ijk}^{kin} = BE_i(Z) - BE_j(Z) - BE_k(Z + \Delta Z) \quad (6.18)$$

where BE_i , BE_j and BE_k are the binding energies of the electron in the shells ($K, L, M, \dots$) involved. Since the Auger electron is emitted from a singly charged ion, its binding energy is larger than that of the same electron in the neutral atom, i.e. Z ($0.5 \leq \Delta Z \leq 1$). The number of possible lines grows rapidly as the number of electrons increases, i.e. with Z . The number of possible Auger lines for a given combination of shells depends upon the type of coupling between angular momentum and spin of electrons (LS, jj or intermediate coupling). For instance, the KLL spectra of very light atoms (LS coupling) consists of five lines, those of very heavy atoms (jj coupling), six lines while those of intermediate atoms should have ten lines. However, even in light atoms, the number of observed lines is more than the number of lines expected on the basis of RS coupling. The weaker additional lines are due to Auger emission from a doubly ionised atom which produces a triply ionised atom, i.e. $A^{++*} \rightarrow A^{+++} + e^-$. Such transitions involving initial double ionisation is quite common when the primary radiations are highly energetic. When the Auger electron excitation is carried out by ions, even higher degree of ionisation occurs, i.e. $A^{+++*} \rightarrow A^{++++} + e^-$, e.g. Ne KLL spectra excited by He^+ , H^+ or O^{+5} beams.

Transitions in which an initial vacancy is filled by an electron from the same shell, e.g. an L_1 vacancy when filled by an electron from the L_{II} shell are called Coster–Kronig transitions. These transitions contribute to the production of Auger electrons and thus to the complexity of their spectrum. BEs' of levels j and k being small compared to BE_i may be neglected. Consequently,

$$E_i^{kin} \propto BE_i$$

Thus, the dependence of the Auger energies upon the atomic number can be obtained from the plot of energies of the initial vacancy against Z . It is found that inner shells can be used if the energy analyser has an upper energy limit of 1500 eV: the K shell up to Al or the L shell up to beyond Ni. Higher Auger-electron energies are not practical because of intensity reasons.

The intensity of an Auger line depends on the probability for creation of an inner shell vacancy, i.e. the ionisation cross-section Q_i and the probability a_{ijk} that is the filling of this vacancy is accompanied by an Auger or Coster–Kronig transition.

$$I(E_{ijk}^{kin}) \approx Q_i a_{ijk} \quad (6.19)$$

In case of ionisation by electrons,

$$Q_i = \frac{a}{BE_i^2} \frac{\ln U}{U} [\text{\AA}^2] \quad (6.20)$$

where BE_i is in eV, $U = \frac{E(\text{energy of incident electron})}{BE_i}$, $a = 960$

The relation holds good for many ionisation processes with 'a' ranging from 600–1100. The function has a maximum at $E_{max} \approx 2.72 BE_i$.

$$Q_i^{max} \approx 0.38a / BE_i^2 [\text{\AA}^2] \quad (6.21)$$

This is lower than the observed value. This leads to a maximum attenuation coefficients $\mu_i^{max} = Q_i^{max} \leq 1 \times 10^{-2} \text{\AA}^{-1}$ for all materials and ionisation energies $BE_i \geq 50$ eV. This reveals that the attenuation due inner-shell ionisation is small compared to attenuation by valence electrons. Equations (6.20) and (6.21) lead to the following values for AES with electrons:

- (i) The energy of the incident beam should be at least $2.5 BE_i$ for efficient ionisation.
- (ii) BE_i should be smaller than about 1500 eV if an ionisation cross section exceeding 10^{-20} cm^2 is to be obtained.

Further, it has been proved for transitions involving K and L shells that nearly all vacancies are filled by Auger transitions ($a_i = \sum a_{ijk} \approx 1$) provided $BE_i > 1500$ eV. At higher BE_i values, x-ray emission becomes increasingly stronger. Thus, AES is efficient below about 1500 eV.

The Auger-electron line width of free atoms is determined from the lifespan of the vacancy i . It ranges from fractions of an eV for small BE_i to about 10 eV for high BE_i values (≈ 1500 eV). This also leads to infer that shells with low ionisation energies are suitable for AES. When atoms are in condensed matter, i.e. atoms are not free, the Auger electron bandwidth increases considerably. This is because of broadening of the valence levels into bands. The removal of the Auger electron causes a disturbance in the atom from which it is removed. The main disturbances are dynamic relaxation and static relaxation which is further divided into two types, namely atomic and extra-atomic relaxations. In addition, the disturbance is also caused by the multiplet coupling in the final state, which causes the splitting. *Dynamic relaxation* describes the rearrangement of an atom accompanying ionisation. The dynamic relaxation energies of electrons are automatically included in Eq. (6.18) for $\Delta Z = 0$ if experimental BE s are used. *Static relaxation* describes the rearrangement of the atoms connected with the transition of the j electron into the i hole. *Static atomic relaxation* is the process which occurs in the free atom, *static extra-atomic relaxation* represents the response of the atomic environment in the solid to the formation of the j hole. The contribution of the various processes to the Auger energy have been determined for the Cu $L_{\text{III}} M_{\text{IV}} M_{\text{IV}}$ -Auger spectrum to be 25 eV, 10 eV and 20 eV for the multiplet, the static atomic and the static extra-atomic relaxation contributions respectively. The Auger energies calculated with Eq. (6.18) for $\Delta Z = 0$ but with the inclusion of these terms agree within 2–3 eV with experiment.

In summary, AES is based upon the measurement of the kinetic energies of the emitted electrons. Each element in a sample being studied will give rise to a characteristic spectrum of peaks at various kinetic energies. It is a surface-sensitive spectroscopic technique used for elemental analysis. It offers high sensitivity (typically, Ca of 1 per cent mono layer) for all elements except H and He, a means of monitoring surface cleanliness of samples, and quantitative compositional analysis of the surface region of specimens, by comparison with standard samples of known composition. Moreover, Auger depth profiling provides quantitative compositional information as a function of depth below the surface. Scanning Auger Microscopy (SAM) provides spatially resolved compositional information of heterogeneous samples.

6.5 PHOTOELECTRON SPECTRUM

The kinetic-energy distribution of the emitted electrons, i.e. the number of emitted electrons as a function of their kinetic energies, is measured with the aid of an instrument called a photoelectron spectrometer and the plot of intensity of electrons, i.e. the number of electrons per unit time at each energy level, against their kinetic energy is termed the *photoelectron spectrum*. A peak is found in the spectrum at each energy $h\nu - IE_j$, corresponding to the binding energy IE_j of an electron in the atom; the BE s of energy levels in solids are conventionally measured with respect to the Fermi level rather than the vacuum level.

When vibrational and rotational motions are also excited on ionisation, the energies of the photoelectrons are defined by

$$E_{\text{kin}} = h\nu - IE_j - E_{\text{vib,rot}}^* \quad (6.22)$$

The spectrum may contain many vibrational lines for each type of electron ionised and the system of lines corresponding to ionisation from a single molecular orbital constitutes a band. In addition to Koopman's theorem, the two simple rules that correlates the PES spectrum with molecular electronic structure are (i) each band in the spectrum corresponds to ionisation from a single molecular orbital, and (ii) each occupied molecular orbital of BE less than $h\nu$ gives rise to a single band in the spectrum. However, the number of bands in the PES is more than expected from valence orbitals in the molecule. The additional bands in the PES may arise due to (i) the ionisation of one electron with the simultaneous excitation of a second electron to an unoccupied excited orbital. The bands generated in such a two-electron process are much weaker compared to simple ionisation bands, (ii) ionisation from a degenerate occupied molecular orbital since the degenerate orbitals in the molecule may not be degenerate in the molecular ion because of spin-orbit coupling and Jahn–Teller effect, and (iii) ionisation from molecules with unpaired electrons such as O_2 , NO. In such cases, many more bands appear than expected on the basis of occupied orbitals in the molecule and neither the Koopman theorem nor the simple two rules are valid.

The relationship between ionisation energies and orbital energies (i.e. Koopman's theorem) has been illustrated in the schematic diagram shown in Fig. 6.6.

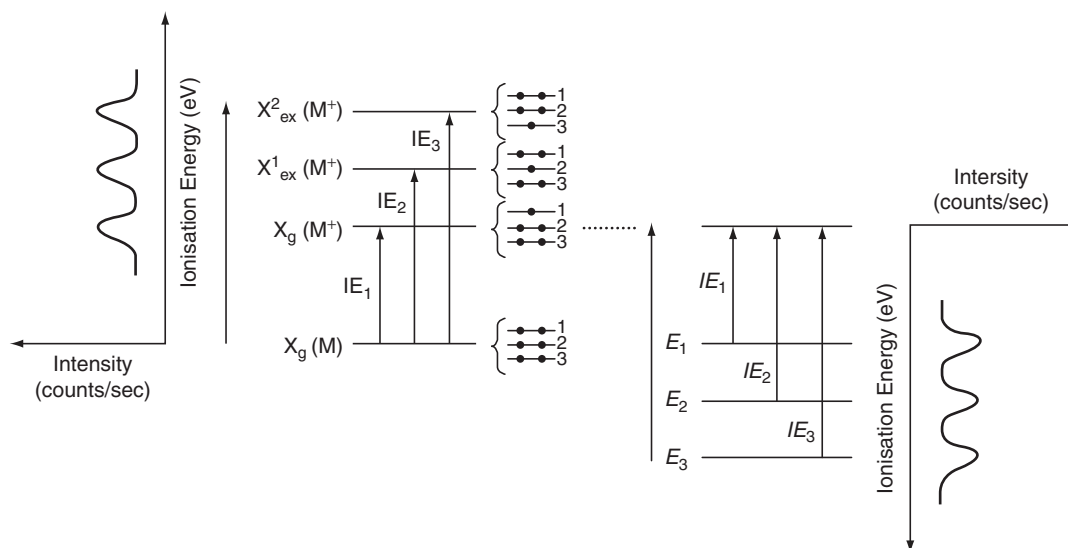


Fig. 6.6 Schematic diagram illustrating the relationship between ionisation energies and the orbital energies (i.e. Koopman's theorem). X_g — the ground state, X_{ex}^I — the excited state, M — the neutral molecule and M^+ — the molecular ion. The dark point (.) represents an electron.

The spectra in PES are recorded and displayed in two ways:

(a) Differential Spectrum When electrons of one energy only at time are able to reach the detector, the spectrum obtained is called the differential spectrum.

(b) Integral Spectrum When all the electrons of more than a certain energy can reach the detector simultaneously, the spectrum is called an integral spectrum.

Note that AES spectra are different from ESCA spectra. AES spectra are plotted as derivatives, i.e. $\frac{dI}{dE_{kin}}$ against kinetic energy (E_{kin}) while ESCA spectra are plotted as integrals. This is so because Auger spectra caused by ionisation lie on top of a very high, scattered electron background and differentiation removes the spectra background. Differentiation of ESCA spectra is not necessary because the primary photobeam produces a lower electron background. The intensity ratio in differential spectra is given by the areas whereas in integral spectrum by the step heights. The hypothetical differential and integral spectra of some systems are shown in Fig. 6.7 (a) and (b) respectively. Differential and derivative AES spectra of Pd metal generated using 2.5 keV electron beam to produce the initial core vacancies and hence to stimulate the Auger emission process have been shown in Fig. 6.8 (a) and (b) respectively. It is to be noted that in PES, differential and derivative spectra are not same but different. So be careful while using these terms.

The other phenomenon related to the interaction of x-ray radiation with matter is the absorption of x-ray photons, i.e. $h\nu'' = h\nu - E_{kin}$ [Fig. 6.5 (a)]. The intensity of the x-ray beam decreases as it passes through the materials and it depends upon the amount of the material. By measuring the absorption as a function of wavelength of x-rays, the absorption spectrum is obtained. The wavelength in the spectrum where a sudden change of absorption occurs is called the *absorption edge*. Absorption edges occur at those wavelengths where the x-ray photon has sufficient energy to excite an electron from a particular energy level to infinity.

For a metal, infinity is taken to be at above the Fermi level and at the bottom of the conduction band for an insulator. The positions of the absorption edges give us information

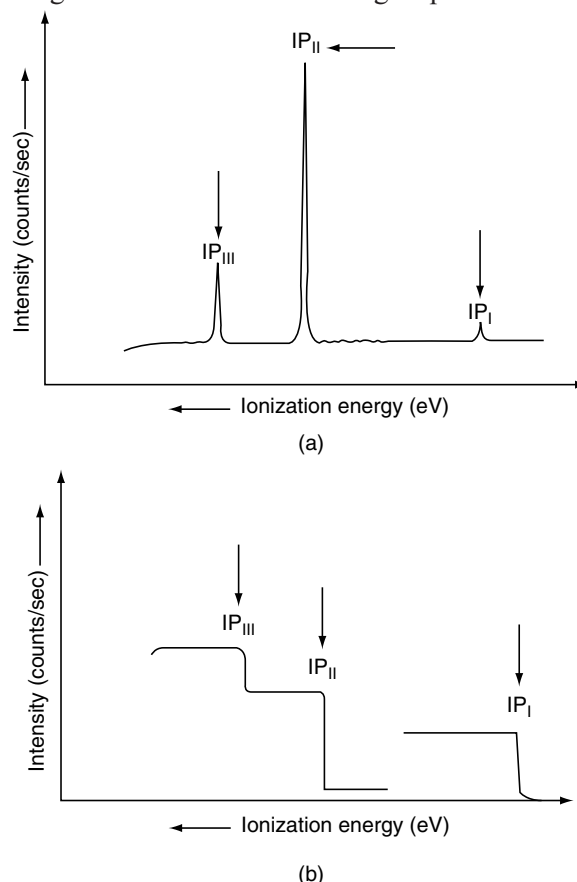


Fig. 6.7 Hypothetical (a) differential, and (b) integral photoelectron spectra of some system. Ionisation potentials (IP): $IP_{III} > IP_{II} > IP_I$.

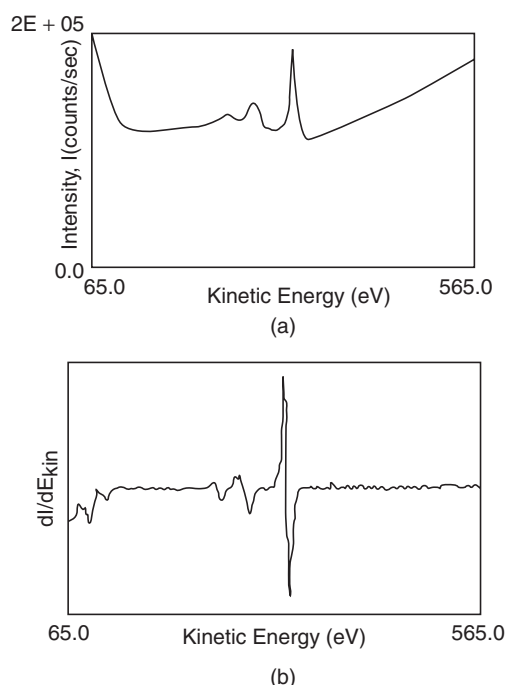


Fig. 6.8 Auger electron spectra of Pd metal produced by using 2.5 keV electron beam: (a) differential spectrum (b) derivative spectrum.

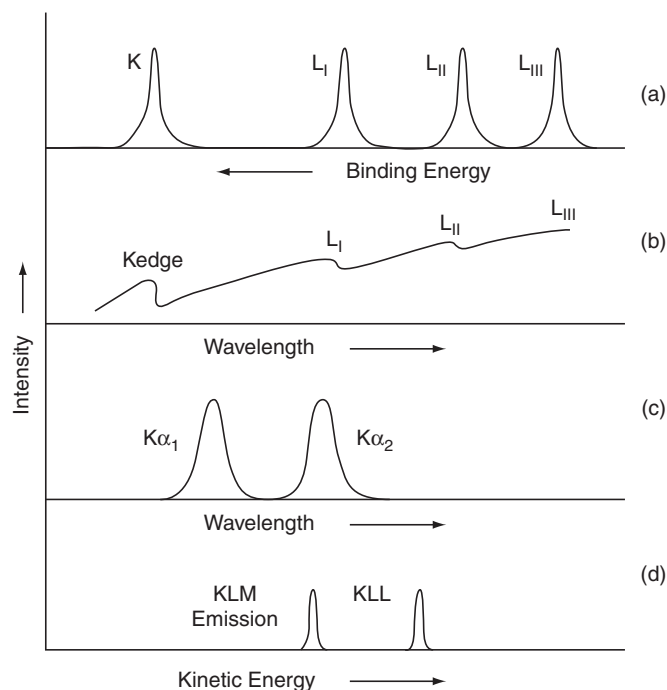


Fig. 6.9 Schematic diagram showing structural features of (a) photoelectron spectrum, (b) x-ray absorption spectrum, (c) x-ray fluorescence spectrum, and (d) Auger electron spectrum.

regarding the electronic energy structure of an atom. Each element has its own characteristics of *K*, *L*, *M*, *N* spectra. The structural features of x-ray absorption, x-ray fluorescence, Auger electron, and x-ray photoelectron spectroscopy are shown in Fig. 6.9. The positions of the photoelectron peaks coincide with the x-ray absorption edges. The peak positions in the other spectra are only relatively calculated with respect to one another.

6.6 BANDWIDTH AND THE FACTORS AFFECTING IT

The photoionised excited state will have lifespan, say τ . According to the Heisenberg uncertainty principle, i.e. $\Delta E \times \Delta t \approx \frac{h}{2\pi}$, the uncertainty in the energy of the ionised excited state will manifest itself in the width, say Γ , of the photoelectron signal.

$$\text{Thus,} \quad \Gamma \tau \approx \frac{h}{2\pi} = \frac{41.346 \times 10^{-16} (\text{eVs})}{2\pi} = 6.577 \times 10^{-10} (\text{eVs})$$

$$\text{or} \quad \Gamma = \frac{h}{2\pi\tau} = \frac{6.577 \times 10^{-16} (\text{eVs})}{\tau} \quad (6.23)$$

$$\text{For} \quad \tau = 10^{-13} \text{ s}$$

$$\Gamma = \frac{6.577 \times 10^{-16} (\text{eVs})}{10^{-13} \text{ s}} = 6.577 \times 10^{-3} \text{ eV} = 0.0065 \text{ eV} = 6.5 \text{ meV}$$

i.e. the natural bandwidth of the photoelectron signal is $0.0065 \text{ eV} = 6.5 \text{ meV}$.

The other factors which contribute to natural bandwidth are Doppler effect, width of the irradiating line, spectrometer broadening, etc.

The Doppler effect arises due to the random thermal motions of the target molecules before ionisation and the motion of the ejected electrons. The target molecules in random thermal motions have components of their velocities in the direction of the ejected electrons and add to their velocities. The electrons that move in a single direction only, the one-dimensional law of thermal distribution of velocity of molecules holds good. In such a situation, the observable line width, ΔV , in millielectron volts is then given by

$$\Delta V = 0.75 \left(\frac{VT}{M} \right)^{\frac{1}{2}} \quad (6.24)$$

where V is the electron energy in electron volts, T is the absolute temperature and M is the mass in atomic mass units.

For $M = 100$ amu; $V = 10$ eV and $T = 298$ K

$$\Delta V = 0.75 \left(\frac{10 \times 298}{100} \right)^{\frac{1}{2}} = 4.09 \text{ meV; which is well below the normal resolution of the differential analysers.}$$

The Doppler effect becomes important for light molecules and high electron energies or gas temperatures. The extreme case is hydrogen ionisation of H_2 , with He (I) 21.22 eV and He (II) 40.8 eV radiations sources respectively. The observable line width in the former is 22 meV and 46 meV in the latter. The Doppler widths can easily be reduced by reducing the effective transverse kinetic temperatures used in Eq. (6.24) to below 10 K. This temperature can be achieved if the target gas is used in the form of a jet or a true molecular beam.

The broadening of width by the irradiating line as well as spectrometer broadening may be judiciously controlled to a certain extent.

6.7 RESOLUTION OF PHOTOELECTRON SPECTRAL PEAK

The ability of a technique to determine the location of two closely spaced peaks/bands in the presence of each other is called *resolution*. It is governed by the width of the spectral band relative to the spacing between the peaks which is influenced not only by Doppler effect but also by the line width of the exciting radiation. Therefore, for high-resolution work, the Doppler widths must be reduced. In PES, this is achieved using target gas in the form of a jet or a true molecular beam in which the transverse kinetic temperature is reduced to below 10 K (see Section 6.6). As stated above, the width of the PES peak is limited by the line width of the excitation radiation which increases as the third power of the frequency. According to this rule, the ratio UPS line width to that

of the XPS should be of the order of $\left[\frac{21.22(\text{eV})}{1486.5(\text{eV})} \right]^3 \approx 10^{-6}$. This means, that the UPS line width is very small

as compared to that of the XPS. Consequently UPS is capable of much better peak resolution than XPS (0.01 eV against 0.5 eV in XPS). Due to better resolution of UPS, the fine structure resulting from the different vibrational and rotational transitions are also observed in the UPS; but not all of these peaks are resolved. However from the fine structure in the high-resolution UPS, some deductions regarding the nature of molecular orbital involved in photoionisation have been made and are so summarised in the tabular form in Section 6.14.4.

The additional complexity in UPS arises due to spin-orbit coupling for heavy atoms and by Jahn–Teller distortion effects in highly symmetric molecules. Even analysis of UPS spectra of atoms and simple molecules is very hard.

6.8 INTENSITIES OF THE PHOTOELECTRON SPECTRAL PEAKS

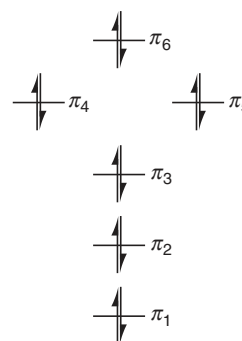
The intensities of the ionisation bands help to analyse the PES of molecules whose ionic states have not been identified. The areas of the photoelectron bands are approximately proportional to the relative probability of ionisations, also called relative partial ionisation cross sections or branching ratios in ionisation, to the different ionic states. For resolved bands, the total intensity of a particular band is equal to the sum of the intensities of all the vibrational lines in that band.

6.8.1 Rules to Predict the Intensities of Ionisation Peaks

The relative intensities of ionisation bands in the photoelectron spectrum not only depend upon ionisation probability but also upon the nature of the orbital, and their size, number of nodes and their localisation in the molecule, etc. Experimental parameters also contribute to the measured intensity. However, the three approximate rules framed to predict the intensities of the peaks in the PES are based purely on the probability of transition and the parameters governing it.

(a) Rule 1 The relative probability of ionisation from a given orbital is proportional to the number of equivalent ionisable electrons. Thus, the intensity of the band because of two equivalent ionisable electrons will be one half of the intensity of the band due to four equivalent ionisable electrons. All orbitals having the same number of ionisable electrons will give rise to bands of equal intensities. This rule is valid when ionisation occurs from molecular orbitals consisting of the same set of atomic orbitals; however even otherwise also, this is the only rule

useful for analysing the spectra of closed-shell molecules, e.g. the partial photoelectron spectrum of biphenyl in the π -electron region, i.e. 8–12 eV exhibits first three bands at 8.4, 9.4 and 9.8 eV in the approximate intensity ratio of 1 : 2 : 1. The π -orbital pattern in biphenyl predicted from the Hückel Molecular Orbital (HMO) calculations is indicated below:



The degenerate π_4 and π_5 orbitals yield a degenerate state which has four electrons. Thus, the experimental intensity ratio of the three π -electron ionisation bands conforms to the π -orbital pattern of biphenyl. The PES of CCl_4 in the 8–18 eV region exhibits four bands at ~ 11.7 , ~ 12.7 , ~ 13.5 and ~ 16.7 eV. The intensity ratios of the first three bands are 1.9:2.6:1.0, which indicate that the third ionisation band is because of e^{-1} ionisation. MO calculations reveal that the nonbonding chlorine p -atomic orbitals generate the outermost occupied orbitals in CCl_4 . In tetrahedral symmetry, these orbitals combine to give the three molecular orbitals t_1 , t_2 and e ; and t_1 and t_2 being triply degenerate while e is doubly degenerate. Thus, the predicted pattern of intensity ratios of the ionised bands will be 3:3:2. The predicted ratios, though do not conform to the experimental ratios of the first three bands, but on comparison show that the first three ionisation bands correspond to the t_1^{-1} , t_2^{-1} and e^{-1} ionisations respectively.

(b) Rule 2 The probability of ionisation is proportional to the statistical weights of the ionic states produced. This rule is equivalent to Rule 1 when ionisation occurs from closed-shell molecules but is different when ionisation takes place from atoms and open-shell molecules, for example the $^2P_{3/2}$ and $^2P_{1/2}$ states of atomic ions of rare gases though originating from the same orbital, have different statistical weights (i.e. $2J + 1$) of 4 and 2 respectively. Further, oxygen on ionisation, produces O_2^+ ion in quartet ($^4\Sigma$) and doublet ($^2\Pi$) states. Thus, the intensity ratios of the bands corresponding to the quartet and doublet states will be 2:1. Note that both rules 1 and 2 hold good for ionisations from closed shells of an open-shell molecule such as oxygen. Furthermore, when ionisation occurs from a filled orbital, the total intensity of the ionised band equals the sum of the intensities of such bands arising from the electronic configuration of the ionised molecule, i.e. ion and the relative intensities of the bands corresponding to single-electron configuration of the ion is proportional to the statistical weights (i.e. $2J + 1$) of the different ionic states, e.g. the electronic configuration of nitrogen oxide $2\pi...4\sigma^2 5\sigma^2 1\pi^4 2\pi$ on $1\pi^{-1}$ ionisation yields a configuration of $4\sigma^2 5\sigma^2 1\pi^3 2\pi$ for NO^+ molecule. This configuration gives rise to six ionic states: $^3\Sigma_1^+$, $^3\Delta_{5/2}$, $^3\Sigma_1^-$, $^1\Sigma_0^-$, $^1\Delta_{1/2}$ and $^1\Sigma_0^+$. Accordingly, $1\pi^{-1}$ ionisation of NO molecule should give six subbands of intensity ratios 3:6:3:1:2:1 in the PES spectrum of NO. Similarly, the ionisation from the 5σ orbital gives $^1\Sigma_0$ and $^3\Sigma_1$ ionic states. Consequently, two subbands in the intensity ratios of 1:3 are expected in the PES spectrum. Accordingly, the total intensity of the $1\pi^{-1}$ ionisation bands due to Σ states = 8 and those of $5\sigma^{-1}$ bands = 4. Thus according to Rule 1, the intensity ratio of the $1\pi^{-1}$ and $5\sigma^{-1}$ ionisations should be 2:1 but experimentally it has not been observed in the spectrum. The discrepancy may be attributed to the fact that while framing the rules which are purely on probabilistic considerations, the character of the orbitals have not been taken into account, e.g. the $6s^{-1}$ and $5d^{-1}$ ionisations bands from atomic mercury have intensity ratios of 1 : 21 whereas orbital occupancies predict a ratio of 1:5. In addition, as mentioned earlier, experimental parameters also contribute to the total intensity of the band measured by the instrument and will be discussed here in Section 6.8.2.

(c) Rule 3 This rule was given by Cox and Orchard who were also the first to enunciate the rules 1 and 2 as they apply to open-shell molecules. The third rule is for ionisation from the open shell of an open-shell molecule. The relative band intensities, are in general, proportion to the coefficients of the fractional parentage. When molecular configuration generates only one term, Rule 3 is equivalent to Rule 2, and this is so if the open shell contains either a single electron or one electron less than the number required for a complete shell. When the molecules have more than one open shell, a more complex rule which is beyond the scope of this book is available in the literature; Cox and Orchard; Chem. Phys. Lett., 7 (1970) 273; Cox, Evans and Orchard, Chem Phys. Lett., 13 (1972) 386; Brink and Satcher, Angular Momentum, Oxford University Press, London (1968).

6.8.2 Measured Intensities of Photoelectron Spectral Peaks

The presence of peaks at particular energies indicates the presence of a specific element in the sample under study—the measured intensity of a peak is related to the concentration of the element within the sampled region. Thus, photoelectron spectroscopy provides a quantitative analysis of surface composition, etc., the accuracy of which will be governed by the accuracy of measured intensities.

The intensity of the PES signal is measured in terms of the number of ejected electrons per second at a particular energy level. In differential PES spectra, the intensities of the peaks depend upon the resolution of the analyser. As resolution increases, the height of the sharp peak apparently increases while the height of the broad peak decreases. Therefore, areas under the peaks, rather than heights, are taken as the true measure of the intensities of the PES signals. On the other hand, this problem is not encountered in integral spectra. The measured step heights in the integral spectra correspond exactly to the areas in differential spectra. The angular distribution of electrons being not even will vary from one band to another in the PES but will affect the intensity. When measurements are made at an angle of $54^\circ 44'/\cos^{-1}(1/\sqrt{3})$, called *magic angle* from the photon beams (for unpolarised light), the variations in the angular distribution have no effect on the intensities. When electrons normal to the photon beam are examined, the intensity due to angular effects alone varies by a factor of two.

The photoelectron angular distributions of a mixture of *s*, *p*, *d*, *f* or higher partial electron angular wave functions have been given by

$$I(\theta) = \frac{\sigma}{4\pi} \left[1 + \frac{\beta}{2} (3\cos^2\theta - 1) \right] \quad (6.25)$$

Here, θ is the observation angle away from the direction of the electric vector of the plane polarised radiation, σ is the total cross section integrated over all angles and β is an anisotropy parameter which determines the angular distribution of the photoelectrons in the ionisation process. For a pure *p*-wave, $\beta = +2$.

For unpolarised radiation (generally used in PES), the distribution of intensity is defined as

$$I(\theta') = \frac{\sigma}{4\pi} \left[1 + \frac{\beta}{2} \left(\frac{3}{2} \sin^2\theta' - 1 \right) \right] \quad (6.26)$$

Here, θ' is the observation angle away from the direction of the radiation beam. The range of β values is from -1 and $+2$ and has the usual meanings. The value of β determines the angular distributions in the ionisation of both the atoms and molecules.

Equations (6.25) and (6.26) are valid for all atoms, for diatomic molecules, and for all molecules. The value of β can be determined experimentally using the relationship

$$I(\theta') = 1 + \frac{3\beta}{4 - 2\beta} \sin^2\theta' \quad (6.27)$$

The value of β can be determined by measuring the intensity at two angles or by making a least-square fit to the theoretical distribution given by Eq. (6.27).

Relationships between β and theoretical parameters that govern the ionisation process, i.e. angular momentum of the electron in the atom (*R-S* coupling holds good), partial cross section for the production of $l-1$ and $l+1$ waves and the phase difference ($\delta_{l+1} - \delta_{l-1}$) between the two waves exist for atoms and diatomics. The formula for atomic ionisation is expressed as

$$\beta = \frac{l(l-1)\sigma_{l-1}^2 + (l+1)(l+2)\sigma_{l+1}^2 - 6l(l+1)\sigma_{l+1}\sigma_{l-1} \cos(\delta_{l+1} - \delta_{l-1})}{(2l+1)[l\sigma_{l-1}^2 + (l+1)\sigma_{l+1}^2]} \quad (6.28)$$

β depends not only on the strengths of the two partial waves but on their phases also, which govern the interference between them. When the interference term is large, β values become negative since both the partial cross sections and the phases depend upon the energy of the electron, so β values of atoms and molecules also depend upon the electron energy and are useful in the analysis of photoelectron spectra. Direct calculation of β values have been carried out on some atoms and molecules but, in general, are hard due to mathematical difficulties. Experimental and theoretical studies reveal that the β values depend almost entirely on the nature of the orbital from which the electrons originate and not on the details of the ionic states produced. β is constant within the vibrational structure of a single band. If two or more bands arise from ionisation out of a single orbital (e.g. because of spin-orbit coupling or Jahn-Teller effects), the β values for such bands are the same. This relationship also probably applies to several bands per orbital produced by ionisation of open-shell molecules provided the electron energies are not very different.

To summarise, it is concluded that the measurements on the angular distribution of electrons photoemitted from atoms or molecules provide a tool to determine which molecular orbital is associated with a given photoionisation peak in the spectrum of a molecule or an atom. The variation in the angular dependence of one orbital compared to another is never very dramatic in the gas phase because the atoms or molecules in the gas phase have

random orientation. On the other hand, a surface can orient all the adsorbed atoms or molecules so that the angular distribution of the emitted electrons has much more structure than the corresponding gas-phase spectra. A proper analysis of the angular dependence can be used to determine the symmetry of the bonding site and potentially the symmetry of each orbital.

Magic Angle in PES As already described, the angle $\theta = 54^\circ 44'$ is called the magic angle since at this angle, the intensity is completely independent of β whether the radiation is polarised or not. When the photoelectron spectrum is recorded at this angle, the relative intensities of the peaks in the spectrum are not disturbed by the angular distributions of the emitted electrons.

6.9 SENSITIVITY AND DETECTION LIMIT OF PHOTOELECTRON SPECTROSCOPY

Sensitivity and detection limits are important for the quantitative application of any spectroscopic technique. The intensity of the signal can be increased using a higher source intensity provided increased source intensity does not cause decomposition of the sample. However, an increase in signal by using a higher source intensity is accompanied by an increase in background called *noise*. Actually, the quantity signal-to-noise ratio determines how much the quantitative information can be obtained from the spectrum.

A typical ESCA spectrum with superimposed background noise is shown in Fig. 6.10.

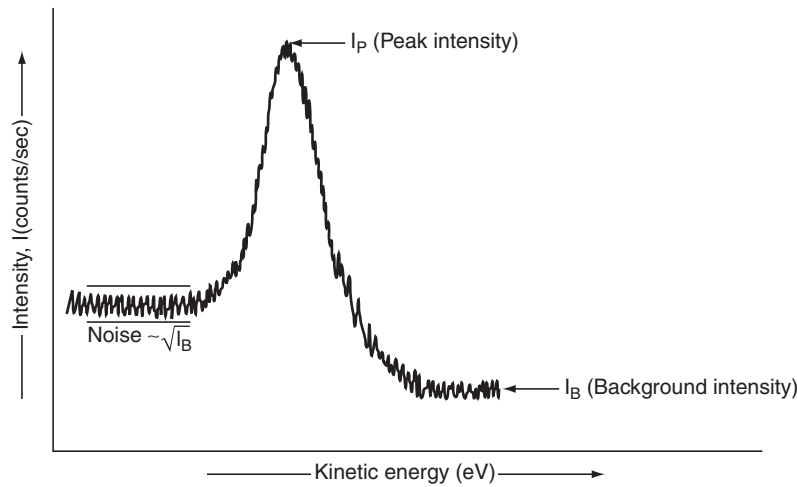


Fig. 6.10 Schematic diagram of a typical ESCA spectrum.

The difference between the peak and background intensities is defined as the signal intensity of the peak. Thus,

$$\text{Signal intensity} = I_P - I_B \quad (6.29)$$

$$\text{and signal-to-background ratio} = \frac{I_P - I_B}{I_B} \quad (6.30)$$

The signal-to-noise ratio is defined as $(I_P - I_B) / \sqrt{\text{RMS noise}}$ and is a more important parameter than signal-to-background ratio. For most spectra, as $I_P \rightarrow I_B$, $\text{RMS noise} \approx \sqrt{I_B}$; consequently,

$$\text{Signal-to-noise ratio} = (I_P - I_B) / \sqrt{I_B} \quad (6.31)$$

The other important factor which is important in any spectroscopic technique is the behaviour of observed intensity with concentration. For most surface techniques, a linear relationship exists between net intensity and concentration, i.e. $I_P - I_B = kC$. Thus, the sensitivity of a spectroscopic technique is defined as the slope of a plot of intensity against concentrations as shown in Fig. 6.11.

Mathematically,

$$\text{Sensitivity} = \frac{dI}{dC} = \frac{\Delta(I_P - I_B)}{\Delta C} \quad (6.32)$$

Further, detection limit is defined as the minimum amount of a material that can be detected using a given spectral line. This represents the concentration for which

$$I_p - I_B = 2 \times \text{RMS noise or } (I_p - I_B) = 2\sqrt{I_B} \quad (6.33)$$

The most sensitive spectral line need not have the lowest detection limit. In Fig. 6.11, line (i) has higher sensitivity (greater slope) and occurs at a higher background, i.e. I_B (i) while line (ii) has lower sensitivity (smaller slope) and occurs at lower background, i.e. I_B (ii). Thus, line (ii) will show a lower detection limit although line (i) shows a higher sensitivity. Detection limits are important and generally the matter of concern is what fraction of a monolayer can give a signal equal to 2 (RMS noise)^{1/2}.

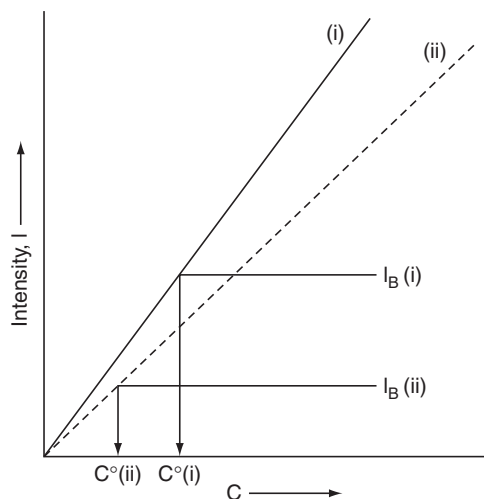


Fig. 6.11 Calibration curve for two spectral lines: (i) greater slope and higher background (ii) lower slope and lower background.

6.10 XPS CHEMICAL SHIFTS OR CORE ELECTRON SHIFTS

The exact *BE* of an electron not only depends upon the level from which the electron originates but also upon (i) the local chemical and physical environments of the atom which is being influenced by the molecular charge distribution on the shielding of core electrons, and (ii) the formal oxidation state of the atom. Changes in either chemical and physical environments or oxidation state of the atom give rise to small shifts in the peak positions in the spectrum which are termed chemical shifts or core electron-shifts. Such shifts are readily observable and interpretable in XP spectra (unlike in Auger spectra) because the XP technique, being a one-electron process is simple to interpret and is of high intrinsic resolution as core levels are discrete and generally of a well defined energy. The chemical shifts need be standardised with respect to the *BE* of some reference compound. The difference between electron binding energy for a particular atom *A* within a given molecule and binding energy of the same electron in a reference molecule is called the standard XPS chemical shift. The standard chemical shift is then defined as

$$\Delta IP(A) = IP(A) - IP(OA) \quad (6.34)$$

where, $IP(A)$ is the *BE* of the electron (say $1s$) in atom *A* in the molecule, and $IP(OA)$ is the *BE* of the electron (say $1s$) in the atom *A* in the reference molecule, e.g. for carbon atom the reference is CH_4 . The $\text{C}, 1s$ PES spectra of CH_4 , CO and CO_2 is shown in Fig. 6.12. Thus $\Delta IP(\text{C}, 1s) = 5.30 \text{ eV}$ for CO and $\Delta IP(\text{C}, 1s) = 7.7 \text{ eV}$ for CO_2 , the $IP(\text{C}, 1s)$ of CH_4 being 290.7 eV . Further, XPS chemical shifts of same atoms in a molecule will be different provided they are in a different chemical environment, e.g. the chemical shift of $1s$ carbon electrons for various carbon atoms of ethylchloroformate (I) and trifluoroacetate (II) follows the order.

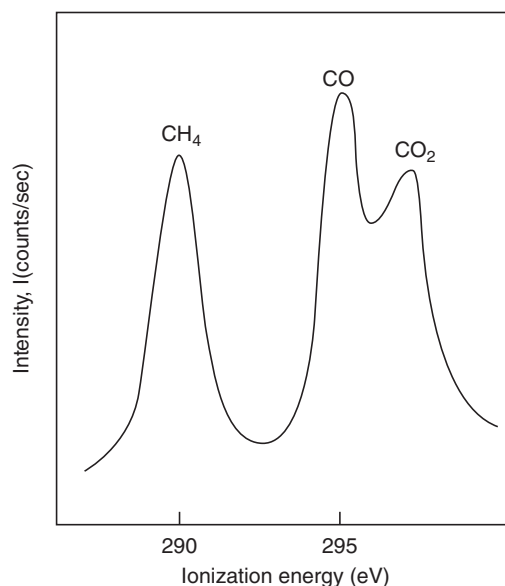
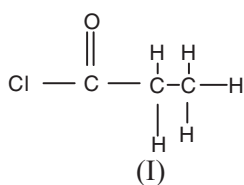
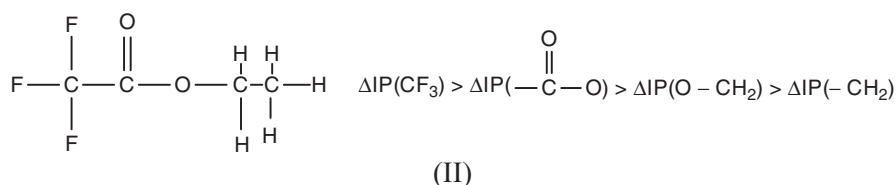


Fig. 6.12 Carbon $1s$ photoelectron spectrum from gas mixture of CH_4 , CO and CO_2 .



and in



This reveals that XPS chemical shift is governed by the electron-withdrawing power of the atoms attached to the atom whose chemical shift is under consideration. The more the withdrawing power of the neighbouring atoms or substituents, the greater the chemical shift. The *BEs* (in eV) of 1s electron of some atoms in compounds are listed here for ready reference. C1s (288), CH₄ (290.7), C₂H₅OH (290.9) CH₃COCH₃ (291.2), CH₃CHO (291.3), CH₃COOH (291.4), CH₃OH (292.3), N1s (403.0), C₆H₅NH₂ (405.5), NH₃ (405.6), N₂ (409.9), NO (410.7), NO₂ (412.9), O1s (538.0), CH₃CHO (537.6), C₂H₅OH (538.6), CH₃OH (538.9), CH₃COCH₃ (539), SO₂ (539.6), H₂O (539.7), CO₂ (540.8), CO (542.1), O₂ (543.1), F1s (694.0), SOF₂ (693.6), SF₆ (694.6), CF₄ (695.0).

As has already been stated, changes in oxidation state also cause XPS chemical shifts (i.e. change in *BE*), e.g. chemical shifts in the *K* and *L*₁ shells of chlorine in a series of inorganic compounds reveal that the chemical shift increases with the increase in the oxidation number, since atoms of higher positive oxidation state exhibit a higher *BE* due to the extra coulombic interaction between the photoemitted electron and the ion core, i.e.



The same argument holds good for S, N, I, Be, Cu, Fe, B, Cr, Eu and C compounds, e.g. for S (2s): oxidation state / chemical shift :: 0/0, +4 /4.5; for N₂ (1s): -1/0, +1/+4.5, +3 /+5.1; for Cl₂ (2p): -1 /0, +3 /+3.8, +5 /+7.1, for I₂ (4s): -1/0, +5 /+5.3.

Accordingly, the chemical shifts permit insight into the nature of bonding and the valency of the atom in the molecule.

6.11 ATOMIC PHOTOELECTRON SPECTRA

Atoms have the simplest photoelectron spectra. The light atoms, i.e. up to alkaline earth metals, obey Russells–Saunders (i.e. *L–S*) coupling where the orbital (*l*) and the spin (*s*) angular momenta of electrons are coupled separately.

$$L = l_1 + l_2 + \dots = \sum_i^n l_i$$

$$S = s_1 + s_2 + \dots = \sum_i^n s_i$$

For two electrons, $S = s_1 \pm s_2 = 0$ or 1. Thus, the total angular momentum is given by $J = L + S$ and the atomic term symbol is $^{2S+1}L_J$. Here, J can take on values $L + S, L + S - 1, \dots, |L - S|$. $|L - S|$ coupling is opposite to $j-j$ coupling which is operative in heavy atoms. The strong coupling between the individual orbital and spin angular momenta is deduced as follows:

$$j_1 = l_1 + s_1$$

$$j_2 = l_2 + s_2$$

$$j_1 + j_2 + \dots = \sum_i^n j_i = J$$

State	<i>L</i>	<i>S</i>	Relative order
Ψ ₁ , Ψ ₂	Same	<i>S</i> ₁ > <i>S</i> ₂	<i>E</i> ₂ > <i>E</i> ₁
Ψ ₁ , Ψ ₂	<i>L</i> ₁ > <i>L</i> ₂	Same	<i>E</i> ₂ > <i>E</i> ₁

The relative order of energies of the orbitals is predicted from the Hund's rule of multiplicity, i.e. For less than half-filled orbitals,

$$\Psi_1, \Psi_2 \quad J_1 > J_2 \quad E_1 > E_2$$

For more than half-filled orbitals,

$$\Psi_1, \Psi_2 \quad J_1 > J_2 \quad E_2 > E_1$$

For carbon atom $2p^2$: ${}^3P_0 < {}^3P_1 < {}^3P_2 < {}^1D_2 < {}^1S_0$
and for mercury atom: $(6s6p) {}^1P_1 > {}^3P_2 > {}^3P_1 > {}^3P_0 > (6s6s) {}^1S_0$

(a) 2p PES of Ne (Atomic Number 10) The electronic configuration of Ne is $1s^2 2s^2 2p^6$, which is a closed shell configuration. Photoionisation of $2p$ electrons will yield Ne^+ ion with a hole in the $2p$ orbital according to the scheme



The atomic states involved in this process are worked out from the general term symbol ${}^{2S+1}L_J$ as follows.

For $\text{Ne}(1s^2 2s^2 2p^6)$: $l = 0, s = 0; L = 0, S = 0. \therefore J = 0$ and ${}^{2S+1}L_J = {}^1S_0$

For $\text{Ne}^+ (1s^2 2s^2 2p^5)$: $l = 1, s = \frac{1}{2}; L = 1, S = 1/2 \therefore J = 1 + \frac{1}{2} = \frac{3}{2};$

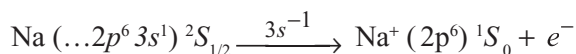
$$l = 1, s = -\frac{1}{2}; L = 1, S = -\frac{1}{2} \therefore j = 1 - \frac{1}{2} = \frac{1}{2}$$

Thus, the possible terms are ${}^{2S+1}L_J = {}^2P_{3/2}$ and ${}^2P_{1/2}$

Thus, the $2p$ PES of Ne^+ will consist of two peaks corresponding to the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ higher energy states respectively. According to Hund's multiplicity rule, the BE of $2p^{-1}$ electron in ${}^2P_{3/2}$ state should be small relative to that of in ${}^2P_{1/2}$ i.e. $BE({}^2P_{1/2}) > BE({}^2P_{3/2})$. It can be noted that the relative intensities of these peaks are directly proportional to the multiplicity of the final states, i.e. the number of $2J + 1$ components, $J, J - 1, J - 2, \dots -J$, thus indicating the type of electron ionised. In other words, we can say that the relative intensity of the peaks reflects the degeneracy of final states, i.e. $g_J = 2J + 1$, which in turn determines the probability of transition to such a state during photoionisation. Accordingly, the ratio of intensities of ${}^2P_{1/2}$ and ${}^2P_{3/2}$ peaks will be 2:4. The predicted $2p$ PES of Ne is consistent with the observed spectrum of Ne using He (II) 40.81 eV radiation source. The two states are separated by 0.1 eV.

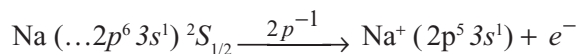
According to Koopman's theorem, one peak is expected per orbital. This rule fails in case of p - and d -orbitals in light as well as in heavy atoms where the number of peaks of an electron in these orbitals corresponds to the number of states corresponding to the orbitals (i.e. characteristic spin-orbit doublets are observed in case of p -, d -, f - orbitals since $l = 2, 3$ and 4 for the p -, d - and f - orbitals respectively. $l = 0$ for s -orbital so there is no spin-orbit splitting). In such cases, a weighted mean of all energies for ionisation from a single orbital must be taken. The splitting of the energy states corresponding to the p - and d -orbitals may be due to either of the two factors: (i) due to spin-orbital, i.e. j - j coupling, e.g. in case of heavy atoms, and (ii) ionic state has both orbital and spin degeneracy, e.g. in case of light atoms.

(b) 3s- and 2p PES of Na (Atomic Number = 11) The electronic configuration of Na is $1s^2 2s^2 2p^6 3s^1$, which is an open-shell configuration. The photoionisation of $3s$ electron is represented as



Thus, $3s$ PES of Na will exhibit a single peak corresponding to ${}^1S_0$ state Na^+ . It conforms to the observed $3s$ spectrum where a single peak has been observed at 5.14 eV using He (II) 40.8 eV radiation source.

Now, when $2p$ electrons are involved in photoionisation, the process is represented as



For $\text{Na} (\dots 2p^6 3s^1)$: $l = 0, s = \frac{1}{2}, L = 0, S = \frac{1}{2} \therefore J = \frac{1}{2}$ and

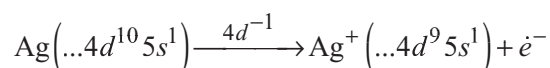
$${}^{2S+1}L_J = {}^2S_{1/2}$$

and for $\text{Na}^+ (\dots 2p^5 3s^1)$: $l_1 = 1, l_2 = 0; L = l_1 + l_2 = 1 + 0 = 1; s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, S = s_1 \pm s_2 = 0, 1$

$\therefore J = L + S = 1 + 1 = 2$ and $1 + 0 = 1$. The possible terms are $^{2S+1}L_J = {}^3P_2$ and ${}^1P_1$. The ${}^3P_2$ term further splits into ${}^3P_1$ and ${}^3P_0$ terms. Thus, the four states of Na^+ are ${}^3P_2$, ${}^3P_1$, ${}^3P_0$ and ${}^1P_1$. Consequently, the $2p$ spectrum of Na will exhibit four peaks corresponding to the ${}^3P_2$, ${}^3P_1$, ${}^3P_0$ and ${}^1P_1$ states respectively. According to Hund's rule of multiplicity, the binding energy of the states should follow the order ${}^1P_1 (J=1) > {}^3P_0 (J=0) > {}^3P_1 (J=1) > {}^3P_2 (J=2)$. According to the $(2J+1)$ multiplicity rule, the intensity ratio of the peaks is 3:1:3:5. The predicted spectrum is consistent with the experimentally observed spectrum obtained by using He (II) 40.8 eV radiation source. Note that the energy of the states follow the order ${}^1P_1 > {}^3P_2 > {}^3P_1 > {}^3P_0$.

(c) 4d PES of Ag and Cd The atomic number of Ag is 47 and that of Cd is 48. These two atoms are selected to see how the multiplet structure in the PES is influenced if the open shell is closed by the addition of an electron.

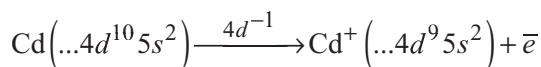
The 4d photoionisation of Ag proceeds according to the scheme



For $\text{Ag}^+(\dots 4d^9 5s^1)$: $s_1 = \frac{1}{2}$, $s_2 = \frac{1}{2}$, $S = \frac{1}{2} \pm \frac{1}{2} = 1, 0$, $l_1 = 2$, $l_2 = 0$, $L = l_1 + l_2 = 2 + 0 = 2$

$\therefore J = 1 + 2 = 3$ and $2 + 0 = 2$ and $^{2S+1}L_J = {}^3D_J$ and ${}^1D_2$. The term ${}^3D_J$ further splits into ${}^3D_3$, ${}^3D_2$ and ${}^3D_1$ terms. Thus, the 4d PES of Ag will consist of four peaks. The BE corresponding to these peaks follows the order: ${}^3D_3 < {}^3D_2 < {}^3D_1 < {}^1D_2$. The intensity ratio of these peaks according to the $(2J+1)$ rule is 7:5:3:5. The predicted spectrum is consistent with experimental spectrum obtained by using He (II) 40.8 eV radiation source.

In case of Cd, the electronic configuration of Cd^+ cation is formed because of 4d photoionisation and is $4d^9 5s^2$. The photoionisation process in this case is represented as



In order to predict the 4d PES of Cd, we are to work out the spectroscopic terms for $\text{Cd}^+(\dots 4d^9 5s^2)$.

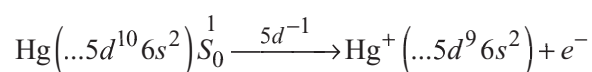
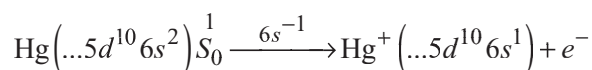
Here $s = \frac{1}{2}$, $S = \frac{1}{2}$; $l = 2$, $L = 2$ $\therefore J = 2 + \frac{1}{2} = 5/2$ and $^{2S+1}L_J = {}^2D_{5/2}$. ${}^2D_{5/2}$ term further splits into ${}^2D_{3/2}$

state (i.e. $s = \frac{-1}{2}$, $S = \frac{-1}{2}$; $l = 2$, $L = 2$ $\therefore J = 2 - \frac{1}{2} = 3/2$). The BE of the ${}^2D_{3/2}$ state will be small as compared to that of the ${}^2D_{5/2}$ state. The intensity ratio of the two peaks is 6:3. Again, the predicted spectrum matches with the experimentally observed spectrum obtained by using He (II) 40.8 eV radiation source. The spectrum reveals that the four peaked structure of the $\dots 4d^9 5s^1$ configuration decreases to double peaked structure by closing one of the open shells ($5s^1$) by the addition of an electron.

(d) PES of Ar (Atomic Number = 18) Uptil now, we have discussed the partial PES arising because of photoionisation of an electron from a particular level of an atom. Let us now apply the rules to work out the complete PES of the Ar atom. The electronic configuration of Ar is $1s^2 2s^2 2p^6 3s^2 3p^6$. The complete PES will result from the photoionisation of 1s, 2s, 2p, 3s and 3p electrons of the Ar atom. The spectroscopic terms corresponding to these five different configurations of photoionised Ar^+ atom are the following:

$1\ {}^2S_{1/2}$, $2\ {}^2S_{1/2}$, $(2\ {}^2P_{1/2}, 2\ {}^2P_{3/2})$, $3\ {}^2S_{1/2}$ and $(3\ {}^2P_{1/2}, 3\ {}^2P_{3/2})$ respectively. Accordingly the complete spectrum will consist of seven peaks. BE of the photoelectrons from different orbitals will follow the order $3p(3\ {}^2P_{3/2} < 3\ {}^2P_{1/2}) < 3s(3\ {}^2S_{1/2}) < 2p(2\ {}^2P_{3/2} < 2\ {}^2P_{1/2}) < 2s(2\ {}^2S_{1/2}) < 1s(1\ {}^2S_{1/2})$. The intensity ratio of the peaks is $(4:2) : 2 : (4:2) : 2 : 2$. The completely resolved experimentally observed spectrum of Ar obtained by combining both ESCA (Cr K_{α} = 5414.7 eV) and PES [He (I) = 21.21 eV] is consistent with the predicted spectrum. The spectrum reveals that only the 3p electrons of Ar are within the range of 6–21 eV of the He (I) radiation source. The BEs corresponding to $3\ {}^2P_{1/2}$ and $3\ {}^2P_{3/2}$ states are 15.933 and 15.755 eV respectively.

(e) 6s and 5d PES of Hg (Atomic Number = 80) Hg is a candidate from heavy atoms with closed-shell structure. The photoionisation of 6s and 5d electrons is represented as



For $\text{Hg}^+ (\dots 5d^{10} 6s^1)$: $s = \frac{1}{2}$, $S = \frac{1}{2}$, $l = 0$, $L = 0$, $\therefore J = L + S = \frac{1}{2}$ and the spectroscopic term $^{2s+1}L_J = {}^2S_{1/2}$

Thus, the 6s PES of Hg should consist of a single line. Indeed the same has been observed experimentally [He (I) 21.22 eV]. The BE corresponding to ${}^2S_{1/2}$ state is 10.44 eV.

Now in order to predict the 5d PES of Hg, we are to write the states for the configuration $\text{Hg}^+ (\dots 5d^9 6s^2)$. In this case, $l = 2$, $L = 2$, $s = \frac{1}{2}$, $S = \frac{1}{2}$ $\therefore J = L + S = 2 + \frac{1}{2} = \frac{5}{2}$.

Thus, the spectroscopic term corresponding to this configuration is $^{2s+1}L_J = {}^2D_{5/2}$. This term splits further into ${}^2D_{3/2}$ terms $\left(\text{i.e. } l = 2, L = 2, s = \frac{-1}{2}, S = \frac{-1}{2}, \therefore J = L + S = 2 - 1/2 = \frac{3}{2} \right)$. Consequently, the 5d PES of Hg

will show two peaks corresponding to the ${}^2D_{5/2}$ and ${}^2D_{3/2}$ states. According to Hund's rule of multiplicity, the energy of the ${}^2D_{5/2}$ state should be on the lower side of the ${}^2D_{3/2}$ state. The experimentally observed data on BE follows the expected trend, i.e., ${}^2D_{3/2}$ (16.71 eV) > ${}^2D_{5/2}$ 14.84 eV. The intensity ratio of the two peaks, as deduced from the $(2J + 1)$ rule, has been found to be 4:6. However, the experimentally observed intensity ratio is 2.4:6 (from integral spectrum). The intensity ratio for the complete 6s and 5d photoionisation from the differential spectrum is $\approx 6 ({}^2D_{3/2}) : 21 ({}^2D_{5/2}) : 1 ({}^2S_{1/2})$. The discrepancy between the observed and theoretical intensity ratios reveals that the relative intensities of the bands are not solely governed by the spin-orbital coupling but by other factors also. To cite a few, the relative probability of ionisation to different ionic states depends on the nature of the orbitals and their size, number of nodes, etc., and angular distribution of electrons.

The ${}^5p_{3/2}$ electron spectral lines of Th metal, V metal, and UO_3 also split whereas the ${}^4f_{5/2}$ and ${}^4f_{7/2}$ spectral lines of the same sample do not split. On the other hand, ${}^5p_{3/2}$ line for gold in some gold compounds varies linearly with MB quadrupole splittings of the compounds. Since quadrupole splitting depends on the symmetry of the electric field around the nucleus of the atom in question, the x-ray photoelectron spectroscopy may also give information about the symmetry of the electronic environment around the atom.

Splitting has also been observed in paramagnetic molecules and transition metal ions. The splitting in paramagnetic species is due to the different behaviour of unpaired electrons towards core electrons. The exchange interaction affects core electrons with α (spin up) and β (spin down) spins differently.

6.12 RULES FOR THE PREDICTION OF ATOMIC PHOTOELECTRON SPECTRUM

The atomic PES can be deduced by making use of the following steps:

1. Write the electronic configuration of the photoionised cation.
2. Using the general term $^{2s+1}L_J$, write the terms for the photoionised states for the cation.
3. The number of peaks in the PES corresponds to the number of photoionised states.
4. According to Hund's rule of multiplicity, the BE's of the states will follow the reverse trend of J 's.
5. The intensity ratio of the peaks can be predicted from the $g_J = (2J + 1)$ multiplicity rule.
6. Draw the stick spectrum and compare with the experimentally observed values if available.

6.13 PHOTOELECTRON SPECTROMETER

The schematic diagram of a photoelectron spectrometer is shown in the self-explanatory Fig. 6.13. The basic elements of the photoelectron spectrometer are radiation source, target, ionisation chamber, electron energy analyser, detector, recorder and ultra high vacuum chamber.

(a) Radiation Sources They form the backbone of the photoelectron spectrometer. In UV-PES, the radiation source is normally a noble gas discharge lamp and sometimes helium mixed with any other noble gas. The energy of the HeI_α line at 584.3 Å (21.22 eV) from the He discharge lamp is sufficient to cause ionisation of the majority of the valence shell electrons. Moreover, this line is not accompanied by any lines of lower energy down to about 4 eV. The HeII_α line at 303.8 Å (40.81 eV) from ionised He (He^+) produced in the He discharge lamp is also used since its energy is sufficient to cause ionisation of most of the valence-shell electrons. Discharge lamps of other inert gases alone or mixed with helium are used to produce low-energy radiations. Discharge in neon gas gives NeI_α lines at 16.67 and 16.85 eV while in argon gas gives ArI_α lines at 11.62 and 11.83 eV and Ar II (Ar^+) lines at 13.30 and 13.48 eV. Lyman $-\alpha$, $-\beta$ and $-\gamma$ lines from hydrogen discharge lamps have energies of 10.198, 12.087 and 12.748 eV respectively.

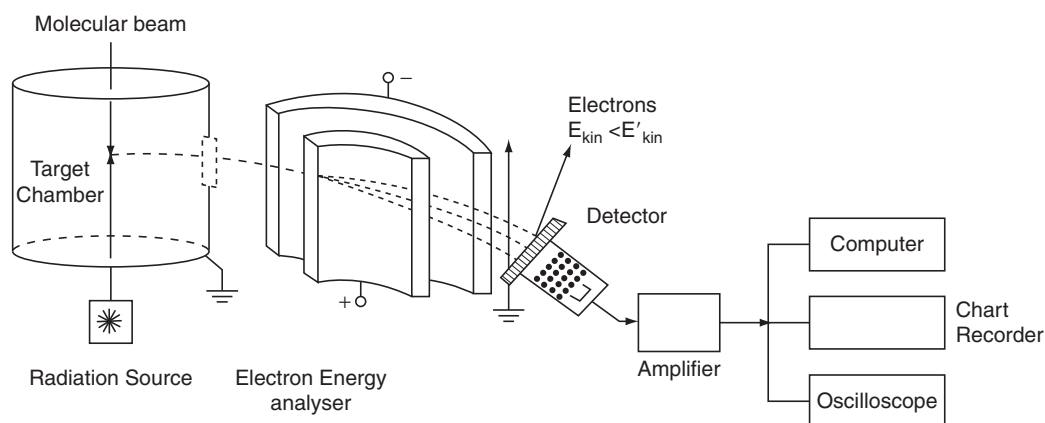


Fig. 6.13 Block diagram of a photoelectron spectrometer.

In XPS, soft x -ray sources which have energies of 1000 eV and higher are most commonly employed, e.g. Mg K_{α} line at 1253.6 eV and Al K_{α} line at 1486.5 eV. The emitted photoelectrons from Mg K_{α} source will have KE's in the range of Ca 0–1250 eV while Ca 0–1480 eV from Al K_{α} . The very soft x -ray sources in the energy range of 130–300 eV can bridge the gap between the UV and x -ray regions. These very soft x -rays were discovered by M A Krause in 1970. 132.3 eV Yttrium line is most useful but its intrinsic line width is 0.6 eV and intensity is also very low. Presently, the synchrotron radiation is the most promising emission source in the intervening wavelength region for photoelectron studies. The synchrotron radiations of variable wavelengths are generated by electron/positron accelerators. The energy range of these sources is Ca 5–5000 eV plus and the intensity is also sufficient for PES. Moreover, the radiation is fully polarised in the plane of electron paths (80 per cent or more) and has a very small angular divergence out of plane. Though such radiation sources have enabled high-resolution studies in photoionisation and adsorption studies of gases and of solids spanning much wider and more complete energy range, such work is, and will remain, limited due to expense, complexity and limited availability of such sources.

(b) Sample and Ionisation Chambers Samples can be in solid, liquid, or vapour form, depending on the pumping techniques. For surface studies, solid samples freed from moisture and other impurities are placed in a suitable sample holder which is mounted in a fixed position close to the monochromatic photoelectron source in the ionisation chamber (not shown in Fig. 6.13); otherwise a stream of volatilised sample or a beam of molecules in cases of gases is introduced from the top into the target chamber where it is irradiated with photons from an appropriate radiation source. The electrons emitted from the sample are made to enter the electron-energy analyser. Liquids at room temperature have been studied by vapourising or freezing. Solutions of $K_3Fe(CN)_6$, $K_4Fe(CN)_6$ and NaCl are examined by this method. XPS of frozen solutions of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ show that the BEs of the Fe 3p electrons differ by about 0.2 eV from the corresponding solid samples.

(c) Ultra High Vacuum Chamber All the electron optics is placed in a chamber fitted with high vacuum pumps to produce high vacuum (10^{-5} mmHg or less) (not shown in Fig 6.13). The ionisation is carried out in a high vacuum environment to enable the emitted electrons to be analysed without interference from gas-phase collisions.

(d) Electron-energy Analysers They are the heart of any photoelectron spectrometer and the function of an analyser is to sort out the emitted electrons according to their kinetic energy. There are many different designs of electron energy analysers but the most commonly preferred and widely used for photoemission experiments is a concentric cylindrical or hemispherical analyser which uses an electrostatic field between the two cylindrical/hemispherical surfaces to deflect or disperse the electrons according to their kinetic energy. Accordingly, they are known as deflection or dispersion analysers.

For cylindrical plates, the kinetic energy E_{kin} of electron is given by

$$E_{kin} = \frac{V_2 - V_1}{2r \log(r_1/r_2)} \quad (6.35)$$

Here, V_1 and V_2 are the plate voltages, r_1 and r_2 the radii of the plates and r is the average radius.

The path of the electrons in the analyser is affected by an external magnetic field. So for better resolution, external fields are reduced to about 0.1 mG ferromagnetic shielding. Magnetic-deflection analysers are also used but they are not very suitable for low-energy electrons because weak magnetic fields are required and it is a problem to nullify the effect of external fields.

The other class of analysers is the *retarding-field analysers*. In these types of analysers, use is made of cylindrical/spherical/slotted geometry and the electrons with energies higher than a retarding potential are permitted to reach the detector. The detector in this case measures the photoelectron current as the retarding potential is varied. The recorded spectrum, thus, should contain a step in the current for each group of photoelectrons of discrete energy. The steps of low-energy electrons are superimposed on the electron current of all electrons of higher energy, and hence it becomes difficult to examine the low-energy electrons. However, they are capable of accepting electrons in a large solid angle and from extended sources. They are equally sensitive to electrons of all energies, particularly low-energy electrons where the differential analysers are usually least sensitive as compared to deflection analysers.

The theoretical resolution of such an analyser is given by

$$\frac{\Delta V}{V} = \left(\frac{r_1}{r_2} \right)^2 \quad (6.36)$$

where ΔV is the smallest resolvable energy difference at the electron energy, r_1 is the radius of the ionisation region and r_2 is the radius of the retarding electrode. The maximum value of resolution achieved is 0.5 meV, but in these type of analysers it is difficult to maintain high resolution in the presence of target high reactive gases since their adsorption on the surface of the retarding electrode will alter the contact potential and hence the resolving power.

(e) Detector The electrons from the electrostatic analyser with varying voltage are introduced into the detector for further analysis. The detector counts the number of electrons per second as a function of their kinetic energy, i.e. all electrons of the same kinetic energy are counted. Note that the electron energy is scanned by the variation of the analyser field or preaccelerating potential, i.e. the potential difference between the target chamber and the analyser entry slit. The latter method is preferred because the analyser is set to transmit electrons of fixed energy for which its resolution and transmission can be optimised and that the resolution of the resulting spectrum is independent of electron energy. However, the contact potential varies from compound to compound and shifts the energy scales as a function of pressure. Hence, it is essential to record the spectrum of a mixture of sample and calibrant. A calibrant should give sharp peaks precisely at known ionisation potentials. The detector is calibrated with known lines of CH_3I , argon, krypton or xenon, (which are useful for ionisation energy range below 15 eV), the recorded half width of which gives a guide to the resolution. Resolution of 10–20 mV (80–160 cm^{-1}) can easily be obtained. Some other gases and different ionising radiations can be used in order to extend the calibration range to higher and lower ionisation energies. Some of the useful calibrant lines due to D R Lloyd are mentioned here in Table 6.1.

Table 6.1 Some calibrant lines due to D R Lloyd.

Substance	Ionic state	Ionising line	Electron energy (eV)	Ionisation potential (eV)
Ne	$^2P_{3/2}$ $^2P_{1/2}$	He II $_{\alpha}$ He II $_{\alpha}$	19.2494, 19.3463	1.9681, 2.0650
He	^2S	He II $_{\alpha}$	16.2268	4.9907
MeI	$^2E_{1/2}$ $^2E_{3/2}$ $^2E_{1/2}$	He I $_{\beta}$, He I $_{\alpha}$ He I $_{\alpha}$	12.922, 11.680, 11.053	8.296, 9.538 10.165
Xe	$^2P_{3/2}$ $^2P_{1/2}$	He I $_{\alpha}$ He I $_{\alpha}$	9.088, 7.782	12.130, 13.436
Kr	$^2P_{3/2}$ $^2P_{1/2}$	He I $_{\alpha}$ He I $_{\alpha}$	7.219 6.533	13.999 14.665
Hg	$^2D_{5/2}$	He I $_{\alpha}$	6.378	14.840
Ar	$^2P_{3/2}$ $^2P_{1/2}$	He I $_{\alpha}$ He I $_{\alpha}$	5.459, 5.281	15.759, 15.937
Hg	$^2D_{3/2}$	He I $_{\alpha}$	4.514	16.704
N ₂	$^2\Sigma_u^+$	He I $_{\alpha}$	2.467	18.751
Ne	$^2P_{3/2}$ $^2P_{1/2}$	He I $_{\beta}$ He I $_{\beta}$	1.5223, 1.4253	19.6952, 19.7922
CH ₃ I	$^2E_{3/2}$	H Lyman $_{\alpha}$	0.661	20.557

(f) Recorders The rate at which electrons of each energy arrive at the detector can then be stored in the computer or displayed on an oscilloscope screen or recorded on an X-Y chart recorder for qualitative analysis.

The XPS spectrum obtained from a Pd metal sample using MgK_{α} radiation on a deflection-type photoelectron spectrometer is shown in Fig. 6.14 (a). The main peaks occur at kinetic energies of Ca 330, 690, 720, 910 and 920 eV. If the energy of the radiation is known, it is a simple matter to transform the spectrum so that it is plotted against BE as opposed to KE . The resultant spectrum in case of Pd spectrum is shown in Fig. 6.14 (b).

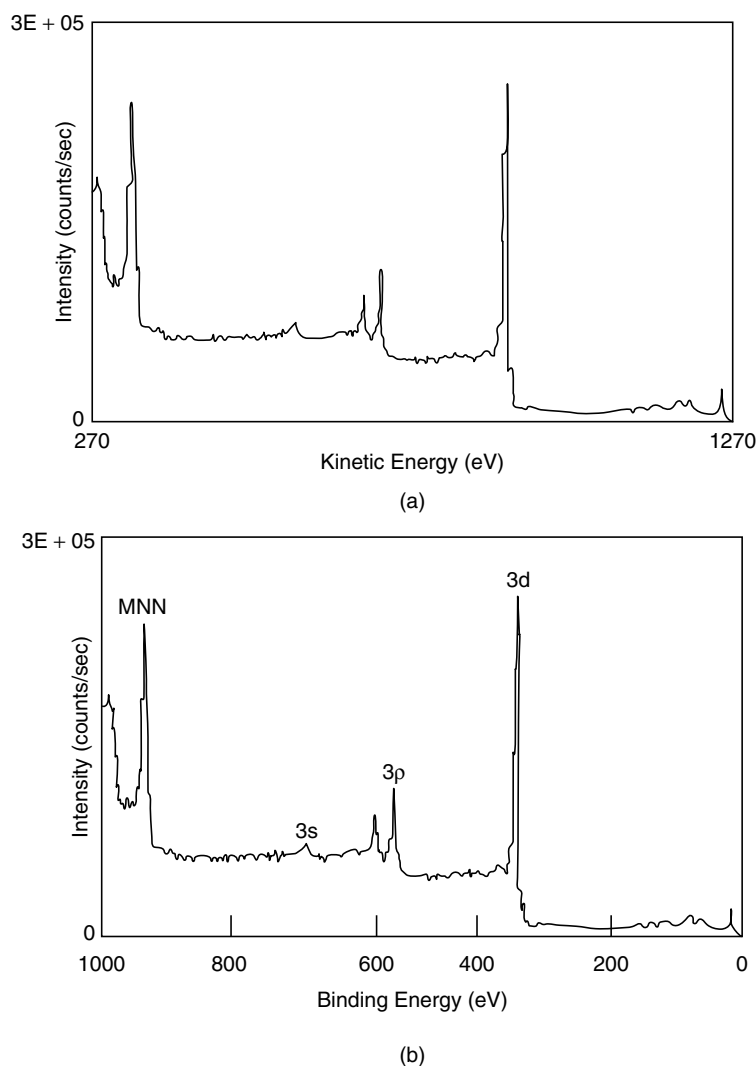


Fig. 6.14 X-ray photoelectron spectra of Pd generated using MgK_{α} 1253.6 eV radiation source: (a) intensity vs kinetic energy (b) intensity vs binding energy.

Problem 6.1: Calculate the wavelength of resonance line of the helium atom if excitation energy of the resonance level is 21.22 eV.

Solution The wavelength λ (in Å) is equal to

$$\lambda = \frac{hc}{\Delta E} = \frac{12404(\text{eV})}{21.22(\text{eV})} = 584.5 \text{ Å}$$

where ΔE is the difference in the potentials of the ground and excited states in eV; h is Planck's constant and c is the velocity of light in vacuum.

Problem 6.2: In the $C(1s)$ photoelectron spectrum of CO_2 and CH_4 mixture, there is one more line between the CH_4 and CO_2 lines at $BE(CH_4) = 290.7 \text{ eV}$ and $BE(CO_2) = 298.4 \text{ eV}$. Calculate the energy of the unknown line if on the screen of the oscilloscope, it is 1.8 mm away from the line of CH_4 and 2.2 mm from the line of CO_2 .

Solution In order to determine the energy of the unknown line that lies between the lines of CH_4 and CO_2 , we need to convert the energy corresponding to the CH_4 and CO_2 lines into wavelength units which are additive in nature.

Thus,
$$\lambda(\text{CH}_4) = \frac{12404(\text{eV}\text{\AA})}{290.7(\text{eV})} = 42.414 \text{\AA}$$

and
$$\lambda(\text{CO}_2) = \frac{12404(\text{eV}\text{\AA})}{298.4(\text{eV})} = 41.320 \text{\AA}$$

we find λ_x as

$$\lambda_x = \lambda(\text{CH}_4) + [\lambda(\text{CO}_2) - \lambda(\text{CH}_4)] \times \frac{d_x}{d}$$

Here, d_x is distance of the unknown line from CH_4 line and d is the distance between the two known lines. Substituting the values of the respective parameters into the above expression, we obtain

$$\begin{aligned} \lambda_x &= 42.414 \text{\AA} + (41.320 \text{\AA} - 42.414 \text{\AA}) \times \frac{1.8 \text{ mm}}{4.0 \text{ mm}} \\ &= 42.414 \text{\AA} - 1.094 \text{\AA} \times 0.450 = 42.414 \text{\AA} - 0.492 \text{\AA} = 41.922 \text{\AA} \end{aligned}$$

The energy of the unknown line $= \frac{12404(\text{eV}\text{\AA})}{41.922 \text{\AA}} = 295.8 \text{ eV}$

Problem 6.3: The x -ray PES of Pd metal produced using MgK_α 1253.6 eV radiation source is shown in Fig. 6.14 (b). It exhibits peaks at BEs (measured with respect to Fermi level) of: 0–8 eV, 54 eV (very weak), 88 eV (very weak), 335 eV (very intense), 534/561 eV (medium), 673 eV (weak), and 924 (strong).

(a) Assign the peaks to the various orbitals involved in photoionisation in the Pd metal, (b) The high-resolution spectrum of Pd metal shows a doublet instead of a single peak at 335 eV as shown below in Fig 6.15. Explain.

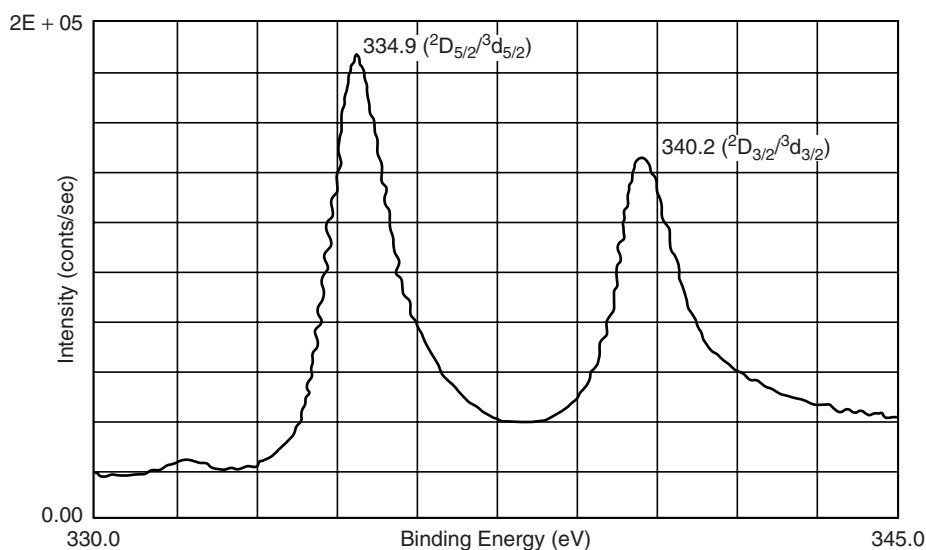


Fig. 6.15 High resolution spectrum of Pd.

Solution The electronic structure of Pd with an atomic number of 46 is

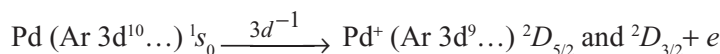
$$\begin{array}{cccc} 1s^2 & 2s^2 2p^6 & 3s^2 3p^6 3d^{10} & 4s^2 4p^6 5s^1 4d^9 \\ K & L & M & N \end{array}$$

In order to assign the various peaks in the problem, let us proceed from the valence electrons towards the nucleus. The BE of electrons will increase as we proceed from the valence electrons towards the nucleus. Thus, (i) The peaks in the BE range of 0–8 eV are attributed to the valence electrons from 4d and 5s orbitals respectively, (ii) The very weak peaks at 54 and 88 eV originates because of photoionisation from 4p and 4s levels/orbitals respectively. (iii) The very strong peak at 335 eV is due to emission of electron from 3d level. (iv) The medium

and weak intensity peaks at 534/561 and 673 eV are attributed to electrons emitted from $3p$ and $3s$ levels respectively. (v) The strong peak at about 924 eV, is due to x-ray induced Auger emission (MNN).

(b) The splitting of the peak at 335 eV into a doublet ($BE \sim 335$ eV, ~ 340 eV) with intensity ratio of 3:2 is because of spin-orbit coupling effects in the palladium ion. The inner-core electronic configuration of the initial state of the Pd is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} \dots$ with all subshells completely full. The removal of an electron from the $3d$ subshell by photoionisation will yield a configuration in which the $3d$ subshell will not be completely full, i.e. $Ar 3d^9 \dots$. Accordingly, the d -orbitals ($l = 2$) have nonzero orbital momentum; consequently, there will be an interaction between the unpaired spin and the orbital angular momenta. The spin-orbit coupling is treated by the $R-S$ coupling model and the $j-j$ coupling model. Let us deduce the splitting of $3d^{-1}$ PES spectrum from $R-S$ model.

Photoionisation of $3d$ electrons will yield Pd^+ ion with a hole in the $3d$ orbital according to the scheme



The atomic states involved in this process are worked out from the general term ${}^{2S+1}L_J$ as follows:

$$\text{For Pd } (Ar 3d^{10} \dots) : l = 0 \quad s = 0 \therefore J = 0 \text{ and } {}^{2S+1}L_J = {}^1S_0.$$

$$\text{For Pd}^+ (Ar 3d^9 \dots) : l = 2 \quad s = \frac{1}{2}, \therefore J = 2 + \frac{1}{2} = 5/2$$

$$\text{and } {}^{2S+1}L_J = {}^2D_{5/2}, l = 2, s = -\frac{1}{2}, \therefore J = 2 - \frac{1}{2} = 3/2$$

and ${}^{2S+1}L_J = {}^2D_{3/2}$, i.e. the ${}^2D_{5/2}$ term further splits into ${}^2D_{3/2}$ terms. (Here, the interaction of $3d^9$ electrons with the valence electrons is ignored). Thus, $3d^{-1}$ PES of Pd will consist of two peaks corresponding to the ${}^2D_{3/2}$ and ${}^2D_{5/2}$ higher energy states respectively. According to Hund's multiplicity rule, the BE of $3d^{-1}$ electron in ${}^2D_{5/2}$ state should be small relative to that of in ${}^2D_{3/2}$ state, i.e. $BE({}^2D_{3/2}) > BE({}^2D_{5/2})$ and the same has been observed indeed. The intensity ratio of these peaks according to the $g_J = 2J + 1$ rule is 2: 3 as expected.

We know that the $R-S$ coupling model approximation is best applied only to light atoms. However, this splitting can alternatively be described using individual electron $l-s$ coupling. In this case, the resultant angular momenta arise from the single hole in the d -shell. A single d shell electron (or hole) has $l = 2$ and $s = \frac{1}{2}$ which gives rise to permitted values of $j = 3/2$ and $5/2$, the former being higher in energy than the latter as expected.

6.14 APPLICATIONS OF PHOTOELECTRON SPECTROSCOPY

The applications of photoelectron spectroscopy are centered around the three parameters namely the position of the photoelectron signal expressed in terms of BE or KE , area under the photoelectron signal, width of the signal and the chemical shift. Based on these parameters, a number of qualitative and quantitative methods have been developed to study the surface properties of metals and alloys, electronic and molecular structure of diatomic and polyatomic molecules, analysis of gases, etc. Some of the typical applications of photoelectron spectroscopy based on the above-said parameters are being described here.

6.14.1 Ionisation Energies

PES provides a direct method for the determination of ionisation energies of the molecules. The first and second ionisation energies can simultaneously be determined. The energy required to evict a single electron from the first highest filled orbital is called *first ionisation energy* and from the second highest filled orbital is called the *second ionisation energy*. The highest bonding molecular orbitals π_2 and π_3 in benzene are degenerate, and so a single ionisation band is expected corresponding to these orbitals. In monosubstituted benzenes, the degeneracy is removed, and consequently two bands corresponding to π_2 and π_3 ionisations are expected and the same has been observed indeed, e.g.

C_6H_6 (9.40); RF (9.5, 9.86), RCl (9.31, 9.71), RBr (9.25, 9.78). RI (8.78, 9.75);

RNH_2 (8.04, 9.11) $RNHCH_3$ (7.73, 9.03), $RN(CH_3)_2$ (7.51, 9.03); ROH (8.75, 9.45),

$ROCH_3$ (8.54, 9.37), $ROC(CH_3)_3$ (8.75, 9.33). R = C_6H_5 and the energies are in eV.

6.14.2 Surface or Interelectronic Structure Studies

XPS, being a surface-sensitive technique, is more sensitive to those atoms which are located near the surface than it is to atoms in the bulk which are well away from the surface, i.e. the main part of the signal comes from the surface region. However, XPS is not completely surface specific, (i.e. it does not give signals due to atoms only in the surface region) in that whilst most of the signal comes from within a few atomic layers of the surface, a small part of the signal comes from much deeper into the solid. Thus, XPS is best described as being only surface sensitive but is not also a surface-specific technique. This can be demonstrated by depositing some metal by evaporation onto a substrate of another material as shown in Fig. 6.16. It is experimentally observed that in such a situation, the XPS signals due to the substrate are rapidly attenuated, whilst those due to the condensed evaporant simultaneously increase to a limiting value. It is possible to measure deposition rates using equipment such as quartz crystal oscillators and thus obtain independent verification of the deposited film thickness. A detailed analysis of the variation of signals due to depositing material and substrate can also give information about the mechanism of film growth. We know that the soft x-rays employed in XPS penetrate a substantial distance into the sample ($\sim \mu\text{m}$). Thus, this method of excitation imparts no surface sensitivity at the required atomic scale. The surface sensitivity arises from the emission and detection of photoemitted electrons. Thus, if the source atom is closer to the surface then a greater fraction of the emitted electron will be detected since; (i) the detector would subtend a greater solid angle at the emitting atom, and (ii) for an electron emitted towards the surface, there would be less chance of inelastic scattering before it escaped from the solid. Note that the former factor is insignificant in real experiments. Thus, the probability of detection depends upon the distance of the emitting atom below the surface. The probability of escape from a given depth, $P(d)$, is determined by the inelastic mean free path, λ (IMFP) also called the penetration (escape) depth of electrons, which is a measure of the average distance travelled by an electron through a solid before it is inelastically scattered.

The IMFP is actually related to the probability of an electron travelling a distance d through a solid without undergoing scattering by the expression.

$$P(d) = \exp(-d/\lambda) \quad (6.37)$$

Further, IMFP depends upon (i) the initial kinetic energy of the electron and $\lambda \propto (\text{KE})^{1/2}$ for 100–10,000 eV kinetic energy range, and (ii) the nature of the solid. Generally, ESCA electrons have KE's of approximately 100–1500 eV with a nominal escape depth of 20 Å while AEs' electrons have KEs of 50–2500 eV with an escape depth of 20 Å. The variation of the IMFP with initial electron energy (eV) is shown in Fig. 6.17.

This behaviour of IMFP with energy is reasonably accurate for most metals, although experimental measurements on different metals show a substantial scatter about the general curve. Other classes of solids also show qualitatively similar universal curves, although the absolute values of the IMFP of electrons in materials such as inorganic solids and polymers differ quite significantly from those in metals. The IMFP data is usually displayed on a log-log plot as shown in Fig. 6.18.

The graph clearly shows how the IMFP varies at low KEs. The IMFP shows a minimum for electrons with a KE of around 50–100 eV; at lower energies the probability of inelastic scattering decreases since the electron has insufficient energy to cause plasmon excitation (the main scattering mechanism in metals), and consequently, the distance between inelastic collisions and the IMFP increases. The IMFP in metals is typically less than

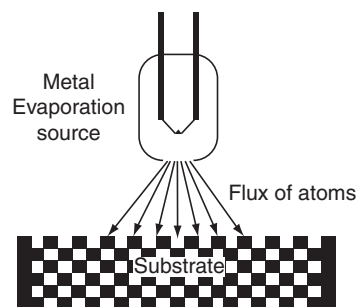


Fig. 6.16 Deposition of one material onto a substrate of another material.

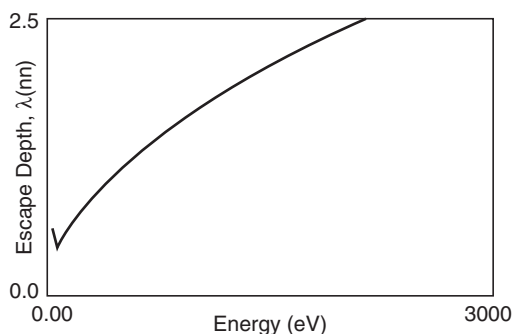


Fig. 6.17 Universal curve for the variation of the escape depth with initial electron energy.

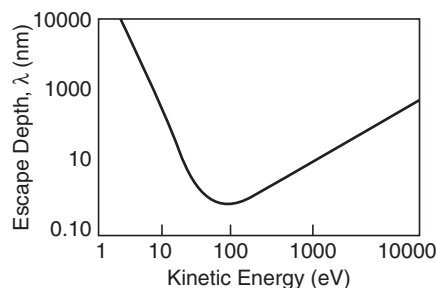


Fig. 6.18 A log-log plot of electron escape depth against kinetic energy of the electron.

10 Å (1nm) for electron energies in the range $15 < E_i \text{ eV} < 350$
 20 Å (2 nm) for electron energies in the range $10 < E_i \text{ eV} < 1400$

i.e. the IMFP of low-energy electrons corresponds to only a few atomic layers.

The IMFP can be used to calculate the thickness of surface films. Let us consider that a substrate or thick film of one material, say *A*, is covered by a thin film of thickness '*t*' of another material, say *B* (Fig. 6.19). The XPS signal from the underlying substrate will be attenuated, i.e. reduced in intensity due to inelastic scattering of some of the photoelectrons as they pass through the thin layer of the covering material.

The probability of such a scattering process for any single photoelectron passing through this layer is given by

$$P = \exp(-t/\lambda) \quad (6.38)$$

Here, *t* is the thickness of layer of the covering material.

Accordingly, the overall intensity of an XPS signal due to the substrate will be reduced by this factor. Thus, if the intensity of this signal in the absence of any covering layer is I_0 then the intensity *I* in the presence of the overlayer of thickness '*t*' is given by

$$I = I_0 \exp(-t/\lambda) \quad (6.39)$$

It follows that it is possible to determine the thickness of a deposited layer from Eq. (6.39) provided the reduction in the substrate signal due to deposition of the covering layer is known.

Note that the degree of surface sensitivity can be increased by collecting the photoelectrons at a more grazing emission angle. Let the atoms be located within a smaller distance, *x*, from the surface (Fig. 6.20) such that

$$x = d \cos \theta \quad (6.40)$$

Here, the photoelectrons have to travel a distance '*d*' which is less than 1λ through the solid in a direction making an angle θ with the normal to the surface. So as the emission angle (θ) is increased, $\cos \theta$ decreases, the analysed region becomes more surface localised and the surface sensitivity is increased.

This effect can be used in the study and diagnosis of surface segregation as is evident from Fig. 6.21 which shows simulated data for the variation of the XPS signal intensities with emission angle for: a random alloy of 10 percent of element *A* in element *B*, with no segregation and the same random alloy, but with surface segregation of *A* to give a surface monolayer, i.e. I_A/I_B is independent of the emission angle.

The average size of particles on a surface is sometimes of interest. The PE signal intensity *I* is related to the size of the particles by the expression

$$I = I_0 \left(1 - \frac{\lambda^2}{12r^2} \right) \quad (6.41)$$

Here, *r* is the radius of the particles on a surface and I_0 is the signal intensity in the limit $r \ll \lambda$.

Further, we know that in XPS, the photon is absorbed by an atom in a molecule or solid leading to ionisation and the emission of core, i.e. inner-shell electron. For each and every element, there is a characteristic binding energy associated with each core atomic orbital, i.e. each element will give rise to a characteristic set of signals in the photoelectron spectrum at KEs determined by the photon energy and the respective BEs. The presence of peaks at particular energies, therefore, indicates the presence of a specific element in the sample under study. Since the intensity of the peaks is related to the concentration of the element within the sample region, the technique provides a quantitative analysis of the surface composition and is known as ESCA. It being surface

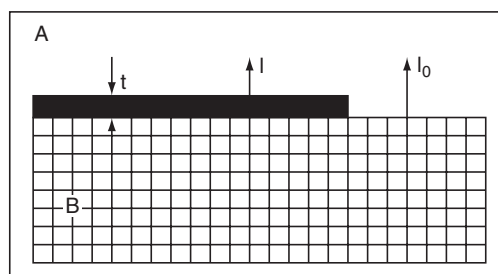


Fig. 6.19 Schematic diagram showing a thick film of material 'A' covered by a thin film of thickness '*t*' of another material *B*.

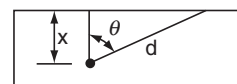


Fig. 6.20 Diagram depicting the effect of grazing emission angle of photoelectrons on the surface sensitivity.

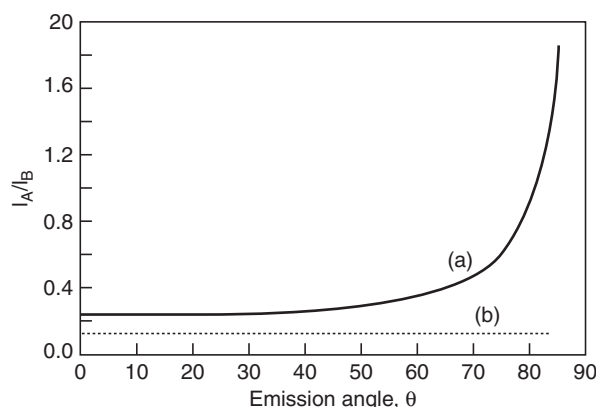


Fig. 6.21 Angular variation of XPS signal ratio for a random alloy of 10 per cent element *A* in element *B* (a) with no segregation, and (b) with surface segregation of *A* to give a surface monolayer of pure element *A*.

sensitive, has been proved to be the most successful and useful tool alone and in conjunction with AES to study the analytical chemistry of surfaces as is evident from the following typical examples. However, before describing the examples let us define a term, called *surface shift*, which is frequently used in XPS. If $E_{\text{ion}}(i)$ is the bond energy of the ion to the surface, after an electron has been removed from the i th orbital, E_{neut} is the bond energy of the atom or molecule to the surface in the ground state then the BE of the i th orbital on surface $E_{BE}^S(i)$ can be related to the BE in the gas phase, $E_{BE}^g(i)$ by

$$E_{BE}^S(i) = E_{BE}^g(i) - E_{\text{ion}}(i) + E_{\text{neut}} \quad (6.42)$$

The surface shift which is $E_{BE}^g(i) - E_{BE}^S(i)$ is given by the difference in the bond strength of neutral and the ionised molecule. This energy difference will depend upon not only the nature of the i th orbital, but the degree of electronic and spatial relaxation of the ion. Let us now compare the penetration depth of various particles and effect of probes on surfaces. The penetration (escape) depth of photons, electrons and ions in the energy range used for surface analysis are given in Table 6.2, while the effect of probes on surfaces is reported in Table 6.3.

Table 6.2 Penetration depths of particles.

Particle	Energy(eV)	Depths (Å)
Photon	1000	10,000
Electron	1000	20
Ions	1000	10

Table 6.3 Effect of probes on surfaces.

Probe	Effects
Photons	Least destructive IR < UV < VUV < x-rays 95 per cent OK
Electrons	More destructive Insulators > Semiconductors > Conductors Charging bad for organic materials
Ion beams	Cause sputtering; All materials sputtered

(a) Presence or Absence of Element on the Surface The ESCA spectrum of Ni/W/Al₂O₃ catalyst using AlK_α x-rays for ionising radiation shows the following peaks not only corresponding to the elements present in the catalyst but an additional peak at 285 eV Table (6.4). The peak at 285 eV (C1s) is attributed to the carbonaceous material present in the atmosphere.

Table 6.4 Peaks in the ESCA spectrum of Ni/W/Al₂O₃ catalyst.

Element	Orbital (≈BE)
O	2p (9 eV)
O	2s (23 eV)
W	4f (38 eV)
Al	2p (73 eV)
Ni	3s (102 eV)
Al	2s (109 eV)
W	4d (244 eV)
C	1s (285 eV)
O	1s (544 eV)
O	KLL Auger line
Ni	LMM Auger lines amplified signals
Ni	2p (866 eV amplified signals)

(b) Determination of Oxidation States on Catalyst Mo 3d ESCA spectrum of Mo/Al₂O₃ (15 percent MoO₃ on Al₂O₃) catalyst shows a low-intensity signal at $BE = 236.1$ eV and a high intensity signal at $BE = 233$ eV. The 3d Mo spectral data of the catalyst as function of reduction time (catalyst reduced by H₂ at 500°C) shown in Fig. 6.22 indicates that initially the Mo is in the +6 state. As the reduction progresses, the rapid fall of the +6 state takes place with the simultaneous increase of +5 and +4 states and after about 40 minutes, all of Mo +6 disappears while the +5 state passes through a maximum. After about 10 hours, the mixture of oxidation states reaches a steady state (60 per cent + 4 and 40 per cent +5) and remains constant.

(c) Differential Rates of Reactions of Two species on a Surface

The ESCA can be used to follow the differential rates of reactions of two species on a catalyst surface. The ESCA spectrum of a pure and fresh catalyst ($\text{Ni}/\text{W}/\text{Al}_2\text{O}_3$) shows two peaks at 37.5 eV and 857.5 eV which are characteristic of tungsten (4f) and nickel (2p) respectively. When $\text{Ni}/\text{W}/\text{Al}_2\text{O}_3$ catalyst surface is exposed to $\text{H}_2/\text{H}_2\text{S}$ mixture, the ESCA signal corresponding to the sulphided Ni (854 eV) is fully developed after some time while the sulphided tungsten peak (31.5 eV) is not fully developed at that particular time and even after longer periods. Some unsulphided tungsten (37.5 eV) remains after very long sulphiding times whereas none of the unsulphided Ni (857.5 eV) is seen.

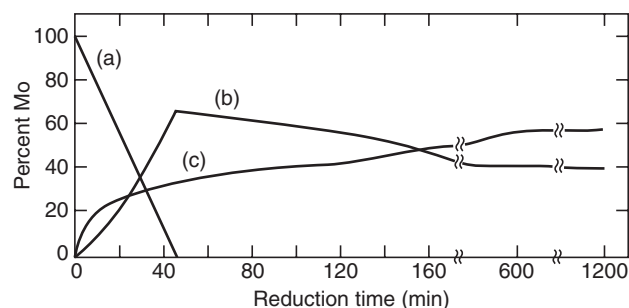


Fig. 6.22 Mo oxidation states as a function of reduction time. (a) Mo (+6), (b) Mo (+5), (c) Mo (+4).

(d) Adsorption of CO on W (100) in Relation to Effects of Different Orbitals on the Surface The BEs of O_{1s} (1σ) and C_{1s} (2σ) levels of α_1 state of CO in the gas phase are 542.6 and 296.2 eV respectively, while that of CO adsorbed on (100) tungsten are 538.0 and 291.2 eV respectively. Thus, the spectral data on the measurements for the α_1 state of CO adsorbed on (100) tungsten show that the surface shift for the C_{1s} level is 5.0 eV which is larger than the surface shift of 4.60 eV for the O_{1s} level. This discrepancy between the magnitudes of the surface shifts is presumably because CO is bonded to the surface standing up with the carbon closer to the surface. Both the C_{1s} and O_{1s} levels have a larger shift than the 1π level ($16.54 - 13.7 = 2.84$ eV), since they are more localised. Thus, the measurements for the α_1 state of CO adsorbed on W (100) illustrate the effects of different orbitals on the surface of the catalyst. In case the value of the surface shift for both the orbitals is constant, it is presumed that both the orbitals have a similar charge distribution relative to the surface, e.g. 1π and 4σ levels of α_2 state of CO on W (100) have a constant value of surface shift, i.e. 3.2 eV.

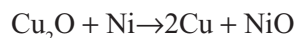
(e) Change in the Nature of Surface Species as a Function of Composition of the Catalyst When the ESCA intensity ratio of Ni/Al peaks in a $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst with different compositions of Ni are plotted against the nickel content in the catalyst, it is found that as the amount of Ni content increases, the intensity also varies linearly and at about 17 per cent of Ni, the slope of the line increases abruptly. This indicates that upto 17 per cent the nickel binds to alumina lattice in a highly dispersive fashion and above 17 per cent crystallites of NiO begin to form on the catalyst surface. Thus depending upon the nature of species in the catalyst surface, the ESCA shows two linear regions which form the basis of detection of the change in the nature of nickel species on the catalyst.

(f) Separation of Polymer from a Metal Surface The ESCA spectrum of clean aluminium surface shows three signals at BEs: 1348 eV, P (2p); 1362 eV, Al (2s) and 1409 eV, Al (2p). The P(2p) signal appears due to contamination of the surface during the cleaning process. The ESCA spectrum of pure bulk polymer shows two signals corresponding to Si (2s) and Si (2p) levels at BEs' of 1329 and 1382 eV respectively. After stripping of the polymer, the aluminium surface still exhibits five signals. Presence of five signals in the spectrum reveals that the tearing occurred within the polymer layer. The polymer layer removed from the aluminium surface shows no signals corresponding to aluminium thereby substantiating the findings that tearing occurred within the polymer layer but not within metal or metal and polymer layers.

(g) Study of Polymer Surface Reactions The ESCA spectrum can be used to study the polymer surface reactions. The ESCA spectrum of Teflon shows Cls (294 eV) and Fls (694 eV) lines from the surface of Teflon. On itching with Na/NH_3 , the fluorine line disappears, carbon shifts to a lower value of 286 eV and an oxygen signal at 535 eV appears. These are the characteristics of carboxylic acid. When the itched surface is treated with chlorox, some of the nonfluorinated polymer formed by Na/NH_3 treatment is dissolved and a high BE carbon line at 294 eV reappears along with fluorine line at BE of 694 eV. The shifted Cls line at 286 eV and the Ols line at 535 eV also persist.

(h) Study of Annealing of Cu-Ni Alloy Use can also be made of Auger lines in the ESCA spectrum for analysis of surfaces. Let us see the effects on copper spectra caused by annealing a Cu-Ni alloy at 250°C. Cu_{LLM} Auger lines in the ESCA spectrum of a Cu-Ni alloy as a function of annealing time indicate that initially Cu is present as copper oxide (Cu_2O) having a peak at 917 eV on the KE scale. During the annealing process, a peak characteristic of elemental Cu appears at 920 eV on the KE scale. During the process, the intensity of the Cu_2O

peak decreases with the increase of annealing time while that of NiO increases. These results conform to the following reaction that occurs in the annealing process:



In addition to ESCA spectra, Auger spectra alone and in conjunction with ESCA can also be used both qualitatively and quantitatively to study the elemental surface composition. All elements ($Z < 10$), except H_2 and He, can be estimated quantitatively. The small escape depth of Auger electrons make them an ideal tool for the study of atomic distribution normal to the surface by successive removal of surface layers. This can be done in several ways but the most convenient method is ion bombardment sputtering which is possible while the Auger spectrum is being measured. Typical sputtering conditions are Ar gas pressure (1–5) $\times 10^{-5}$ Torr, Ar^+ beam energy 0.5–2 keV, Ar^+ beam current density 0.2–20 $\mu\text{A}/\text{cm}^2$ and beam diameters on the specimen of several mm to 1 cm. If the ultimate depth resolution as determined by the escape depth of Auger electron ($\approx 10 \text{ \AA}$) is to be achieved, then the ion-beam current density must be constant over an area larger than the diameter of the primary electron beam. Otherwise, the area from which the Auger electrons are emitted is not flat and the Auger signal represents an average over a range of depths. At sufficiently low sputtering rates (1–10 $\text{\AA}/\text{min}$ depending upon concentration gradients), several Auger lines can be monitored sequentially. The in depth analysis of silicon wafer oxidised after phosphorous pre-deposition is shown in Fig. 6.23. Four peaks, the oxygen 511 eV, phosphorous 120 eV, silicon 92 eV and the silicon 75 eV line characteristic of Si in SiO_2 are measured while the oxide layer is sputtered away. The limitations of this technique are that the sputtering cross sections vary from atom to atom and depend upon its chemical environment, for example removal of equal amounts of Mo deposited on various surfaces. Mo forms on W a uniform film with a normal sputtering profile while on Cu, Au and Al, it agglomerates and can be observed over a large depth range. Roughening of surface especially in impure material occurs during sputtering. The ion bombardment induced movement of ions in insulating films results in accumulation of such ions on boundaries of the film. Further, it is to be noted that in contrast to low-energy electron diffraction (Leed), AES neither requires a periodic nor a flat surface. Thus it can be applied to unusual samples as fracture surfaces or rocks from the moon or other such planets. The use of ion sputtering in conjunction with AES not only allows depth analysis but also studies in relatively dirty vacuum because the contamination can be removed continuously. AES is at present, by far, the most universal surface analysis method with sensitivities down to less than $\frac{1}{100}$ of a monolayer, except for hydrogen and helium which are not detectable.

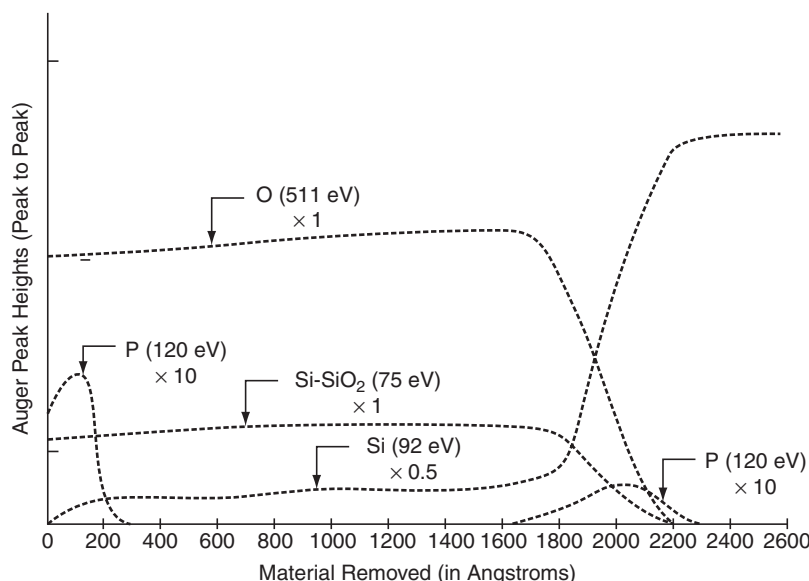


Fig. 6.23 The indepth analysis of silicon wafer oxidised after phosphorous pre-depositlon.

The Auger spectrum of Ni–Fe–Cr–B alloy shows a signal to each component (Table 6.5).

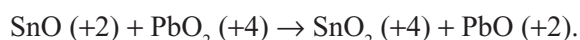
The presence of S, Si and C peaks at 156, 88, and 275 eV respectively on the KE scale indicates the presence of impurities in the alloy while a strong peak at 513 eV, characteristic of oxygen (O), reveals that the surface is heavily oxidised. The percentage composition of the constituents can be estimated from the relative intensities of the respective signals after calibration.

Sometimes it becomes necessary to combine ESCA and AES surface techniques for a particular study. The chemical shift obtained from ESCA coupled with the depth profiling capability of AES is the most common

Table 6.5 Peaks in the Auger spectrum of Ni-F-Cr-B alloy.

Element	KE(eV)
Si	88
S	156
B	175
C	275
O	513 (Strong)
Cr	538
Fe	600,650,706
Ni	716,788,855

combination for the study of surfaces. Note that AES spectra are plotted as derivatives while ESCA spectra are integrals. Let us now see how such a combination is effective to study the chemical effects on a surface when it is corroded by reactive gases, e.g. ESCA spectrum of solder before melting shows peaks characteristics of SnO_2 ($\text{Sn}3d_{5/2}$) at BE = 486 and PbO_2 (Pb 4f) at BE = 143 and 138 eV. After melting, in addition to the peak of SnO_2 at 486 eV an additional peak at 485 eV characteristic of tin (Sn) metal appears in the spectrum whereas in case of Pb, the entire spectrum of PbO_2 except a very weak peak at 138 eV disappears with the appearance of two new peaks at 141 eV and 137 eV which are characteristic of lead metal. Further, the ESCA studies of the effect of oxygen exposure on the Pb/Sn and O/Pb + Sn ratios show that Pb/Sn ratio drops as the log (Langmuir of oxygen exposed) increases while $\frac{\text{O}}{\text{Pb+Sn}}$ ratio increases indicating that alloy is oxidised, the reactive metal tin tends to concentrate on the surface. AES (2 keV) depth profile of oxidised solder, i.e. the plot of Pb/Sn ratio against Ar sputtering time and $\frac{\text{O}}{\text{Pb+Sn}}$ ratio against Ar sputtering time, indicate that the $\frac{\text{O}}{\text{Pb+Sn}}$ ratio falls off rapidly on sputtering in, say, time t_{sp} (second) and then tends to be constant, while the $\frac{\text{Pb}}{\text{Sn}}$ ratio first increases and passes through a maximum at about time $t = t_{\text{sp}}$ (second) and then decreases, approaching the bulk value. Further, when the changes in oxidation states of solder during oxidation by NO_2 are followed by ESCA (i.e. from the plot of composition of Pb in alloy as a function of oxidation time), it is found that for Pb, PbO_2 (+4) and PbO (+2) are the initial products, the former being dominant species. As the oxidation proceeds, PbO_2 (+4) and PbO (+2) increase, and after about 60 minutes when the former passes through a maximum, and then drops as PbO (+2) becomes the predominant species and even at longer periods remain constant, the latter, i.e. PbO (+2), grows and then becomes constant. The sputtering suggests that as the PbO (+2) moiety drops with sputtering time, the Pb (0) moiety grows. On the other hand, for Sn, the initial products are Sn (0) and SnO (+2). As the oxidation proceeds, the oxidation process is simple: $\text{Sn}/\text{SnO} \rightarrow \text{SnO}_2$, during the entire oxidation time. The sputtering shows that as the SnO_2 moiety decreases, the Sn (0) and SnO (+2) species grow. The data show that initially a thin film of SnO_2 and PbO_2 is formed on the surface. As the tin diffuses outward, the film becomes oxygen-poor forming some SnO (+2) which combines with PbO_2 (+4) to give SnO_2 and PbO according to the reaction



Thus, in the oxidation process, a steady-state film is formed consisting mainly of SnO_2 and PbO.

6.14.3 Analysis of Gas Mixtures

The most powerful aspects of PES is that the core electron binding energy of an atom is often a significant function of the chemical environment of the atom in a molecule and the band intensities are proportional to the partial pressure of the constituent gases of the mixture. Both these aspects make the tool of PES applicable to the analysis of gas mixtures qualitatively and quantitatively. Only those gases which exhibit at least one sharp and characteristic peak in the PES are most suitable for quantitative analysis. Moreover, such a peak should dominate the peaks overlapping it. The following gases qualify the above characteristics: N_2 , O_2 , CO, CO_2 , N_2O , CS_2 , COS, NO, H_2S , C_2H_2 and all atomic species. The sample of COS has been quantitatively analysed for CS_2 and CS_2 impurities. The analysis of a mixture of gases by PES has the advantage over low-resolution mass spectrometry in cases where the PES spectra are different while the mass spectra are almost the same e.g. $\text{N}_2\text{-CO}$, $\text{N}_2\text{O-CO}_2$, CO-CO_2 pairs. PES is also preferred for compounds where mass spectra contain no molecular ion peak but only fragment ions. Moreover, for analyses of gases in the upper atmosphere and in space, the photoelectron spectrometer is preferred over the mass spectrometer because of its volume and lighter weight.

The electronic structure of free radicals and other transient moieties is useful to understand the mechanism of kinetically controlled reactions. The ionisation energies and ionic excited states of radicals are directly relevant to mass spectrometry and to the study of ionic decomposition, for which knowledge of the energy levels of fragment ions are required. Photoelectron spectroscopy can impart the necessary information provided the transients can be produced in sufficient amounts to yield a signal when ionised in the spectrometer source. Transients produced by microwave discharge on high-temperature pyrolysis in a flowing gas stream exhibiting PES are H, N, O, F, Cl, Br (monoatomics); SO, CS, P₂ (diatomics); NF₂, ClO₂, S₂O (triatomics) and larger molecules. PES of stable molecules in excited states can also be observed, e.g. oxygen in its first electronically excited state ¹Δ_g.

Problem 6.4: Calculate the thickness of a deposited layer on some virgin surface if the intensity of the photoelectron signal due to the virgin surface is reduced by the covering layer by 5 per cent $\lambda = 20 \text{ \AA}$.

Solution In order to determine the thickness of the covering layer on the virgin surface, use is made of Eq. (6.39) i.e.

$$I = I_0 e^{-t/\lambda} \quad (\text{Eq. 6.39})$$

Substituting the values of the given parameters into Eq. (6.39), we get.

$$\frac{95}{100} = e^{\frac{-t}{20(\text{\AA})}}$$

Taking log on both sides and solving for 't', we get

$$\ln 0.95 = \frac{-t}{20(\text{\AA})} \ln e (=1)$$

$$\text{or } t = +5.129 \times 10^{-2} \times 20 (\text{\AA}) = 1.025 \text{ \AA}$$

Problem 6.5: The photoelectron spectrum of CO and CO₂ produced from a gas mixture of CO and CO₂ is characterised by the presence of the peaks of the Cls electrons of CO and CO₂ with ionisation potentials of 296 eV and 298.4 eV respectively. Determine the percentage composition of the mixture if the intensity ratio of the bands corresponding to CO and CO₂ is 2:3.

Solution The content of CO in the binary gas mixture is determined by the formula:

$$x = \frac{I_{\text{CO}} \times 100}{I_{\text{CO}} + I_{\text{CO}_2}}$$

where, I_{CO} and I_{CO_2} are the band intensities of the CO and CO₂ being determined in the PES.

$$\text{Thus, } x = \frac{2}{5} \times 100 = 40 \text{ per cent}$$

Similarly, the content of CO₂ in the mixture is given by the formula

$$y = \frac{100}{R_{\text{CO}_2} + 1} = \frac{3}{5} \times 100 = 60 \text{ per cent}$$

6.14.4 Molecular Orbital Models

PES provides a tool to develop qualitative molecular orbital models and vice versa which helps not only to understand the electronic structure of the molecules but also the other molecular properties of the molecules. This is demonstrated by taking the example of the nitrogen molecule. The possible combination of *s* and *p* orbitals in N₂ can be characterised according to their behaviour with respect to the three symmetry elements of the molecule: an axis of rotation (C₂), a reflection plane (σ_{yz}) and centre of inversion (i) (Fig. 6.24 Table 6.6). The interaction or mixing of two orbitals is governed by their relative energies. In general, when there is a large energy difference between the

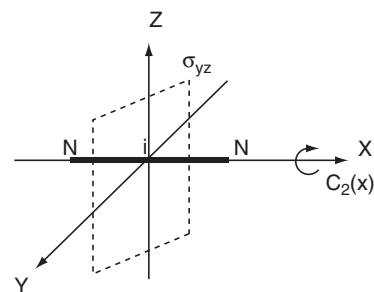


Fig. 6.24 Symmetry elements of N₂ molecule in relation to the characterisation of the possible combination of *s* and *p* orbitals in the molecule.

two orbitals, the interaction between them decreases, for example in the argon atom, for a given primary quantum number n , $E(ns) > E(np)$.

Accordingly, in the first approximation for N_2 , only mixing between two similar orbitals is considered, i.e. $2s$ with $2s$ and $2p$ with $2p$ (Fig. 6.25). The $1s$ electrons of nitrogen are tightly bound to their respective nuclei, and hence their contracted orbitals do not overlap effectively and they remain almost localised. The resulting first orbital scheme, filled with electrons according to Aufbau and Pauli exclusion principles is compared with the PES spectrum of N_2 in Fig. 6.26.

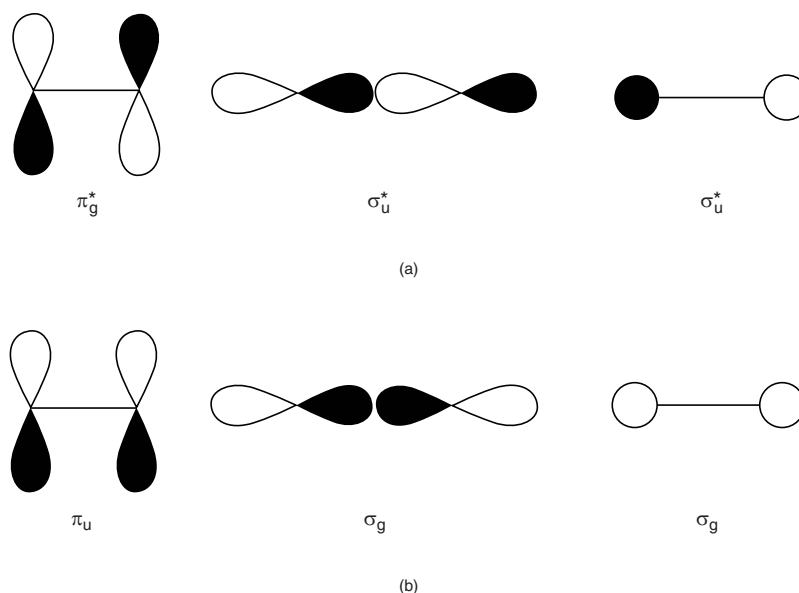


Fig. 6.25 1st order mixing between two similar orbitals: (a) antibonding and (b) bonding configurations.

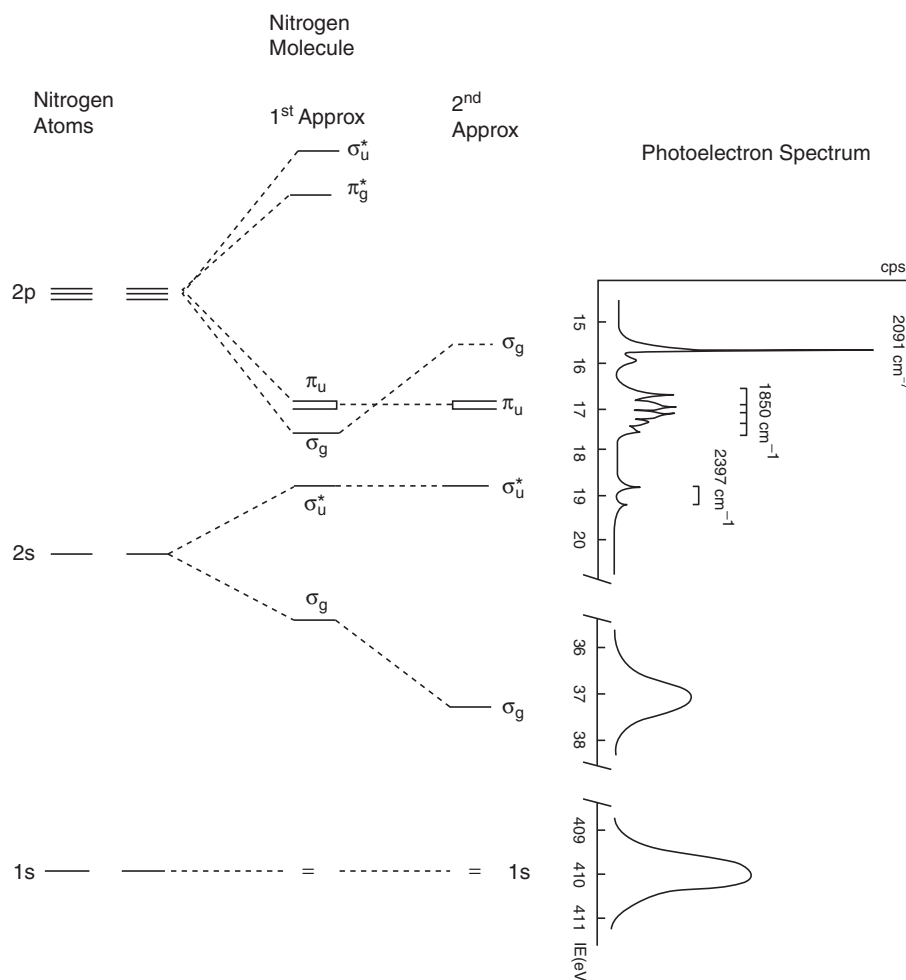


Fig. 6.26 Schematic diagram showing the observed photoelectron spectrum of N_2 molecule in relation to the 1st and 2nd order molecular orbitals.

The photoelectron spectrum of N_2 from various energy sources exhibit five bands expected for 14 electrons of the nitrogen molecule, assuming degenerate $1s$ and π_u orbitals. Besides ionisation potentials, other information can be gathered from the spectrum. The shape of the band imparts information regarding the bonding character of molecular orbital:

Table 6.6 Symmetry elements of N_2 in relation to characterization of bonding character of orbitals.

	$C_2(x)$	σ_{yz}	i
Symmetric	σ	Percent (bonding)	g (gerade)
Antisymmetric	π	*(antibonding)	u (ungerade)

Strong, sharp spikes followed by a few other weak bands characterise the nonbonding electrons whose orbitals are localised, e.g. the low-energy bands in the 15–20 eV region, the broad bands whose maxima occur towards the centre of the band characterise both the very strongly bonding and antibonding electrons which are delocalised. Moreover, the bands in the PES spectrum may exhibit a resolvable fine structure, the spacing in which corresponds to particular vibrational modes of the molecular cation. Ionisation from a nonbonding orbital does not affect the vibrational frequency very much but from a bonding orbital, decrease the frequency and from an antibonding orbital, increase the frequency. A comparison of the vibrational frequencies manifested in the ionisation spectral bands with that of the fundamental vibrational mode at 2345 cm^{-1} of the neutral ground state of N_2 molecule suggests that the first, second and third ionisation energy bands of N_2^+ molecular ion correspond to very slightly bonding, strongly bonding and slightly antibonding orbitals respectively. However, this deduction does not conform to the first-order molecular orbital scheme according to which out of the three highest occupied orbitals, two have significantly bonding character. Accordingly, the first-order molecular orbital scheme needs to be modified in order to explain the experimental facts. This is done by taking into consideration the idea that orbitals of the same symmetry interact so as to increase the difference in their energies. Based on the idea, in the second-order molecular orbital scheme, interaction between the two occupied σ_g orbitals, i.e. $1\sigma_g$ and $2\sigma_g$ is taken into account and is shown in Fig. 6.27. The good agreement between the second-order molecular orbital and observed experimental results confirms the rule: two molecular orbitals of like symmetry admix in such a way that the low-energy orbital of the first (less stable), i.e. $1\sigma_g$ interacts with the high-energy orbital of the second (more stable) i.e. $2\sigma_g$ in an antibonding destabilising fashion, i.e. $(2\sigma_g - 1\sigma_g)$ while the admixture of type $2\sigma_g + 1\sigma_g$ results in a stable configuration as shown in Fig. 6.27.

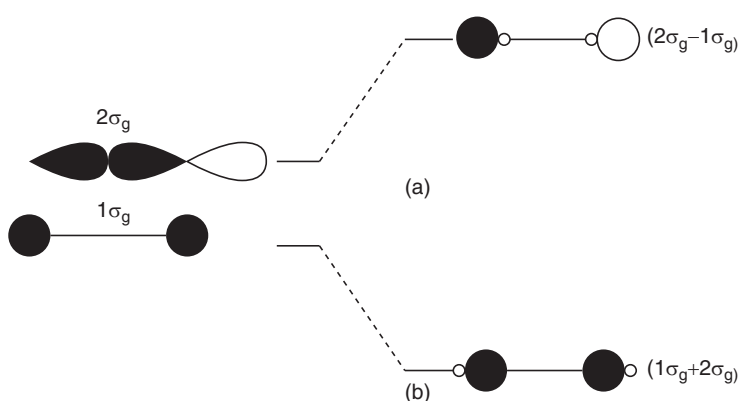


Fig. 6.27 Second-order interaction between two occupied σ_g orbitals of like symmetry (a) antibonding, and (b) bonding configurations.

To summarise, we arrive at the following deductions. The photoelectron spectrum provides data on ionisation energies, band shapes and vibrational frequencies. The experimentally observed data can satisfactorily be explained with a qualitative molecular orbital scheme. The experimental data in conjunction with molecular orbital scheme enables to develop a model which satisfactorily interprets the photoelectron spectrum. This model can further be applied to explain the other molecular properties of nitrogen, e.g. the only small increase in bond length on ionisation (bond length in N_2 is $1.09\text{ \AA}$ while in N_2^+ is $1.11\text{ \AA}$). The band at 410 eV in the ESCA region consists of only one peak. This suggests that the inner shell $1s$ orbitals fail to interact and only the valence electrons need be considered. Vibrational fine structure imparts information regarding the nature of the molecular orbital and the relationship between nature of peak and the orbital involved in ionisation is given here in Table 6.7.

Such studies have also been carried out successfully on various types of polyatomic molecules such as H_2O , H_2S , C_6H_6 , etc.

Table 6.7 Deductions based on vibrational fine structure of the nature of molecular orbital involved in ionisation.

Nature of peak	Orbital involved in ionisation	Remarks
Sharp peak without any vibrational fine structure	Nonbonding or very weakly bonding	r_e is not effected $I_{\text{adiabatic}} = I_{\text{vertical}}$ i.e no vibrational changes
Sharp peak with number of vibrational structures	Bonding or antibonding	Decrease in frequency (bonding) or Increase in frequency (antibonding)
Broad band	Very strongly bonding or antibonding	Dissociation or predissociation

6.14.5 Anharmonicity Constant and Changes in Molecular Geometry on Ionisation

The position of the photoelectron band indicates the energy of an ionic state whereas the vibrational structure of the band gives information about the structure and bonding of the ions in that state. When the coarse vibrational structure manifested in an ionisation band is resolvable, the identities and frequencies of the modes excited on ionisation and the intensities of the vibrational lines can be examined. All of these can be used to make direct deductions about the nature of the ionic state produced, about the differences between the ionic state and molecular ground state from which ionisation occurs and the changes in molecular geometry.

(a) Intensity of the Vibrational lines in an Ionisation Band To the relative intensity of a vibrational transition in an ionisation band is given by Franck–Condon Factor (FCF) which is equal to the square of the overlap integral between the vibrational wave functions $\Psi_{V'}$ and $\Psi_{V''}$

$$\text{FCF} = |\langle \Psi_{V''} | \Psi_{V'} \rangle|^2 \quad (6.43)$$

Here, V' denotes the vibrational level in the neutral molecule, i.e. the target molecule and V'' denotes the vibrational level in the molecular ion produced on ionisation of the neutral molecule. The deductions regarding the intensities of vibrational lines are made from Eq. (6.43) and are recorded in Table 6.8.

Table 6.8 Deductions regarding the intensities of vibrational lines based on Franck-Condon Factor.

Change in bond lengths or force constants on ionization i.e. change in PE surface	Values of vibrational quantum numbers in both the levels	Ortho-gonality of wave functions	Overlap integral	Intensity
No change	Different ($V' \neq V''$)	Orthogonal	Zero	Zero
No change	Same $V' = V''$	Orthogonal	Zero	Zero
Little change	Same ($V' = V''$)	Orthogonal	Large value	Strong
	Different ($V' \neq V''$)	Orthogonal	Small value	Weak

In PES, the target molecules are in their vibrational ground states so the adiabatic transitions are most intense. However, if there is a change in bond length on ionisation so that the equilibrium position of the nuclei are different then the vibrational mode or modes that corresponds most closely to the change in nuclear position are most strongly excited. This is the basis of relationship between the localisation of bonding character of particular electrons and the structure of the ionisation bands.

When two or more vibrational modes are strongly excited in a transition, the band structure consists of progressions of progressions, i.e. each line corresponding to the excitation of a number of quanta of one mode is the starting point for a progression in the other band. Progressions of progressions in the PES of carbonyl fluoride (F_2CO) are shown in Fig. 6.28.

(b) Selection Rules The selection rules for vibrational modes which can be excited on ionisation are summarised in Table 6.9. The selection rules for degenerate vibrations are the same as those for antisymmetric vibrations but only weak transitions in units of two quanta are allowed. For certain point groups, the odd quantal states of degenerate vibrations are also antisymmetric with respect to at least one element of symmetry and rule $\Delta V = 0, \pm 2, \pm 4, \pm 6$ is strictly obeyed. In other instances, transitions with $\Delta V = \pm 3, \pm 5, \pm 7, \dots$ may be weakly allowed, but $\Delta V = \pm 1$ is strictly forbidden. Double quantal excitation of such a degenerate vibration is observed in the PES of ethylene.

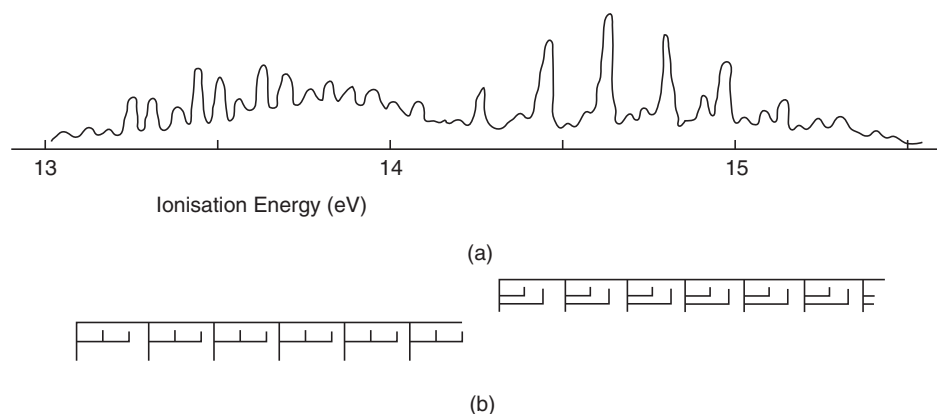


Fig. 6.28 (a) Photoelectron spectrum of carbonyl fluoride (13–16 eV) showing progressions of vibrational bands (b) Vibrational analysis.

Table 6.9 Selection rules for vibrational modes.

Symmetry of vibrational modes	Symmetry of vibrational wave functions	Vibrational quantum number or quantal state	Selection rule	Intensity
Symmetric	Symmetric	Even or odd	$\Delta V = 0, \pm 1, \pm 2, \pm 3 \dots$	—
Antisymmetric (CO ₂ , CS ₂)	Antisymmetric Symmetric	Odd Even	$\Delta V = 0, \pm 2, \pm 3$	$I_0 \gg I_{\pm 2}, I_{\pm 4}, I_{\pm 6} \dots$ since maxima of vibrational wave functions lie in a symmetrical position directly above the vibrationless ground state on a <i>F-C</i> diagram

(c) Determination of Anharmonicity Constant When a long vibrational progression is observed in an ionisation band, the spacing between two adjacent lines, i.e. ΔG is measured on the vibrational levels $V = 1, 2, 3, 4 \dots$ in order to determine the anharmonicity constant x_{ii} (See Chapter 3 on infrared spectroscopy).

The energy of a vibrational level above the vibrationless ground state ($V = 0$) for excitation of a single vibrator ‘*i*’ can be written as

$$E(V \geq 1) = hc \bar{\nu}_i V_i + hc x_{ii} \bar{\nu}_i V_i^2 \quad (6.44)$$

where, $\bar{\nu}_i$ is the wave number in cm^{-1} and V_i is the vibrational quantum number.

The spacing between two adjacent lines can be worked out as follows:

$$EV_i = hc \bar{\nu}_i V_i + hc x_{ii} \bar{\nu}_i V_i^2$$

$$EV_{i+1} = hc \bar{\nu}_i (V_i + 1) + hc x_{ii} \bar{\nu}_i (V_i + 1)^2$$

For the spacing between two adjacent lines, we write

$$\Delta G = \frac{EV_{i+1} - EV_i}{hc} = \bar{\nu}_i + x_{ii} \bar{\nu}_i (2V_i + 1)$$

or

$$\Delta G = \bar{\nu}_i (1 - x_{ii}) + 2x_{ii} \bar{\nu}_i V_i \quad (6.45)$$

The plot between ΔG and V_i will be a straight line with slope of $2x_{ii} \bar{\nu}_i = m$ and intercept of $\bar{\nu}_i (1 - x_{ii}) = I_{\text{int}}$. From the slope and intercept, one can determine the anharmonicity constant,

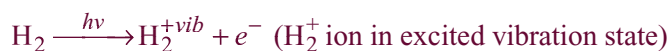
i.e.

$$x_{ii} = \frac{m}{2I_{\text{int}} + m} \quad (6.46)$$

When the spacing, i.e. the vibrational interval decreases with the increasing V_p , the anharmonicity is said to be positive, e.g. progression in $X^2 \sum_g^+$ band of H_2^+ . On the other hand, when the spacing increases with the increasing V_p , the anharmonicity is said to be negative, although the anharmonicity constant x_{ii} is positive. Actually the nomenclature originates from Franck–Condon principle. The potential energy curves for most diatomic molecules lead to negative values of x_{ii} , indicating thereby that the vibrational levels converge as they approach the dissociation limit which is normally expected, and thus x_{ii} is positive. Negative anharmonicity is observed most commonly in progressions due to bending vibrations since in such vibrations the restoring force instead of decreasing with increasing amplitude, rather increases by steric interactions when the vibrating groups approach each other, e.g. second band in the spectra of H_2O , H_2S , H_2Se , H_2Te , etc., and the first bands in the spectra of NH_3 and related molecules show the same effect.

Note that the rotational fine structure can also appear in the ionisation band if the resolving power of the current instruments could be increased 10–100 fold, which of course seems to be hard. However, pure rotational fine structure has been observed in the PES of H_2 recorded on an instrument having a resolution of 4 meV. Note that hydrogen is a special case not because of its large rotational intervals but also because both H_2 and H_2^+ exist in ortho and para states in which the spins of the two nuclei are parallel and antiparallel respectively. The selection rule of electronic transitions (spins are not affected in electronic transitions) $\Delta J = 0, \pm 2, \pm 4$ and a related rule are also applicable to photoionisation of any molecule with identical nuclei in equivalent positions, e.g. O_2 , CO_2 , C_2H_2 and NH_3 . Photoionisation of He (I) line showed that transition with $\Delta J = 0$ is much more intense than those with $\Delta J = 2$.

Problem 6.6: When the hydrogen molecule is excited by the helium resonance line (21.22 eV), it undergoes the following processes:



The PES spectrum corresponding to the $H_2^+ 1 \sum_g^+ (V' = 0) \rightarrow H_2^+ 2 \sum_g^+ (V'' = 0, 1, 2, 3 \dots)$ transition exhibits a long vibrational progression given below:

V''	0	1	2	3	4	5	6	7	8	9
IP (eV)	15.45	15.72	15.98	16.21	16.43	16.63	16.83	17.01	17.17	17.32

Calculate (a) the anharmonicity constant for H_2^+ ion, (b) compare the force constant of H_2^+ ion with that of the H_2 molecule, and (c) the lifetime of the H_2^+ ion if the width of the lines is about 0.1 eV.

Solution Proceeding as in Problem 3.29 of Chapter 3 on infrared spectroscopy, the average value of $-\Delta^2 G$ comes out to be 0.015 eV ($= 0.015 \times 8065.7 \text{ cm}^{-1} = 120.98 \text{ cm}^{-1}$).

Thus,
$$w_e x_e = w_0 x_0 = \frac{120.98}{2} \text{ cm}^{-1} = 60.49 \text{ cm}^{-1}$$

From Eq. (3.53) for $V=1$, we obtain

$$\Delta G \left(V + \frac{1}{2} \right) = 0.27 \times 8065.7 \text{ cm}^{-1} = w_0 - w_0 x_0 - 2 w_0 x_0 \times 1$$

$$2177.74 \text{ cm}^{-1} = w_0 - 60.49 \text{ cm}^{-1} - 2 \times 60.49 \text{ cm}^{-1}$$

Rearranging, we get

$$w_0 = (2177.74 + 60.49 + 120.98) \text{ cm}^{-1} = 2359.21 \text{ cm}^{-1}$$

From Eq. (3.36), i.e.

$$w_0 = w_e - w_e x_e,$$

we write
$$2359.21 = w_e - 60.49$$

Thus, $w_e = 2455.70 \text{ cm}^{-1}$

Since $w_e x_e = w_0 x_0$

Therefore, $x_e = \frac{w_0 x_0}{w_e} = \frac{60.49 \text{ cm}^{-1}}{2455.70 \text{ cm}^{-1}} = 24.63 \times 10^{-3}$

and $D_e = \frac{w_e}{4x_e} = \frac{2455.70 \text{ cm}^{-1}}{4 \times 24.63 \times 10^{-3}} = 24926 \text{ cm}^{-1} = 298 \text{ kJ/mole}$

For H_2 molecule; $w_e = 4400 \text{ cm}^{-1}$, $x_e = 27.4 \times 10^{-3}$, and $D_e = 435.9 \text{ kJ/mole}$

(b) In order to compare the force constant of the hydrogen molecule ion with that of the hydrogen molecule, we make use of Eq. (3.19).

Thus, $w_e(\text{H}_2^+) = 1303.16 \sqrt{\frac{k(\text{H}_2^+)}{\mu_m(\text{H}_2^+)}}$

$$w_e(\text{H}_2) = 1303.16 \sqrt{\frac{k(\text{H}_2)}{\mu_m(\text{H}_2)}}$$

Since $\mu_m(\text{H}_2^+) = \mu_m(\text{H}_2)$

Therefore, $\frac{w_e(\text{H}_2^+)}{w_e(\text{H}_2)} = \sqrt{\frac{k(\text{H}_2^+)}{k(\text{H}_2)}}$

or $\frac{k(\text{H}_2^+)}{k(\text{H}_2)} = \frac{[w_e(\text{H}_2^+)]^2}{[w_e(\text{H}_2)]^2} = \frac{[2455.70 \text{ cm}^{-1}]^2}{[4400 \text{ cm}^{-1}]^2} = 0.31$

or $k(\text{H}_2^+) = 0.31 k(\text{H}_2)$

or $k(\text{H}_2) = \frac{k(\text{H}_2^+)}{0.31} = 3.22 k(\text{H}_2^+)$

i.e. the force constant of the H_2 molecule is 3.22 times large as compare to that of the hydrogen molecule ion, H_2^+

(c) We know that

$$\Gamma = \frac{h}{2\pi\tau} = \frac{6.577 \times 10^{-16} (\text{eV s})}{\tau}$$

Since $\Gamma = 0.1 \text{ eV}$

Therefore, the lifetime of H_2^+ ion $\tau = \frac{6.577 \times 10^{-16} (\text{eV s})}{0.1 \text{ eV}} = 6.5 \times 10^{-15} \text{ s}$, i.e. of the order of 10^{-14} s .

Problem 6.7: The first ionisation band (i.e. $^2A_1$) in the PES of NH_3 exhibits a long progression as shown Fig. 6.29. The approximate values of ionisation potentials (i.e. vibrational frequencies) on quantum number $V'' = 0, 1, 2, 3 \dots 13$ as measured from Fig. 6.29 are listed in Table 6.10.

Solution In order to determine the anharmonicity constant, the vibrational intervals ΔG on different vibrational quantum numbers $V'' = 1, 2, 3 \dots 13$ need to be determined first. Now by making use of Eq. (3.53), ΔG for different values of V'' have been calculated and are listed here in Table 6.11.

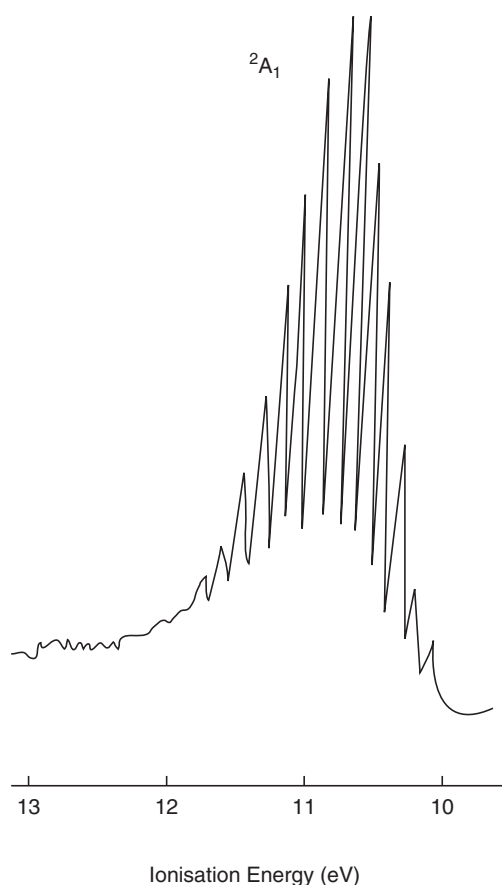


Fig. 6.29 Photoelectron spectrum of NH_3 , showing negative anharmonicity in the $^2A_1$ band.

Table 6.10 Ionisation potentials from the photoelectron spectrum of NH_3 .

V''	IP (eV)
0	10.110
1	10.220
2	10.338
3	10.456
4	10.575
5	10.695
6	10.816
7	10.940
8	11.066
9	11.194
10	11.323
11	11.452
12	11.584
13	11.718

Table 6.11 ΔG for different values of V'' .

V''	IP (eV)	ΔG (meV)
0	10.110	
1	10.220	110
2	10.338	118
3	10.456	118
4	10.575	119
5	10.695	120
6	10.816	121
7	10.940	124
8	11.066	126
9	11.194	128
10	11.323	129
11	11.452	129
12	11.584	132
13	11.718	134

Solution The increase in the vibrational interval ΔG at high vibrational quantum number indicates negative anharmonicity in the vibrational progression of the $^2A_1$ ionisation band in the photoelectron spectrum of ammonia.

The anharmonicity constant x_{ii} is then determined from the plot of ΔG against V'' shown in Fig. 6.30.

Here, Intercept $I_{\text{int}} = 113$ meV and slope $m = 1.65$ meV

Using Eq. (6.46), we get

$$x_{ii} = \frac{m}{2I_{\text{int}} + m} = \frac{1.65(\text{meV})}{2 \times 113(\text{meV}) + 1.65 \text{ meV}} = \frac{1.65}{227.65} = 7.25 \times 10^{-3}$$

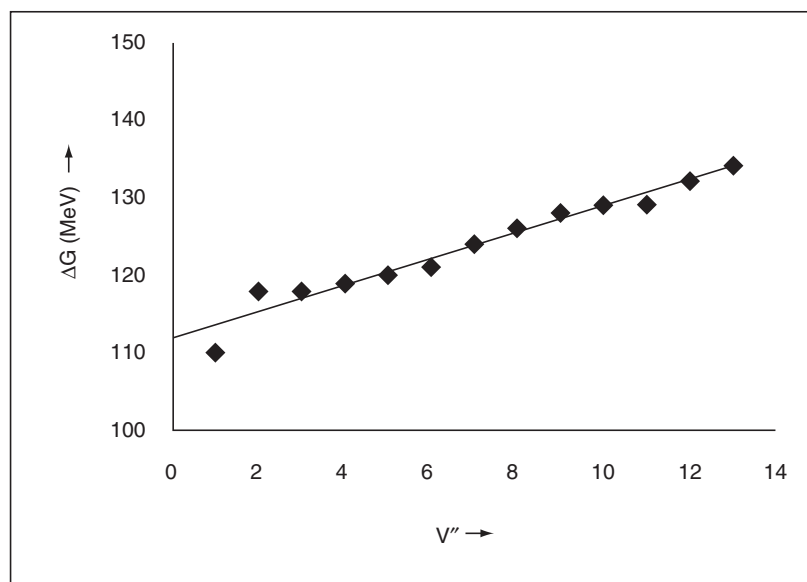


Fig. 6.30 Plot of vibrational intervals in the $2A_1$ ionisation band of NH_3 against vibrational quantum number.

(d) Determination of Geometrical Changes in Molecules on Ionisation From the measured vibrational frequencies in a particular ionisation band in different states of the molecule or ion, one can estimate the force constants while from the intensity distributions in the vibrational progression, the changes in molecular geometry, i.e. the changes in the equilibrium bond length or bond angle can be determined. It is simple to carry out such studies in diatomics since the normal modes of vibration in them are not localised. But it is not so in polyatomics where most of the normal modes of vibrations are not localised. However, the stretching modes of diatomics, totally stretching vibration of linear BAB , tetrahedral AB_4 , octahedral AB_6 , square planar AB_4 or planar AB_3 molecules qualify for the above studies. Bending vibrations of nonlinear BAB and the umbrella bending vibration of pyramidal AB_3 molecules are also totally symmetric.

According to the Franck–Condon principle, the vibrational wave functions for high vibrational quantum numbers (V'') have their greatest amplitude near the PE curve itself, which gives the position of the turning points of the classical vibrational motion. The largest Franck–Condon factor for a transition from the ground state and therefore the maximum intensity in a vibrational progression, occurs when the turning point in the ionic state V'' comes at the same bond distance or the angle as the equilibrium position in the ground state of the molecule (V''). The energy of the classical vibrator that represents vibrations in the ion is proportional to the square of the vibrational amplitude at the turning of the classical vibrational motion can be set equal to the experimental vibration energy in the ion at the vertical ionisation potential.

For a stretching vibration in a diatomic molecule.

$$2\pi^2 \mu_m \bar{\nu}_{\text{ion}}^2 (\Delta r)^2 = \left(V''_{\text{max}} + \frac{1}{2} \right) h \bar{\nu}_{\text{ion}} = I_{\text{vert}} - I_{\text{ad}} \quad (6.47)$$

where, $\bar{\nu}_{\text{ion}}$ is the vibrational frequency in the ion, μ_m is the reduced mass appropriate for the vibration, V''_{max} is the vibrational quantum number at the maximum intensity in the band and Δr is the difference in equilibrium bond distance between the ion and molecule, i.e. $\Delta r = r_e(\text{ion}) - r_e(\text{molecule})$. The same equation is valid for a bending vibration also.

$$\text{For a bending vibration,} \quad \Delta r = l \delta\theta \quad (6.48)$$

Here, l is the bond length and $\delta\theta$ is the change in equilibrium bond angle.

Thus, the Eq. 6.47) can be written as

$$(\Delta r)^2 = (l\delta\theta)^2 = 5.439 \times 10^5 \times \frac{(I_{\text{vert}} - I_{\text{ad}})}{\mu_m \bar{\nu}_{\text{ion}}^2} \quad (6.49)$$

Here, Δr and l are in Å, $\delta\theta$ in radians, I_{vert} and I_{ad} in eV, μ_m in atomic mass units and $\bar{\nu}_{\text{ion}}$ in cm^{-1} .

For BAB triatomic molecules, the energy of the classical vibrator is expressed in terms of the AB bond length is $4\pi^2\mu_m\bar{\nu}_{\text{ion}}^2(\Delta r_{AB})^2$. In such cases, Eq. (6.48) becomes

$$(\Delta r)^2 = (l\delta\theta)^2 = 2.719 \times 10^5 \times \frac{(I_{\text{vert}} - I_{\text{ad}})}{\mu_m \bar{\nu}_{\text{ion}}^2} \quad (6.50)$$

The equation holds good only for large vibrational quantum numbers, i.e. when there is a large change in shape and hence long vibrational progressions are observed.

A more general method to estimate the changes in molecular geometry on ionisation is due to Heilbronner, Muszkat and Schaublin, i.e. HMS method. This is based on calculated Franck–Condon factors for transitions between two harmonic vibrators which can be expressed in the analytical form.

The geometrical changes in some diatomic and triatomic molecules determined by different methods are compared in Table 6.12.

Table 6.12 Geometrical change in some diatomic and triatomic molecules.

Molecule	Orbital ionised	Ionic state	Change in bond length on ionisation (Å)		
			(a)	(b)	(c)
H ₂	$\sigma_g(b)$	$X^2\Sigma_g^+$	0.33	0.35	0.32
O ₂	$\pi_u(b)$	$a^4\Pi_u$	0.17	0.20	0.19
	$\pi_g(ab)$	$X^2\Pi_g$	−0.08	−0.09	−0.08
CO ₂	$\pi_g(nb)$	$X^2\Pi_g$	0.015	0.015	—
	$\pi_u(b)$	$A^2\Pi_u$	0.066	0.074	0.062
	$\sigma_u(b)$	$B^2\Pi_u$	0.018	0.015	—
CS ₂	$\pi_u(b)$	$A^2\Pi_u$	—	0.08	0.07

(a) From microwave spectroscopy, (b) From PES by HMS method (c) from (6.49)

Problem 6.8: Calculate the change in bond length on ionisation of H₂ molecule if the difference between the vertical and adiabatic ionisation potentials is 0.57 eV and the vibrational frequency of the H₂⁺ ion (in $\sum_g^+$ state) and that of the H₂ molecule is 2455.70 and 4400 cm^{-1} respectively. The bond distance of the molecule is 0.741 Å.

Solution Substituting the given values into Eq. (6.49), we get

$$(\Delta r)^2 = 5.439 \times 10^5 \times \frac{0.57(\text{eV}) \times 2}{(2455.70 \text{ cm}^{-1})^2} = 0.103 \text{ Å}^2$$

or

$$\Delta r = 0.32 \text{ Å}$$

Since the vibrational frequency of the H₂ molecule decreases on ionisation, the bond length of the H₂⁺ ion will be large as compared to that of H₂ molecule. Thus $r(\text{H}_2^+ \sum_g^+) = (0.741 + 0.32) \text{ Å} = 1.061 \text{ Å}$.

Problem 6.9: Calculate the change in bond length on ionisation of O₂ molecule ($\text{O}_2, X^3\Sigma_g^- \rightarrow \text{O}_2^+, ^2\Pi_g$), the difference between the vertical and adiabatic ionisation potentials is 0.32 eV and the vibrational frequency of the O₂⁺ ion (in $^2\Pi_g$ ionic state) is 1850 cm^{-1} . Compare the bond distance so determined with that of the O₂ molecule (1.21 Å) if the vibrational frequency of the O₂ molecule is 1580 cm^{-1} .

Solution Substituting the given values into Eq. (6.49), we obtain

$$(\Delta r)^2 = 5.439 \times 10^5 \times \frac{0.32(\text{eV}) \times 32}{(1850 \text{ cm}^{-1})^2 \times 16 \times 16} = 6.356 \times 10^{-3} \text{ Å}^2$$

or

$$\Delta r = 0.08 \text{ Å}$$

Since the vibrational frequency of the O_2 molecule increases on ionisation, the bond length of the O_2^+ ion will be small as compared to that of the oxygen molecule. Thus, $r(O_2^+ \ ^2\Pi_g) = (1.21 - 0.08) \text{ \AA} = 1.13 \text{ \AA}$.

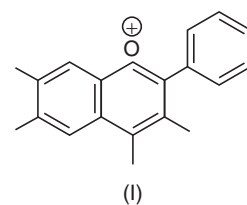
6.14.6 Molecular Charge Distribution

The ionisation potentials of inner shell electrons vary slightly with the chemical environment of the atoms in a molecule. Thus, the chemical shifts are due to changes in the electrical potentials of the inner electrons caused by charges within the molecules. The changes in potential are defined as

$$\Delta U = \frac{q}{r} + \sum_i \frac{\delta q_i}{R_i} \quad (6.51)$$

where R_i is the distance from the atom of interest to the i th other atom carrying charge δq_i . The atomic charge q can be computed provided that the constant $(\frac{1}{r})$ is known and the Madelung potential ΔU can be estimated.

Here, the ionisation potential shift is equated with the Madelung potential. Since the ionisation potential shifts in molecules with respect to some standard can be measured, the charge distribution in molecules can be accomplished by photoelectron spectroscopy, e.g. a comparison of OIs ionisation shift of the ring oxygen in flavylum compounds which are usually shown as under (I) with that of known oxygen groups showed that oxygen is slightly negative and the charge is strongly localised. This demonstrates the power of PES for probing the charge on individual atoms in the complex molecules.

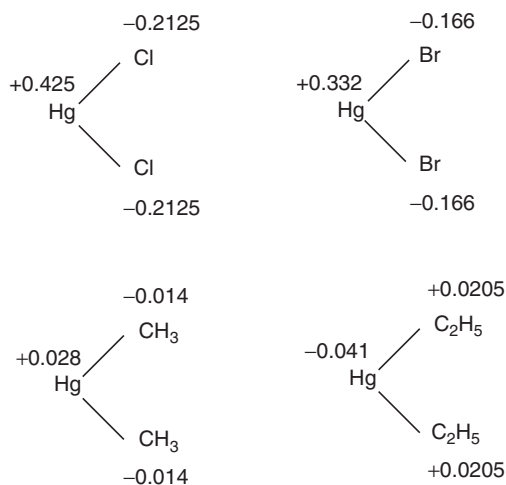


The photoelectron spectra of $HgBr_2$ exhibit $5d^{-1}$ ionisation bands (above 15 eV) at 16.4 (sharp), 16.8 and 18.3 eV while that of $(CH_3)_2Hg$ at 15.0 (sharp), 15.4 and 16.9 eV. These bands are assigned to $Hg \ 5d^{-1}$ ionisations, since they appear in the spectrum of every mercury compound, the relative spacing of the three bands remain almost constant i.e. ≈ 0.4 and 1.5 eV, the spacing of the two outer bands is ≈ 1.5 eV which is close to 1.86 eV, the spin-orbit splitting of the ^2D state of Hg^+ .

The shift between the sharp ($J = 5/2$) peak and the $^2D_{5/2}$ ionisation potential of atomic mercury is a direct measure of the difference between mercury atom in a molecule and a free mercury atom. Thus the charge on mercury atom in a molecule can be calculated from Eq. (6.51) provided the constant $\frac{1}{r}$ is known. The constant is equal to the change in ionisation potential of the d shell produced by unit positive charge in the outer $6s$ shell, and it can be obtained from the atomic spectrum of mercury. The atomic charges from $5d^{-1}$ ionisation potentials in some typical mercury compounds (II) are given here:

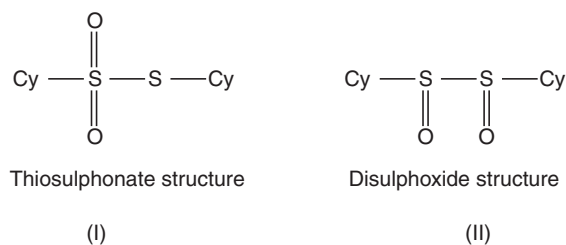
Compound	$HgCl_2$	$HgBr_2$	CH_3HgCl	CH_3HgBr	$(CH_3)_2Hg$	$(C_2H_5)_2Hg$
Shift from $^2D_{5/2}$ (eV)	1.87	1.56	0.95	0.84	0.11	-0.16
Charge on Hg (units of e)	0.425	0.332	0.218	0.182	0.028	-0.041

The negative charge on mercury in case of $(C_2H_5)_2Hg$ shows that the electron-attracting power of mercury atom is intermediate between that of the methyl and the ethyl groups.



6.14.7 Structural Elucidation

Since the photoelectron signal due to the atom of an element in a molecule is characteristic of its electronic environment, the PES lines due to atoms of the same element in a molecule will be different and discernible, consequently this can be fixed as criterion for resolving the structural problems in organic and inorganic molecules. Moreover, correlation tables could help in the final selection of functional groups, e.g. N 1s ESCA spectrum of sodium azide (NaN_3) shows two peaks with relative areas under the peaks in the ratio 2:1. This suggests that there are two types of nitrogens in sodium azide. The two similar-end nitrogens are different from the central nitrogen. Thus, ESCA spectra can also impart information about the number of each kind of atom in a molecule. Doubly oxidised cystine (CySO_2SCy) can either have thiosulphonate (I) or disulphoxide structure (II).



The thiosulphonate structure is expected to give two signals of equal intensity corresponding to the two oxidation states of S atom in the molecule while only one peak is expected in the disulphoxide structure since both the S atoms in the molecule exist in the same oxidation state. S (2p) ESCA spectra of cystine and doubly oxidised cystine shown in Fig. 6.31 suggest that oxidised cystine has a thiosulphonate structure (I) since two signals corresponding to two oxidation states of S are observed at 162 and 166 eV. The former corresponds to the low oxidation state while the latter to the high oxidation states of sulphur since the S (2p) signal in Cy SS Cy is observed at 164 eV.

The oxidation states of central metal in oxides like $\text{W}_3\text{V}_5\text{O}_{20}$, WV_2O_6 can also be established by comparing ESCA spectra of these compounds with their simple oxides. It is found that in the former, V is in +5 and +4 oxidation states while in the latter, V is in +5, +4 and +3 oxidation states.

Further, the change in electronic structure takes place in going from a linear molecule to a bent molecule since the degenerate orbitals in the former become nondegenerate in the latter. Thus, the number of photoelectron bands will increase and their shapes will also change markedly. This is attributed to the excitation of bending vibrations in ionisation from the orbitals which are angle determining in a bent molecule. This can be fixed as a criterion to resolve any doubt about the linearity of a molecule. Photoelectron spectrum is also useful to resolve the problem regarding the planar and nonplanar nature of the molecules, e.g. butadiene and 1, 1, 4, 4-tetrafluorobutadiene are planar molecules. The two π^* and one σ^* bands of butadiene appear at 9, 11.5 eV and 12.2 eV respectively while at 10.5, 11.5 eV and 14.5 eV in case of pentafluorobutadiene. Thus the shift of σ^* bands to higher ionisation potential is greater as compared to π^* bands due to perfluoro effect. The strong band near 17 eV in the spectrum of pentafluoro compound is due to ionisation of the fluorine lone-pair electrons. The difference in energy between the first (outermost π -orbital) and the second ionisation bands is above 2 eV in case of butadiene and 1, 1, 4, 4-tetrafluorobutadiene. However, this difference is about (11.5–10.5) eV $\approx$ 1 eV in pentafluorobutadiene. This suggests a nonplanar nature of the molecule since in a bent molecule, conjugation across the central bond will be less. Consequently, ionisation-energy difference between two π -orbital bands will also be reduced. Optical absorption data in conjunction with photoelectron spectral data suggest that pentafluorobutadiene has a *cis*-nonplanar configuration having a dihedral angle of 42 degrees. This conclusion conforms to the x-ray diffraction studies on the molecule.

The partial x-ray photoelectron spectrum of ethylchloroformate is shown in Fig. 6.32. The presence of C and Cl is established by the electron peaks at 284 and 270 eV respectively. Similarly, the presence of O could be established by electron peak at 532 eV. The chemical shifts apparent in the Fig. 6.32 give evidence for the presence of C in different valence states. The C (1s) peak intensity ratio 1:1:1 indicates that the compound contains equal number of carbon atoms in three different groups. Since the XPS chemical shifts are governed by the electron-withdrawing power of atoms attached to the atom whose chemical shift is under consideration, the peak at 284 eV is attributed to

C (1s) $\text{Cl}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}$ in groups and the following two peaks to C (1s) in $-\text{O}-\text{CH}_2$ and $-\text{CH}_3$ groups respectively.

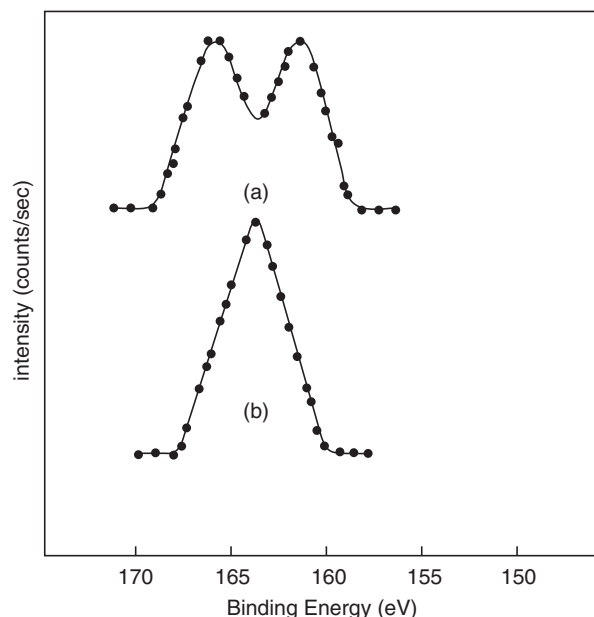


Fig. 6.31 S (2p) ESCA spectra of (a) doubly oxidised cystine, and (b) cystine.

6.14.8 Nature of Chemical Bonding

Based on the photoelectron spectral data on pentacarbonyl manganese derivatives, it has been accomplished that the *BE* of pure ligand orbitals > the metal to ligand bonding orbitals > the metal *d*-orbitals, i.e. complexation stabilises both the ligand σ -orbitals and the metal *d*-orbitals as compared to their energies in the free ligand molecule and the metal atom as expected. This rule aids in interpreting the photoelectron spectra and conforms to the fact that metal *d*-orbitals determine many of the chemical properties of the complexes.

Molecule	BE(eV)
PF ₃	12.2, 16.2, 17.7, 19.7
Mo(PF ₃) ₆	9.2, 12.4, 13.5, 14.5, 16.2, 17.7, 19.7
Mo(CO) ₆	8.4, 13.2, 14.8

Let us now examine the HeI photoelectron spectral data of Mo (PF₃)₆ and Mo (CO)₆ given below in relation to the nature of chemical bonding in these compounds in the light of this rule.

The lowest ionisation energy band in the PES of Mo (PF₃)₆ appears at 9.2 eV while an 8.4 eV in the PES spectrum of Mo (CO)₆. The shift of 0.8 eV on the change of ligand from PF₃ to CO is attributed to the ionisation from metal *d*-orbitals. In octahedral low-spin complexes, the six *d*-orbitals reside in *t_{2g}* orbitals, so the *d*-electron ionisation bands are single.

Ionisation potential of the PF₃ complex is greater than that of the CO complex showing thereby that PF₃ causes greater stabilisation compared with the CO ligand and it is a better π -acceptor than CO. The PES spectra of PF₃ and Mo (PF₃)₆ are almost identical in the ionisation region of 15–20 eV suggesting thereby that the fluorine lone-pair orbitals or the P–F bonding orbitals are weakly affected by complexation. The lowest-energy ionisation band of PF₃ at 12.2 eV which disappears in the complex is attributed to the ionisation from the lone pair of electrons of *P* atom, the orbital from which σ -donation occurs. In octahedral symmetry, the six ligand lone-pair orbitals become *t_{1u}*, *e_g* and *a_{1g}* molecular orbitals, and are stabilised by the empty Mo *p*, *d* or *s* orbitals respectively on complexation. The three bands at 12.4, 13.5 and 14.5 eV having area ratio of 3:2:1 in the PES spectrum of Mo(PF₃)₆ correspond to ionisation from *t_{1u}*, *e_g* and *a_{1g}* orbitals respectively as expected. All these three orbitals are stabilised compared with lone-pair orbitals of free PF₃. In case of Mo(CO)₆, the band at 13.2 eV corresponds to *t_{1u}* orbital while at 14.8 eV is from orbitals located in the CO molecule (bands due to uncomplexed CO orbitals fall in the range of $\approx$ 14–20 eV). The bands due to other σ -bonding orbitals, i.e. *e_g*, *a_{1g}* might have overlapped with the bands from orbitals located in the CO molecule.

Let us now correlate the photoelectron spectra of Ni(PF₃)₄: Ionisation energy bands [(9.6, 10.6), 12.3, 13.1, 14.5, 15.8, 17.4, 19.3 eV] and Ni (CO)₄ [(8.9, 9.8), 14–20 eV] in order to understand the nature of chemical bond in these complexes. Both these tetrahedral complexes have completely filled *t₂* and *e* orbitals as nickel in these complexes is in zero oxidation state. The lowest ionisation energy band in both the complexes appear as a doublet, the bands at 9.8 and 8.9 eV are the components of the doublet of CO complex while at 10.6 and 9.6 eV are the components of doublet of PF₃ complex. The ratio of areas of bands constituting a doublet in both the complexes is 3:2 as expected for *t₂*⁻¹ and *e*⁻¹ ionisations. The splitting between the ²*T₂* and ²*E* states which is a measure of the strength of the ligand field is almost the same, i.e. about 1 eV in both the complexes but the ionisation potential of

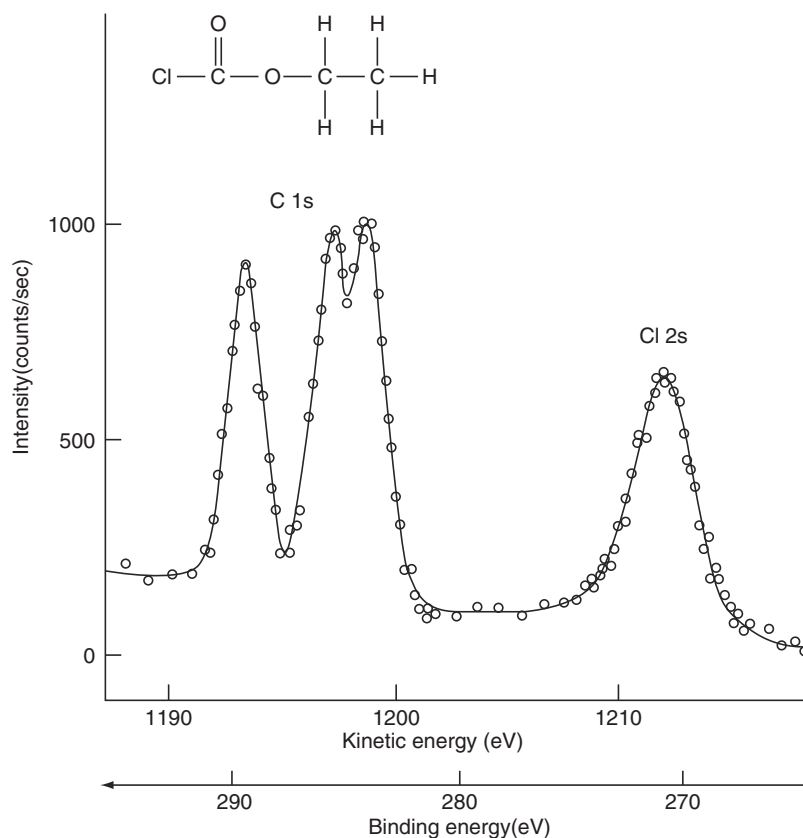


Fig. 6.32 Partial photoelectron spectrum of ethylchloroformate.

the PF_3 complexes (10.6 eV, 9.6 eV) is higher than that of CO complex (9.8 eV, 8.9 eV). This indicates that though ligand-field strength in both these complexes is about the same but PF_3 is a better π -acceptor as compared to CO ligand, i.e. PF_3 causes greater stabilisation than CO. Just like the low-spin octahedral complex $\text{Mo}(\text{PF}_3)_6$, the PES spectra PF_3 and $\text{Ni}(\text{PF}_3)_4$ are almost identical in the ionisation region of 15–20 eV indicating that the P–F bonding orbitals are weakly affected by complex formation. The lowest ionisation band of PF_3 at 12.2 eV is attributed to the ionisation from the lone pair σ -donating orbitals of P-atom which are stabilised in the complex as is evident from the ionisation bands at 12.3, 13.1 and 14.5 eV.

To summarise, the bonding in these complexes involves the donation of σ -electrons from the ligands into empty metal d orbitals accompanied by back donation from metal d orbitals into empty ligand π orbitals of appropriate symmetry, the latter, i.e. $\text{P} \leftarrow \text{M} \pi$ back bonding seems to be the most important for the stability, i.e. neutrality of the complexes.

He (I) photoelectron spectrum of chloroform exhibits bands at 11.5, 11.9, 12.8, 16 and 17.1 eV whereas its silicon analogue, i.e. SiHCl_3 , shows a broadened band (not all) at 11.8, 12.3, 13.1, (14.8 shoulder, 15.2 eV) and 18.1 eV. The ionisation energies from equivalent lone-pair orbitals of SiHCl_3 are at higher potentials as to that of CHCl_3 while the ionisation bands involving σ -orbitals are observed at lower ionisation energies, as expected. The broadening of some of the bands in going from CHCl_3 to SiHCl_3 , i.e. halomethanes to halosilanes, is attributed to the presence of $d\pi$ - $p\pi$ interaction between chlorine and silicon which can stabilise certain orbitals and increase their bonding character. Si-F bonding in fluorosilanes has less $d\pi$ - $p\pi$ character than Si-Cl bonding in chlorosilanes. These observations conform to theoretical models in which $d\pi$ - $p\pi$ interaction is incorporated. Photoelectron spectra of thiophene and its derivatives, halophosphenes also exhibit $d\pi$ - $p\pi$ interaction in the molecules.

6.14.9 Substituent Effects

PES, like all other spectroscopic methods, provides a tool of measuring substituent effects via ionisation potential in organic molecules. The high accuracy of measurement of PES ionisation potentials (either adiabatic or vertical) compared with other spectroscopic methods makes it a better tool to study the substituent effects. The ionisation potentials of lone-pair electrons may be influenced by the following:

- (i) *Conjugative (bonded or nonbonded) interaction with other orbitals in the molecule* may either raise or lower the ionisation potential. Width of the lone-pair ionisation bands gives an estimate of the strength of conjugative interactions. Many lone pairs being angle determining, give broad spectral bands so width test is of little practical use to measure strength of conjugative, effects.
- (ii) *Spin-orbit coupling* in halogen lone-pair ionisations splits the ionisation band symmetrically. Such an effect can be distinguished from the other two by taking the average from two peaks.
- (iii) *Local electric charges and electrostatic effect of the nearby dipoles* shifts the body of the ionisation bands. Such effects constitute the inductive effects. The simple presence of charge in large molecules with nonrigid skeletons may cause changes in molecular geometry by polarisation effects and consequently, broadening of bands occurs. Thus, it is very hard to separate the conjugative and inductive effects.

In spite of the limitations of separating out these effects quantitatively, correlations have been made between ionisation potentials of lone pairs of heteroatoms in homologous series, between ionisation potentials and substituent constants and between ionisation potentials and electronegativities.

A linear relationship between the ionisation potentials of molecules belonging to several homologous series and a new substituent parameter μ_R is given by the equation

$$IP_{RX} = IP_{MeX} + \mu_R \chi_{RX} \quad (6.52)$$

where, χ_{RX} are the sensitivity parameters.

The sensitivity parameters for a series of compounds are obtained from the slope of the plot between lone-pair ionisation potentials of alkyl iodides (RI) on the X -axis and those of other aliphatic homologous series (RX) on the Y -axis. Alkyl iodides are used as standard because they exhibit sharp ionisation bands. The slope of RI is taken as unity. The numerical values of sensitivities of adiabatic ionisation potentials to alkyl substitution are recorded in Table 6.13 and those of alkyl group substituent parameters, μ_R , in Table 6.14.

$\text{R-CN}-n^*$ – nitrogen lone-pair ionisations and $\text{R-CN}-\pi^* - n$ orbital ionisations of the alkyl cyanides.

The sensitivities grow as we move from iodides to bromides and from thiols to alcohols. The sensitivities are higher for lone pairs on atoms adjacent to the alkyl groups as compared to lone pairs which are farther away from the alkyl groups. The sensitivity of the π -electron ionisations in cyanides is largest of all and that of n -electron ionisations in the same compounds is moderate.

Table 6.13 Sensitivities of lone-pair adiabatic ionisation potentials in different homologous series.

Series RX	Sensitivity, χ_{RX}	Ionisation potential of methyl homologue $IP_{MeX}(eV)$
RNCS	≈ 0.57	9.25
RNH ₂	0.66	8.97
RCO, <i>t</i> -Bu	0.84	9.14
RSH	0.94	9.44
RI (standard)	1.00	9.54
HCOOR	1.00	10.81
RNO ₂	1.00	11.08
RCOMe	1.12	9.71
RCN- n^*	≈ 1.2	13.14
RBr	1.25	10.53
RCHO	1.40	10.22
ROH	1.72	10.85
RCN- π^*	2.00	12.22

R-CN- n^* -nitrogen lone-pair ionisations and R-CN- Π^* - Π orbital ionisations of alkali cyanides

Table 6.14 Substituent parameters for the alkyl-group substituents.

Alkyl group	Substituent parameter, μ_R
Methyl	0.0 (standard)
Ethyl	-0.20
<i>n</i> -Propyl	-0.29
<i>n</i> -Butyl	-0.34
<i>n</i> -Pentyl	~ -0.35
Isopropyl	-0.36
Isobutyl	-0.38
<i>t</i> -Butyl	-0.52

The new substituent parameter, μ_R reflects the effects of different alkyl groups on the ionisation potentials and bears a close linear relationship with Taft's σ^* constants, indicating thereby that the alkyl substitution affects the ionisation potential mainly through inductive effects; the role of other two effects, if any, is negligibly small.

In case of aromatic compounds, the following deductions are based on the PES spectrum of monosubstituted and para-disubstituted benzenes. The first ionisation band at 9.40 eV in the PES of benzene is due to ionisation from the two degenerate orbitals, π_2 and π_3 . The introduction of an electron donating group such as —OH, —OR and —NR₂ cause splitting of the first band into two components (i.e. 8.75 eV, 9.45 eV; 8.54 eV, 9.37 eV; and 8.04 eV, 9.11 eV respectively) by conjugative mechanism. The splitting is due to the nondegenerate character of the π_2 and π_3 orbitals in the substituted benzenes. One of the bands remains near the original position whereas the other band shifts to the lower ionisation potentials. The shift in the latter case is due to the interaction of substituent with a new nondegenerate π -orbital without a node at the substituent position. The other nondegenerate π -orbital with a node at the substituent position does not interact with the substituent, so the position of the band remains unaffected. On the other hand, electron-withdrawing groups such as CF₃, NO, NO₂, CN, COCH₃, COOCH₃, —CHO, etc., operates through inductive mechanism and does not produce detectable splitting but shifts the first band of benzene (i.e. 9.40 eV) to higher potentials, e.g. —CF₃ (9.90 eV) —NO (9.97 eV), —NO₂ (10.26 eV), —CN (10.02 eV), —CHO (9.80 eV), etc. When two substituents are introduced into the benzene ring at the *p*-position, the experimental splittings and shifts are approximately additive. Thus, photoelectron spectrum of benzene derivatives enables to distinguish some conjugative and inductive effects. Halogen substituents operate via both the effects and cause splitting and shifting of both the bands, e.g. C₆H₅F (9.5 eV, 9.86 eV), C₆H₅Cl (9.31 eV, 9.72 eV), C₆H₅Br (9.25 eV, 9.76 eV), C₆H₅I (8.78 eV, 9.75 eV). The splitting of the ionisation band follows the order: I > Br > Cl > F, while the shifts (i.e. mean ionisation potential of the first two bands minus the first ionisation potential of benzene) follows the reverse trend of splitting, i.e. F > Cl > Br > I. When all the hydrogens in benzene molecule are replaced by

fluorine, σ electron ionisation bands of the unsubstituted molecules are shifted to much higher ionisation energy as compared to those of π electron ionisation bands. A clear separation between π^- and σ^- ionisation bands is seen in the PES spectrum. Both aliphatics and aromatics exhibit such an effect called the *perfluoro effect*.

Problem 6.10: Calculate the lone-pair adiabatic ionisation energies of $\text{C}_2\text{H}_5\text{NO}_2$, $n\text{-C}_3\text{H}_7\text{NO}_2$ and $\text{iso-C}_3\text{H}_7\text{NO}_2$.

Solution Substituting the values of the needed parameters from tables 6.5 and 6.6 into Eq. (6.52), we get

$$\text{IE}(\text{C}_2\text{H}_5\text{NO}_2) = 11.08 - 1 \times 0.20 = 10.88 \text{ eV (10.88 eV)}$$

$$\text{IE}(n\text{-C}_3\text{H}_7\text{NO}_2) = 11.08 - 1 \times 0.29 = 10.79 \text{ eV (10.81 eV)}$$

$$\text{IE}(\text{iso-C}_3\text{H}_7\text{NO}_2) = 11.08 - 1 \times 0.36 = 10.72 \text{ eV (10.71 eV)}$$

The quantities with in brackets are the literature values.

6.14.10 Nonbonded Interactions

Interactions between electrons of atoms or groups within molecules which are not represented by bonds are called nonbonded interactions. Such interactions are generally ignored in simple molecular orbital models. But in some cases they are strong enough to influence the electronic structure, particularly the nature of the outermost orbitals in molecules. Examples are mutual interactions between the halogen lone pairs in the halides of carbon and silicon, interactions of lone pairs of heteroatoms in large organic molecules, hyper conjugation (one form of through bond interaction), homo conjugation (through space interactions), e.g. nonboradiene, barrelene, cis, cis, cis-1, 4, 7-cyclo nonatriene—the interactions in these compounds are called isolated double bond interactions, the last compound being the representative of homoaromatic compounds.

PES is most sensitive to nonbonded interactions as compared to other physical techniques and such interactions manifest themselves in the form of splitting and shifting of ionisation bands under observations in the photoelectron spectrum of the molecule. The transitions due to lone pair on heteroatoms in cyclic organic compounds have low ionisation energies and relatively narrow bands as compared to that of bonded electrons. However, if the molecules are conjugated, interactions between occupied π -orbitals also exhibit narrow bands. In such a situation, the band due to lone-pair interaction can only be identified by molecular orbital calculations on model compounds and comparison with photoelectron spectrum. Thus, experimental studies together with empirical molecular orbital calculations provide an aid to understand the nature of molecular electronic structure. Note that PES deals with ions but not with the neutral molecules; conjugation being much stronger in ionised form compared with the neutral molecule.

The most interesting deductions regarding the nature of nonbonded interactions in cyclic compounds containing oxygen, nitrogen and sulphur as heteroatoms based on molecular orbital calculation on model compounds and comparison with the photoelectron spectrum and vice versa are the following: The interactions between lone pair of electrons on heteroatoms in a series of organic compounds may occur through space or bonds. The magnitude of both these effects in cyclic compounds containing heteroatoms such as O or N or S depend markedly on molecular geometry and on different accessible conformations in open-chain molecules. The different interactions in different conformations result in overlapping of bands in the lone-pair region of the photoelectron spectrum. Due to this very reason, it is preferred to study lone-pair interactions in the relatively rigid-ring compounds.

When the interaction is through space, the symmetrical combination of atomic orbitals, i.e. positive overlap integral will have higher ionisation potential (lower energy) but the unsymmetrical combination of orbitals will have lower ionisation energy if the overlap integral is negative. The reverse is true for the through-bond interaction. The through-bond interaction makes a new orbital containing mainly a symmetrical combination of lone pairs energetically outermost, giving the opposite ordering to that expected on a through-space mechanism and it also shifts the centre of gravity of the bands. The effects of the through-space and through-bond interactions on the lone-pair orbital energies are shown in Fig. 6.33.

The extent of dominance of either of these interactions, i.e. through space and bonds depends upon not only on the number of carbon centres separating the heteroatoms but also on the nature of the heteroatom. The above mechanism also holds good for through-space interactions, e.g. in case of 2 (1,4-diazabicyclo [2,2,2] octane) (DABCO), the through-bond interaction is dominant. The centre of gravity of the doublet (7.52 eV, 9.65 eV) at 8.6 eV undergoes a shift of +0.58 eV relative to the lone-pair band of quinuclidine at 8.02 eV. The energy difference between two lone-pair ionisations is 2.13 eV. The first-order splitting, i.e. through space interaction is expected to be small due to the large separation between the two nitrogen centres of about 3 Å. The number of bands in the photoelectron spectrum

may or may not correspond to the number of equivalent lone pairs even if the heteroatoms are separated by a number of bonds, e.g. only a single doublet at 8.6, 9.0 eV and at 8.8, 9.4 eV has been observed in 1, 4-dithiane and in 1, 3, 5-trithiane respectively. The splitting of the lone-pair band in a series of compounds passes through a minimum and rises again. The alteration in the magnitude of splitting is the characteristic of the transition from through-space to through-bond interaction and the negative sign indicates the reversal in the order of the symmetrical and antisymmetrical orbitals combinations in passing from through-space to through-bond interactions, e.g. the splittings in case of *o*-, *m*- and *p*-diazines are 2.0 eV, 1.5 eV and -1.7 eV respectively.

The through-space interaction is dominant when the two heteroatoms are neighbours and it remains dominant even if they are separated by one carbon centre, e.g. the magnitude of splitting in a doublet (8.6 eV, 9.0 eV) of 1,4-dithiane is 0.4 eV whereas in a doublet (8.8 eV, 9.4 eV) of 1,3, 5-trithiane, it is 0.6 eV.

The spectral data of some model cyclic compounds having N, O and S as heteroatoms has been summarised in Table 6.15.

Table 6.15 Characteristic spectral parameters of heteroatom lone pairs of some cyclic systems.

Molecular system	Heteroatom lone pair ionisation potential band (eV)	Splitting (eV)	Centre of gravity of doublet (eV)	Shift of centre of gravity relative to original band	Dominant interaction
	8.5	—	—	—	—
	8.6, 9.0 (Doublet)	0.4	8.8	0.3	Bond
	8.8, 9.4 (Doublet)	0.6	9.1	0.6	Space
	—	2.0	—	—	Space
	—	1.50	—	—	Space
	—	-1.70	—	—	Transition from space to bond
	—	—	—	—	—
	8.02	—	—	—	—
	7.52, 9.65 (Doublet)	2.13 [1.6]	8.6	0.58 [0.37]	Bond

The quantities within square brackets are from the molecular orbital model.

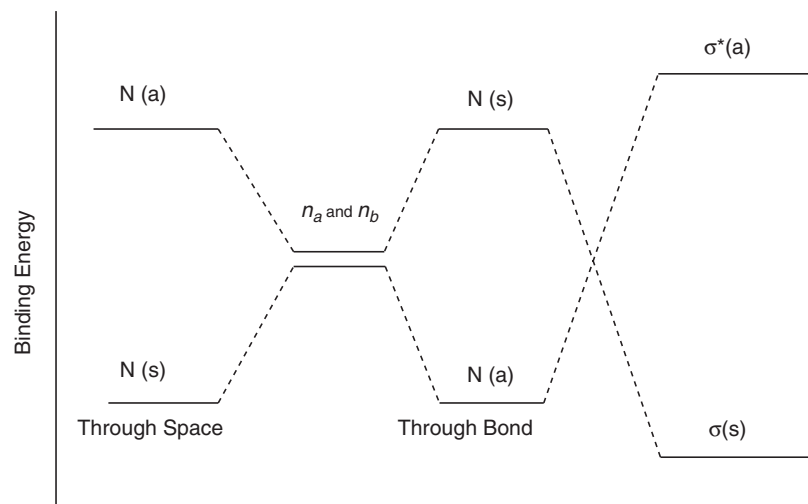
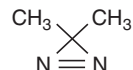
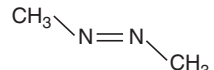
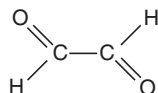


Fig. 6.33 Schematic molecular-orbital-energy diagram illustrating the effects of through-space and through-bond interaction on the ionisation potential of lone-pair orbitals: *s*-symmetrical, *a*-asymmetrical, *N*-nitrogen.

The splittings between lone-pair ionisation potentials of heteroatoms in some typical molecules have been given here.

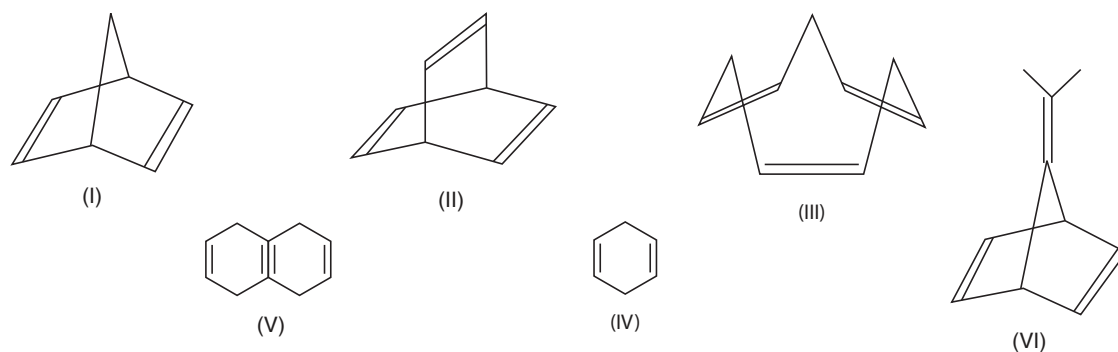
	3.6 eV		0.55 eV	$t\text{-Bu} \cdot \text{S}-\text{S} \cdot t\text{-Bu}$	0.64 eV
	3.3 eV		-1.6 eV		-0.45 eV
$\text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$	0.5 eV		0.25 eV		0.41 eV
	-0.3 eV				
	-2.1 eV		-1.22 eV		

Lone-pair interactions occur in halogen compounds also but are complex relative to lone-pair interactions in cyclic compounds containing heteroatoms such as N, O and S. A single halogen atom has two lone pairs and will give two lone-pair bands in the photoelectron spectrum either because of spin-orbit interaction or because one halogen p -orbital interacts more strongly than the other with the remainder of the molecule, e.g. in case of methyl iodide (CH_3I) four distinct bands in the form of two doublets at 9.5 eV, 9.6 eV (doublet with peak height ratio 15:1) and at 10.2 eV, 10.3 eV (doublet with peak height ratio 13:1) are observed in the spectrum. The strong peaks of equal intensities at 9.5 and 10.2 eV are due to spin-orbit coupling, i.e. first-order effect, the spin-orbit splitting being ≈ 0.7 eV whereas the two doublets are because of Jahn–Teller effect, i.e. second-order effect; the Jahn–Teller splitting being ≈ 0.1 eV. CH_3Br also shows a similar spectrum but the intensities of the strong bands at 10.6 eV and 10.8 eV are quite different, the intensity ratio of the two peaks is ≈ 1.5 . This is attributed to the removal of degeneracy of orbitals not only by spin-orbit coupling but also by Jahn–Teller effect, as casual, the latter being still smaller than the former. Further, in a molecule with two halogen atoms each having two lone pairs, four lone-pair ionising bands are expected and the same has been observed in the experimental photoelectron spectrum of dichloroethylene. The photoelectron spectrum of diiodomethane also exhibits four distinct bands at 9.4, 9.8, 10.3 and 10.7 eV while that of dichloromethane (CH_2Cl_2) shows only two bands at 11.4 and 12.3 eV. The separation of two bands in the spectrum of CH_2Cl_2 into four in the spectrum of CH_2I_2 may be due to spin-orbit splitting which is partially true since spin-orbit splitting can arise from accidental degeneracy as well as symmetry-based degeneracy, i.e. when two orbitals are nearly degenerate, the second order effects become as strong as the first-order effects. The degeneracy is removed by distortions brought about by excitation of one or more degenerate vibrational modes of the molecule, which are called the Jahn–Teller vibrations.

Let us now consider the nonbonded interactions between isolated double bonds, i.e. π -orbitals instead of lone-pair electrons on heteroatoms in cyclic compounds. Both types of nonbonded interactions, i.e. through space as well as through bond are also operative between isolated π -orbitals. The through-space interaction between isolated π -orbitals is called homo-conjugative interaction while it is called hyper-conjugative interaction when it operates through bond.

Just like nonbonded interactions between lone pairs on heteroatoms, the isolated double-bond interactions are also accomplished on the basis of molecular orbital calculation data in conjunction with the observed photoelectron spectral data on some model compounds. The model candidates for through-space interaction are norbornadiene (I) barrelene (II); cis, cis, cis-1,4,7-cyclononatriene (III), etc., and for through-bond interaction are 1, 4-cyclohexadiene (IV); 1,4,5,8-tetrahydronaphthalene (V), etc.; the typical overlap integrals for the former and similar molecules in an Huckel molecular treatment is about 1 eV as compared to 2–3 eV for normal double bonds and the unsymmetrical π -orbitals combination, i.e. negative overlap integrals has a lower ionisation potential than the symmetrical combination as required by the through-space interaction while the reverse is true for through-bond interaction, i.e. symmetrical combination of π -orbitals has lower ionisational potential compared with unsymmetrical combination.

Let us now examine the photoelectron spectrum of the candidates for through-space interaction. Both the π -orbitals of norbornadiene (I) are singly degenerate but its PES exhibits two bands at 8.69 and 9.55 eV. Thus the splitting of π -levels which does occur in norbornadiene and its 7-isopropylidene derivative (VI) is the result of π -bond interaction. This π -bond interaction is through-space since through-space splitting is expected to be small (0.86 eV) due to the large π -bond separation of about 2.5 Å compared with that in butadiene (3.15 eV) with a π -bond separation of 1.483 Å.



The through-space interaction between π -orbitals in norbornadiene (I) and such molecules can also be accomplished by the general method proposed by E Heilbronner. In this method, the PES of the system under observation, i.e. the parent molecule, is compared with the PES of a similar system having the parent molecule in its structure also. Here, the spectrum of 7-isopropylidene derivative of norbornadiene (VI) is compared with that of norbornadiene (I), the parent molecule. Isopropylidenenorbornadiene (VI) has three π -bonds out of which the two π -bonds in the parent structure are equivalent and the dihedral angle between them is almost the same as in the parent molecule itself. The new π -bond because of its symmetry interacts with the unsymmetrical combination of the two equivalent π -orbitals giving rise to three ionisation bands at 9.54, 9.25 and 7.97 eV in the photoelectron spectrum of the compound (VI). Thus, the higher ionisation energy band of the parent compound at 9.55 eV remains unperturbed while the lower energy band at 8.69 eV splits into two separate bands at 7.97 and 9.25 eV in its 7-isopropylidene PES spectrum. This effect proves that the outermost π -orbitals in norbornadiene has an unsymmetrical combination as demanded by the through space interactions.

6.14.11 Study of Biological Systems

XPS proved to be a convenient tool for studying the presence of metals in metalloproteins. This technique is especially suitable for those metals which cannot be studied by means of Mössbauer or ESR spectroscopy. In some cases, even the site of the metal in metalloproteins can be located by XPS. This is demonstrated here by comparing x -ray photoelectron spectral data of $\text{Cu } 2\text{P}_{3/2}$ and $\text{Zn } 2\text{P}_{3/2}$ in erythrocyte with the corresponding values of different Cu/Zn amino acid chelates.

The intensity ratio of the signals in Cu/Zn amino acid chelates is approximately the same (Zn:Cu). However, in case of erythrocyte, a marked change has been noticed. The intensity ratio of the signals has been found to be 1:2.5 (Zn: Cu). Since two gram atoms of each metal are present in erythrocyte, it is inferred that Cu is located in the outer sphere of the protein portion while Zn must be less accessible to the Mg K_α radiation. The Zn $2\text{P}_{3/2}$ signals are observed at 1021.5 eV in the amino acid chelates and the aquo complex, and an identical value of the 1020.5 eV is measured in erythrocyte. On the other hand, the Cu $2\text{P}_{3/2}$ signal at 934.2 eV in the amino acid chelates is observed at 931.9 eV in erythrocyte. But in case of Cu $[\text{Cu}(\text{Asp})_2]$, two signals have been observed at 932 and 934.2 eV. The former signal at (932 eV) is attributed to extraneous Cu^{2+} while the latter (at 934.2 eV) is attributed to the binding energy of inner Cu $2\text{P}_{3/2}$. It is interesting to note that the copper in Cu $[\text{Cu}(\text{Asp})_2]$ is identical to that of copper in erythrocyte.

System	BE(eV)	Intensity ratio of Zn:Cu in Cu/Zn amino acid complexes	Intensity ratio of Zn:Cu in erythrocyte
$\text{Cu}[\text{Cu}(\text{Asp})_2]$ (Cu $2\text{P}_{3/2}$)	934.2 932	Same	1:2.5
Bovine erythrocyte (Cu $2\text{P}_{3/2}$)	931.9		
$\text{Zn}[\text{Zn}(\text{Asp})_2]$ (Zn $2\text{P}_{3/2}$)	1021.5		
Bovine erythrocyte (Zn $2\text{P}_{3/2}$)	1020.5		

PROBLEMS

1. (a) Draw the 3p photoelectron spectra of Kr and Xe atoms.
 (b) The 3p PES of Kr and Xe atoms using He (I) 21.22 eV radiation source show that the photoelectron kinetic energies for the two different states of Kr are 7.23 and 6.57 eV and that of Xe are 9.093 and 7.793 eV. Calculate
 (i) the BEs for the different states of Kr and Xe, and
 (ii) the weighted mean of the ionisation energies of Kr and Xe atoms as well.

[Ans: (b); (i) Kr. 13.99 eV, 14.65 eV; Xe: 12.127 eV, 13.427 eV (ii) Kr 14.210 eV, Xe: 12.560 eV]

2. The figure given below shows an energy-level diagram for sodium with approximate BEs for the core levels as determined from XPS spectrum of NaCl obtained by using MgK_α ($h\nu = 1253.6$ eV) radiation. At what kinetic energy will the Na, 1s, 2s and 2p photoelectron peaks be observed?

_____	Vacuum level
_____	VB
-----	2p (BE = 31 eV)
_____	2s (BE = 64 eV)
_____	1s (BE = 1072 eV)

[Ans: 2p (1222.6 eV, 2s (1189.6 eV); and 1s (181.6 eV)]

3. Calculate the probability of escape of a photoelectron through a solid without undergoing scattering for $\lambda = 20.0$ Å

and $d = 100$ Å. At what value of d or $\frac{d}{\lambda}$ will the probability of escape be maximum? [Ans: $67 \cdot 10^{-4}$, d or $\frac{d}{\lambda}$]

4. Calculate the probability $P(d)$ of escape of an electron through a solid without undergoing scattering when $d =$

$1\lambda, 2\lambda, 3\lambda \dots 8\lambda$. Draw a graph between $P(d)$ and $\frac{d}{\lambda}$ and

then from the graph find out at what value of d will the probability of escape of the electron tend to be zero?

[Ans: $d = 5\lambda$]

5. Calculate the escape depth of an electron in a solid if its kinetic energy is 1000 eV.

[Ans: $31 \cdot 6$ Å]

6. Using the data in Problem 6.6, draw a graph of the vibrational interval of H_2^+ ion ($X \Sigma_g^+$) against the upper-state

vibrational quantum numbers, i.e. V'' . From the graph, find the maximal value of vibrational quantum number at which the vibrational interval is zero and using this value of V'' , determine the dissociation energy of hydrogen molecule ion and compare it with the one computed by nongraphical method in Problem.

[Ans: $V''_{\max} = 16 D_e = 24051 \text{ cm}^{-1}$]

7. The fourth ionisation band of $\text{O}_2^+(B \Sigma_g^-)$ in the photoelectron spectrum of oxygen (O_2) exhibits a vibrational progression. The ionisation potentials in the vibrational progression on different vibrational quantum numbers are given here:

(a) Calculate the dissociation energy of the O_2^+ ion by the graphical and nongraphical methods and compare the values so obtained with that of the oxygen molecule listed in the appendix of the book.

V''	IP(eV)
0	20.29
1	20.42
2	20.55
3	20.67
4	20.78
5	20.88
6	20.96

(b) Compare the force constant of O_2^+ ion with that of the oxygen molecule if the vibrational frequency of the latter is 1580 cm^{-1} .

8. The vibrational frequency of $\text{O}_2^{+4}\pi_u$ ion as determined from the vibrational progression in the PES of O_2 molecule (using He (I) resonance line $h\nu = 21.22$ eV) is 1129 cm^{-1} . Calculate the change in bond length on ionisation of O_2 molecule if the difference between the vertical and adiabatic ionisation potentials is 0.67 eV. Also, determine the bond length of O_2^+ ion if the bond length of O_2 molecule is 1.21 Å and its vibrational frequency is 1580 cm^{-1} .

[Ans: 0.19 Å; 1.40 Å]

9. The argon $^2\text{P}_{3/2}$ peak is often used as a standard test resolution. Calculate the observable widths at 300 K and 10 K when ionisation of Ar is carried out by He (I): 21.22 eV and He (II) 40.81 eV radiation lines respectively. The natural line width of PES signal is 6.5 meV and atomic mass of Ar is 39.95 amu.

[Ans: At 300 K; 9.5 meV; 13.1 meV, At 10K; 1.7 meV; 2.4 meV]

10. The width of ionised band of H_2 , i.e. H_2^+ , when recorded using He (I); 21.22 eV radiation line is 22 meV and is 46 meV when He (II) 40.81 eV radiation line is used. Calculate the theoretical line widths of H_2 ionised bands obtained by He (I) and He (II) radiation lines at 298 K if the natural PES line width is 6.5 meV.

[Ans: He (I), 42.17 meV; He (II), 58.48 meV.]

11. (a) Calculate the thickness of the covering layer of some material on the surface of a catalyst if the photoelectron signal intensity of the catalyst surface in the

absence of the covering layer is reduced to $\frac{1}{4}$ th of its

value in the presence of the covering layer, and (b) find at what value of the thickness of the covering layer on the surface of the catalyst is $I = I_0$? $\lambda = 20$ Å.

[Ans: (a) 1.38 nm, and (b) $r = 0$ Å]

12. The BEs of valence electrons of Pd metal with respect to the vacuum level lie in the energy range 0–8 eV. What will be the BE range with respect to the Fermi level if the energy gap between the two scales is 4 eV?

[Ans: 4–12 eV]

13. What will be the ratio of He (I) excitation radiation line width to that of He (II) excitation radiation line width?

[Ans: $\approx 1:7$]

14. By making use of the data in tables 6.13 and 6.14, generate the lone-pair ionisation energies of $\text{C}_2\text{H}_5\text{NH}_2$, $n\text{-C}_3\text{H}_7\text{NH}_2$, $\text{iso-C}_3\text{H}_7\text{NH}_2$, $n\text{-C}_4\text{H}_9\text{NH}_2$, $\text{iso-C}_4\text{H}_9\text{NH}_2$ and $\text{tert-C}_4\text{H}_9\text{NH}_2$.

[Ans: 8.84 (8.86); 8.78 (8.78); 8.73(8.72) 8.74 (8.71); 8.72 (8.70) and 8.63 (8.64) eV. The quantities within parenthesis are the literature values.]

15. The partial ESCA spectra of a mixture of carbon dioxide, carbon monoxide and methane is presented in the figure 6.34. From the spectra, determine the percentage composition of the gas mixture.

[Ans: CO₂;28.4 percent CO;36.3 percent CH₄35.3 percent]

16. Calculate the Fermi energy of a free electron in the highest energy state in (a) Cu and (b) Ag, and (c) Al. Density (Cu) = 8.96 g/ml, Density (Ag) = 10.5 g/ml; Density (Al) = 2700 kg/m³; Molecular mass (Cu) = 63.54 g/mole; Molecular mass (Ag) = 107.870 g/mole; Molecular mass (Al) = 27g/mole.

[Ans: (a) 7.0 eV, (b) 5.5 eV]

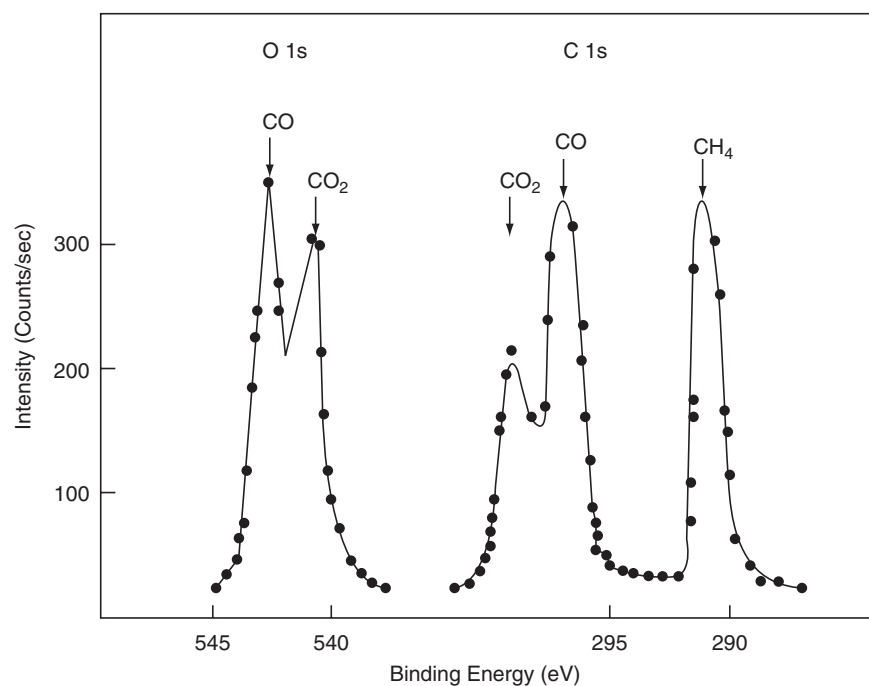


Fig. 6.34 O 1s and C 1s ESCA spectra of a mixture of CO₂, CO and CH₄.

CHAPTER 7 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Discoveries and inventions are not terminals. They are fresh starting points from which we can climb to new knowledge.

—Whitney

It is the intuition of unity among diversity which impels the mind to form science.

—Hoffman

7.1 INTRODUCTION

Nuclear Magnetic Resonance (NMR) spectroscopy is based on the measurement of absorption of electromagnetic radiation in the radio-frequency region of roughly 4–900 MHz by the analyte placed in an external magnetic field. The purpose of the external field is to cause the nuclei to develop the energy states required for the absorption of radiation.

The theoretical basis for NMR spectroscopy was proposed by W Pauli in 1924. He suggested that splitting of energy levels of atomic nuclei will take place under the influence of an external magnetic field provided these nuclei have properties of spin and magnetic moment.

The first nuclear magnetic resonance experiment in the strict sense was performed on hydrogen in 1939 by I Rabi, S Millman and P Kusch. However, the most successful experiments in the field of NMR were conducted independently in 1946 by F Bloch, W W Hansen and M E Packard, and by E M Purcell, H C Torrey and R V Pound. The impact of this phenomenon was so great that within five years after the discovery, when it was found that NMR frequencies depend upon chemical environment of the nuclei, commercial instruments capable of resolving NMR lines separated by 0.1 ppm became available. The day of the chemists in NMR dawned when WG Proctor and FC Yu in 1951 discovered two NMR lines in NH_4NO_3 corresponding to nitrogen in NH_4^+ and NO_3^- ions. This was the experimental evidence to the fact that frequency depends on the electronic surroundings in which the nuclei are placed. In 1952, the independent discoveries of Bloch at Stanford and Purcell at Harvard were recognised in the form of the Nobel Prize in physics. The technique, though discovered by physicists, proved to be a boon for chemists as an analytical tool as well as for structural elucidation of molecules. The second Nobel Prize in NMR was awarded in 1992 to Richard R Ernst of Switzerland for his contribution to Fourier transform NMR spectroscopy. Currently, two broad classes of NMR are (i) high-resolution continuous wave (CW) NMR, i.e. CWNMR; and (ii) pulsed or Fourier transform NMR, i.e. FTNMR. In CWNMR, the behaviour of nuclear spins is monitored by frequency-sweep methods. The excitation is moved across the whole frequency range of interest and the magnetic field is kept constant. But in FTNMR, the behaviour of nuclei is manipulated with the aid of sequences of pulses of varying duration, phase, frequency and amplitude and the external magnetic field is also maintained constant. The capabilities of NMR have been extended to two and three dimensions, hence transforming NMR into a molecular structure determination tool competing with x-ray crystallography.

7.2 CHARACTERISTICS OF MAGNETIC NUCLEI

The nucleus of an atom is characterised by its mass, charge, spin quantum number or intrinsic angular momentum. The angular momentum of the nucleus is due to its spin or rotation about an axis. The circulatory charge of the spinning nucleus generates a magnetic field and hence such nuclei have magnetic moments. The nuclear magnetic dipole moment (μ_I) is 1000 times smaller than that of an electron and is given by the relation

$$\mu_I = g_N \left(\frac{e}{2M_N} \right) \hbar \sqrt{I(I+1)} \quad (7.1)$$

where g_N is the nuclear g factor, M_N is the mass of the nucleus, e is the electronic charge, $\sqrt{I(I+1)}$ is the magnitude of the spin angular momentum, and I is the spin quantum number. Magnetic-dipole moment and spin angular momentum act in the same direction in case of nuclei, whereas in opposite directions in the case of an electron.

The laws governing the vector addition of nuclear spins are not yet known, so the spin of a particular nucleus cannot be predicted in general. However, on the basis of observed spins, certain empirical rules have been framed. The rules are the following:

- For nuclei, $I = 0$, $eQ = 0$ where, Q is a measure of deviation of charge distribution from the spherical symmetry, i.e. there is no net circulation of nuclear charge in these types of nuclei and hence their magnetic moment is zero, e.g. ^{12}C , ^{32}S , ^{16}O , ^{28}Si , etc. Thus, all nuclei with even mass number (A) and even charge number (Z) do not have magnetic moments and are NMR-inactive. The spherical nonspinning nucleus is shown in Fig. 7.1(a).
- When $I = 1/2$, $eQ = 0$, these types of nuclei have spherical charge distribution and hence have magnetic moments and are NMR-active, e.g. ^{13}C , ^1H , ^3H , ^{19}F , ^{31}P , ^{15}N , etc. Thus, all nuclei with odd mass numbers and even or odd charge numbers possess magnetic moments. The spherical spinning nucleus is shown in Fig. 7.1(b).
- For $I > 1$, $eQ > 0$ or $eQ < 0$. In such types of nuclei, there is also a net circulation of either positive or negative charge and hence they have magnetic moments and are also NMR-active. The charge distribution in these types of nuclei is nonspherical and, therefore, besides nuclear magnetic moment they also possess electric quadrupole moment and hence are NQR (Nuclear Quadrupole Resonance)-active also, e.g. ^2H , ^{14}N , ^{10}B , ^{11}B , ^{35}Cl , ^{37}Cl , etc. Thus, all nuclei with odd charge numbers and even or odd mass numbers possess magnetic dipole as well as quadrupole moments. The nonspherical spinning nucleus is shown in Figs 7.1(c) and (d).

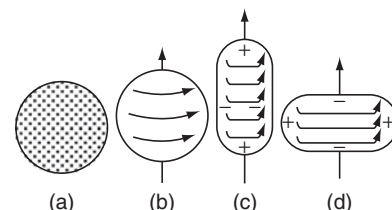


Fig. 7.1 Various representations of nuclei; (a) $I = 0$, $eQ = 0$; (b) $I = 1/2$, $eQ = 0$; (c) $I \geq 1$, $eQ > 0$; and (d) $I \geq 1$, $eQ < 0$. A positive value of eQ indicates that the protonic charge is oriented along the direction of the applied field while negative values for eQ indicate that the charge is oriented perpendicular to the direction of the applied field.

7.3 CONCEPT OF MAGNETIC ENERGY STATES

When a tiny bar magnet is suspended, it will align itself parallel to the direction of the earth's magnetic field (geographical). The magnet in this situation is said to be in low-energy state. In order that it should flip in a direction anti-parallel to the direction of the earth's magnetic field, some energy has to be supplied from an external source, and this state of the magnet is termed as the *excited state*. This behaviour of a bar magnet in the earth's magnetic field is shown in Fig. 7.2 and it forms the basis of nuclear magnetic resonance. Nuclei with nonzero spins also behave as tiny bar magnets under the influence of an external magnetic field. The energy to flip the nuclei from a direction parallel to the external magnetic field to that anti-parallel to the field is supplied in the form of radiation in the radio frequency region. In the text, the low-energy state, i.e. parallel, is denoted by α or $+1/2$ while the high-energy state, by β or $-1/2$.

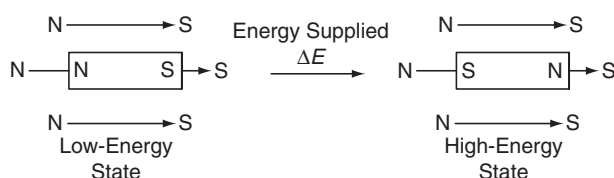


Fig. 7.2 Behaviour of a bar magnet in the earth's magnetic field.

7.4 LARMOR THEOREM

According to this classical theorem, a spinning bar magnet in its N-S direction, free from all frictional forces, under the influence of a steady magnetic field, precesses about the direction of the applied magnetic field as the spinning mechanical top or gyroscope precesses in the direction of the gravitational field, shown in Fig. 7.3.

It is to be noted that because of gyroscopic effect, the force applied by the applied magnetic field to the axis of rotation of the spinning magnet does not move the magnet in the plane of the force but perpendicular to this plane. Consequently, the rotational axis of the spinning magnet moves in a circular path, i.e. precesses around the axis of the applied magnetic field. The angular velocity of this rotation, ω , in radians per second is given by

$$\omega = \gamma H \quad (7.2)$$

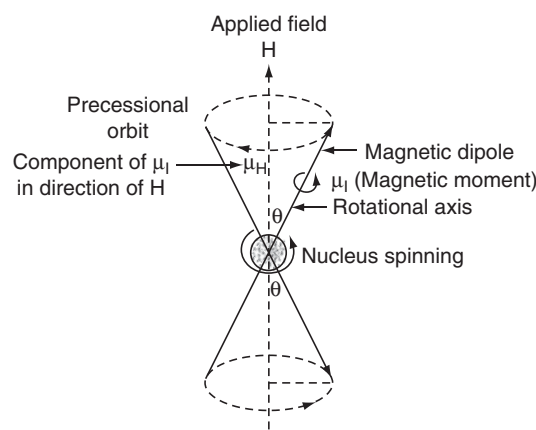


Fig. 7.3 Precession of a spinning top of spinning nucleus in a magnetic field.

where $\omega = 2\pi\nu$, ν is the frequency of precession, also called *Larmor frequency*, γ is the gyromagnetic constant also known as *gyromagnetic ratio*, i.e. the ratio of magnetic dipole moment and spin angular momentum. Thus, Eq. (7.2) can also be expressed as

$$\nu = \frac{\gamma H}{2\pi} \quad (7.3)$$

The classical Larmor frequency is identical to the frequency of absorbed radiation derived quantum mechanically. This theorem is helpful in understanding the adsorption of radio frequency radiations by a magnetic nucleus under the influence of external magnetic field.

7.5 ENERGY OF THE MAGNETIC STATES

We know that all nuclei with nonzero spin behave as tiny bar magnets. Thus when placed in a uniform magnetic field of strength H , the nuclear magnetic dipole will precess about the axis of the applied field. The frequency of precession of a spinning magnetic moment is given by

$$\nu = \frac{\gamma H}{2\pi}$$

where, $\gamma = \frac{\mu_I}{\sqrt{I(I+1)}\hbar}$ and is different for different nuclei.

The potential energy E of the precessing nuclei which is due to the interaction between the applied magnetic field and magnetic moment of the nucleus is given by

$$E = -\mu_I H \cos \theta \quad (7.4)$$

where θ is the angle between the direction of the magnetic dipole and the direction of the applied field H . On the basis of classical mechanics, θ can take on any value so that energy varies continuously. But according to quantum mechanics, θ can take on only certain permissible values since angular momentum is quantised in space. Thus, when radio frequency energy is absorbed by the nucleus, its angle of precession changes. It is to be noted that since magnetic moment of a circularly polarised radiation of a suitable frequency has the characteristics of a precessing nucleus, it is absorbed by the nucleus for its flipping. The relation between angular momentum for $I = 1/2$ and its component along the axis of external magnetic field, i.e. its direction of quantisation, is shown in Fig. 7.4.

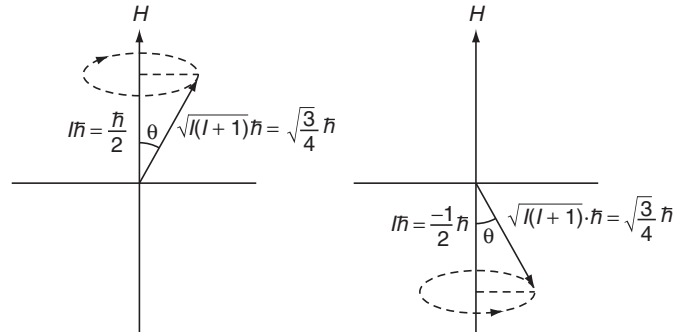


Fig. 7.4 Nuclear spin angular momentum and its components along the applied magnetic field.

For $I = 1/2$, θ can take on only two values, i.e. either $35^\circ 15'$ or $144^\circ 45'$ as shown here. The projection of the spin angular momentum on the axis of applied field

$$= I\hbar = \frac{-\hbar}{2} = M_I \hbar \quad (7.5)$$

The spin magnetic quantum number M_I can have $(2I+1)$ values, i.e. $M_I = I, I-1, I-2, \dots, -I$. Thus, for $I = 1/2$, the two values for M_I are $+1/2$ and $-1/2$. Therefore, θ in this case is either $35^\circ 15'$ or $144^\circ 45'$ since

$$\sin \theta = \frac{\hbar/2}{\sqrt{3/4}\hbar} = \frac{1}{\sqrt{3}} = \sin 35^\circ 15'$$

The same is true for magnetic moment.

Let μ_H be the component of μ_I in the direction of the field; then

$$\cos \theta = \frac{\mu_H}{\mu_I} \quad (7.6)$$

Form Eqs (7.4) and (7.6), we obtain

$$E = -\mu_H H \quad (7.7)$$

where,

$$\mu_H = g_N \beta_N M_I \quad (7.8)$$

Here, g_N is the nuclear g -factor (for proton $g_H = 5.5837$) and β_N is the nuclear magneton.

$$\beta_N = \frac{eh}{4\pi m_p c} = 5.046 \times 10^{-27} \text{ JT}^{-1} \quad (7.9)$$

where c is the velocity of light, $c = 2.997925 \times 10^{10} \text{ cms}^{-1}$, m_p is the mass of the proton $= 1.67252 \times 10^{-24} \text{ g}$, e , the electron charge $= 4.803 \times 10^{-10} \text{ esu}$ and the Planck's constant $h = 6.623 \times 10^{-27} \text{ erg s} = 6.623 \times 10^{-34} \text{ J s}$.

Combining Eqs (7.7) and (7.8), we obtain

$$E = -g_N \beta_N H M_I \quad (7.10)$$

Thus, the total number of the energy levels in the magnetic system is governed by M_I for a given value of I , and each energy level is characterised by its magnetic quantum number.

For $I = 1/2$, M_I can take on two values, i.e. $M_I = \pm 1/2$

Further, for $M_I = +1/2$, Eq. (7.8) becomes

$$E_{+\frac{1}{2}} = \frac{-1}{2} g_N \beta_N H \quad (7.11)$$

This corresponds to low-energy orientation in which the magnetic field of the nucleus is aligned with the external field.

Similarly, for $M_I = -1/2$,

$$E_{-\frac{1}{2}} = \frac{1}{2} g_N \beta_N H \quad (7.12)$$

This corresponds to the high-energy orientation in which the magnetic field of the nucleus is anti-parallel to that of the external field.

In the absence of an external magnetic field, the two orientations, i.e. substates, are said to be degenerate. This degeneracy is removed with the aid of an external applied field (Zeeman effect) as shown in Fig. 7.5(a). Similarly, for $I = 3/2$, M_I can have four values, i.e. $3/2, 1/2, -1/2, -3/2$. The Zeeman splitting in this case is shown in Fig. 7.5(b).

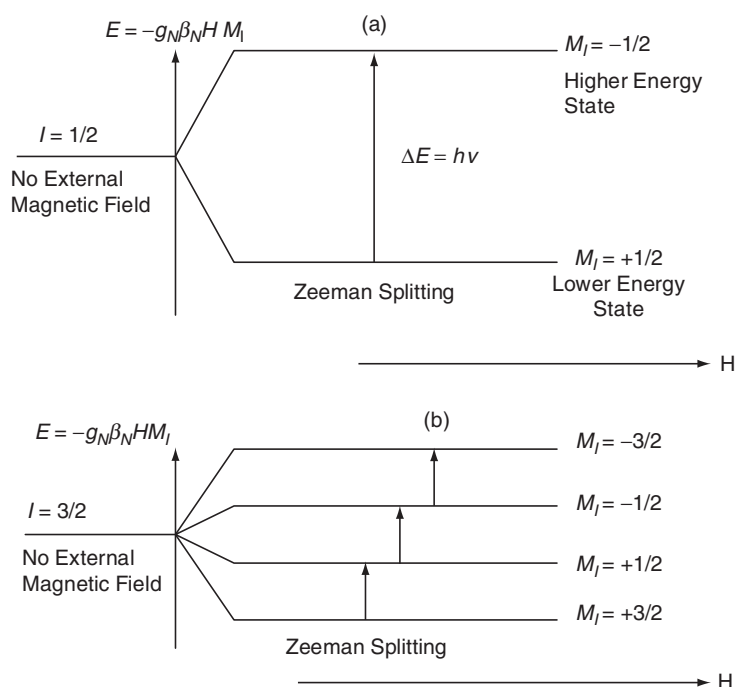


Fig. 7.5 The splitting of magnetic energy level under the influence of an external magnetic field (a) $I = 1/2$, and (b) $I = 3/2$.

7.6 GENERAL SELECTION RULES FOR THE TRANSITION BETWEEN MAGNETIC STATES

The transition probability is proportional to the integral

$$\int (\Psi_n I \Psi_m d\tau)^2$$

The selection rule evolved from the solution of the integral is $\Delta M_I = \pm 1$. A nonresonant nucleus does not change its quantum stage, hence absorption ($\Delta M_I = +1$) rather than emission ($\Delta M_I = -1$) is considered which of course is not so in vibrational and rotational spectra. The general selection rule is supplemented by the condition that the resultant M_I of one and only one basic group, i.e. ΣM_p , must change by unity in every observable transition, e.g. ΣM_I for CH_3 group = 3/2. In other words, we can say that chemically equivalent nuclei are magnetically equivalent also and hence they are characterised by only one quantum number which is the sum total of quantum numbers of individual nuclei, e.g. for CH_2 ,

$$M_I = \frac{1}{2} + \frac{1}{2} = 1.$$

7.7 SPACING BETWEEN TWO CONSECUTIVE MAGNETIC LEVELS

The energy of any magnetic state is given by $E = -g_N \beta_N H M_I$ (Eq. 7.10)

For

$$M_I = I, I-1, I-2, \dots, -I$$

$$E_I = -g_N \beta_N H I \quad (7.13)$$

$$E_{I-1} = -g_N \beta_N H (I-1) \quad (7.14)$$

Subtracting Eq. (7.13) from Eq. (7.14),

$$\Delta E_d = E_{I-1} - E_I = g_N \beta_N H \quad (7.15)$$

Thus, the space ΔE_d between two consecutive states is independent of magnetic quantum number but does depend upon the strength of the external field and g -factor of the nuclei. For a specific nucleus, ΔE_d depends only on the strength of the external field.

Units of field strength = 1 tesla T = 10^4 Gauss = $1 \text{ kg s}^{-2} \text{ A}^{-1}$

Problem 7.1: Determine the distance between any two successive states of the ^1H nuclei at a field strength of 13,500 gauss.

Solution We know that

$$\Delta E_d = g_N \beta_N H$$

For hydrogen nuclei, $g_H = 5.5854$, $H = 13500 \text{ gauss} = 1.35 \text{ T}$, $\beta_N = 5.0504 \times 10^{-27} \text{ J T}^{-1}$.

Thus,

$$\begin{aligned} \Delta E_d &= 5.5854 \times 5.0504 \times 10^{-27} (\text{JT}^{-1}) \times 1.35 (\text{T}) \\ &= 38.08 \times 10^{-27} \text{ J} = 19.17 \times 10^{-4} \text{ cm}^{-1} \end{aligned}$$

7.8 TRANSITION BETWEEN MAGNETIC LEVELS

The transition from low energy to higher energy state can occur only if the nuclei under the influence of external magnetic field absorb a suitable quantum of radio frequency energy $\Delta E = h\nu$. The nuclei in the lower energy state absorb energy so as to flip in a direction anti-parallel to that of the applied field as already shown in Fig. 7.2. The energy difference between two energy levels as determined from Eqs (7.11) and (7.12) and selection rule $\Delta M_I = \pm 1$ comes out to be

$$\Delta E = g_N \beta_N H \quad (7.16)$$

which is equal to the gap between any two successive magnetic states given by Eq. (7.15).

Thus the energy difference for a specific nucleus depends upon the strength of the applied field. The system of nuclei in a magnetic field is capable of absorbing small quanta if the condition $h\nu = \beta_N g_N H$ is satisfied. The frequency of radiation at which absorption occurs is called *resonance frequency*, and the phenomenon itself is known as *nuclear magnetic resonance*. When the frequency exceeds the resonance frequency, the quantum condition is not qualified and the absorption stops. Consequently, the NMR signal appears in the form of a narrow peak. NMR spectrum is represented by plotting the absorption intensity on the vertical axis versus the strength of the external magnetic field on the horizontal axis. The resonance frequency of different nuclei, say ^1H , ^{19}F , ^{31}P , ^{13}C , etc., sharply differ from one another because of different g_N factors and hence their NMR spectra never overlap.

The characteristic parameters of some common nuclei are listed in Table 7.1. When the nucleus under consideration is hydrogen, the nuclear magnetic resonance is called *proton magnetic resonance* and is abbreviated as PMR or simply ^1H -NMR. Similarly, ^{13}C -NMR, ^{19}F -NMR, ^{31}P -NMR, etc., stand for ^{13}C , ^{19}F - and ^{31}P , etc., nuclear magnetic resonance respectively.

Problem 7.2: (a) Calculate the value of g_N for ^{13}C if its resonance frequency in MHz at a field strength of 10 kilogauss is 10.705.

(b) Determine the resonance frequency of ^{19}F in MHz at a field strength of 1 T if its g_N value is 5.2532.

Solution (a) $\beta_N = 5.05 \times 10^{-27} \text{ J T}^{-1}$,

$$H = 10 \text{ kilogauss} = 1 \text{ T}$$

$$h = 6.623 \times 10^{-34} \text{ J s}$$

$$\nu = 10.705 \text{ MHz} = 10.705 \times 10^6 \text{ cps}$$

Substituting these values in the Eq. (7.16), we get

$$\begin{aligned} g_N(^{13}\text{C}) &= \frac{6.623 \times 10^{-34} (\text{J s}) \times 10.705 \times 10^6 (\text{cps})}{5.05 \times 10^{-27} (\text{J T}^{-1}) \times 1 (\text{T})} \\ &= 1.4039 \end{aligned}$$

(b) Equation (7.16) may be expressed as

$$\nu = \frac{g_N \beta_N H}{h}$$

Using the value of the respective parameters from part (a) and part (b) of the problem:

$$\begin{aligned} \nu &= \frac{5.2532 \times 5.05 \times 10^{-27} (\text{J T}^{-1}) \times 1 (\text{T})}{6.623 \times 10^{-34} (\text{J sec})} \\ &= 4.0055 \times 10^7 \text{ cps} \\ &= 40.055 \text{ MHz} \end{aligned}$$

Problem 7.3: Show that as the field strength grows, the energy difference between magnetic levels also grows.

Solution This can be shown by determining the energy difference, ΔE , between the levels at different values of H .

$$\text{For } H = 10,000 \text{ G}$$

$$\begin{aligned} \Delta E &= g_N \beta_N H = (5.585) \times (5.051 \times 10^{-31} \text{ J G}^{-1}) \times (10,000 \text{ G}) \\ &= 2.820 \times 10^{-26} \text{ J} \end{aligned}$$

Since, $\Delta E = h\nu$

$$\therefore \nu = \frac{2.820 \times 10^{-26} (\text{J})}{6.625 \times 10^{-34} (\text{J s})} = 42 \text{ Mcps}$$

Table 7.1 Nuclear magnetic resonance data of some common nuclei.

Isotope	Spin	Relative Abundance in Nature	Gyromagnetic Ratio γ in units of 10^3 radian (Gauss) $^{-1}$ (s) $^{-1}$	Magnetic Moment μ_I in Multiple of Nuclear Magnetron (eh/4 π m $_p$ c)	g_N	Relative NMR Sensitivity for Equal Number of Nuclei, i.e. 1000		NMR Resonance Frequency in MHz at a Magnetic Field of 10 kG	Electric Quadrupole Moment Q in Multiples of $e \times 10^{-24}$ cm ^{2}
						At Constant Field	At Constant Frequency		
^1H	1/2	99.9844	26.7519	2.79270	5.5837	1.0	1.0	42.5759	
$^2\text{H/D}$	1	0.0156	4.106	0.85738	0.8571	9.64×10^{-3}	0.409	6.53566	2.77×10^{-3}
^6Li	1	7.46	—	0.82191	—	8.51×10^{-3}	0.392	6.265	4.6×10^{-4}
^7Li	3/2	92.57	—	3.2560	—	0.294	1.94	16.547	-4.2×10^{-2}
^{10}B	3	18.83	2.875	1.8006	0.6000	1.99×10^{-2}	1.72	4.575	0.111
^{11}B	3/2	81.17	8.853	2.6880	1.7914	0.165	1.60	13.660	3.55×10^{-2}
^{13}C	1/2	1.11	6.726	0.70216	1.40394	1.59×10^{-2}	0.251	10.705	
^{14}N	1	99.64	1.933	0.40357	0.4034	1.01×10^{-3}	0.193	3.076	2.0×10^{-2}
^{15}N	1/2	0.365	-2.711*	-0.28304	-0.5659	1.04×10^{-3}	0.101	4.315	
^{17}O	5/2	0.037	-3.627*	-1.8930	-0.7504	2.91×10^{-2}	1.58	5.772	-4.0×10^{-3}
^{19}F	1/2	100.0	25.167	2.6273	5.2532	0.834	0.941	40.055	
^{23}Na	3/2	100.0	7.0789	2.2161	1.476	9.27×10^{-2}	1.32	11.262	0.1
^{25}Mg	5/2	10.05	—	-0.85471	—	2.68×10^{-2}	0.714	2.606	
^{27}Al	5/2	100.0	6.971	3.6385	1.4549	0.207	3.04	11.094	0.149
^{29}Si	1/2	4.70	5.317	-0.55477	-1.1095	7.85×10^{-2}	0.199	8.460	
^{31}P	1/2	100.0	10.829	1.1305	2.2605	6.64×10^{-2}	0.405	17.235	
^{33}S	3/2	0.74	2.052	0.64274	0.4283	2.26×10^{-3}	0.384	3.266	-6.4×10^{-2}
^{35}Cl	3/2	75.4	2.261	0.82089	0.5472	4.71×10^{-3}	0.490	4.172	-7.97×10^{-2}
^{37}Cl	3/2	24.6	2.182	0.68329	0.4553	2.72×10^{-3}	0.408	3.472	-6.21×10^{-2}
^{39}K	3/2	93.08	—	0.39094	—	5.08×10^{-4}	0.233	1.987	
^{43}Ca	7/2	0.13	—	-1.3153	—	6.39×10^{-2}	1.41	2.865	
^{47}Ti	5/2	7.75	—	-0.78712	—	2.10×10^{-3}	0.659	2.400	
^{49}Ti	7/2	5.51	—	-1.1023	—	3.76×10^{-3}	1.19	2.401	
^{50}V	6	0.24	—	3.3413	—	5.53×10^{-2}	5.58	4.245	
^{51}V	7/2	~100.0	—	5.1392	—	0.383	5.53	11.193	0.3
^{53}Cr	3/2	9.50	—	-0.4735	—	1.0×10^{-4}	0.29	2.406	
^{55}Mn	5/2	100.0	—	3.4610	—	0.178	2.89	10.553	0.5
^{57}Fe		2.245	—	≤ 0.05	—	—	—	—	—
^{59}Co	7/2	100.0	6.350	4.6388	1.3132	0.281	4.83	10.103	0.5
^{63}Cu	3/2	69.09	—	2.2206	—	9.38×10^{-2}	1.33	11.285	-0.15
^{65}Cu	3/2	30.91	—	2.3790	—	0.116	1.42	12.090	-0.14
^{67}Zn	5/2	4.12	—	0.8735	—	2.86×10^{-3}	0.730	2.635	
^{75}As	3/2	100.0	—	1.4349	—	2.51×10^{-2}	0.856	7.292	0.3
^{79}Br	3/2	50.54	6.704	2.0990	1.3989	7.86×10^{-2}	1.26	10.667	0.33
^{81}Br	3/2	49.46	—	2.2626	1.5957	9.84×10^{-2}	1.35	11.498	0.28
^{95}Mo	5/2	15.78	—	-0.9099	—	3.22×10^{-3}	0.761	2.774	
^{97}Mo	5/2	9.60	—	-0.9290	—	3.42×10^{-3}	0.776	2.833	
^{107}Ag	1/2	51.35	—	-0.1130	—	6.69×10^{-5}	4.03×10^{-2}	1.722	

(Continued)

Table 7.1 Nuclear magnetic resonance data of some common nuclei—Cont'd.

¹⁰⁹ Ag	½	48.65	—	−0.1299	—	1.01×10 ^{−4}	4.66×10 ^{−2}	1.981	
¹¹¹ Cd	½	12.86	—	−0.5922	—	9.54×10 ^{−3}	0.212	9.028	
¹¹³ Cd	½	12.34	—	−0.6195	—	1.09×10 ^{−2}	0.222	9.444	
¹¹⁵ Sn	½	0.35	—	−0.9132	—	3.50×10 ^{−2}	0.327	13.22	
¹¹⁷ Sn	½	7.67	—	−0.9949	—	4.53×10 ^{−2}	0.356	15.77	
¹¹⁹ Sn	½	8.68	−9.971*	−1.0409	—	5.18×10 ^{−2}	0.373	15.87	
¹²¹ Sb	5/2	57.25	—	3.3417	—	0.160	2.79	10.19	−0.8
¹²³ Sb	7/2	42.75	—	2.5334	—	4.57×10 ^{−2}	2.72	5.518	−1.0
¹²⁷ I	5/2	100.0	—	2.7939	1.1173	9.35×10 ^{−2}	2.33	8.519	−0.75
¹³³ Cs	7/2	100.0	—	2.5642	—	4.74×10 ^{−2}	2.75	5.585	≤ 0.3
¹⁹⁹ Hg	½	16.92	4.783	0.4993	0.9983	5.72×10 ^{−3}	0.179	7.612	
²⁰¹ Hg	3/2	13.24	—	−0.607	—	1.90×10 ^{−3}	0.362	3.08	0.5
²⁰⁷ Pb	½	21.11	—	0.5837	—	9.13×10 ^{−3}	0.209	8.899	
Electron	½	—	17.6×10 ³	−1836	2.0023192 [#]	2.85×10 ⁸	658	27944	

* The angular momentum vector and the vector of the magnetic dipole are anti-parallel.

Lande g factor for the electron. The positive value of g_N indicates that the magnetic moment and angular momentum are parallel and anti-parallel for negative value of g_N .

For $H = 14000$ G, $\Delta E = 3.949 \times 10^{-26}$ J, and $\nu = 60$ Mcps

For $H = 24500$ G, $\Delta E = 6.911 \times 10^{-26}$ J, and $\nu = 104$ Mcps

Thus, as H increases, the energy difference between the magnetic levels also increases. Same is true for frequency also or since g_N and β_N are constants of a nucleus, so $\Delta E/\nu \propto H$.

7.9 NUCLEI POPULATION IN DIFFERENT STATES

The ratio of nuclei population in the two magnetic states is governed by Boltzmann's law, i.e.,

$$\frac{N_{+\frac{1}{2}}}{N_{-\frac{1}{2}}} = e^{\Delta E / \kappa T} \quad (\text{since population density} \propto e^{-E/\kappa T}) \quad (7.17)$$

where, $\Delta E = g_N \beta_N H$.

The population difference, Δn is given

$$\Delta n = N_{+\frac{1}{2}} - N_{-\frac{1}{2}} = \frac{N \Delta E}{2\kappa T} - \frac{Ng_N \beta_N H}{2\kappa T} \quad (\text{since } \kappa T < 1) \quad (7.18)$$

where, $N_{-\frac{1}{2}} + N_{+\frac{1}{2}}$ is the total number of nuclei in both the populations.

Hint:

$$N_1 = \frac{N_0 e^{-E_1/\kappa T}}{e^{-E_1/\kappa T} + e^{-E_2/\kappa T}}$$

$$N_2 = \frac{N_0 e^{-E_2/\kappa T}}{e^{-E_1/\kappa T} + e^{-E_2/\kappa T}}; \quad N_0 = N_1 + N_2$$

The lower magnetic level has more nuclei than the higher level. Thus, if there were no thermal motion, all nuclei would be at the lower energy level. The energy of thermal motion tends to bring the populations of the levels into accord with Boltzmann law. The population difference Δn varies inversely to absolute temperature and directly to field strength, H .

Problem 7.4 Show that the distribution of magnetic nuclei between two magnetic states can be expressed as

$$\frac{N_{-\frac{1}{2}}}{N_{+\frac{1}{2}}} = \left[1 - \frac{g_N \beta_N H}{\kappa T} \right] = \left[1 - \frac{h\nu}{\kappa T} \right]$$

Solution We know that

$$\frac{N_{-\frac{1}{2}}}{N_{+\frac{1}{2}}} = e^{-\Delta E/\kappa T} = e^{-g_N \beta_N H / \kappa T}$$

Applying the expansion, $e^x = 1 + x + \frac{x^2}{2} + \frac{x^3}{3} + \dots$ and considering only the first two terms, we obtain

$$\frac{N_{-\frac{1}{2}}}{N_{+\frac{1}{2}}} = \left[1 - \frac{g_N \beta_N H}{\kappa T} \right] = \left[1 - \frac{h\nu}{\kappa T} \right] \text{ (since } g_N \beta_N H = h\nu \text{)}$$

Problem 7.5: Determine the ratio of the proton nuclei population at 300 K when the field strength is 13500 G. $\kappa = 1.3806 \times 10^{-23} \text{ JK}^{-1}$.

Solution The population ratio can be determined as follows.

$$\begin{aligned} \Delta E &= g_N \beta_N H = 5.585 \times (5.051 \times 10^{-31} \text{ JG}^{-1}) \times (13500 \text{ G}) \\ &= 3.808 \times 10^{-26} \text{ J} \\ \frac{N_{+\frac{1}{2}}}{N_{-\frac{1}{2}}} &= e^{3.808 \times 10^{-26} \text{ (J)} / (1.3806 \times 10^{-23} \text{ JK}^{-1}) \times 300 \text{ K}} = e^{0.000009} = 1.000009 \end{aligned}$$

The lower energy level has nine proton nuclei more than the higher energy level if its population scale is kept 1,000,000.

Problem 7.6: Determine the population difference of proton nuclei between two magnetic states at 300 K if the strength of the external field is 13500 G and the total population of the nuclei is 1,000,000.

Solution The population difference between two states can be calculated with the aid of Eq. (7.18).

$$\Delta n = \frac{Ng_N \beta_N H}{2\kappa T}$$

Using the value of $g_N \beta_N H$ from Problem 7.5, we get

$$\Delta n = \frac{1,000,000 \times 3.808 \times 10^{-26} \text{ J}}{2 \times 300 \text{ K} \times 1.3806 \times 10^{-23} \text{ (JK}^{-1})} = 4.59 = 5$$

Problem 7.7: Using the expression for the distribution of magnetic nuclei between two states from Problem 7.4 and data of Problem 7.5, calculate $N_{-1/2}/N_{+1/2}$.

Solution From Problem 7.4, we write

$$\frac{N_{-\frac{1}{2}}}{N_{+\frac{1}{2}}} = \left[1 - \frac{g_N \beta_N H}{\kappa T} \right]$$

Substituting the needed data from Problem 7.5:

$$\begin{aligned} \frac{N_{-\frac{1}{2}}}{N_{+\frac{1}{2}}} &= \left[1 - \frac{3.808 \times 10^{-26} \text{ (J)}}{(1.3806 \times 10^{-23} \text{ JK}^{-1}) \times 300 \text{ K}} \right] \\ &= 1 - 0.0000091 = 0.9999909 \end{aligned}$$

Since $N_{-1/2}/N_{+1/2} < 1$ the upper state is thinly populated as compared to the lower state.

7.10 LINE SHAPE AND LINE WIDTH

There are two important types of line shape in the NMR absorption curves: (i) Lorentzian line (L) shape, and (ii) Gaussian line (G) shape. The main difference between the two types of line shapes is that the outerwings of the L-line are much longer and drop more slowly than those of the Gaussian lines [see Figs 1.5(a) and (b)]. The shape of the absorption line in some cases is an admixture of these two types of lines. These two types of spectral lines are characterised by the measurable experimental parameters recorded in Table 7.2.

Table 7.2 Properties of Lorentzian and Gaussian Lines.

Parameter	L-shape	G-shape
Half width at half height	$\Delta H_{1/2}$	$\Delta H_{1/2}$
Peak amplitude	$I_0 = \frac{1}{\pi \Delta H_{1/2}}$	$I_0 = \left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{1}{\pi \Delta H_{1/2}}$
Equation for absorption line	$I = \frac{I_0 (\Delta H_{1/2})^2}{(\Delta H_{1/2})^2 + (H - H_r)^2}$	$I = I_0 \exp \left[\frac{-\ln 2 (H - H_r)^2}{(\Delta H_{1/2})^2} \right]$

H_r is the field resonance at the line centre, I is the intensity of the absorption line as a function of field H for L and G -line shapes.

7.11 FACTORS INFLUENCING THE INTENSITY OF NMR LINES

The NMR emission or absorption can only be detected when there is a population difference between the two spin states. The transition between two spin states $E_{-1/2}$ and $E_{+1/2}$, can occur either by emission or by absorption. The rates of both processes are proportional to (i) the population of the state considered, (ii) the radiowave energy density, and (iii) the square of the transition matrix element.

The radiowaves of the oscillating magnetic field ($h\nu$) induce two types of transition: (i) from upper state to the lower state (the emission process), and (ii) from the lower state to the upper state (the absorption process). When the nuclear-spin population is equally divided between the upper population and the lower population, the emission of radiowave quanta is higher than the absorption of these quanta, and no observable signal is obtained. When the population of the nuclear spin is higher in the lower state than in the upper state, a radio frequency absorption is observed. We know that the ratio of the two populations in equilibrium is determined by

$$\frac{N_{-1/2}}{N_{+1/2}} = \exp \left[\frac{-g_N \beta_N H}{\kappa T} \right] \quad (\text{Eq. 7.17})$$

The NMR signal recorded in an NMR spectrometer increases with increasing ratio between $N_{-1/2}$ and $N_{+1/2}$ because the absorption more and more predominates over the emission. The signal intensity is also increased when the temperature decreases. We have already shown that the population difference between two magnetic levels is given by

$$\Delta n = \left(\frac{N g_N \beta_N H}{2 \kappa T} \right) \quad (\text{Eq. 7.18})$$

The NMR signal intensity is directly proportional to Δn , which varies inversely to absolute temperature and directly to field strength H and concentration of nuclei in the analyte, N . Thus for any nuclei, the intensity of the absorption signal at low temperature will be higher than at room temperature. The dependence of signal sensitivity on magnetic field strength has led manufacturers to produce magnets with field strength as large as 14T.

The intensity (I) of the absorption signal as a function of the external magnetic field of strength, H for Lorentzian and Gaussian line shapes is given by

$$\text{L-line shape: } I = \frac{I_0}{1 + T_2^2 (H - H_r)^2} \quad (7.19)$$

$$\text{G-Line shape: } I = I_0 \exp \left[-b (H - H_r)^2 T_2^2 \right] \quad (7.20)$$

Here, T_2 is the spin-spin relaxation time, also called the *line-width parameter*, and will be discussed under spin-relaxation processes, and b is a constant.

For a given experimental set-up at constant temperature, the signal strength at a given frequency ν is proportional to

$$N(I+1)\mu_I\nu^2 \quad (7.21)$$

and at a given field H ,

$$N\left[\frac{I+1}{I^2}\right]\mu_I^3H^2 \quad (7.22)$$

These expressions indicate that for the same value of H , proton nuclei are ≈ 4000 times more sensitive than ^{13}C nuclei.

7.12 MEASUREMENT OF NMR SIGNAL INTENSITY

The absolute intensity of an NMR line is a complex function of sample parameters, instrument parameters and operating conditions and hence difficult to measure. However, the relative intensities of different bands in a typical NMR spectrum often follow general rules. The integrated intensity of NMR signal represents the total energy absorbed by the nuclei in an analyte at resonance conditions and is expressed by the total area under the resonance curve. This area is proportional to the number of nuclei, say protons, of a particular functional group in the sample and hence can be used in their determination. The area under the curve can be measured by (i) paperweight method, and (ii) integration method. The latter, however, is widely used in NMR spectroscopy. All modern NMR recorders are equipped with electronic or digital integrators to measure areas under absorption peaks.

7.13 SPIN-RELAXATION PROCESS

The probability of transition between allowed energy states is proportional to the radio-frequency energy density. The signal intensity grows to a maximum with the growth of incident radiowave energy. The further increase of power of radio frequency decreases and broadens the signal and ultimately it results in the disappearance of the signal. This is due to the saturation process where the population in the lower and upper nuclear magnetic levels become equal, i.e. $N_{-1/2} = N_{+1/2}$. At this stage, the probability of upward and downward transition is equal and hence no further absorption can take place. The return of the spin system to equilibrium is known as *relaxation process*. The relaxation processes are exponential and are characterised by '*relaxation times*'.

$$M_T = M e^{-T/\lambda} \quad (7.23)$$

where M_T is the bulk magnetisation after time T and λ is a relaxation constant. So for $T = \lambda$; $\frac{M_T}{M} = 1/e$. Thus, the time during which the nuclei spin in the excited state dissipate a fraction $1/e = 0.37$ of the excess spin energy to the environments or other spins in order to return to the ground state without emission of any energy is called the relaxation time.

7.13.1 Types of Relaxation Processes

The two spin relaxation processes which influence the equilibrium ratio $N_{-1/2}/N_{+1/2}$, and are of interest to chemists are: (i) spin-lattice ($s-l$) process, and (ii) spin-spin ($s-s$) process.

(a) $s-l$ Process The $s-l$ relaxation process is due to the interaction of the spin of the system with its environment, i.e. lattice in case of solids. The term 'environment' also refers to the solvent, electrons in the system and other different types of atoms or ions in the system. The $s-l$ mechanism involves the thermal equilibrium of the spin system with the atomic vibrations of crystal lattice or tumbling motion of liquids or gases. Consequently, the transference of energy from the excited state to the environments occurs and the spins return or relax back to the lower state and the population difference is maintained. In other words, we can say that *the radiationless transition from equilibrium is called $s-l$ relaxation since the excess energy passes from the spins to lattice, i.e. surroundings, as heat.*

The s - l process is characterised by s - l relaxation time, also called *longitudinal relaxation time* T_1 which is a measure of the average lifetime of the nuclei in the higher energy state. It is the time taken for a dissipation of fraction $1/e = 0.37$ of the excess energy to the environments. T_1 for specific nuclei not only depends on the isotope and its chemical environment but also on the physical state of the analyte. T_1 is of the order of 10^{-2} – 10^4 second for solids and 10^{-4} – 10 second for liquids. The shorter time for liquids is because of free motion of molecules which causes large fluctuations of magnetic field in the neighbourhood of the nuclei. The various nuclei constituting the gaseous or liquid lattice are in violent vibrational and rotational motions. Such a motion generates a complex field around each magnetic nucleus. The resultant complex field has a continuum of magnetic components. The phase and frequency of some of the components correspond to the precessional frequency of the nuclei in the analyte. Thus, these vibrationally and rotationally developed components exchange energy with the spins in the excited state and the nuclei move to the lower spin state, the absorbed energy then simply increases the amplitude of the thermal vibrations or rotations. This change produces a very small temperature rise in the analyte. In crystalline solids and viscous liquids, where the mobility of the lattice is low, T_1 is large.

(b) s - s Relaxation Process The s - s relaxation process occurs when two neighbouring nuclei of the same kind having identical precessional frequencies but different quantum numbers, interact with each other. *In the process, the nucleus of one atom in the higher energy level imparts its energy to an atom in the lower energy level. Consequently, the nuclei in the lower state moves to the higher state while the excited state nuclei relaxes back to the lower energy state. Nevertheless, the net number of nuclei in the excited state remains unchanged, i.e. population ratio is not affected. However, the average lifespan of a particular excited nucleus is shortened.*

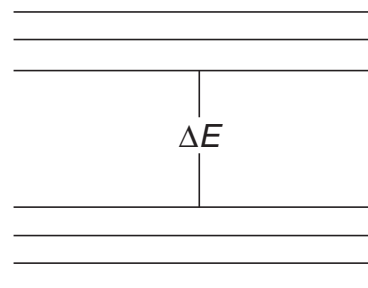


Fig. 7.6 Spread of nuclear spin energy of the upper and lower states due to spin-spin interaction.

The s - s process is characterised by s - s relaxation time, also called transverse relaxation time, T_2 . Because of s - s interaction, the energy levels corresponding to the upper and lower states are not well defined but they spread over a certain value of spin energy which is represented in Fig. 7.6. The time required for the spin energy to spread over a certain value is called the s - s relaxation time. For solids, T_2 is of the order of 10^{-4} second and for liquids $T_1 = T_2$.

Both the s - s and s - l mechanisms increase the line width of the NMR signals and are related to line width parameter τ by the expression

$$\frac{1}{\tau} = \frac{1}{T_1} + \frac{1}{T_2} \quad (7.24)$$

In addition to these two types of relaxation processes, another type which is of little importance to chemists is the spin-rotation (s - r) relaxation processes.

(c) s - r Relaxation Process The interaction between the nuclear magnetic moment and the magnetic field generated at the nucleus by the rotation of a molecular magnetic moment arising from the electron structure of the molecule is called spin-rotational interaction. The relaxation process in this case is due to the energy transfer from the nuclear spin system to the molecular rotation. This mechanism is important in spin $\frac{1}{2}$ nuclei in the gas phase and in liquid phase generally with small molecules at relatively higher temperatures. As already has been pointed out, s - r relaxation process is of little use to chemists. However, the nuclear spin-internal rotation (s -int-rot) is of interest to chemists. Here, the internal rotation of a group relative to the larger molecule to which it is attached is the source of relaxation. The s - r and s -int-rot mechanisms become more important at higher temperatures. The s -int-rot relaxation process is important in ^1H -NMR of freely rotating $-\text{CH}_3$, ^{31}P -NMR of freely rotating $-\text{OPO}_3$, proton decoupled ^{13}C -NMR of freely rotating $-\text{CH}_2\text{X}$ and ^{19}F -NMR of free rotating $-\text{CF}_3$, etc., groups attached to larger molecules.

7.14 WIDTH OF NMR SIGNAL AND RELAXATION TIMES

According to the Heisenberg uncertainty principle,

$$\Delta E \Delta t = \frac{h}{2\pi} = 10^{-34} \text{ J s}$$

On rearrangement, we get

$$\frac{\Delta E}{h} = \Delta\nu = \frac{1}{2\pi\Delta t} = \frac{0.1}{\Delta t} \text{ cps}$$

where ΔE is the energy spread over an excited state (not well-defined) and $\Delta\nu$ is the corresponding frequency spread, Δt is the lifetime of the state; $\Delta t = 1/2\pi\Delta\nu$. $\Delta\nu$ is the uncertainty in energy of the excited state and manifests itself in the width of the NMR signal. This Heisenberg bandwidth of the NMR signal is influenced both by the s - l and s - s relaxation times, i.e. T_1 and T_2 . When T_1 and T_2 are large, i.e. lifetime of nuclear spin state is large; $\Delta\nu$ is large. For a typical liquid, $T_1 = T_2 = 1$, $\Delta\nu = 0.1$ cps and for solids $T_2 = 10^{-4}$ second and hence $\Delta\nu = 1000$ cps. Thus, inherent NMR bandwidth is large in solids as compared to liquids. Hence, solids rarely give high-resolution spectra. Some liquids may give spectra having broad lines, provided T_1 and T_2 are small. Such liquids are generally viscous or contain paramagnetic ions which increase the efficiency of relaxation processes. In general, we can say that the natural width of NMR spectral line varies inversely to the average time the system spends in the excited state.

In addition to T_1 and T_2 the applied field H also contributes to line broadening in two ways provided it differs slightly from nucleus to nucleus. In such cases a band of frequencies, say $\nu \pm \delta\nu_1, \nu \pm \delta\nu_2, \nu \pm \delta\nu_3, \dots$ rather than a single frequency ν is absorbed by the nucleus of interest. First, the presence of other spatially fixed neighbouring magnetic nuclei present in the analyte whose spins generate local magnetic fields that may interact with H to increase or decrease its impact on the nucleus under consideration. In gases and liquids, these local magnetic fields cancel each other since the nuclei producing them are in violent motion. However, in solids and viscous liquids, a range of field strengths, i.e. $H \pm \delta H_1, H \pm \delta H_2, H \pm \delta H_3, \dots$ is generated by the local magnetic fields, $\delta H_1, \delta H_2, \delta H_3, \dots$ and thus a corresponding range of absorption frequencies, $\nu + \delta\nu_1, \nu + \delta\nu_2, \nu + \delta\nu_3, \dots$. Second, the variations in the static magnetic field may occur if the applied field, H , is not homogeneous. This affect is minimised by spinning the analyte in the magnetic field.

7.15 FOURIER TRANSFORM NMR (FTNMR) SPECTROSCOPY

Our discussion on FTNMR is based on a rotating reference frame rather than a fixed laboratory reference frame. The rotating reference frame is one in which the Z -axis is the field direction but the X - and Y -axes rotate about the Z -axis at a frequency $\omega = \gamma H$. The angular component due to precession in the laboratory frame becomes fixed; we have, in effect, switched off the H -induced precession.

Due to thermal motion, the magnetic moments associated with nuclei spins in a sample are randomly oriented. Since the magnetic moment is quantised on the application of an external magnetic field of strength H , the magnetic moments of nuclei (denoted by narrow arrows) orient themselves randomly in the direction of the applied field which is defined as the Z -axis as shown in Fig. 7.7(a). The net resultant magnetic moment, i.e. bulk magnetisation M (shown by broad arrow) of these spins is static with the field direction [Fig. 7.7(a)]. Now when a $\pi/2$ pulse of radio frequency field of strength H_{rf} (also static in the rotating reference frame) is applied in a direction perpendicular to the Z -direction which is taken as the X -axis, it will strike the sample, due to which the bulk magnetisation will sense with each pulse a torque and is tipped from the Z -axis into the Y - Z plane by an angle θ_f (the tip angle or the flip angle) given by

$$\theta_f = \gamma H_{rf} \tau \quad (7.25)$$

where θ_f is the angle of rotation in radians and τ is the duration of the pulse. The urge of the net magnetic moment to move away from the Z -axis at the instant the pulse just strikes the sample is shown in Fig. 7.7 (b), whereas the rotation of M due to torque of radio frequency field around X -axis in the Y - Z plane is presented in Figs. 7.7(c) and (d).

We can determine the relationship between duration of the pulse or pulse width τ and the tip angle by varying the length of the pulse and examining the resulting signal intensity. The signal intensity will be maximum for a tip angle of $\pi/2$, a null at π when magnetisation is along Z -axis, a negative maximum at $3\pi/2$ and return to null at 2π with magnetisation back at Z . For a given pulse, $\tau = 1 - 10\mu\text{s}$, $= \pi/2$ radians.

Further, on the termination of the pulse, the torque due to the applied magnetic field causes the relaxation of the nuclei in the Y -direction to return to their equilibrium position instantaneously as shown in Fig. 7.7(e) and then to the original state after several seconds via s - s and s - l relaxation processes operating independent of each other as depicted in Fig. 7.7(a). The relaxation of the nuclei is recorded as a function of time and the signal due to relaxation process is called *free induction decay* (FID)—free of the influence of radio frequency field along X -axis and decaying back to the original state. The FID is then converted to the normal frequency domain signal by a mathematical tool, of Fourier transformation.

When a nucleus returns to its equilibrium state as shown in Fig. 7.7(e), there is a decrease in the magnetic moment M_y along the Y -axis and an increase in the magnetic moment M_z along the Z -axis. The mechanisms of

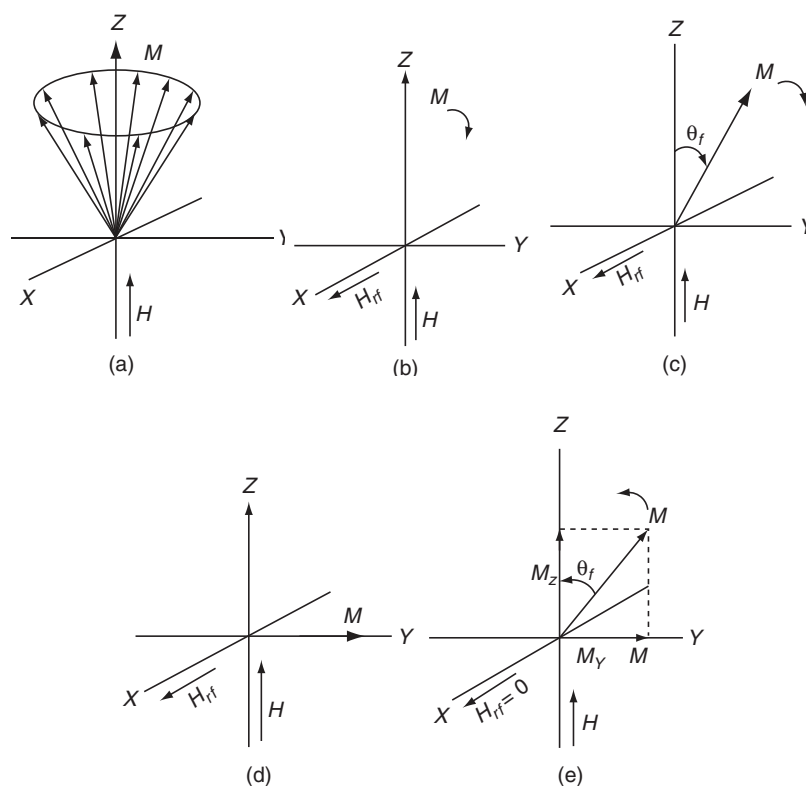


Fig. 7.7 Behaviour of magnetic moments of nuclei in rotating field of reference.

s - s and s - l processes now in the stationary frame of reference are shown in Fig. 7.8. In the first-order relaxation process, i.e. s - l relaxation process, the magnetic moment along Z -axis grows until it returns to its original value as shown in Fig. 7.8(a). On the other hand, in s - s relaxation mechanism, exchange of energy takes place between the nuclei spins, due to which some nuclei precess faster than the Larmor frequency while the others precess slowly. Consequently, the spins begin to fan out or dephase in the X - Y plane as shown in Fig. 7.8(b). Ultimately, the magnetisation along Y -axis reduces to zero. There is no residual component of M in the X - Y plane by the time relaxation is complete along the Z -axis, which means $T_2 \leq T_1$.

The s - s relaxation rate constant R_2 in the X - Y plane is related to the relaxation time constant T_2 by the relation

$$R_2 = \frac{1}{T_2} \quad (7.26)$$

The factors which contribute to the signal decay may be intrinsic to the molecules, such as exchange processes, or may be purely experimental such as poor skimming of magnetic field. The intrinsic relaxation rate and time constants are denoted by R_2 and T_2 respectively, while the actual rate and time constant of decay observed in FID are R_2^* and T_2^* respectively. For large R_2^* or small T_2^* , the line in the spectrum is broad. Conversely, if the line is sharp, R_2^* is small and T_2^* is long, the s - s relaxation is slow. The resonance line width $\Delta\nu_{1/2}$ and R_2^* are related by

$$\Delta\nu_{1/2} = \frac{R_2^*}{\pi} = \frac{1}{T_2^* \pi} \quad (7.27)$$

or

$$T_2^* = \frac{1}{\pi \Delta\nu_{1/2}}$$

7.16 TIME PERIODS INVOLVED IN MULTIPLE PULSE FT

In multiple pulse sequences, three distinct time periods: (a) preparation period, (b) evolution period, and (c) detection period are involved. The spin system is perturbed from its normal position by a pulse or pulses or by some other effect such as decoupling in the preparation period. After perturbation, the system is allowed to evolve by relaxation processes for some period called *evolution period* (t_1) and then detected with a pulse called the *detection or acquisition pulse* (t_2) to find out what happened to the system in the evolution period. The evolution is not detected directly but may be mapped by studying the system with different evolution periods. The spectrum that is finally obtained depends on the nature of preparation and on the length of the evolution period. Thus, the mechanisms affecting the

magnetisation during the evolution period and those affecting it during the acquisition period can be studied by multiple pulse sequences.

7.17 THEORY OF MEASUREMENT OF RELAXATION-RATE CONSTANTS BY MULTIPLE PULSE FT

Let us now examine the effects of multiple pulse sequence and intervening delays on simple spin systems to detect the rates at which the magnetization returns to its normal position after perturbation by a pulse. Based on the nature of multiple pulse sequences, the methods to determine the s - l and s - s rate constants are termed as inversion recovery and spin echo, respectively.

Inversion Recovery When a π pulse is applied in a direction perpendicular to the bulk magnetization of the sample along Z -axis, i.e. X -axis, it will rotate M through π -radians, the bulk magnetisation is inverted from M initially aligned along Z -axis to $-M$ along $-Z$ as shown in Figs 7.9(a) and (b) respectively. The excited nuclei will give up their energy to the surroundings because of which M will become smaller, pass through zero and then grow upwards until it attains its original position. This relaxation of bulk magnetisation from the inverted ($-M$) state to the initial ($+M$) state is exponential and is depicted in Fig. 7.9(c). There is no magnetization in the X - Y plane and hence no signal will be observed by the receiver coil along Y -axis.

In order to detect the relaxation process of bulk magnetisation from $-M$ to $+M$, we must have its component in the X - Y plane. This is generated by a $\pi/2$ pulse which rotates any Z -magnetisation into X - Y plane producing a signal amplitude A , which is proportional to the remaining Z -magnetisation. The $\pi/2$ pulse transfers information from the Z -axis where it is not observable into the X - Y plane where it can be detected by the receiver coil. Now the s - l relaxation mechanism may be detected with a pulse sequence represented as $\pi - t_D - \pi/2 - \text{Acquire (AQ)}$ and shown in Fig. 7.10. Here, π is the preparation pulse, $\pi/2$ is an acquisition pulse and t_D is the delay which is under the control of the operator. The width of π pulse is twice that of the $\pi/2$ pulse. The π pulse is a nonselective, 'hard' pulse applied with the high-power transmitter, and t_D is of the order of milliseconds to seconds while the length of the π pulse is of the order of a few milliseconds. Note that the notations $(\pi)_x$ and $(\pi)_{-x}$ indicate that π pulses are 180° out of phase with each other.

Let us now visualise the inversion-recovery experiment through vector diagrams. For short t_D , the magnitude of inverted M will almost remain unchanged and the $\pi/2$ pulse will rotate it to the Y -axis as shown in Fig. 7.9(d). The signal is inverted compared with the signal produced by a $\pi/2$ pulse on the Z -magnetisation. Now if t_D is lengthened before applying the $\pi/2$ pulse, the magnitude of M will decrease as shown in Fig. 7.9(e). The $\pi/2$ pulse will rotate the magnetisation in the $-Y$ -axis producing an inverted signal with smaller amplitude as shown in Fig. 7.9(f). Further, if the delays between the π and $\pi/2$ pulses are prolonged, the magnetisation, will pass through zero [Fig. 7.9(g)] so that $\pi/2$ pulse produces a $+Y$ magnetisation, a positive signal [Fig. 7.9(h)] and ultimately magnetisation will recover its original value M [Fig. 7.9(i)] and the $\pi/2$ pulse will produce a positive signal with maximum amplitude as shown in Fig. 7.9(j). The effect of inversion-recovery sequence on bulk magnetisation may also be presented by Fig. 7.9(c).

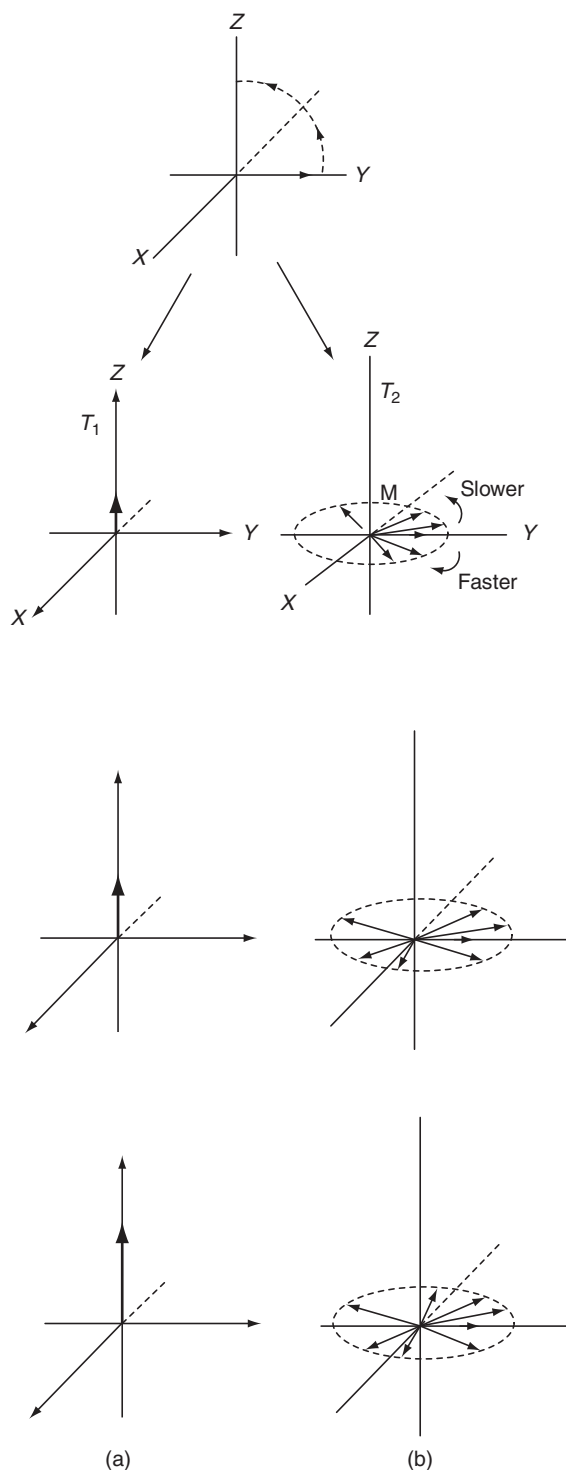


Fig. 7.8 Relaxation processes in the X - Y plane: (a) Longitudinal/spin-lattice relaxation, and (b) transverse/spin-spin relaxation.

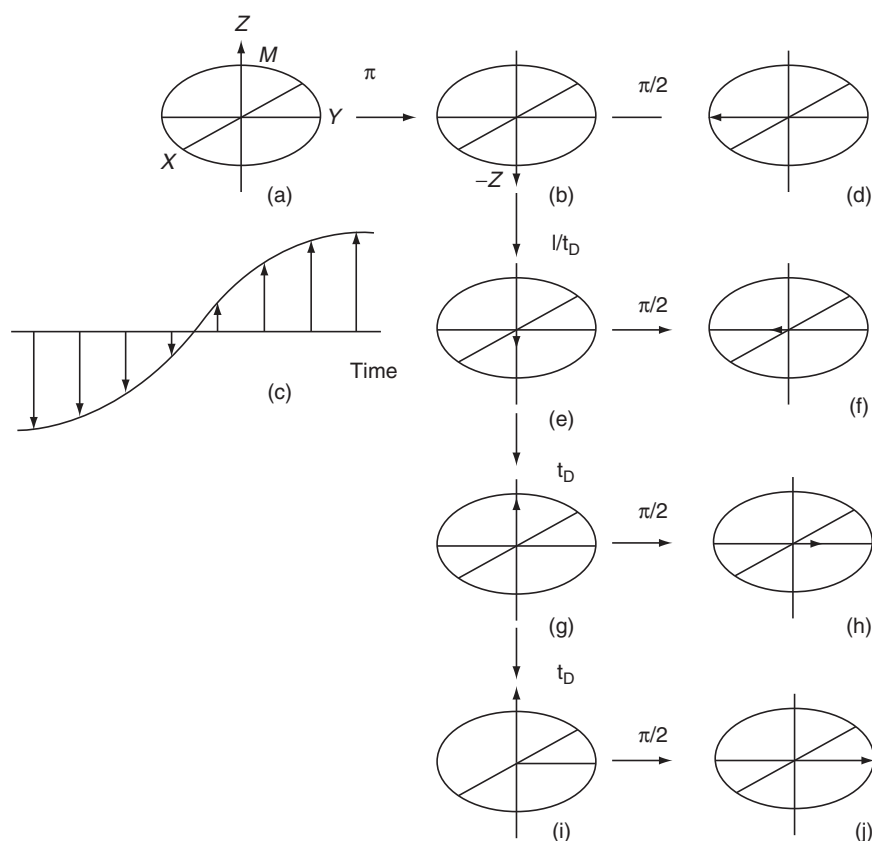


Fig. 7.9 Vector diagram for the inversion recovery pulse sequence.

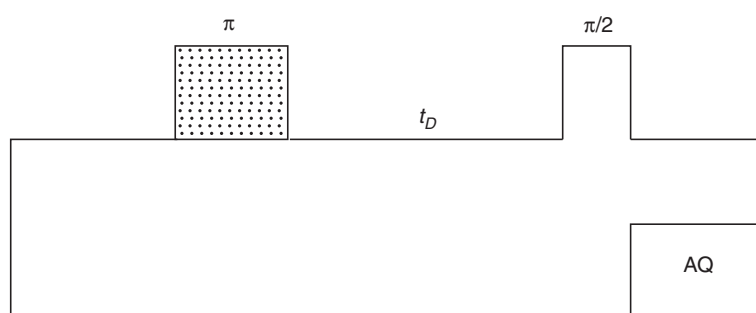


Fig. 7.10 The inversion-recovery pulse sequence.

Now, if t_D between π and $\pi/2$ pulses is longer, the system will relax back to its original state by the time the $\pi/2$ pulse is applied. The amplitude A_∞ of the signal will be the same when the π pulse is not applied. On the other hand, if t_D is small, the magnetisation will be inverted and its amplitude will be $-A_\infty$. For intermediate delays between π and $\pi/2$ pulses, the exponential decay of the magnetisation is given by

$$A_t = A_\infty [1 - 2 \exp(-R_1 t)] \quad (7.28)$$

This expression may be used to determine the s - l relaxation rate constants.

These days, a computer attached to the spectrometer is used to control the whole process of measurement. It times the original π pulse, selects increasing t_D values, times the $\pi/2$ pulse, and collects and measures the signal intensity. A hypothetical spectra of a single-spin system produced by inversion-recovery pulse sequence is shown in Fig. 7.11 while in Fig. 7.12 is displayed the inversion recovery spectra of *m*-dinitrobenzene.

7.18 MEASURING OF S - L RELAXATION RATES

Relaxation rates depend upon solvent, temperature, concentration, paramagnetic impurities and method of measurement. So, care should be taken about these parameters while measuring the relaxation rates. We will describe here only the inversion recovery and saturation recovery methods for the estimation s - l of relaxation rates.

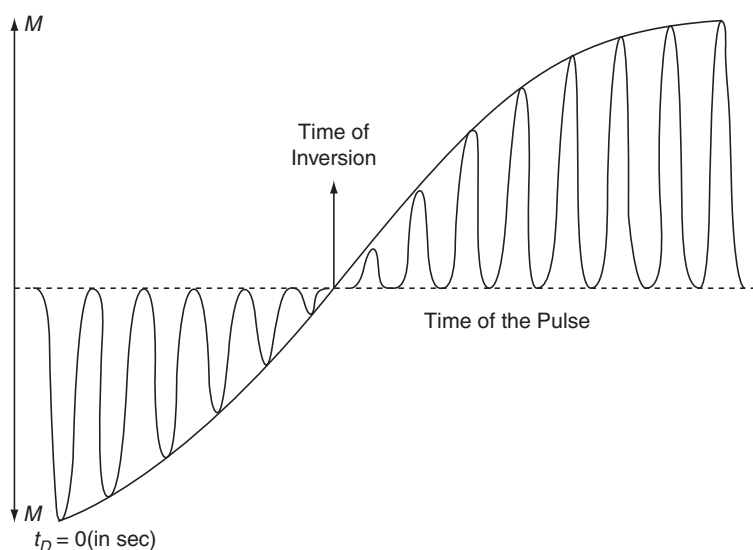


Fig. 7.11 Hypothetical spectra of a single-spin system produced by an inversion recovery pulse.

(a) Inversion Recovery This is the classical method of measuring constants. The system is observed under the influence of π - t_D - $\pi/2$ - Acquire pulse sequence. t_D is varied in a series of experiments. If the original bulk magnetisation is M , the magnetisation after π -pulse will be $-M$. The return of Z-magnetisation to the original state is governed by

$$M_t = M [1 - 2\exp(-R_1 t)] \quad (7.29)$$

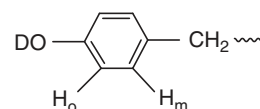
$$A_t = A_0 [1 - 2\exp(-R_1 t)] \quad (\text{Eq. 7.28})$$

Here, M_t/A_t is the Z-magnetisation/amplitude at time t after the π -pulse. The signal amplitude A_t , detected in the X-Y plane after the $\pi/2$ pulse, will grow exponentially from $-A$ to A .

When, $M_t = 0$, Eq. (7.29) yields

$$R_1 t = \ln 2 \text{ or } t_n = 0.693 T_1 \quad (7.30)$$

where, t_n is the null point. Thus, the relaxation time, T_1 is about 1.5 times the time taken for the signal to decay to zero intensity. The relaxation rates may be obtained from the plot of $\ln(A_0 - A_t)$ against t_D . The slope of the straight line is $-R_1$. However, this method of determining R_1 is not preferred since for latter points when the relaxation is least, $A_0 - A_t$ will be small due to which the relaxation is likely to be non-exponential. So, it is better to fit the exponential curve directly to obtain R_1 . Trial values of A_0 are selected in order to obtain the best fit between observed peak intensities and Eq. (7.28). The s - l relaxation rates for the two aromatic signals corresponding to H_o and H_m protons of peptide tyrala, (I) are 0.48 s^{-1} and 0.91 s^{-1} , respectively.



(b) Saturation Recovery The preparation step used to measure s - l relaxation time constants may be saturation rather than inversion of the original magnetisation. The saturation may be carried out by a series of hard pulses with only short delays between them so that there is not enough time for the system to return to its original position. The whole spectrum becomes saturated by this technique. This type of saturation is achieved by using $\pi/2$ pulses and a delay scheme in which the time interval is decreased during the train pulses as shown in Fig. 7.13. The saturation of proton magnetisation may also be done by a burst of broad band ^1H decoupling for ^1H relaxation measurements.

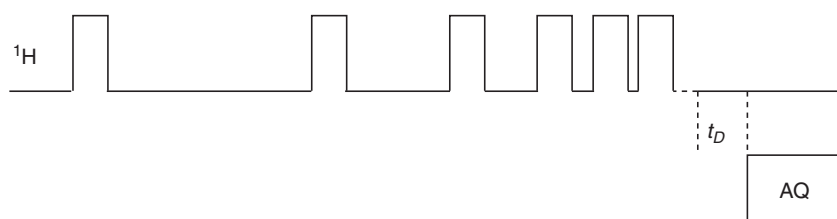


Fig. 7.13 Pulse sequence for saturation recovery using a converging pulse train to ensure saturation.

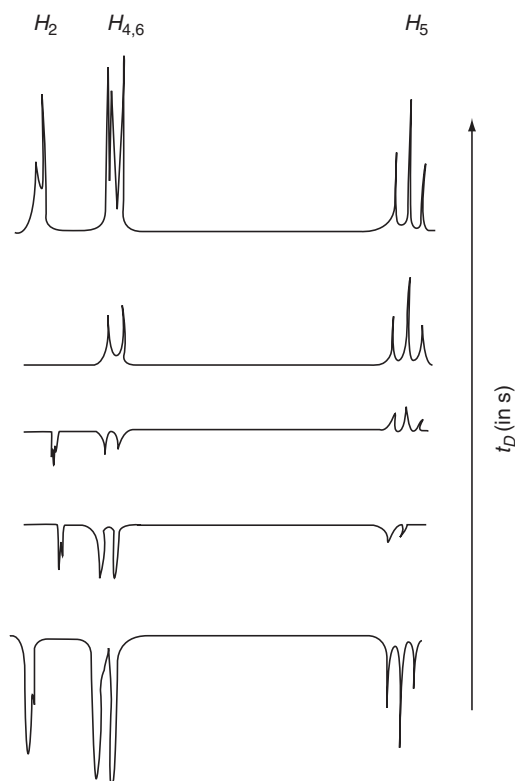


Fig. 7.12 250 MHz ^1H inversion recovery spectra for *m*-dinitrobenzene.

Once the saturation is attained, the system is allowed to evolve during the delay t_D , and then detected with a $\pi/2$ pulse. The evolution is measured as a function of varying evolution delay, t_D . The signal intensity is given by

$$A_t = A_0 [1 - \exp(-R_1 t_D)] \quad (7.31)$$

The slope of the line between $\ln(A_0 - A_t)$ and t_D will give the value of R_1 . The saturation-recovery methods are less time consuming than inversion-recovery method. This method is particularly useful for slow relaxing nuclei, i.e. nuclei with low sensitivity such as ^{15}N .

7.19 SPIN ECHO

In order to measure s - s relaxation time constant T_2 , the s - s relaxation process is to be disentangled from other processes which can cause the spin to precess at different frequencies, mainly the field inhomogeneities. The effect of field inhomogeneity is that the chemically identical spins in different parts of the sample tube will experience different effective magnetic fields. They will, therefore, precess at average of frequencies rather than a single frequency. The effect of inhomogeneity which appears in the form of line broadening is removed using a pulse sequence represented as $\pi/2 - t_D - \pi - t_D - \text{Echo}$, where terms and symbols have their usual meanings.

When, a $\pi/2$ pulse is applied along the X-axis, via the transmitter coil, it tips the bulk magnetisation M along Z-axis [Fig. 7.14(a)] to the Y-axis [Fig. 7.14(b)]. During the evolution time t_D , the magnetisation decoupled into fast (F) and slow (S) components in the X-Y plane as shown in Figs 7.14(c) and (d), and the signal observed in the receiver coil will result from the sum of the components of magnetisation. As the individual components fan out, the sum decreases and the intensity of the net signal decay rapidly. At this stage, a π pulse is applied along the X-axis and its effect is to rotate the components of magnetisation by 180° about the X-axis [Fig. 7.14(e)]. The sum of components and the resulting signal intensity will increase to form an echo of maximum amplitude at the end of delay period equal to the first [Fig. 7.14(f)]. After that moment, the decoupling of magnetisation will start and the signal will decay but at the peak of echo, all effects of field inhomogeneity have been removed. The decay process continues up to $3t_D$ and further application of π pulse will cause rebunching of the F and S components at $4t_D$. The whole process is shown in Fig. 7.15, where (a) represents the spin-echo pulse timing, and (b) the detector output.

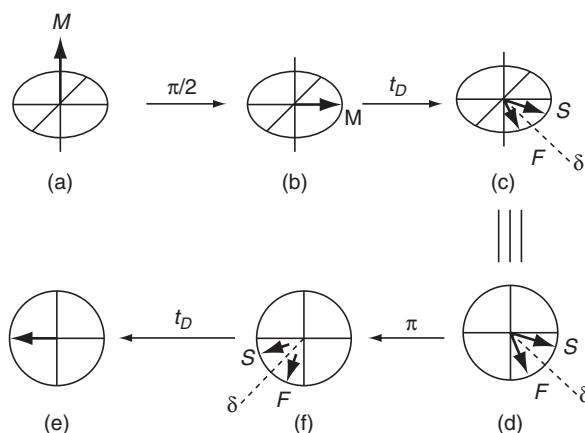


Fig. 7.14 Vector diagram of the effect of the spin-echo sequence on the signal which is broadened by field inhomogeneity.

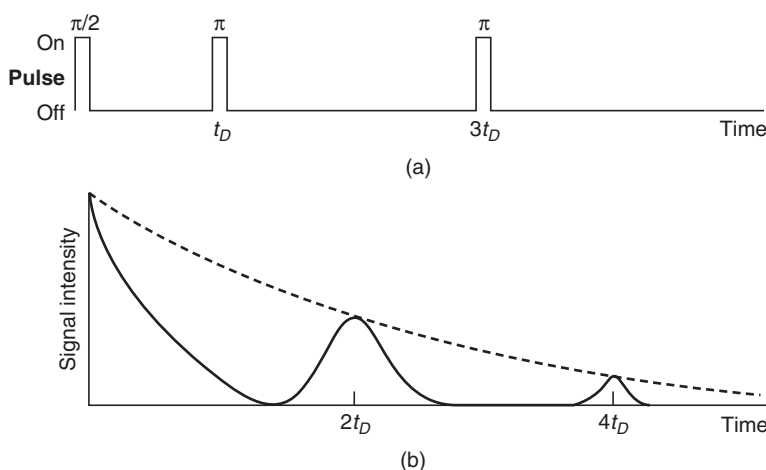


Fig. 7.15 The pulse timing of $\pi/2 - t_D - \pi$ sequence, and (b) the resultant spin echoes.

7.20 CHEMICAL SHIFT AND SHIELDING CONSTANT

The resonance condition $h\nu = \beta_N g_N H$ is derived on the assumption that the interaction between nuclear magnetic moment of bare nuclei, say proton, and applied field of strength H occurs. However, the bare nucleus seldom exists. The nuclei in molecules are surrounded by electrons. The external field H induces currents in the electron

clouds of the molecules. These currents, in turn, produce their own secondary magnetic fields at the sites of the magnetic nuclei which shift the resonance away from the bare nucleus. This shift from the bare nucleus is called *chemical shift*. The magnitude of the induced secondary field is proportional to the external field H and in isotropic environments, its direction is along the external field. H . An isotropic environment is effectively produced in gases, liquids and solutions. Under these conditions, the effective magnetic field experienced by the nucleus is given by

$$H_{\text{eff}} = H - \sigma H = H(1 - \sigma) \quad (7.32)$$

Thus, the resonance condition for a nucleus $\left(I = \frac{1}{2}\right)$, i.e. proton, in going from a bare nucleus to the shielded nucleus is given by

$$\Delta E' = h\nu' = g_N \beta_N H(1 - \sigma) \quad (7.33)$$

and is also shown in Fig. 7.16.

The dimensionless parameter σ is known as *screening* or *shielding constant* of the nucleus in the environment considered. The value of σ for hydrogen nuclei in diamagnetic samples varies over a range of some 10–20 ppm. σ is somewhat greater for heavier nuclei because currents can be easily induced in their electron clouds. The shielding constant is, therefore, a function of molecular environment of the nucleus of interest, say proton, and is largely determined by the density of the surrounding electron cloud.

Let us now consider two resonance lines due to two magnetically non-equivalent protons, say A and B , as shown in Fig. 7.17. The difference between resonance frequencies or fields of A and B is called chemical shift. In other words, we can say that the measurable distance between two resonance signals in terms of frequency or magnetic field is the chemical shift.

Applying Eq. (7.32) to both the nuclei, we get

$$H_{\text{eff}}(B) - H_{\text{eff}}(A) = H(\sigma_A - \sigma_B) = H\delta_{AB} \quad (7.34)$$

where $\delta_{AB} = \frac{H_{\text{eff}}(B) - H_{\text{eff}}(A)}{H} \times 10^6$ is called the chemical shift.

Similarly, in terms of resonance frequencies of the two nuclei, i.e. $\nu_r(A)$ and $\nu_r(B)$, the chemical shift is expressed as

$$\delta_{AB} = \frac{\nu_r(B) - \nu_r(A)}{\nu} \times 10^6 \text{ ppm} \quad (7.35)$$

Here, ν (in MHz) is the operating frequency of the NMR spectrometer, a factor of 10^6 is introduced so that δ_{AB} can be expressed in convenient numbers. δ_{AB} is measured in dimensionless units—ppm and is independent of the strength of the applied magnetic field, H .

Quantitatively, the chemical shift should be measured with respect to some standard reference, and for protons, chemical shifts are usually reported with reference to tetramethylsilane (TMS), $(\text{CH}_3)_4\text{Si}$. TMS has twelve equivalent protons and hence will give narrow intense line at a higher field than the signals of hydrogen atoms present in most of the organic compounds. TMS is chemically inert, has low BP (300 K) and thus can easily be removed from most of the analytes after use. Generally, 5 per cent TMS is added to the analyte. For aqueous solutions, sodium 2,2-dimethyl-2 silapentane-5-sulphonate, i.e. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{SO}_3^- \text{Na}^+$, called DSS is preferred since TMS is insoluble in water. The CH_3 groups of DSS resonate in the same position as those of TMS. Weak peaks due to methylene protons interfere so in order to eliminate the undesirable peaks, DSS with methylene groups deuterated is used. The other standards for protons are cyclohexane, tetramethylammonium ion, hexamethyldisiloxane (HMDS). The chemical shift relative to TMS is given by

$$\delta_{\text{analyte. TMS}} = \frac{\nu_{\text{analyte}} - \nu_{\text{TMS}}}{\nu} \times 10^6 \text{ ppm} \quad (7.36)$$

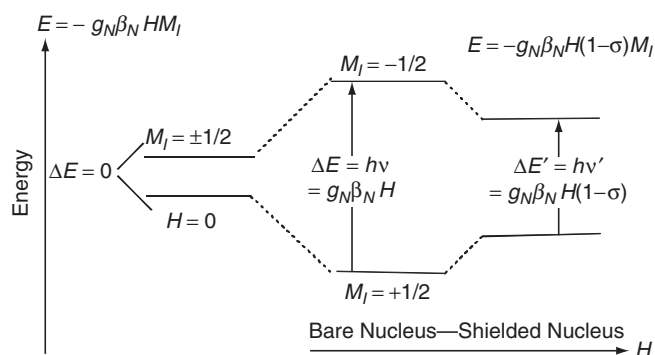


Fig. 7.16 A sketch depicting the comparison of the resonance condition for a bare and shielded nucleus.

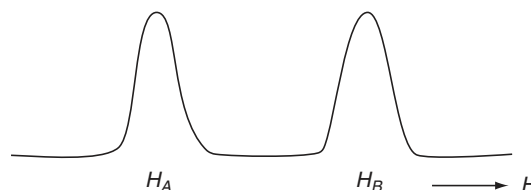


Fig. 7.17 Hypothetical resonance signals due to two magnetically non-equivalent protons, A and B .

The chemical shifts of most of the protons fall in the range of 1–15 ppm. The chemical shifts of H-bonded protons, NH, OH, SH, etc., are temperature, concentration, pH and solvent dependent. The NMR signals are often broadened. H-bonding causes low field shift relative to unbonded state. Thus increase in δ value is because of deshielding effect. In other words, we can say that hydrogen bonding decreases the electron density around the proton, and thus moves the proton to lower field, i.e. higher δ values. Intramolecular hydrogen bonds are less affected by their environment than are intermolecular hydrogen bonds. The up-field shift of the hydroxyl proton resonance of ethanol with increase of temperature or on diluting the ethanol with CCl_4 is attributed to breaking of intermolecular H-bonds. At present, there are two scales for measuring chemicals — the delta (δ) and the tau (τ) scales. The δ -scale is recommended for PMR by American Society for Testing and Materials (ASTM, Manual of Feb. 1966, sponsored by Committee E-13). The sign convention used in δ -scale is that the frequency and chemical shift increase down the field. The other scale, called τ -scale, is contrary to that of δ -scale is due to Tiers (GVD Tiers, *J. Phys. Chem.* 62 (1958), 1151) and is recommended by the Chemical Society of London. The parameter τ is defined as

$$\tau = 10 - \delta \quad (7.37)$$

Standard Reference and Chemical Shift of Some Other Nuclei Standard references for ^{13}C -nucleus are CS_2 and TMS. ^{13}C -chemical shifts with respect to TMS can be converted to some other standards where the up-field shifts have been regarded as positive (contrary to the convention for proton chemical shifts) by

$$\begin{aligned} \delta(\text{TMS}) &= -[\delta(\text{C}_6\text{H}_6)_{\text{ext}} - 129] \\ &= -[\delta(\text{CS}_2)_{\text{ext}} - 194] \\ &= -[\delta(\text{CH}_3\text{C}^*\text{OOH})_{\text{ext}} - 179] \end{aligned} \quad (7.38)$$

CF_4 and trifluoroacetic acid are used as standards for ^{19}F while 85 per cent phosphoric acid is used for ^{31}P nucleus.

The range of chemical shifts for other nuclei is greater because of associated $2p$ -electrons, e.g. ^{13}C -chemical shifts lie in the range 0–220 ppm. In some cases, the range may extend to 400 ppm or even more. For ^{19}F , the range may be 800 ppm while 300 ppm or more for ^{31}P nucleus. Chemical shift for ^{35}Cl and ^{37}Cl cover a range of about 1000 ppm. The range of chemical shifts of ^{205}Tl and ^{207}Pb exceeds even 14000 ppm or more.

The chemical shifts of some typical protons are listed in Table 7.3 Chemical shift is taken as the centre of the peak or of the multiplet (see Figs. 7.21 and 7.22).

Table 7.3 δ and τ values of some typical protons.

Types of Proton	$\tau(\delta)$, ppm	Types of Proton	$\tau(\delta)$, ppm
$\text{Si}(\text{CH}_3)_4$	10(0)	$\text{F}-\text{CH}_3$	5.7(4.3)
CH_4	9.8(0.2)	$\text{Cl}-\text{CH}_3$	7.0(3.0)
$\text{R}-\text{CH}_3$	9.1(0.9)	$\text{Br}-\text{CH}_3$	7.3(2.7)
R_2-CH_2	8.7(1.3)	$\text{I}-\text{CH}_3$	7.8(2.2)
$(\text{R})_3\text{C}-\text{H}$	8.5(1.5)	$\text{R}-\text{CH}_2-\text{OH}$	6.4(3.6)
$\text{CH}_3-\text{C}(=\text{O})\text{OH}$	7.9(2.1)	$\text{R}_2-\text{CH}_2-\text{OH}$	6.4(3.6)
CH_3NO_2	5.7(4.3)	$(\text{R})_2-\text{CH}-\text{OH}$	6.1(3.9)
CH_3NH_2	7.9(2.1)	$\text{R}_2\text{C}=\text{CH}_2$	5.4(4.6)
CH_3-Ar	7.7(2.3)	$(\text{R})_2\text{C}=\text{CHR}$	4.8(5.2)
$\text{R}-\text{C}\equiv\text{C}-\text{H}$	7.7(2.3)	$\text{Ar}-\text{H}$	2.7(7.3)
$\text{O}=\text{C}(\text{R})-\text{CH}_3$	7.7(2.3)	$\text{R}-\text{C}(=\text{O})\text{H}$	0.1(9.9)
$\text{R}-\text{O}-\text{CH}_3$	6.7(3.3)	RSH	9–8(1–2)
ArSH	7–6(3–4)	ArOH	5.5–3.5(4.5–6.5)
ROH	9.5–5.5 (0.5–4.5)	$\left. \begin{array}{l} \text{ArNH}_2 \\ \text{ArNHR} \end{array} \right\}$	7–4(3–6)

Table 7.3 δ and τ values of some typical protons—Cont'd.

$\text{RNH}_2, \text{RNHR}$	9–5(1–5)	$\left. \begin{array}{l} \text{RCONH}_2 \\ \text{RCONHR} \end{array} \right\}$	5–(–2)(5–12)
$\text{C}=\text{N}-\text{OH}$	1–(–2)(9–12)	RCOOH	1–(–3)(9–13)
$\text{C}=\text{O} \cdots \text{H}-\text{O}-\text{C}-$	3–(–3)(7–13)		

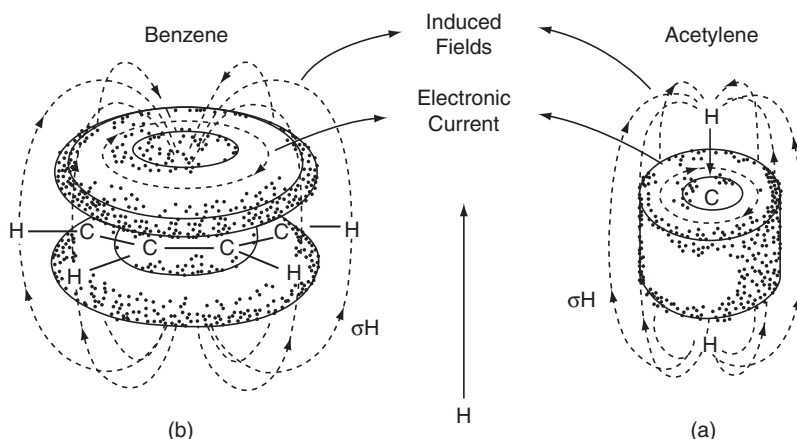


Fig. 7.18 (a) Shielding of protons of acetylene, and (b) deshielding of protons of benzene.

In the case of metal derivatives the proton attached to the carbon atom is shielded much more than the proton of TMS. Thus the chemical shift has a negative value, but the influence of metal atom on the neighbouring carbon atoms decreases sharply in comparison to the electronegative element. For examples, the δ for the protons attached to the carbon atom immediate to the metal atom is having a negative δ with respect to TMS. But these values become positive for the protons attached to the second carbon atom, as shown below:

CH_3Li	$\text{CH}_3\text{CH}_2\text{Li}$	$(\text{CH}_3-\text{CH}_2)_2\text{Mg}$
–1.30	1.33–0.99	1.26–0.64

There are three types of contributions to the screening constant, i.e. diamagnetic (σ_d), paramagnetic (σ_p) and solvent (σ_s). Thus,

$$\sigma = \sigma_d + \sigma_p + \sigma_s$$

σ is related to the induced precession of electrons bonding the nucleus say proton, around the nucleus in a plane perpendicular to the magnetic field. This induced circulation of electrons generates a secondary magnetic field opposed to the external field H . This diamagnetic effect results in shielding the nucleus by electrons from the external field. Consequently, the external field is increased to cause resonance.

Diamagnetic shielding of protons of acetylene is shown in Fig. 7.18 (a). In acetylene bond, the symmetrical distribution of π -electrons about the bond axis permits electrons to circulate around the bond. σ_d is difficult to be computed but qualitatively it is proportional to the charge densities. The electron-loving (electronegative) groups or atoms adjacent to protons reduce the density of the electron cloud around the protons of interest and hence the shielding constant. The resonance, therefore, occurs at lower modified external field or higher frequency. The most common electron attracting groups are NO_2 , F, Br, I, Cl, CN, OR, COOR. The reverse effect is exhibited by electron repelling (electropositive) groups such as CH_3 , NH_2 . Protons of tetramethylsilane, i.e. $(\text{CH}_3)_4\text{Si}$ are highly shielded and, therefore, are observed at high magnetic fields. Si is relatively positive.

σ_p is related to anisotropy in the electron distribution around the nucleus. The electron circulation around the nucleus in such a case produces a magnetic field in the direction of the applied field. This is a paramagnetic effect and it results in deshielding the nucleus. Consequently, the external field is decreased to cause resonance. Thus σ_p is negative. The π -electrons of benzene may be thought of precessing around the ring and thus give rise to ring current which causes deshielding. Deshielding will occur only if the external field is perpendicular to the plane of the ring. This effect is either absent or self-cancelling in other orientations of the ring. Deshielding of protons of benzene is shown in Fig. 7.18(b).

Deshielding is also exhibited by ethylenic or carbonyl double bonds. π -electrons in these bonds are not symmetrically distributed along the bond axis as in the case of acetylene. Thus, the circulation of π -bonds around the bond axis is prohibited by the nodal plane in the distribution of a double bond. π -electrons in these types of bonds

can be thought of circulating in a plane along the bond axis, when the molecule is oriented with the field as shown in Fig. 7.19. Further, it is observed that the observed chemical shift (δ) for a given nucleus in a molecule in dilute solution is different from the shift in the gaseous phase (δ_{gas}). The difference between these two chemical shifts is called the solvent screening constant (σ_s). It depends on the nature of the solvents and causes deshielding.

$$\sigma_s = \delta_{\text{gas}} - \delta \quad (7.39)$$

σ_s in part has contributions from the bulk diamagnetic susceptibility difference of the solution and reference samples (σ_b), the solvent magnetic anisotropy (σ_a) and weak dispersion, i.e. van der Waals forces between solute and solvent molecules (σ_w). In case of polar solutes, a polar effect (σ_e) also contributes to the solvent screening constant. This effect arises due to the secondary electric field in the solvent owing to its polarisation by the permanent dipole moment of the solute. The specific complex formation in solution, say solute-solvent complex (σ_c) may also contribute to σ_s . We may, therefore, write

$$\sigma_s = \delta_{\text{gas}} - \delta = \sigma_b + \sigma_a + \sigma_w + \sigma_e + \sigma_c \quad (7.40)$$

σ_b can be eliminated using unreactive internal reference. In favourable cases, σ_w , σ_a and σ_e are small as compared to σ_c . σ_c is eliminated by measuring the chemical shift of solute molecules over a wide range of concentrations and extrapolating to zero.

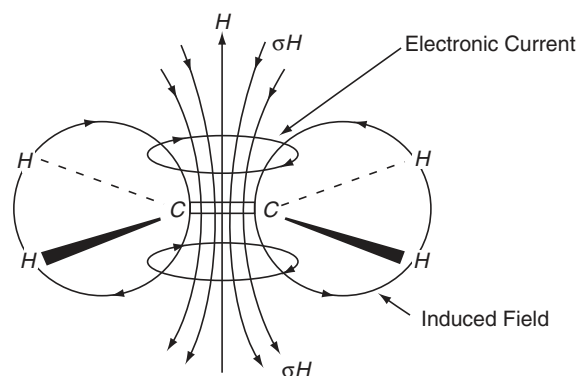


Fig. 7.19 Deshielding of protons of ethylene.

7.21 ESTIMATION OF PROTON CHEMICAL SHIFTS IN COMPOUNDS OF KNOWN STRUCTURES

The chemical shift of a proton bonded to carbon follows the additivity rule; the value of shift is the sum of the contributions along the other three bonds to the carbon, together with the effects of nearby unsaturation. Thus, the NMR shifts of protons attached to carbon in compounds of known structures can be estimated from the deshielding values of atoms, bonds and rings recorded in Table 7.4.

Table 7.4 Deshielding values of atoms, bonds and rings.

System				Deshielding values (ppm)
(a)	B, Si, Sn			-0.3
	H			0.2
	C, P			0.7
	N, S			1.7
	O, Cl, Br, I			2.7
	F			3.7
(b)	Double bond	If the carbonation participates	DB	4.2
		If one carbonation intervenes	dB	0.8
	Benzene ring; also, pyridine, and diazines			
		If the carbonation participates	BZ	6.0
		If one carbonation intervenes	bZ	1.2
(c)	Additional values, more subject to steric effects than those above:			
			TB	2.1
			tb	0.8
	Triple bond	If the carbonation atom intervenes	TB	2.1
		If the carbonation intervenes	tb	0.8
	Four-membered ring		R ₄	0.7
	Three-membered ring		R ₃	-0.7

Table 7.5 Calculated and observed chemical shifts for some selected molecules.

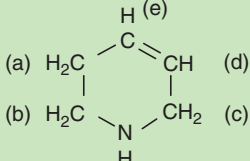
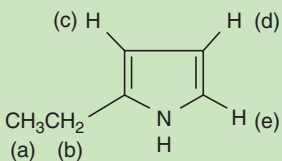
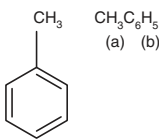
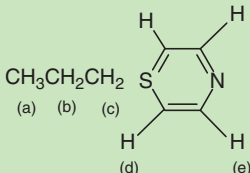
System	Proton(s)	Contributors to Chemical Shift	Chemical Shift (δ) (in ppm)	
			Calculated	Observed
Methanol: CH_3OH (a)	(a)	H, H, O	3.1	3.6
Ethanol: $\text{CH}_3\text{CH}_2\text{OH}$ (a) (b)	(a)	H, H, C	1.1	1.2
	(b)	H, C, O	3.6	3.7
Tetramethyltin: $(\text{CH}_3)_4\text{Sn}$ (a)	(a)	H, H, Sn (= B)	0.1	0.1
Sodium 2, 2-dimethyl-2-silapentane sulphonate: $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{SO}_3(-)\text{Na}(+1)$	(a)	H, H, Si	0.1	0.0
	(b)	H, C, Si	0.6	0.6
	(c)	H, C, C	1.6	1.9
	(d)	H, C, S	2.6	2.8
1, 2, 5, 6-Tetrahydropyridine: 	(a)	H, C, C, db	2.4	2.1
	(b)	H, C, N	2.6	3.0
	(c)	H, C N, db	3.4	3.3
	(d)	C, C, DB	5.6	5.7
			5.6	5.8
	(e)	C, C, DB	5.6	5.8
2-Ethylpyrrole 	(a)	H, H, C	1.1	1.2
	(b)	H, H, C, db	2.4	2.6
	(c)	C, C, DB, db	6.4	6.0
	(d)	C, C, DB, db	6.4	6.2
Tolene 	(a)	H, H, C, bz	2.3	2.3
	(b)	C, C, Bz	7.4	7.2
Diphenyl-methylbromide $(\text{C}_6\text{H}_5)_2\text{CHBr}$ (a)	(a)	C, C, Br (= O)	6.5	6.3
		bz, bz		
1-propyl-4pyridylthioether 	(a)	H, H, C	1.1	1.1
	(b)	H, H, C	1.6	1.7
	(c)	H, C, S (= N)	2.6	2.9
	(d)	C, C, BZ	7.4	7.1
	(e)	C, N, BZ	8.4	8.4
2-Pyropyne-1-ol $\text{HC}\equiv\text{CCH}_2\text{OH}$ (a) (b)	(a)	C, TB	2.8	2.5
	(b)	H, C, O, tb	4.4	4.3
β -Methoxypropionitrile $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CN}$ (a) (b) (c)	(a)	H, C, C, tb	2.4	2.6
	(b)	H, H, O	3.1	3.4
	(c)	H, C, O	3.6	3.6

Table 7.5 *Calculated and observed chemical shifts for some selected molecules.*

System	Proton(s)	Contributors to Chemical Shift	Chemical Shift (δ) (in ppm)	
			Calculated	Observed
Trimethy-leneoxide				
(a) $\begin{array}{c} \text{H}_2\text{C} - \text{CH}_2 \\ \quad \quad \\ \text{H}_2\text{C} - \text{O} \end{array}$ (b)	(a)	H, C, C, R ₄	2.3	2.7
(b) $\begin{array}{c} \text{H}_2\text{C} - \text{O} \\ \quad \quad \\ \text{H}_2\text{C} - \text{CH}_2 \end{array}$	(b)	H, C, O, R ₄	4.3	4.7
Phenylcyclo-propane				
(a) $\begin{array}{c} \text{H}_2\text{C} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} \quad \text{C}_6\text{H}_5 \end{array}$ (b)	(a)	H, C, C, R ₃	0.9	0.7
(b) $\begin{array}{c} \text{H}_2\text{C} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} \quad \text{C}_6\text{H}_5 \end{array}$	(b)	C, C, C, bz, R ₃	2.6	2.8
(a) $\begin{array}{c} \text{H}_2\text{C} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} \quad \text{C}_6\text{H}_5 \end{array}$ (c)	(c)	C, C, BZ	7.4	7.1
Ethyleneimine				
(a) $\begin{array}{c} \text{H}_2\text{C} \\ \quad \diagup \\ \text{H}_2\text{C} \quad \text{NH} \end{array}$	(a)	H, C, N, R ₃	1.9	1.6

*in CDCl_3

Within a saturated compound, the δ value for a proton is the sum of the deshielding values of the other three substituents on the carbon atom. For alkenes and arenes, the chemical shift of a proton on an unsaturated carbon atom is the sum of the contributions from the other two substituents, plus the effect of π -electrons at the carbon. Based on these rules, the computed values of chemical shifts are compared with the observed values of some selected molecules in Table 7.5.

7.22 DISPLAY OF NMR SPECTRUM

Equations (7.35) and (7.34) show that the NMR spectrum of an analyte can be recorded either by field sweep or by frequency-sweep method, respectively. In the field-sweep method, the external field is varied and the frequency is maintained constant while frequency is varied and applied field is kept constant in the frequency-sweep method. The universally accepted mode of displaying NMR spectrum is a left (L) to right (R) arrangement in which H , in a field-sweep spectrum increases from L-R and consequently ν in a frequency-sweep spectrum decreases from L-R. The NMR spectrum is obtained by plotting δ against absorption intensity on the horizontal and vertical axis respectively. The zero value of δ scale corresponds to TMS signal. The hypothetical spectrum of a proton is shown in Fig. 7.20.

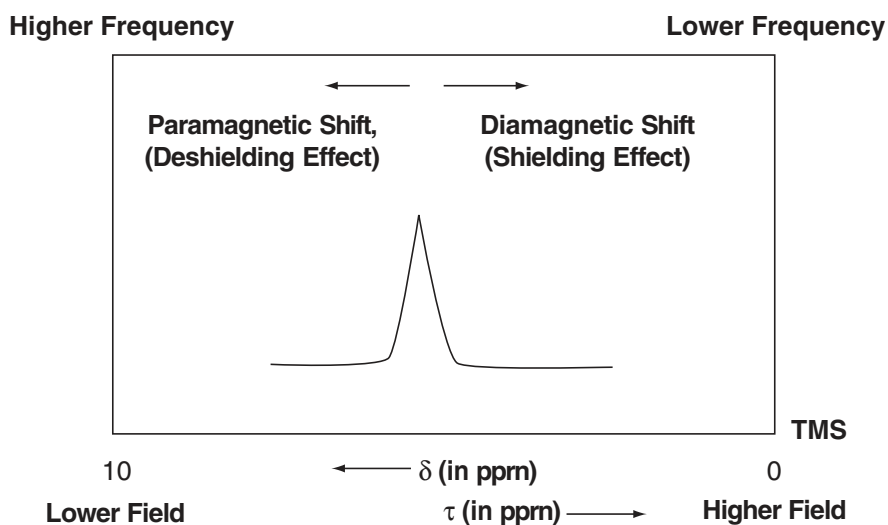


Fig. 7.20 A hypothetical NMR spectrum of a proton.

7.23 DIPOLE-DIPOLE (*D-D*) INTERACTION

Dipole-dipole interaction takes place directly through space. Let us consider two protons, say *A* and *B*, separated by a distance *r*. The interaction between the two magnetic dipoles is given by

$$H_{d-d} = g_N^2 \beta_N^2 \left[\frac{I_A I_B}{r^3} - \frac{3(I_A \cdot r)(I_B \cdot r)}{r^5} \right] \quad (7.41)$$

where I_A and I_B are the nuclear spins of protons *A* and *B* respectively, H_{d-d} is the Hamiltonian for *d-d* interaction. As a result of interaction between the two magnetic dipoles, there will be an additional magnetic field, H_{add} , at the proton *A* due to proton *B* and vice versa, and is given by

$$H_{\text{add}} = \pm \frac{3g_N \beta_N}{4} \cdot \frac{1 - 3\cos^2 \theta}{r^3} \quad (7.42)$$

where θ is the angle between the applied field *H* and the line joining the nuclei. The sign $\pm$ appears due to the fact that the magnetic dipole of the proton *B* can be parallel or antiparallel to that of the proton *A*. Same is true for proton *A*. Thus the effective field at each nucleus is

$$H_{\text{eff}} = H \pm H_{\text{add}} = H \pm \frac{3g_N \beta_N}{4} \cdot \frac{1 - 3\cos^2 \theta}{r^3} \quad (7.43)$$

Consequently, the absorption spectrum will be a doublet with a separation of

$$\Delta H = H_{\text{eff}} - H = \frac{3}{2} g_N \beta_N \frac{1 - 3\cos^2 \theta}{r^3} \quad (7.44)$$

e.g. the NMR spectrum of the single crystal of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, gives rise to four lines (two doublets). The interaction between each pair of equivalent protons should only give rise to a doublet. However, we get two doublets. This will lead us to infer that two water molecules in each unit have different orientations.

This type of magnetic interaction vanishes in nonviscous liquids due to the rapid tumbling motion of the molecules. When a molecule tumbles in solution, the angle ' θ ' changes continuously, and if the frequency of tumbling is equal or greater than the energy due to *d-d* interaction (in frequency units), this effect will be averaged out to zero. However when the correlation time for molecular reorientation is of the order of 10^{-11} second, only a very weak line broadening effect remains of that *d-d* interaction. The broadening due to this effect becomes uncertain or obscure normally if the external magnetic field is not homogeneous. *d-d* interaction in solids produces a structure having a line width of 10–20 kHz. This width is sufficient to smear out all structures caused by chemical shifts and internuclear *s-s* coupling, i.e. *J* coupling. Thus, high-resolution NMR spectrum in solids is impossible unless the *d-d* interactions are annihilated or reduced to minimum. If a nonspherical molecule is dissolved in a liquid crystal matrix, the motional averaging may become slightly anisotropic and in that case *d-d* interactions may produce additional structure in a high-resolution NMR spectrum. This forms the basis of applications of liquid crystals in the study of *d-d* interactions and will be discussed later on under the heading 'liquid crystals in high-resolution NMR spectroscopy'.

7.24 SPIN-SPIN (*S-S*) COUPLING AND SPIN-LATTICE (*S-L*) COUPLING CONSTANTS

So far we have considered only the interaction between the magnetic moment of a nucleus and applied field *H*. However, in molecules, the protons may be closely spaced and the net interaction between these types of protons may be due to (i) direct *d-d* interaction through space, and (ii) indirect *s-s* interaction through bonds. As we have already discussed, the former averages out to almost zero in case of isotropic fluids. The isotropic *s-s* interaction in liquids is mediated by the electron-nuclear and electron-electron interactions in the molecule. This interaction imparts a fine structure to the NMR signals. The energy of *s-s* interaction is proportional to the product of spins of the nuclei considered and is given by

$$E = J_{AB} I_A I_B \quad (7.45a)$$

where I_A and I_B are the spins of the coupled nuclei *A* and *B* respectively. J_{AB} is the spin coupling constant between *A* and *B* and has dimensions of frequency. The coupling constant is independent of applied magnetic field while

Table 7.6 Characteristic values of s-s coupling constants for some typical fragments.

Fragment	J, cps	Fragment	J, cps	Fragment	J, cps
$H_2(CH_4)$	280 (12.4)		1-3		$J_{23} = 1.6-2.0$ (4.6-5.8)
	12.5		2-3		$J_{24} = 0.6-1.0$ (1.0-1.8)
	0.35-2		$J_{aa} = 9-13$		$J_{25} = 1.3-1.8$ (2.1-3.3)
	2-9		$J_{ee} = 2-4$		$J_{34} = 3.2-3.8$ (3.0-4.2)
	6-14		$J_{AB} = 7-10$		$J_{AB} = 3-4$
	11-18		$J_{AA'} = 2-3$		$J_{AC} = 0.6-1$
	0.5-2		$J_{AB} < 1.5$		$J_{BC} = 1.8-2$
	10-13		$J_{AB} = 7.5-8$		
			$J_{AA'} = 1.4-2$		
			$J_{AB} = 5.2-5.5$		
			$J_{AB'} = 0.9$		$J_{HH} = 0$

 $J_{HH} = 6.5 J_{HD}$ (provided the two protons are in the same position)

chemical shift is proportional to it. Theoretically, both positive and negative values of J_{AB} are possible. However, the appearance of NMR spectrum depends only on the absolute magnitude of J_{AB} , i.e. $|J_{AB}|$. The sign and magnitude of J_{AB} depends upon the number of bonds and the type of bonds through which nuclei interact in addition to the geometrical orientations of those nuclei, e.g.

- (i) $J(\text{C} \equiv \text{C}) > J(\text{C} = \text{C}) > J(\text{C} - \text{C})$
- (ii) $J(\text{trans}) > J(\text{cis})$
- (iii) $J(\text{axial-axial}) > J(\text{axial-equatorial})$ and $J(\text{equatorial-equatorial})$
- (iv) $J(\text{FHCCl}_2) > J(\text{HCCl}_2\text{CCl}_2\text{F}) > J(\text{HCCl}_2\text{CCl}_2\text{CCl}_2\text{F})$

The s - s coupling constants of some fragments of organic molecules are listed in Table 7.6. Note that the coupling constant is taken as the distance between any two adjacent peaks in a multiplet as shown in Figs 7.21 and 7.22.

Further, it is to be noted that spin-coupling constants J_{AB} (in Hz) between different combinations of nuclear species can be meaningfully compared only when signs and magnitudes of the magnetogyric ratios of the nuclei are accounted for. Thus, it is useful to consider a reduced coupling constant K_{AB} which may be defined as

$$K_{AB} = \left(\frac{2\pi}{\hbar \gamma_A \gamma_B} \right) J_{AB} = \left(\frac{4\pi^2}{\hbar \gamma_A \gamma_B} \right) J_{AB} \quad (7.45b)$$

where γ_A and γ_B are the magnetogyric ratios of nuclei A and B . In the cgs system, the unit of K_{AB} is cm^{-3} , in the SI it is $\text{N A}^{-2}\text{m}^{-3}$, e.g. the reduced Cl coupling constant for

$$\text{HCl} \begin{cases} J_{1\text{H}^{35}\text{Cl}} = 41 \pm 2 \\ J_{1\text{H}^{37}\text{Cl}} = 35 \pm 2 \end{cases} \text{ is } 35 \pm 2 \times 10^{20} \text{ cm}^{-3}$$

and is $19 \pm 1 \times 10^{20} \text{ cm}^{-3}$ for

$$\text{HBr} \begin{cases} J_{1\text{H}^{79}\text{Br}} = 57 \pm 3 \\ J_{1\text{H}^{81}\text{Br}} = 62 \pm 3 \end{cases}$$

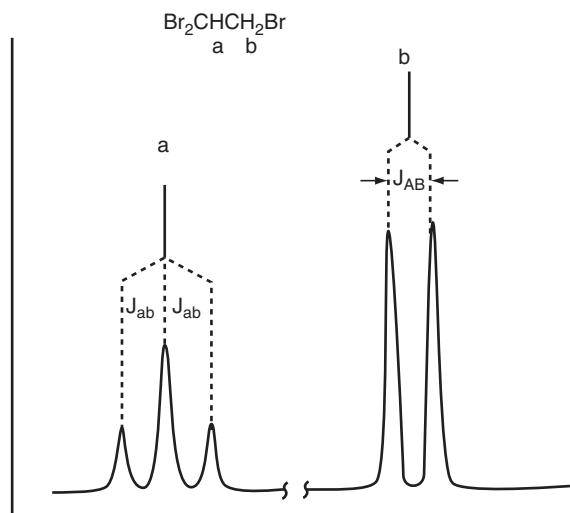


Fig. 7.21 NMR spectrum of 1,1,2-tribromoethane.

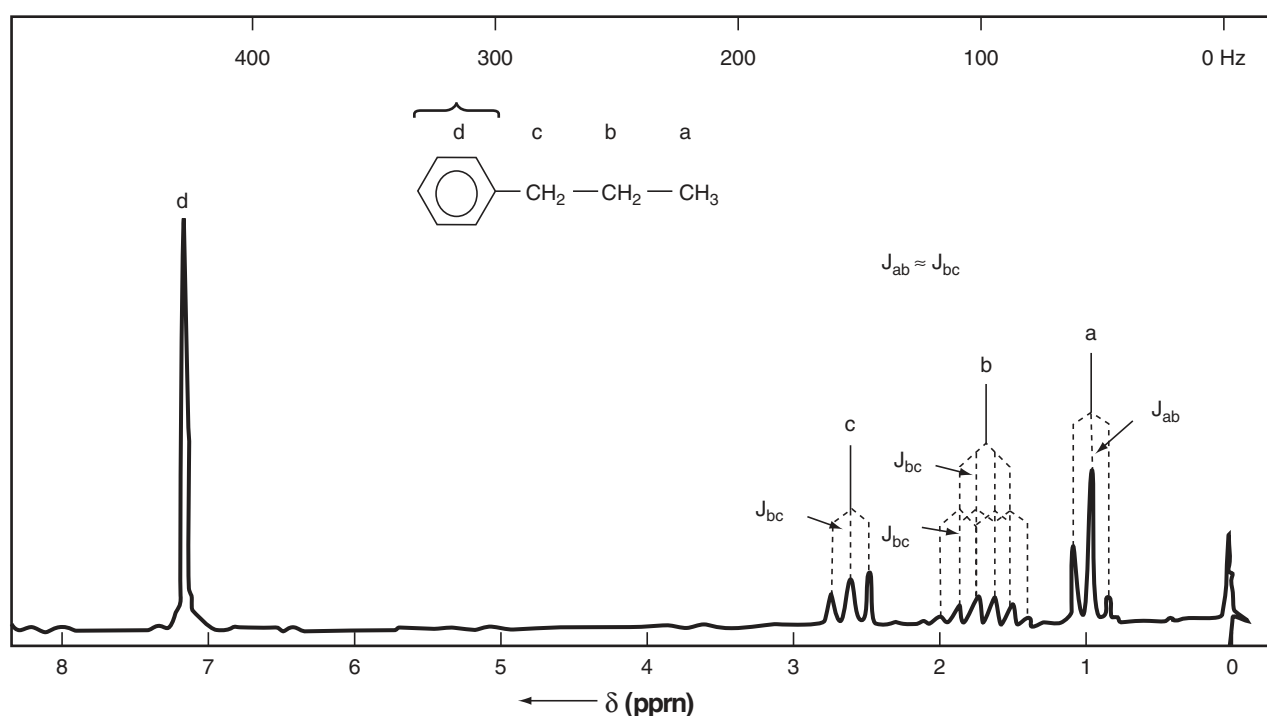
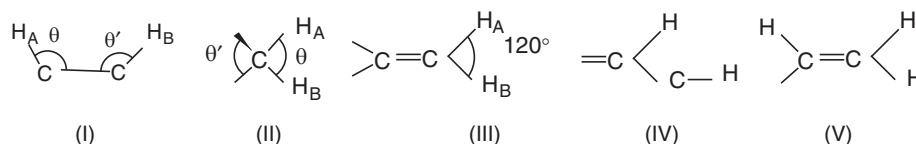


Fig. 7.22 NMR spectrum of 3-phenylpropane.

7.25 TYPES OF S-S COUPLING CONSTANTS AND FACTORS AFFECTING THEM

We know that *s-s* interaction between two nuclei takes place through bonds and is measured in terms of a constant called *coupling constant* (J). In general, J decreases as the number of intervening bonds increases. Depending upon the number of intervening bonds, *s-s* coupling is of two types: (i) short range, and (ii) long range. Long-range interactions are common in π -systems. The number of intervening bonds in short-range interactions is two or three and the magnitude of J in such type of interactions is of the order of 0–20 Hz. On the other hand, the number of bonds through which long-range coupling occurs is four or five and the value of J lies in the range of 0–3 Hz. Further, on the basis of nature and geometrical orientation of nuclei (protons), short-range interactions are characterised as vicinal, geminal and vinylic whereas long-range interactions are classified as substituted benzenes ($J = 0$ –10 Hz), allylic (0–3 Hz) and homoallylic (0–2 Hz) couplings. In vicinal coupling (I), protons are attached to the adjacent carbon atoms and the coupling constant J_{vic} is of the order of 5–10 Hz, e.g. in ethylene J_{HH} (gauche) = 2–4 Hz and J_{HH} (anti) = 5–12 Hz. On the other hand, in geminal coupling (II, III), the protons are attached to the same carbon atom and J_{gem} lies in the range 10–20 Hz. The vinylic coupling in the fragment, (IV) is 4–10 Hz whereas 6–14 Hz for *cis* protons and 11–18 Hz for the *trans* protons in the (V) fragment. The coupling constants are sensitive to various parameters such as bond angle, bond length, electronegativity, etc., and the behaviour of these factors towards coupling constant is reported here.



7.25.1 Vicinal Coupling (J_{vic})

(a) Effect of Dihedral Angle The vicinal coupling is very sensitive to the dihedral angle φ between the planes containing the protons and obeys the relation called *Karplus equation*:

$$J_{\text{HH}'} = A + B \cos \varphi + C \cos 2\varphi \quad (7.46)$$

where A , B and C are constants.

$$\begin{aligned} \text{or} \quad J_{\text{HH}'} &= 8.5 \cos^2 \varphi - 0.28, & 0 \leq \varphi \leq 90 \\ &= 9.5 \cos^2 \varphi - 0.28, & 90 \leq \varphi \leq 180 \end{aligned} \quad (7.47)$$

The behaviour of $J_{\text{HH}'}$ with φ is shown in Fig. 7.23 which shows that $J_{\text{HH}'}$ (transplanar protons, $\varphi = 180^\circ$) $>$ $J_{\text{HH}'}$ (cis-coplanar protons) $>$ $J_{\text{HH}'}$ ($\varphi = 90^\circ$).

Equation 7.47 when applied to the chair form of cyclohexane indicates

$$J_{\text{aa}} (\varphi_{\text{aa}} = 180^\circ) = 9 \text{ Hz} > J_{\text{ae}} (\varphi_{\text{ae}} = 60^\circ) = 1.8 \text{ Hz} = J_{\text{ee}} (\varphi_{\text{ee}} = 60^\circ) = 1.8 \text{ Hz}$$

The observed values of J for cyclohexane in the chair form are: $J_{\text{aa}} = 10$ –13 Hz, $J_{\text{ae}} = J_{\text{ee}} = 2.5$ Hz. A modified version of the Karplus equation when applied to vicinal coupling in olefins, $\text{H}-\text{C}=\text{C}-\text{H}'$ shows, that $J_{\text{HH}'}$ (*cis* $\varphi = 0$) $\text{h} = 7$ –11 Hz $>$ $J_{\text{HH}'}$ (*trans*, $\varphi = 180^\circ$) = 12.18 Hz.

(b) Effect of Electronegativity In a freely rotating alkyl chain, $\text{CH}_3\text{CH}_2\text{CH}_2\text{X}$, where X is an electronegative substituent atom, i.e. X = Cl, F, etc., the behaviour of J with electronegativity is governed by the equation

$$J_{\text{HH}'} = 7.9 - 0.7n \Delta\chi \quad (7.48)$$

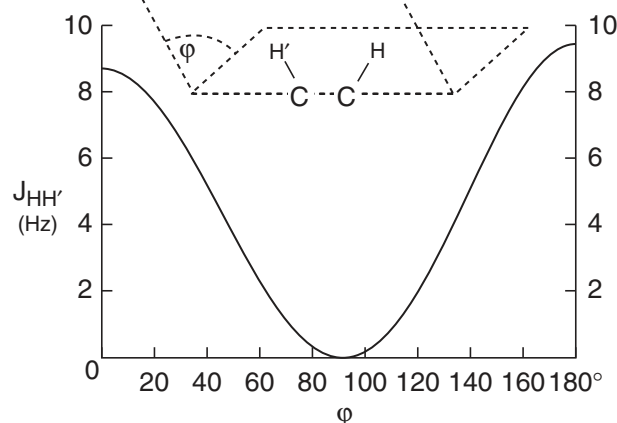


Fig. 7.23 Behaviour of coupling constant ($J_{\text{HH}'}$) with dihedral angle (φ).

Here, n is the number of substituent atoms, and $\Delta\chi$ is the difference between the electronegativities of the substituent atom and proton, i.e. $\Delta\chi = \chi_x - \chi_H$. Here, $\chi_H = 2.10$, and $\chi_{Cl} = 3.0$ and $\chi_F = 4.0$. The equation fairly holds good for di- and tri-substitution by electronegative atoms. According to this equation, the value of $J_{HH'}$ should decrease with the increase in the electronegativity of the substituent atoms in an alkyl chain provided their number is maintained constant ($n = \text{constant}$), e.g.

$$J_{HH'}(\text{FCH}_2\text{CH}_2\text{F}) < J_{HH'}(\text{ClCH}_2\text{CH}_2\text{Cl})$$

and

$$J_{HH'}(\text{FCH}_2\text{CHF}_2) < J_{HH'}(\text{ClCH}_2\text{CHCl}_2).$$

On the other hand, if $\Delta\chi$ is constant and the number of substituent atoms of the same kind are varied in the alkyl chain, the coupling constant decreases with the growth of substituent atoms, e.g.

$$J_{HH'}(\text{Cl}-\text{CH}_2-\text{CH}_2-\text{Cl}) < J_{HH'}(\text{Cl}-\text{CH}_2-\text{CH}-\text{Cl}_2)$$

$$J_{HH'}(\text{F}-\text{CH}_2-\text{CH}_2-\text{F}) < J_{HH'}(\text{F}-\text{CH}_2-\text{CH}-\text{F}_2)$$

Problem 7.8: With the aid of Eq. (7.48), compute the value of $J_{HH'}$ in (a) 1, 1, 2-trichloroethane, (b) 1, 1, 2-trifluoroethane, (c) 1, 2-dichloroethane, and (d) 1, 2-difluoroethane.

Solution We know that $\chi_F = 4.0$, $\chi_{Cl} = 3.0$ and $\chi_H = 2.10$.

By Eq. (7.48),

$$J_{HH'} = 7.9 - 0.7 n \Delta\chi$$

For (a) and (b); $n = 3$,

Hence,

$$J_{HH'}(1, 1, 2\text{-trichloroethane}) = 7.9 - 0.7 \times 3 (3.0 - 2.10) = 6.01 \text{ Hz}$$

The observed value is 6 Hz.

$$(b) J_{HH'}(1, 1, 2\text{-trifluoroethane}) = 7.9 - 0.7 \times 3 (4.0 - 2.10) = 3.91 \text{ Hz}$$

For (c) and (d); $n = 2$,

Therefore,

$$J_{HH'}(1, 2\text{-dichloroethane}) = 7.9 - 0.7 \times 2 (3.0 - 2.10) = 6.64 \text{ Hz}$$

$$J_{HH'}(1, 2\text{-difluoroethane}) = 7.9 - 0.7 \times 2 (4.0 - 2.10) = 5.24 \text{ Hz}$$

(c) Effect of Bond Length For constant bond angles and hybridisation, J_{vic} decreases as the C–C bond length increases, e.g. *cis* olefinic coupling constant follows the reverse trend of π -bond order, i.e.

$$J_{\text{ethylene}}(B.O = 1) = 11.5 \text{ Hz} > J_{\text{benzene}}(B.O = 0.67)$$

$$= 8.0 \text{ Hz} > J_{\text{naphthalene}} \left\{ \begin{array}{l} H_2 - H_3 \text{ B.O} = 0.60 \\ H_1 - H_2 \text{ B.O} = 0.72 \end{array} \right\} = \begin{array}{l} 6.4 \text{ Hz} \\ 8.1 \text{ Hz} \end{array}$$

$$> J_{\text{pyridine}} \left\{ \begin{array}{l} H_2 - H_3 \text{ B.O} = 0.70 \\ H_3 - H_4 \text{ B.O} = 0.64 \end{array} \right\} = \begin{array}{l} 5.5 \text{ Hz} \\ 7.5 \text{ Hz} \end{array}$$

(d) Effect of C–C–H Bond Angles The vicinal coupling constant is also very sensitive to the angles (θ and θ') between the olefinic protons and in cyclic olefins obeys the reverse trend of the bond angles, i.e.

$$\begin{aligned} J_{(\text{cyclopropene})} &= 0.5 - 2.0 \text{ Hz} \\ < J_{(\text{cyclobutene})} &= 2.5 - 4.0 \text{ Hz} \\ < J_{(\text{cyclopentene})} &= 5.1 - 7.0 \text{ Hz} \\ < J_{(\text{cyclohexene})} &= 8.8 - 10.5 \text{ Hz} \end{aligned}$$

In other words, as the ring size increases, the vicinal coupling also increases.

Problem 7.9: Predict the trend of vicinal coupling constants J_{23} in five-membered heterocyclic ring compounds, i.e. furan, pyrrole and thiophene. What will happen to J_{23} if carbon atom at the position 4 is replaced by nitrogen atom in the thiophene ring?

Solution C = C bond length in five-membered heterocyclics is almost constant whereas the angle θ at the position 2 decreases slightly and the electronegativity of the hetero atom also decreases as we move from furan (χ_O , 134°) $\rightarrow$ pyrrole (χ_N , 131°) $\rightarrow$ thiophene (χ_S , 128°). The vicinal coupling constant follows the opposite trend of electronegativity as well as of the bond angle. Therefore, J_{23} obeys the following order:

$$J_{23}(\text{furan}) < J_{23}(\text{pyrrole}) < J_{23}(\text{thiophene}).$$

When nitrogen is also present in the thiophene ring, the total electronegativity increases, consequently J_{23} decreases. These predictions conform to the observed values of J_{23} in the ring systems, i.e. $J_{23}(\text{furan}) = 1\text{--}2$ Hz, $J_{23}(\text{pyrrole}) = 2\text{--}3$ Hz, $J_{23}(\text{thiophene}) = 4.5\text{--}5.5$ Hz and $J_{23}(\text{thiophene with N at position 4}) = 3.4$ Hz.

7.25.2 Geminal Coupling (J_{gem})

The geminal coupling is negative and opposite to that of vicinal which is nearly always positive.

(a) Effect of Electronegativity Coupling constant of methylene protons (CH_2X) increases algebraically with the electronegativity of the atom X, i.e.

$$J_{\text{CH}_2\text{F}} (-9.6 \text{ Hz}) > J_{\text{CH}_2\text{OH}} (-10.8 \text{ Hz}) > J_{\text{CH}_4} (-12.4 \text{ Hz}).$$

Direct determination of $J_{\text{gem}}(\text{HH})$ is not possible in this system. However, by deuteration of one of the equivalent protons, $J_{\text{gem}}(\text{HD})$ is observed and the H-H coupling constant is then computed from the equation

$$J_{\text{HH}} = 6.55 J_{\text{HD}} \quad (7.49)$$

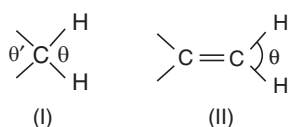
On the other hand, J_{gem} follows algebraically the reverse trend of electronegativity of a substituent X, attached to the carbon atom adjacent to the geminal protons in a series of monosubstituted 1, 1-dichloro-cyclopropanes, i.e. $J_{\text{gem}}(\text{OAc}) = -9.7 \text{ Hz} < J_{\text{gem}}(\text{COOH}) = -6.8 \text{ Hz} < J_{\text{gem}}(\text{Si}(\text{CH}_3)_4) = -4.9 \text{ Hz}$. The opposite effects of electronegativity of atom X on J_{gem} , in these two different types of systems indicate that changes in J_{gem} cannot simply be attributed to the direct inductive effect of the substituent.

(b) Effect of π -bonds The magnitude of coupling constant is very sensitive to the number of π -bonds adjacent to the methylene or methyl group and decreases algebraically as the number of π -bonds increases, e.g.

$$\begin{aligned} \text{CH}_4(0) &= -12.4 \text{ Hz} > \text{C}_6\text{H}_5-\text{CH}_3(1) = -14.5 \text{ Hz} > \text{CH}_3\text{CN}(2) \\ &= -16.2 \text{ Hz} > \text{CH}_2(\text{CN})_2(4) = -20.3 \text{ Hz} \end{aligned}$$

The quantities within brackets correspond to the number of π -bonds in the respective systems.

(c) Effect of Bond Angle The geminal coupling constant is very sensitive to the angle θ between the interacting geminal protons, i.e. (I) J_{gem} varies from 0 at 125° to 20 Hz at 105° . In cycloalkanes, when θ , i.e. ring size, decreases, θ increases, and consequently J_{gem} increases. Hence, $J_{\text{gem}}(\text{Cyclohexane}) = -(12\text{--}14) \text{ Hz} < J_{\text{gem}}(\text{Cyclopentane}) = -(10\text{--}14) \text{ Hz} < J_{\text{gem}}^*(\text{Cyclobutane}) = -(7\text{--}14) \text{ Hz} < J_{\text{gem}}(\text{Cyclopropane}) = -(4\text{--}9) < J_{\text{gem}}(\text{II}) = 0\text{--}3 \text{ Hz}$. The terminal methylene group in J_{gem} which carbon atom is sp^2 hybridised, $\theta = 120^\circ$. In strain-free cyclohexane and cyclopentane, the angle $\theta = 109^\circ$ is close to the tetrahedral angle in methane. Consequently, J_{gem} of these compounds is very close to that of methane. Further, when one of the carbon atoms in cycloalkanes ring is replaced by the oxygen atom then (i) J_{gem} also increases with decrease in ring size and even becomes positive for cyclopropane, and (ii) J_{gem} of the respective rings also increases as expected, since the coupling constant of methylene protons of a system RCH_2X increases algebraically with increasing electronegativity of the atom X.



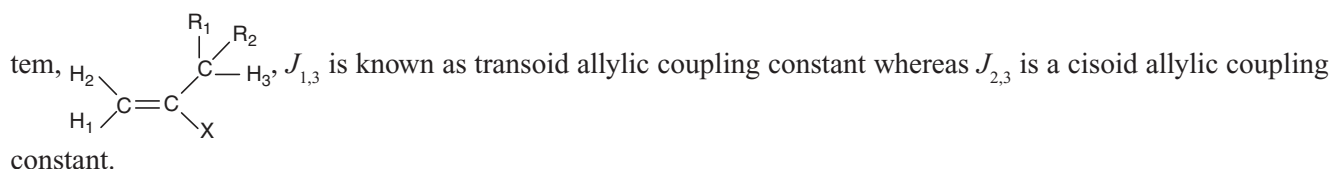
(d) Long-range Coupling Constant As mentioned earlier, in long range s - s interactions, the number of intervening bonds between the interacting protons is four or five and the coupling constant lies in the range 0–3 Hz. Long-range coupling occurs in substituted benzenes as well as in allylic and homoallylic systems.

(i) Substituted Benzenes The coupling constant in substituted benzenes $\left(\begin{array}{c} \text{H}_p \quad \text{H}_a \\ | \quad | \\ \text{C}_6\text{H}_4 \\ | \quad | \\ \text{H}_m \quad \text{H}_o \end{array} \right)$ decreases as the number of intervening bonds between the interacting protons increases.

Thus

$$J_{H(Ao)} (\text{ortho}) = 6-10 \text{ Hz} > J_{H(Am)} (\text{meta}) = 1-3 \text{ Hz} > J_{H(Ap)} = 0-1 \text{ Hz}.$$

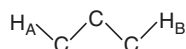
(ii) **Allylic Coupling** Allylic ($\text{H}-\text{C}-\text{C}=\text{C}-\text{H}$) coupling constants are around 0–3 Hz. In an unsaturated system,



(iii) **Homoallylic Coupling** Homoallylic ($\text{H}-\text{C}-\text{C}-\text{C}=\text{C}-\text{H}$) couplings are usually negligible and may have value about 1.6 Hz.

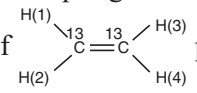
(iv) **Coupling through Conjugated Polyalkyne Chains** This may occur even through nine bonds.

(v) J_{AB} **Coupling Constant (≈ 7 Hz)** in the bicyclo [2.1.1] hexane system, is attributed to the 'W conformation' of the four σ bonds between H_A and H_B i.e.



7.26 CONCEPT OF MAGNETICALLY EQUIVALENT PROTONS

The nuclei which are indistinguishable in all their NMR interactions and can be permuted at will without changing the physical state of the spin system are said to be magnetically equivalent. In other words, we can say that the magnetically equivalent nuclei have the same chemical shift and the same $s-s$ coupling constant with every other nucleus that does not have the same chemical shift, e.g. all the protons of ethylene ($\text{H}_2\text{C}=\text{CH}_2$) are magnetically equivalent. The NMR spectrum will exhibit only one sharp resonance line, centered at the ethylene proton Larmor frequency. However, the protons of ^{13}C -ethylenes ($\text{H}_2^{13}\text{C}=\text{CH}_2$) are not magnetically equivalent. The asymmetric isotopic substitution reduces the symmetry of the molecule, since the directly bonded $=^{13}\text{CH}_2$ protons belong to one group of symmetrically equivalent nuclei and the vicinal protons ($=\text{CH}_2$) belong to the second group of this type. The effect of ^{13}C isotope on proton chemical shift is very small, i.e. $\pm 15 \times 10^{-4}$ ppm. So, all the four protons will show one absorption peak. In spite of this, protons are not magnetically equivalent since ^{13}C ($I = 1/2$) affects the coupling constants of the two types of protons, i.e.

$J(=^{13}\text{CH}_2) = 156.4 \text{ Hz}$ and $J(=\text{CH}_2) = 2.5 \text{ Hz}$. In case of  protons, H(1) and H(2) are not mag-

netically equivalent with protons H(3) and H(4), because these two pairs of nuclei are unequally coupled to a particular ^{13}C nucleus. By definition, protons H_1 and H_2 will also not form a group of magnetically equivalent nuclei since $J_{H(1),H(4)} (19 \text{ Hz}) \neq J_{H(2),H(4)} (11.7 \text{ Hz})$. Two protons of $\text{F}_2\text{C}=\text{CH}_2$ are magnetically non-equivalent since $J_{\text{HF}} (\text{cis}) \neq J_{\text{HF}} (\text{trans})$. All the three protons of methyl the group of ethanol are magnetically equivalent if

the rotation about the C-C bond is rapid. On the other hand, two protons of  are not equivalent even

if the rate of rotation about the C-C bond is fast since both of them have different atoms as spatial neighbours. Magnetic equivalence which arises due to free rotation about a single bond is temperature dependent. At room temperature, all the three protons of CF_3-CH_3 are magnetically equivalent since the internal rotation about the C-C bond produces averaged H-F spin couplings that are the same for all the possible HF pairs. However at low temperatures, one particular rotational conformer of the molecule is in the frozen state. Thus, the three protons and the fluorine nuclei would not form groups of magnetically equivalent nuclei since the vicinal H-F spin interactions depend upon the dihedral F-C-C-H angle. None of the protons of pyridine are magnetically equivalent since $J_{23} \neq J_{36}$, $J_{25} \neq J_{56}$, etc.

Protons of furan and thiofuran are also non-equivalent since they have different coupling constants (see Table 7.6).

7.27 MECHANISM OF S-S INTERACTION

In order to understand the mechanism of *s-s* interaction, consider a molecule with two different interacting protons, say *A* and *B*. The proton *A* will have only two orientations in the external magnetic field, i.e. parallel $\left(M_1 = +\frac{1}{2}\right)$ and antiparallel $\left(M_1 = -\frac{1}{2}\right)$ to the applied field. The proton *B* thus will experience two fields ($H_{eff} - x$) and ($H_{eff} + x$) where x is the correction due to the magnetic moment or field due to the nucleus *A*. Consequently, the signal of the proton *B* will appear as a doublet. Similarly, the signal of the proton *A* will also split into two lines of equal intensity. This may be represented in terms of spin and spin quantum number in the tabular form as follows:

M_I	Proton A	Degeneracy	M_I	Proton B	Degeneracy
$+\frac{1}{2}$	α	1	$+\frac{1}{2}$	α	1
$-\frac{1}{2}$	β	1	$-\frac{1}{2}$	β	1

For protons *A* and *B*, $I = 1/2$, $M_1 = (2I + 1) = 2$ and the states corresponding to $M_1 = 2$ are $+1/2$ and $-1/2$.

Thus, the spectrum of *AB* system consists of two doublets, each of equal intensity, since the statistical weight of $+1/2$ and $-1/2$ states is equal.

Let us now consider the *s-s* interaction in HD molecule, Here, we know that $I(H) = \frac{1}{2}$ and $I(D) = 1$. Hence, $M_I(H) = +\frac{1}{2}, -\frac{1}{2}$ and $M_I(D) = +1, 0, -1$.

The possible combinations of spin orientations of H and D in HD are

M_I	Proton A	Degeneracy	M_I	Deuteron	Degeneracy
$+\frac{1}{2}$	α	1	$+1$	$\alpha\alpha$	1
$-\frac{1}{2}$	β	1	0	$\alpha\beta, \beta\alpha$	2
			-1	$\beta\beta$	1

Thus, the signal due to a proton will consist of a triplet with intensity ratio 1 : 2 : 1 while the deuteron will be a 1 : 1 doublet. The values of net spin moment '0' are two times more probable than the values of $+1$ and -1 in D. On the other hand, the probability of $+1/2$ and $-1/2$ states of *H* is equal.

Let us now apply the mechanism of *s-s* interaction to $C_2H_5NO_2$. It contains two different groups of magnetically equivalent protons, i.e. $-CH_3$ and $-CH_2$. Thus, in this case, $I(CH_3) = 3/2$; $I(CH_2) = 1$. Consequently, $\sum M_I(CH_3) = 2I + 1 = 2 \times 3/2 + 1 = 4$; $+3/2, +1/2, -1/2, -3/2$ and $\sum M_I(CH_2) = 2I + 1 = 2 \times 1 + 1 = 3$; $+1, 0, -1$. The possible combinations of spin and spin quantum number for $-CH_2$ and $-CH_3$ groups are:

$\sum M_I$	$-CH_2$	Degeneracy	$\sum M_I$	$-CH_3$	Degeneracy
$+1$	$\alpha\alpha$	1	$\frac{3}{2}$	$\alpha\alpha\alpha$	1
0	$\alpha\beta, \beta\alpha$	2	$\frac{1}{2}$	$\alpha\alpha\beta, \alpha\beta\alpha, \beta\alpha\alpha$	3
-1	$\beta\beta$	1	$-\frac{1}{2}$	$\beta\beta\alpha, \beta\alpha\beta, \alpha\beta\beta$	3
			$-\frac{3}{2}$	$\beta\beta\beta$	1

Thus, the signal due to protons of $-\text{CH}_3$ group will split into triplet with intensity ratio of 1 : 2 : 1 while that of $-\text{CH}_2$ group will appear as a quartet with intensity ratio of 1 : 3 : 3 : 1.

Based on the above pattern of splitting of NMR signal into multiplets of same or varying intensity, some empirical rules are deduced to interpret the first-order NMR spectra, $|J| < \nu \delta$. The theory of first and different ordered NMR spectra will be discussed later on.

(a) Rule 1 Let n_A , n_B and n_C be the number of magnetically equivalent protons on atoms A , B and C respectively in a hypothetical chemical molecule $A-B-C$. If these three types of protons are magnetically non-equivalent, i.e. they are in different chemical environments, the multiplicity of protons on $A = (n_B + 1)$ on $B = (n_A + 1)(n_C + 1)$ and on $C = (n_B + 1)$. If the neighbouring protons of B , i.e. A and C are magnetically equivalent, the multiplicity of the signal is given by $(n_A + n_C + 1)$.

(b) Rule 2 The relative intensities or areas of peaks that are symmetrical around the mid-point of the multiplet are proportional to the coefficients of the binomial expansion

$$(1+x)^n = 1 + nx + \frac{n(n-1)}{2}x^2 + \frac{n(n-1)(n-2)}{6}x^3 + \dots$$

Here, n is the number of protons on the atom adjacent to atom x .

Problem 7.10: Deduce theoretically the NMR spectra of the following: (a) $\text{CH}_3-\text{CHCl}-\text{CH}_3$; (b) $\text{CH}_2\text{Br}-\text{CHBr}_2$; (c) $\text{ClCH}_2\text{CH}_2\text{Cl}$; and (d) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$.

Solution

(a) In $\text{CH}_3-\text{CHCl}-\text{CH}_3$, both the CH_3 groups are magnetically equivalent. Thus, the signal due to proton of CH group will appear as a $[(6 + 1) = 7]$ septet with intensity ratio 1 : 7 : 21 : 35 : 21 : 7 : 1 while that of protons of end CH_3 groups will be a doublet (1 : 1). CH protons being deshielded will be observed at higher δ values as compared to protons of CH_3 groups, i.e. $\delta_{\text{CH}} > \delta_{\text{CH}_3}$.

(b) In $\text{CH}_2\text{Br}-\text{CHBr}_2$, protons of $-\text{CH}_2$ and $-\text{CH}$ groups are in different chemical environments, hence they are magnetically non-equivalent. Thus the signal due to protons of $-\text{CH}_2$ group will appear as a doublet (1 : 1) while that of $-\text{CH}$ group will be a triplet (1 : 2 : 1). Protons of $-\text{CH}$ group being highly deshielded as compared to protons of $-\text{CH}_2$ group, will be observed at higher δ value, i.e. $\delta_{\text{CH}} > \delta_{\text{CH}_2}$.

(c) In $\text{ClCH}_2\text{CH}_2\text{Cl}$, the spin of protons on both the carbon atoms is the same, i.e. $\frac{1}{2} + \frac{1}{2} = 1$, hence they are magnetically equivalent. Consequently, a single line spectrum without any multiplicity will be observed.

(d) Protons of $-\text{CH}_2$ and $-\text{CH}_3$ groups of identical ethyl groups of $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ are magnetically non-equivalent. Therefore, the signal of $-\text{CH}_2$ protons will consist of a quartet (1 : 3 : 3 : 1) while that of $-\text{CH}_3$ protons will be triplet with intensity ratio 1 : 2 : 1. Protons of $-\text{CH}_2$ group being highly deshielded as compared to protons of $-\text{CH}_3$ group, will be observed at low field, i.e. high δ values, or $\delta_{\text{CH}_2} > \delta_{\text{CH}_3}$.

Problem 7.11: What will be the number of signals and their intensity ratio in (a) toluene, (b) *p*-xylene, and (c) mesitylene?

Solution

(a) There are two groups of magnetically non-equivalent protons in toluene, i.e. three methyl protons and five benzene protons. Thus, the NMR spectrum of toluene will exhibit two signals, one corresponding to methyl protons and the other corresponding to benzene protons. Since the intensity of an NMR signal is directly proportional to the number of protons that cause it, so the ratio of areas under these signals will be 3($-\text{CH}_3$) : 5($-\text{C}_6\text{H}_5$). The methyl protons will be observed at lower δ values than the protons of the benzene ring, i.e. $\delta(-\text{CH}_3) < \delta(-\text{C}_6\text{H}_5)$.

(b) *p*-xylene will exhibit two lines spectrum, The ratio of areas under these two lines will be 2 ($-\text{C}_6\text{H}_4$) : 3 ($-\text{CH}_3-\text{CH}_3$) and $\delta(-\text{C}_6\text{H}_4) > \delta(-\text{CH}_3)$.

(c) Two bands corresponding to methyl and benzene protons will be observed in the PMR spectrum of mesitylene. The ratio of areas of these two bands will be $3(-\text{CH}_3)_3 : 1(-\text{C}_6\text{H}_3)$, and $\delta(-\text{C}_6\text{H}_3) > \delta(-\text{CH}_3)$.

Problem 7.12: Predict the number of signals in (a) ethylchloride, (b) isopropyl chloride, (c) *n*-propylchloride, (d) isobutylene, (e) 2-bromopropane, (f) vinyl chloride, (g) methylcyclopropane, and (h) 1,2-dichloropropane.

Solution According to the concept of magnetic equivalence of nuclei, the number of signals in (a), (b), (d) and (e) is two while in (c), (f), (g) and (h) is three, three, four, and four respectively.

Problem 7.13: Predict and explain the NMR spectra of ethanol in the presence and absence of a mineral acid or a base and compare it with the observed spectra displayed in Fig. 7.24.

Solution Hydroxyl protons in ethanol ($\text{CH}_3-\text{CH}_2-\text{OH}$) are hydrogen bonded, i.e. $\text{O}-\text{H}\cdots\text{O}$. In the presence of a mineral acid or a base, the movement of H-bonded proton gets accelerated and becomes too fast to be experienced by the methylene group ($-\text{CH}_2$). So in such a situation, the signal corresponding to the protons of methylene group will appear as a quartet ($3 + 1 = 4$) with an intensity ratio of $1 : 3 : 3 : 1$ due to the coupling of $-\text{CH}_2$ group with the protons of CH_3 group. The signal of the methyl group will consist of a ($2 + 1 = 3$) triplet with an intensity ratio of $1 : 2 : 1$ due to the interaction of protons of $-\text{CH}_3$ group with that of $-\text{CH}_2$ group. A singlet is expected corresponding to the proton of $-\text{OH}$ group. Due to the inductive effect of $-\text{OH}$ group, the signal corresponding to a methyl group will appear up-field as compared to that of methylene group and $-\text{OH}$ group, i.e. $\delta_{\text{CH}_3} < \delta_{\text{CH}_2} < \delta_{\text{OH}}$. The same has been observed experimentally [Fig. 7.24(a)]. In the absence of a mineral acid or a base, the spins of protons of $-\text{CH}_2$ group and of $-\text{OH}$ group interact with one another. Consequently, the $-\text{OH}$ group will appear as a ($2 + 1 = 3$) triplet with intensity ratio of $1 : 2 : 1$ whereas an $[(3 + 1)(1 + 1) = 8]$ eight-line multiplet is expected for the protons of $-\text{CH}_2$ group. However, at moderate resolution a quintet has been observed experimentally [Fig. 7.24 (b)].

These rules are also equally applicable to nuclei with spin $I = \frac{1}{2}$, i.e. ^{13}C , ^{31}P , ^{19}F , etc., other than protons in *AB* and *ABC* (where *A* and *C* are magnetically equivalent groups) types of systems, e.g. ^{31}P -NMR spectrum of $\text{P}(\text{OCH}_3)_3$ consists of a ten-line multiplet with intensity ratio $1 : 9 : 36 : 84 : 126 : 126 : 84 : 36 : 9 : 1$ while that

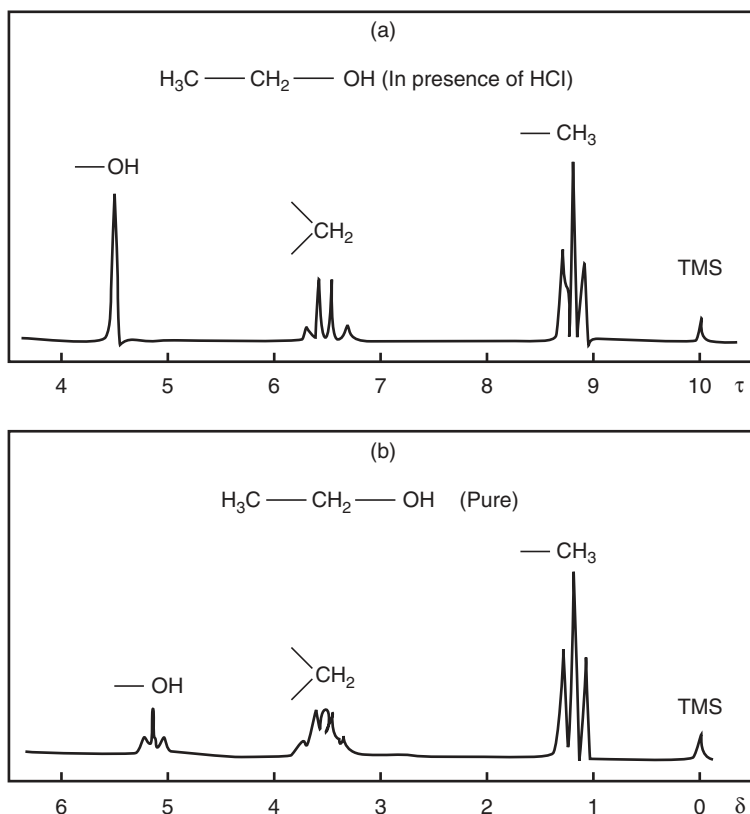


Fig. 7.24 NMR spectrum of ethanol (a) in presence of hydrochloric acid, and (b) in absence of hydrochloric acid.

of triphosphosphate is a doublet (1 : 1) and a triplet (1 : 2 : 1). ^{13}C spectrum of $(\text{CH}_3)_2\text{O}$ is a quartet with intensity ratio 1 : 3 : 3 : 1 while that of $^{13}\text{C}_6\text{H}_6$ is a doublet (1 : 1).

7.28 QUANTUM MECHANICS OF S-S INTERACTION

In the presence of an external magnetic field of strength H , the various magnetic interactions are given by the Hamiltonian

$$H = H_{\text{zeeman}} + H_{d-d} + H_{s-s} \quad (7.50)$$

Here, H_{Zeeman} represents the interaction of nuclear spin with the external magnetic field and is given by

$$H_{\text{Zeeman}} = -g_N \beta_N I_z(A) H (1 - \sigma_A) - g_N \beta_N I_z(B) H (1 - \sigma_B) \quad (7.51)$$

where $I_z(A)$ and $I_z(B)$ are the nuclear spin quantum numbers of nuclei A and B in the spin system AB in the direction of the applied magnetic field, i.e. Z . The Hamiltonian H_{s-s} represents the interaction between nuclear spins I_A and I_B and is represented by

$$H_{s-s} = J_{AB} I(A) I(B) \quad (7.52)$$

The interaction between the two magnetic dipoles is represented by the Hamiltonian

$$H_{d-d} = g_N^2 \beta_N^2 \left[\frac{I(A)I(B)}{r^3} - \frac{3(I(A)r)(I(B)r)}{r^5} \right] \quad (7.53)$$

where the terms and symbols have their usual meanings. In case of liquids, the $d-d$ interactions averages out to zero, i.e. $H_{d-d} = 0$.

Thus, Eq. (7.50) can be written as

$$H = -g_N \beta_N I_z(A) H (1 - \sigma_A) - g_N \beta_N I_z(B) H (1 - \sigma_B) + J_{AB} I(A) I(B) \quad (7.54)$$

In frequency units, Eq. (7.54) becomes

$$H = -\nu(1 - \sigma_A) I_z(A) - \nu(1 - \sigma_B) I_z(B) + J_{AB} I(A) I(B) \quad (7.55)$$

where

$$I(A)I(B) = I_x(A) I_x(B) + I_y(A) I_y(B) + I_z(A) I_z(B) \quad (7.56)$$

The energy of various magnetic levels due to $s-s$ interaction can be worked out from the Schrodinger wave equation

$$H\psi = E\psi \quad (7.57)$$

where ψ is the exact wave function and can be written as a linear combination of the basic spin function ϕ , i.e.

$$\psi = \sum_i C_i \phi_i \quad (7.58)$$

For a two-nuclei spin system having $I(A) = I(B) = \frac{1}{2}$, the four possible combinations of spins are

$$\left. \begin{aligned} \phi_1 &= \alpha(A)\alpha(B), \phi_2 = \alpha(A)\beta(B) \\ \phi_3 &= \beta(A)\alpha(B), \phi_4 = \beta(A)\beta(B) \end{aligned} \right\} \quad (7.59)$$

If Ψ is normalised,

$$E = \int \psi H \psi d\tau \quad (7.60)$$

E is determined by solving the determinant (7.62) with the aid of raising and lowering ladder operators I^+ and I^- respectively given by

$$\begin{aligned} I^+ &= I_x + iI_y \\ I^- &= I_x - iI_y \end{aligned} \quad (7.61)$$

The determinant is

$$\begin{vmatrix} H_{11} - E & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} - E & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} - E & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} - E \end{vmatrix} = 0. \quad (7.62)$$

The properties of ladder operators are

$$I^+ \alpha = 0, I^+ \beta = \alpha.$$

$$I^- \alpha = \beta, I^- \beta = 0. \quad (7.63)$$

Consequently,

$$I(A+)I(B-) = \{I_x(A)I_x(B) + I_y(A)I_y(B)\} + i\{I_y(A)I_x(B) - I_x(A)I_y(B)\} \quad (7.64)$$

$$I(A-)I(B+) = \{I_x(A)I_x(B) + I_y(A)I_y(B)\} - i\{I_y(A)I_x(B) - I_x(A)I_y(B)\} \quad (7.65)$$

and

$$I_x(A)I_x(B) + I_y(A)I_y(B) = \frac{1}{2}[I(A+)I(B-) + I(A-)I(B+)] \quad (7.66)$$

Combining Eqs (7.55), (7.56) and (7.66), we get

$$\begin{aligned} H = & -v(1 - \sigma_A)I_z(A) - v(1 - \sigma_B)I_z(B) \\ & + J_{AB} \left[I_z(A)I_z(B) + \frac{1}{2}\{I(A+)I(B-) + I(A-)I(B+)\} \right] \end{aligned} \quad (7.67)$$

If ϕ_i and ϕ_j have different values of M_l then

$$\int \phi_i H \phi_j d\tau = \int \phi_j H \phi_i d\tau = 0 \quad (7.68)$$

The various H_{ij} terms of determinant (7.62) are evaluated as

$$H_{11} = -\frac{v}{2}x_A - \frac{v}{2}x_B + \frac{J_{AB}}{4}$$

$$H_{22} = +\frac{v}{2}x_A - \frac{v}{2}x_B - \frac{J_{AB}}{4}$$

$$H_{33} = -\frac{v}{2}x_A + \frac{v}{2}x_B - \frac{J_{AB}}{4}$$

$$H_{44} = \frac{v}{2}x_A + \frac{v}{2}x_B + \frac{J_{AB}}{4}$$

$$H_{23} = H_{32} = \frac{J_{AB}}{2}$$

other terms, $H_{12}, H_{21}, H_{13}, H_{31}, H_{14}, H_{41}, H_{24}, H_{42}, H_{34}$ and H_{43} are all zero.

Here, $1 - \sigma_A = x_A$ and $1 - \sigma_B = x_B$

Thus, the determinant (7.62) becomes

$$\begin{vmatrix} -\frac{v}{2}x_A - \frac{v}{2}x_B + \frac{J_{AB}}{4} - E & 0 & 0 & 0 \\ 0 & \frac{v}{2}x_A - \frac{v}{2}x_B - \frac{J_{AB}}{4} - E & 0 & 0 \\ 0 & 0 & \frac{J_{AB}}{2} & 0 \\ 0 & 0 & 0 & \frac{J_{AB}}{2} \end{vmatrix}$$

$$\begin{vmatrix} 0 & 0 \\ \frac{J_{AB}}{2} & 0 \\ -\frac{\nu}{2}x_A + \frac{\nu}{2}x_B - \frac{J_{AB}}{4} - E & 0 \\ 0 & \frac{\nu}{2}x_A + \frac{\nu}{2}x_B + \frac{J_{AB}}{4} - E \end{vmatrix} = 0 \quad (7.69)$$

Solution of determinant (7.69) gives

$$E_1 = \nu \left(-1 + \frac{\sigma_A}{2} + \frac{\sigma_B}{2} \right) + \frac{J_{AB}}{4} \quad (7.70)$$

$$E_4 = \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{J_{AB}}{4} \quad (7.71)$$

E_2 and E_3 are determined from the solution of the determinant (7.72).

$$\begin{vmatrix} \frac{\nu}{2}x_A - \frac{\nu}{2}x_B - \frac{J_{AB}}{4} - E & \frac{J_{AB}}{2} \\ \frac{J_{AB}}{2} & -\frac{\nu}{2}x_A + \frac{\nu}{2}x_B - \frac{J_{AB}}{4} - E \end{vmatrix} = 0 \quad (7.72)$$

$$E_2 = -\frac{J_{AB}}{4} - \frac{1}{2} \sqrt{\nu^2 \delta_{AB}^2 + J_{AB}^2} \quad (7.73)$$

$$E_3 = -\frac{J_{AB}}{4} + \frac{1}{2} \sqrt{\nu^2 \delta_{AB}^2 + J_{AB}^2} \quad (7.74)$$

where,

$$\delta_{AB} = x_B - x_A = \sigma_A - \sigma_B$$

Using the expansion, $(1+x)^{1/2} = 1 + \frac{x}{2} + \frac{x^2}{4} + \dots$, Eqs (7.73) and (7.74) may be written as

$$E_2 = -\frac{J_{AB}}{4} - \frac{1}{2} \nu \delta_{AB} \left[1 + \frac{J_{AB}^2}{2\nu^2 \delta_{AB}^2} + \dots \right] \quad (7.75)$$

and

$$E_3 = -\frac{J_{AB}}{4} + \frac{1}{2} \nu \delta_{AB} \left[1 + \frac{J_{AB}^2}{2\nu^2 \delta_{AB}^2} + \dots \right] \quad (7.76)$$

The negative and positive signs in the energy expressions correspond to attraction and repulsion respectively.

To evaluate the perturbation energy due to s - s interactions in the various levels, we proceed as follows

(i) For a bare nuclei, $\sigma = 0$, $J_{AB} = 0$

$\therefore$

$$E_1 = -\nu$$

$$E_4 = \nu \quad (7.77)$$

$$E_2 = 0$$

$$E_3 = 0.$$

(ii) In case there is no s - s interaction, the coupling constant J_{AB} becomes zero. This is called zero-order interaction. Thus, the energy of the magnetic levels becomes

$$E_1 = \nu \left(-1 + \frac{\sigma_A}{2} + \frac{\sigma_B}{2} \right)$$

$$E_4 = v \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) \quad (7.78)$$

$$E_2 = \frac{-v\delta_{AB}}{2} = -v \left(\frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right)$$

$$E_3 = \frac{v\delta_{AB}}{2} = v \left(\frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right)$$

Thus, the perturbation with respect to bare nuclei, when $J_{AB} = 0$ is given by

$$\begin{aligned} \delta E_1 &= \frac{1}{2}v(\sigma_A + \sigma_B) \\ \delta E_4 &= -\frac{1}{2}v(\sigma_A + \sigma_B) \\ \delta E_2 &= -\frac{1}{2}v(\sigma_A - \sigma_B) \\ \delta E_3 &= \frac{1}{2}v(\sigma_A - \sigma_B) \end{aligned} \quad (7.79)$$

- (iii) When $|J_{AB}| < v\delta_{AB}$, there is weak interaction between the nuclei A and B and the system is known as AX instead of AB . The spectra corresponding to this case are called *first-order spectra*. For a rigorous first-order spectra, $J_{AB}/v\delta_{AB} < 0.05$. When the nuclei are strongly coupled, $|J_{AB}| > v\delta_{AB}$ and the spin system is said to be AB . The energies of the magnetic levels for an AX spin system are given by

$$\begin{aligned} E_1 &= v \left(-1 + \frac{\sigma_A}{2} + \frac{\sigma_B}{2} \right) + \frac{J_{AB}}{4} \\ E_4 &= v \left(+1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{J_{AB}}{4} \\ E_2 &= -\frac{J_{AB}}{4} - \frac{1}{2}v\delta_{AB} = -\frac{J_{AB}}{4} - \frac{1}{2}v(\sigma_A - \sigma_B) \\ E_3 &= -\frac{J_{AB}}{4} + \frac{1}{2}v\delta_{AB} = -\frac{J_{AB}}{4} + \frac{1}{2}v(\sigma_A - \sigma_B) \end{aligned} \quad (7.80)$$

The perturbations relative to bare nucleus in this case are

$$\begin{aligned} \delta E_1 &= v \left(\frac{\sigma_A}{2} + \frac{\sigma_B}{2} \right) + \frac{J_{AB}}{4} \\ \delta E_4 &= -v \left(\frac{\sigma_A}{2} + \frac{\sigma_B}{2} \right) + \frac{J_{AB}}{4} \\ \delta E_2 &= -\frac{J_{AB}}{4} - \frac{1}{2}v\delta_{AB} \\ \delta E_3 &= -\frac{J_{AB}}{4} + \frac{1}{2}v\delta_{AB} \end{aligned} \quad (7.81)$$

- (iv) When $|J_{AB}| \sim v\delta_{AB}$ or $|J_{AB}| \sim v(\sigma_A - \sigma_B)$, the s - s interaction is of second order and the energies of magnetic levels are

$$E_1 = v \left(-1 + \frac{\sigma_A}{2} + \frac{\sigma_B}{2} \right) + \frac{J_{AB}}{4}$$

$$E_4 = \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{J_{AB}}{4} \quad (7.82)$$

$$E_2 = -\frac{J_{AB}}{4} - \frac{1}{2}\nu(\sigma_A - \sigma_B) - \frac{J_{AB}^2}{4\nu\delta_{AB}}$$

$$E_3 = -\frac{J_{AB}}{4} + \frac{1}{2}\nu(\sigma_A - \sigma_B) + \frac{J_{AB}^2}{4\nu\delta_{AB}}$$

The perturbations with respect to bare nucleus/first-order interactions are

$$\begin{aligned} \delta E_1 &= \nu \left[\frac{\sigma_A + \sigma_B}{2} \right] + \frac{J_{AB}}{4} / 0 \\ \delta E_4 &= -\nu \left[\frac{\sigma_A + \sigma_B}{2} \right] + \frac{J_{AB}}{4} / 0 \end{aligned} \quad (7.83)$$

$$\delta E_2 = -\frac{J_{AB}}{4} - \frac{1}{2}\nu[\sigma_A - \sigma_B] - \frac{J_{AB}^2}{4\nu\delta_{AB}} / -\frac{J_{AB}^2}{4\nu\delta_{AB}}$$

$$\delta E_3 = -\frac{J_{AB}}{4} + \frac{1}{2}\nu[\sigma_A - \sigma_B] + \frac{J_{AB}^2}{4\nu\delta_{AB}} / \frac{J_{AB}^2}{4\nu\delta_{AB}}$$

The perturbations with respect to bare nucleus in the zeroth-, first- and second-order interactions/spectra are shown in Fig. 7.25(a). In the second-order perturbation case, the energy states originally corresponding to $\alpha\beta$ and $\beta\alpha$ are mixed and are represented by linear combinations of the type $(\alpha\beta \pm \beta\alpha)$.

(a) Selection Rule The transition between the magnetic levels n and m is induced by applying radio frequency field (H_{rf}) to the sample placed in the external magnetic field of strength H . The radio frequency field is adjusted to oscillate in the direction (X) which is perpendicular to the direction of the applied field $H(Z)$. The interaction between the field, H_{rf} and nuclear magnetic moment is given by

$$H' = \mu_x H_{rf} \quad (7.84)$$

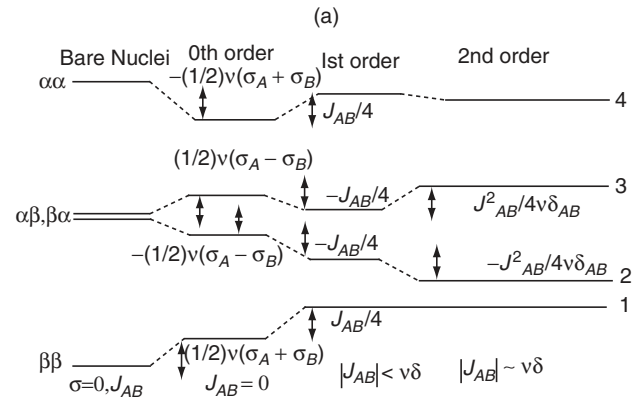


Fig. 7.25 (a) The zeroth-, first-, and second-order perturbation of an AB system. Transitions are: $1 \rightarrow 2$, $1 \rightarrow 3$; $2 \rightarrow 4$; $3 \rightarrow 4$.

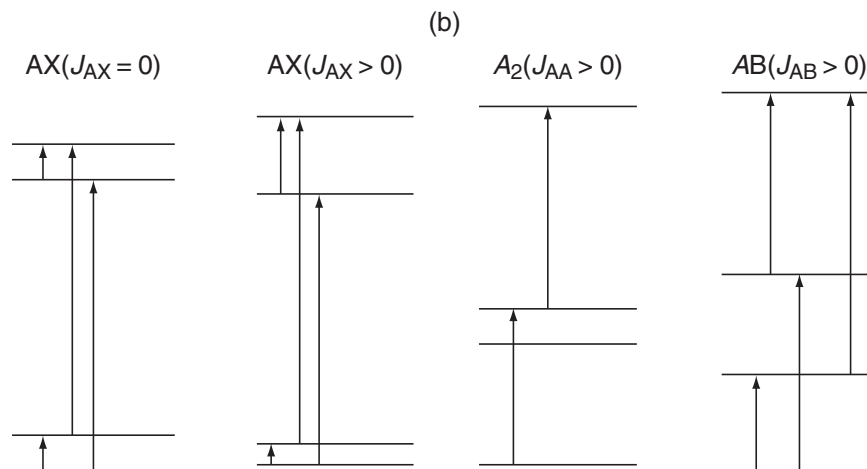


Fig. 7.25 (b) The four energy levels of a two-spin system for various relative values of $\nu(\sigma_A - \sigma_B)$ and J . $\nu|\sigma_A - \sigma_B| \gg J$ for AX system; $\nu|\sigma_A - \sigma_B| = 0$ for A_2 and $\nu|\sigma_A - \sigma_B| \approx J$ for AB.

where, μ_x is the component of nuclear magnetic moment μ_1 in the X -direction. The transition probability is proportional to

$$\left[\int \psi_n (\mu_x H_{rf}) \psi_m d\tau \right]^2 \quad (7.85)$$

Since, $\mu_x = I_x \hbar \gamma$ (7.86)

Therefore, transition probability is proportional to simply

$$(\psi_n I_x \psi_m d\tau)^2 \quad (7.87)$$

Taking $I_x = \frac{I^+ + I^-}{2}$, the solution of the integral results into the selection rule

$$\Delta M_I = \pm 1 \quad (7.88)$$

(b) Transition Between Allowed Energy Levels (Spectrum of AB System) According to the selection rule $\Delta M_I = \pm 1$, the permissible transitions (in frequency units) are

Eqs. (7.75–7.70)

$$\nu_{12} = E_2 - E_1 = \frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) - \frac{1}{2} \nu \delta_{AB} \left(1 + \frac{J_{AB}^2}{2\nu^2 \delta_{AB}^2} + \dots \right) \quad (7.89)$$

Eqs. (7.76–7.70)

$$\nu_{13} = E_3 - E_1 = -\frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{1}{2} \nu \delta_{AB} \left(1 + \frac{J_{AB}^2}{2\nu^2 \delta_{AB}^2} + \dots \right) \quad (7.90)$$

Eqs. (7.71–7.75)

$$\nu_{24} = E_4 - E_2 = \frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{1}{2} \nu \delta_{AB} \left(1 + \frac{J_{AB}^2}{2\nu^2 \delta_{AB}^2} + \dots \right) \quad (7.91)$$

Eqs. (7.71–7.76)

$$\nu_{34} = E_4 - E_3 = \frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) - \frac{1}{2} \nu \delta_{AB} \left(1 + \frac{J_{AB}^2}{2\nu^2 \delta_{AB}^2} + \dots \right) \quad (7.92)$$

Now, when

(i) $J_{AB} = 0$

$$\begin{aligned} \nu_{12} &= \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) - \frac{1}{2} \nu \delta_{AB} \\ \nu_{13} &= \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{1}{2} \nu \delta_{AB} \\ \nu_{24} &= \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{1}{2} \nu \delta_{AB} \\ \nu_{34} &= \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) - \frac{1}{2} \nu \delta_{AB} \end{aligned} \quad (7.93)$$

Thus, the spectrum of AB spin system will consist of two lines positioned at $\nu_{12} = \nu_{34}$ and $\nu_{13} = \nu_{24}$ respectively and is represented in Fig. 7.26(a).

(ii) If $J_{AB} < \nu \delta_{AB}$, the system is weakly coupled and is called AX instead of AB system, e.g. ethanol at 40 MHz. The frequencies of the lines under this condition are

$$\begin{aligned} \nu_{12} &= -\frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) - \frac{1}{2} \nu \delta_{AB} \\ \nu_{13} &= -\frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{1}{2} \nu \delta_{AB} \end{aligned} \quad (7.94)$$

$$\nu_{24} = \frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{1}{2} \nu \delta_{AB}$$

$$\nu_{34} = \frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) - \frac{1}{2} \nu \delta_{AB}$$

Thus, the spectrum in this case consists of two sets of lines, i.e. ν_{12} , ν_{34} and ν_{13} , ν_{24} and each separated by J_{AB} and is represented in Fig. 7.26(b).

- (iii) If $J_{AB} > \nu \delta_{AB}$, the spin-spin system is said to be strongly coupled. This is a true case of AB spin system, e.g. ethanol at 60 MHz. Under this condition,

$$\begin{aligned} \nu_{12} &= -\frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) - \frac{1}{2} \nu (\sigma_A - \sigma_B) - \frac{J_{AB}^2}{4\nu \delta_{AB}} \\ \nu_{13} &= -\frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{1}{2} \nu (\sigma_A - \sigma_B) + \frac{J_{AB}^2}{4\nu \delta_{AB}} \\ \nu_{24} &= \frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{1}{2} \nu (\sigma_A - \sigma_B) + \frac{J_{AB}^2}{4\nu \delta_{AB}} \\ \nu_{34} &= \frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) - \frac{1}{2} \nu (\sigma_A - \sigma_B) - \frac{J_{AB}^2}{4\nu \delta_{AB}} \end{aligned} \quad (7.95)$$

The spectrum in this case also consists of two sets of lines, i.e. ν_{12} , ν_{34} and ν_{13} , ν_{24} . The intensity ratio between the outer to inner lines will always be < 1 . The schematic spectrum for this case is shown in Fig. 7.26(c).

- (iv) If $\nu \delta_{AB} = 0$ then

$$\begin{aligned} \nu_{12} &= -\frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) \\ \nu_{13} &= -\frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) \\ \nu_{24} &= \frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) \\ \nu_{34} &= \frac{J_{AB}}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) \end{aligned} \quad (7.96)$$

The spectrum in such a case will consist of only one line centred at $\frac{|J_{AB}|}{2} + \nu \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right)$ and is shown in Fig. 7.26(d), e.g. benzene exhibits only a one-line spectrum.

The stick spectra of AB spin system reveal that it is better to record the spectra at the highest field possible so that most spectra have the first-order appearance due to increase in chemical shift. The analysis of an NMR spectrum is carried out by making tentative guesses of J_{AB} s and $\nu \delta_{AB}$ s and then drawing a theoretical spectra comparable to the observed one.

The selection rules from Section 7.28 give allowed transitions $1 \rightarrow 2$, $1 \rightarrow 3$, $2 \rightarrow 4$ and $3 \rightarrow 4$ for non-equivalent protons are shown in Fig. 7.25(b). The selection rules differ for non-equivalent and equivalent protons. The rules for the latter are $1 \rightarrow 3$, $3 \rightarrow 4$ [Fig. 7.25(b)].

7.29 INTENSITY OF NMR LINES IN AB SPIN SYSTEM

The intensity and position of lines in an NMR spectrum depend upon the magnitude of interaction but the area under the observed spectrum remains the same in all the cases. The general structure of NMR spectrum which arises due to s - s interaction in the AB system is shown in Fig. 7.26.

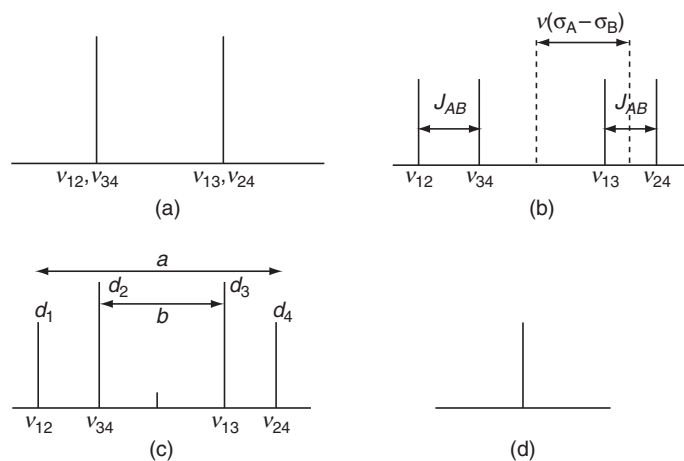


Fig. 7.26 Theoretical stick spectra of an AB system: (a) $J_{AB} = 0$, (b) $|J_{AB}| < v \delta_{AB}$, (c) $|J_{AB}| > v \delta_{AB}$, (d) $v \delta_{AB} = 0$.

The relative intensities of the outer to inner lines in an AB or AX system and the difference in chemical shifts ($|\Delta\delta|$) = $|v_A - v_B|$, are calculated from the following expressions:

$$\text{Relative intensity} \left(\frac{\text{Line 1}}{\text{Line 2}} \right) = \frac{Q - J}{Q + J} \quad (7.97)$$

$$\Delta\delta = (Q^2 - J_{AB}^2)^{\frac{1}{2}} \quad (7.98)$$

and

$$\bar{\nu} = \frac{\nu_A + \nu_B}{2} \quad (7.99)$$

Here,

$$J_{AB} = d_1 - d_2 \text{ or } d_3 - d_4 \text{ (in Hz)} \quad (7.100)$$

$$\nu_A = \frac{d_1 + d_2}{2}, \nu_B = \frac{d_3 + d_4}{2} \quad (7.101)$$

$$Q = d_1 - d_3 \text{ or } d_2 - d_4 \text{ (in Hz)} \quad (7.102)$$

$$|\Delta\delta| = \sqrt{(d_1 - d_4)(d_2 - d_3)} \quad (7.103)$$

$$|J_{AB}| = \frac{(d_1 - d_4) - (d_2 - d_3)}{2} \quad (7.104)$$

Or the relative intensities of four resonance frequencies for a two-spin system are also expressed as

Frequency	Relative Intensity*
$\nu_{1 \rightarrow 2}$	$(I_r - 1)^2 / (I_r + 1)^2$
$\nu_{1 \rightarrow 3}$	1
$\nu_{2 \rightarrow 4}$	$(I_r - 1)^2 / (I_r + 1)^2$
$\nu_{3 \rightarrow 4}$	1

*where

$$I_r = \left[\frac{(\Delta^2 + J^2)^{1/2} + \Delta}{(\Delta^2 + J^2)^{1/2} - \Delta} \right]^{1/2}$$

and

$$\Delta = v(\sigma_A - \sigma_B)$$

Problem 7.14: In the PMR spectrum (60 MHz) of *cis*- β -phenylmercaptostyrene, $\delta_{AB} = 6.48$ ppm for two ethylenic hydrogens, $J_{AB} = 10.7$ Hz and $\Delta\delta_{AB} = 0.095$ ppm. Compute the intensity ratios of outer to inner lines in the spectrum.

Solution $J_{AB} = 10.7$ Hz. Using Eq. (7.98), we can compute the value of Q , i.e. $60 \times 0.095 = (Q^2 - 10.7 \times 10.7)^{1/2}$. $Q = 12.123$. From Eq. (7.97), we get

$$\frac{I_1}{I_2} \text{ or } \frac{I_4}{I_3} = \frac{12.123 - 10.7}{12.123 + 10.7} = \frac{1.423}{22.823} = 0.062$$

The observed intensity ratio is 0.056.

Problem 7.15: The NMR spectrum of *cis*- β -ethoxystyrene, when recorded on a 60 MHz spectrometer gives ethylenic protons at $\delta_A = 5.18$ ppm for and $\delta_X = 6.06$ ppm $J_{AX} = 7.2$ Hz. Calculate the intensity ratios of the outer to inner lines in the spectrum.

Solution In AX system, the lines become more equal in intensity as compared to AB system. Here, $\Delta\delta = (6.06 - 5.18) = 0.98$ ppm $= 0.98 \times 60$ Hz $= 58.8$ Hz.

From Eq. (7.98), we obtain

$$58.8 = (Q^2 - 7.2 \times 7.2)^{1/2}$$

$$Q = 59.23 \text{ Hz}$$

Thus,

$$\frac{I_1}{I_2} \text{ or } \frac{I_4}{I_3} = \frac{59.23 - 7.2}{59.23 + 7.2} = \frac{52.03}{66.43} = 0.78$$

The observed intensity ratio is 0.77.

Problem 7.16: The PMR spectrum of 2, 3-dibromothiophene on a 56.4 MHz spectrometer (15 per cent by weight in CDCl_3) exhibits four lines at 410.39, 404.65, 390.64 and 384.87 Hz down-field from TMS. Calculate the intensity ratio between the outer and inner lines.

Solution Using Eq. (7.103), we get

$$\begin{aligned} |\Delta\delta| &= \sqrt{(410.39 - 384.87)(404.65 - 390.64)} \\ &= 18.91 \text{ Hz} \end{aligned}$$

and from Eq. (7.104),

$$J_{AB} = \frac{25.52 - 14.01}{2} = 5.70 \text{ Hz}$$

According to Eq. (7.98),

$$18.91 = (Q^2 - 5.70 \times 5.70)^{1/2}$$

Hence,

$$Q = 19.75 \text{ Hz}$$

From Q and J_{AB} , we get

$$\frac{I_1}{I_2} \text{ or } \frac{I_4}{I_3} = \frac{19.75 - 5.70}{19.75 + 5.70} = \frac{14.05}{25.45} = 0.552$$

which compares well with the experimental value of 0.606.

Problem 7.17: The PMR spectrum of *trans*-1-bromo-2-chloroethene on 56.4 MHz instrument (in hexafluorobenzene) gives $d_1 - d_4 = 25.80$ Hz, $d_2 - d_3 = 0.89$ Hz and $J_{AB} = 12.46$ Hz. Calculate the intensity ratio between the inner and outer lines.

Solution Using Eq. (7.103), we get

$$\Delta\delta = \sqrt{25.80 \times 0.89} = 4.79 \text{ Hz}$$

From Eq. (7.98), we obtain

$$Q = \sqrt{(4.79)^2 + (12.46)^2} = 13.35$$

Thus, the intensity ratio between the inner and outer lines

$$= \frac{13.35 + 12.46}{13.35 - 12.46} = \frac{25.81}{0.89} = 29$$

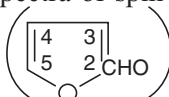
The observed value of intensity ratio is 20. This discrepancy is due to the fact that the two inner strong lines are easily saturated because of their large transition probability. The outer lines are very weak and might even escape detection. This is the collapse of AB pattern into an A_2 pattern.

7.30 SECOND-ORDER EFFECTS

Perfect first-order spectra are seldom observed in homonuclear spin systems. The deviation (λ_{AB}) from the near first-order spectra is given by

$$\lambda_{AB} = \frac{J_{AB}}{(\nu_A - \nu_B)} \quad (7.105)$$

The spacing between multiplets depends linearly on the perturbation parameter λ_{AB} . Second-order corrections become simplest in spectra of spin systems in which every basic group contains only one nucleus of spin 1/2,

e.g. 2-furan aldehyde . The spin coupling between two of the coupled nuclei, A and K , produces a

shift of the whole A multiplet pattern by $J_{AK}^2 / 2(\nu_A - \nu_B)$ and of the K multiplet pattern by $J_{AK}^2 / 2(\nu_K - \nu_A)$. The second-order shift tends to increase the separation between the A and K multiplets beyond the value $|\nu_A - \nu_K|$.

In a first-order spectrum, the multiplet pattern of any basic multiplet displays a perfect mirror image symmetry relative to its centre frequency. On the other hand, when two basic groups are sufficiently strongly coupled to make λ_{AB} non-negligible, this mirror image symmetry is lost in such a way that the intensities of those parts of the two bands which are nearest to each other increases at the expense of the intensities of the outer parts of the multiplets. *This is called roofing effect.* The roofing effect is discernible in the H_3 and H_4 bands of 2-furaldehyde and is of great diagnostic value in the analysis of NMR spectra when certain resonances are hidden under broad absorption bands. In a spin system containing several magnetically equivalent nuclei in a basic group, the second-order effects result in further line splitting and the line spacing within a basic multiplet will no longer depend linearly on the coupling constant.

Coupling constants are smaller than 20 Hz and chemical shifts are higher (of the order of several thousand Hz) in a second-order spectra. Splitting can be explained by the rules of first-order spectrum. However, when $J/\nu \cdot \delta > 0.1 - 0.15$, the rules of first-order spectrum hold no more and when $\nu \delta \rightarrow J$ roofing effect appears in the spectrum. These effects manifest themselves in the spectrum of 2-furaldehyde, 5-methyl-4-thiolen-2-one and ethylbromide, etc. The spectrum of ethylbromide on a 60 MHz instrument exhibits a quartet due to CH_2 group at 3.46 ppm and a triplet due to CH_3 group at 1.67 ppm. The coupling constant is 7.35 Hz. The perturbation parameter

$$\lambda_{AB} = \frac{7.35}{1.79 \times 60} = 0.068 \text{ and the second-order shift is } \frac{(7.35)^2}{214.8} = 0.25. \text{ Thus, the second-order shifts are significant.}$$

Consequently, the first-order estimates of the chemical shifts should have an analytical error of the order of 0.25 Hz. Moreover, the basic groups of ethyl bromide contain groups of magnetically equivalent nuclei due to which additional splittings of the order of 0.25 Hz will arise in the multiplet lines through second-order effects. Asymmetry and roofing effects are also observed in the two multiplets as shown in Fig. 7.27.

Spectrum of 2-furaldehyde on 60 MHz instrument exhibits δ_{H_4} (four doublets) = 398.5 Hz, δ_{H_3} (two doublets) = 438.9 Hz, δ_{H_5} (pentet) = 467.4 and δ_{CHO} (two doublets) = 581.6. $J_{34} = 3.70$ Hz, $J_{45} = 1.70$ Hz, $J_{35} = 0.75$ Hz, $J_{CHO-4} = 0.30$ Hz, $J_{CHO-3} =$ vanishingly small and $J_{CHO-5} = 0.65$ Hz. The maximum value of perturbation parameter in this case,

$$\lambda_{34} = \frac{3.70}{(438.9 - 398.5)} = \frac{3.70}{40.4} = 0.09$$

This value is large enough to make second-order effects appear visible in the spectrum. The second-order shift is $\frac{(3.70)^2}{80.8} = 0.17$ Hz and is almost negligible.

The PMR spectrum of 5-methyl-4-thiolen-2-one on 40 MHz instrument (in cyclohexane) exhibits a simple first-order pattern and even 60 MHz PMR spectrum exhibits no second-order effects. δCH_3 (three doublets, 1 : 2 : 1) = 2.07 ppm, δCH_2 (pentet, 1 : 4 : 6 : 4 : 1) = 3.37 ppm and δCH (triplet of quartets; intensity ratio of three quartets = 1 : 2 : 1; the lines within each quartet has intensity ratio = 1 : 3 : 3 : 1) = 5.54 ppm. $J_{\text{CH}_3-\text{CH}_2} = 2.5$ Hz; $J_{\text{CH}_3-\text{CH}} = 1.5$ Hz, and $J_{\text{CH}_2-\text{CH}_2} = 2.5$ Hz. The largest perturbation parameter

$$\lambda = \frac{2.5}{(3.37 - 2.07)40} = \frac{2.5}{52} = 0.048$$

and it causes second-order shift = $\frac{(2.5)^2}{104} = 0.06$ Hz and is negligible.

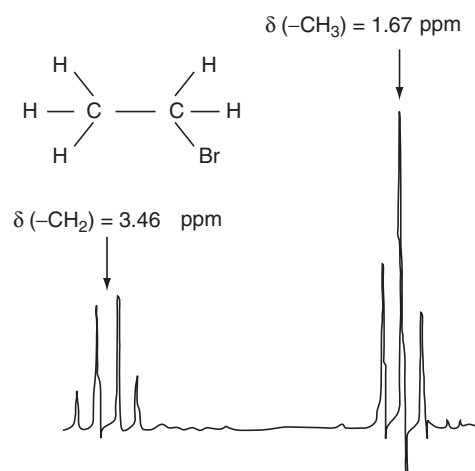


Fig. 7.27 NMR spectrum at 60 MHz of neat ethyl bromide.

7.31 EFFECT OF CHEMICAL ENVIRONMENT ON SHAPE OF NMR SIGNAL

The spectrum of a nucleus which exists in more than one chemical environments depends upon its lifetime in these environments. The lifetime of nucleus on sites I and II, i.e. τ_1 and τ_2 , are long as compared to the NMR transition time. The populations on sites I and II are P_I and P_{II} respectively such that

$$P_I = \frac{\tau_1}{\tau_1 + \tau_2} \quad (7.106)$$

and

$$P_{II} = \frac{\tau_2}{\tau_1 + \tau_2} \quad (7.107)$$

Thus, the probability of nucleus jumping from site I to site II will be $1/\tau_1$ while from II to I will be $1/\tau_2$. The jumping of the nucleus at the same site has no effect on magnetisation. Let us suppose that the population and lifetime of the nucleus in the two environments are the same, i.e. $\tau_1 = \tau_2 = \tau$ and $P_I = P_{II}$. In such a case, the lifetime τ can be determined from the expression

$$\frac{(\delta_I - \delta_{II})_{obs}}{(\delta_I^0 - \delta_{II}^0)} = \left[1 - \frac{1}{2\pi^2\tau^2(\delta_I^0 - \delta_{II}^0)^2} \right]^{1/2} \quad (7.108)$$

Here $(\delta_I^0 - \delta_{II}^0)$ is the difference between the chemical shifts of the two absorptions for large values of τ [Fig. 7.28(a)]. $(\delta_I - \delta_{II})_{obs}$ is the chemical shift difference between the coalescing peaks [Fig. 7.28(b)–(d)], and in this case the mean lifetime $\tau = \tau_1/2$ or $\tau_2/2$. When the peaks have just submerged into a single line [Fig. 7.28(e)], then $(\delta_I - \delta_{II})_{obs}$ becomes zero and the expression for mean lifetime is

$$\tau = \frac{1}{\sqrt{2} \pi (\delta_I^0 - \delta_{II}^0)} \quad (7.109)$$

This is the case of intermediate rates of exchange between two sites. The transverse relaxation times are large, i.e. $1/T_2(I) = 1/T_2(II) \approx 0$ and $P_I = P_{II} = 1/2$.

- (i) $\tau \gg \frac{1}{\sqrt{2} \pi (\delta_I^0 - \delta_{II}^0)}$. In this condition, two lines are observed, provided the absorptions at δ_I^0 and δ_{II}^0 appear as singlet. This is the case of slow rates of exchange between the two different sites. By NMR

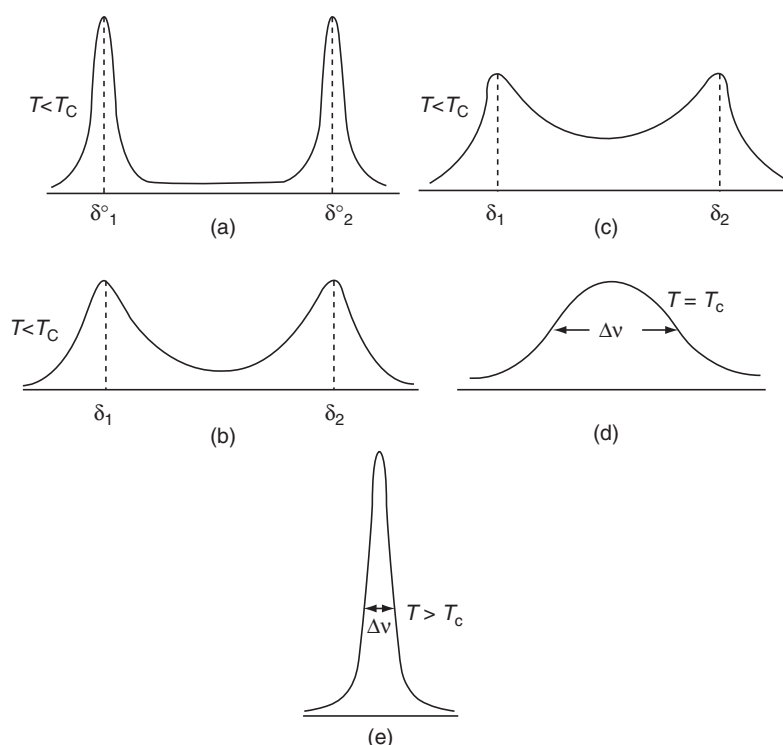


Fig. 7.28 Changes in the shape of the NMR resonance signal for an increasing exchange rate between two positions, I and II, with equal populations. T_c is the coalescence temperature.

criterion, under these conditions, the molecules are said to have rigid structures, e.g. cyclotriborazane (MeNHBH_2)₃. In this case the lifetime at site I, i.e. τ_1 is related to the transverse relaxation times as

$$\frac{1}{T_2^1} = \frac{1}{T_2} + \frac{1}{\tau_1} \quad (7.110)$$

The effective time T_2^1 is determined from resonance line width $\Delta\nu$, i.e.

$$T_2^1 = \frac{1}{\pi\Delta\nu} \quad (7.111)$$

T_2 is the transverse relaxation time in the absence of exchange. The rate constant k for exchange = $1/\tau_1$ which can be obtained from the increased broadening caused by exchange. Similarly, we can determine τ_2 . The drawback for determining k from line broadening is that τ_1 must be accurately known.

- (ii) $\tau < \frac{1}{\sqrt{2}\pi(\delta_I^0 - \delta_{II}^0)}$. Under such a condition, only a single time-averaged line is observed. This is the case

of rapid rates of exchange between two sites, i.e. τ_1 and τ_2 are small. By NMR criterion, under these conditions the molecules are said to have nonrigid structures, e.g. inversion of NH_3 and cyclohexane. In such molecules often two or more (but not always) nuclear configurations are possible. Single ^{13}C resonance line is maintained up to 210 K in $\text{Fe} (^{13}\text{CO})_5$ while a single ^{19}F doublet ($J_{\text{PF}} = 916 \text{ Hz}$) is maintained down to 113 K in $\text{P} ^{19}\text{F}_5$, $\text{Si} ^{19}\text{F}_5$, $\text{MeP} ^{19}\text{F}_4$, etc. Actually in both the cases two peaks are expected in the ratio 3:2.

The position of the observed chemical shift δ depends upon the relative populations in the two environments, i.e.

$$\delta = P_I \delta_I + P_{II} \delta_{II} \quad (7.112)$$

In general, we can say that any change in the system which perturbs the relative populations P_I and P_{II} will affect the observed chemical shift, δ . The factors which may alter the populations are temperature, concentration and nature of donor or acceptor in the case of electron donor-acceptor or H-complexes.

In the limit of rapid exchange, the line width $\Delta\nu$ of a single resonance peak at δ is

$$\Delta\nu = \frac{1}{\pi T_2} \text{ such that } \frac{1}{T_2} = \frac{P_I}{T_2(I)} + \frac{P_{II}}{T_2(II)} \quad (7.113)$$

For weak interactions, the exchange rates between different environments at normal experimental temperatures are comparable to rates of very fast reactions. However, when interactions are of covalent type, the rate of chemical

exchange is of the same order or less than the exchange rate between the magnetic states of the nucleus, for which line broadening or separate lines will be observed, e.g. a single resonance line due to proton is observed under all experimental conditions in the $\text{H}_2\text{O}-\text{H}_2\text{O}_2$ system since the exchange rate of proton between the two situations is large as compared to its lifetime in the two situations. In aliphatic alcohols, the collapse of spin multiplets also occurs through proton exchange. The spin coupling between the hydroxyl proton and a vicinal CH proton is of the order of 7 Hz. If the residence time τ of hydroxyl proton in any particular molecule is greater than 0.2 second ($2\pi J\tau > 10$) the s - s splittings will still be resolved in the spectrum but the multiplet lines are broadened. However, in the presence of an acid or a base, the proton exchange rate increases due to which residence time, τ of the hydroxyl protons in a given molecule reduces to less than 0.01 second. In this situation, the s - s splittings caused by spin coupling to hydroxyl protons are no longer observable. The collapse of the spin multiplets occurs both in the OH and CH absorption bands of the molecule, e.g. $\text{C}_2\text{H}_5\text{OH}$, the NMR line due to $-\text{OH}$ group will appear as a singlet while due to CH_2 group as a quartet. In the case of *N,N*-dimethylformamide and *N,N*-dimethylacetamide, three broad NMR signals of interchanging (due to rotation around C-N bond) non-coupled nuclei are observed. The collapse of spin multiplets in this case is by quadrupole relaxation. Splitting due to s - s interaction between a proton (or some other nucleus with spin $I = 1/2$) and nuclei with spin $I > 1/2$ is rendered unobservable by the rapid quadrupole relaxation of such nuclei. The interactions between the nonspherical charge distribution of nuclei with $I > 1/2$ and randomly varying in homogeneous molecular electric fields induces thermal transitions between the magnetic spin states of such nuclei, i.e. spin $I > 1/2$. When the rates of these thermally induced transitions are large as compared to the spin coupling constant, the spin-coupled proton only senses the vanishing average value of this interaction over the $2I + 1$ spin states of the $I > 1/2$ nucleus. (In case of nitrogen $I = 1$, so $2I + 1 = 3$. Hence, the three spin states are $+1, 0, -1$.) At intermediate relaxation times of the $I > 1/2$ nucleus, a spin-coupled proton experiences a line broadening only. The quadrupole relaxation of the nuclei of halogen atoms Br, Cl and I (except F, which has spin $I = 1/2$) are fast enough to eliminate all evidence of proton-halogen spin coupling effects in proton resonance spectra of these halogenated compounds.

The extended view of the effect of exchange rate between two sites I and II, with equal populations, on the NMR signal is shown in Fig. 7.28(a) to (e).

7.31.1 Effect of Temperature

Let us now discuss the effect of temperature on the NMR spectra of cyclohexane in relation to their conformations. Cyclohexane and its derivatives can assume two types of conformations: the chair and boat forms. The first is more stable (it has a lower energy) and is generally regarded as the only form in which cyclohexane actually exists. Monosubstituted chair cyclohexanes may have two conformations: one with an axial and the other with an equatorial substituents; the latter has a low energy. The conformational equilibrium can be obtained by spectroscopic methods such as infrared spectra and combination scattering, in particular by NMR method.

The PMR spectrum of cyclohexane is shown in Fig. (a). At room temperature, the spectrum cyclohexane contains only one sharp singlet. This is associated with the very rapid flipping of one chair conformation of the ring to the other chair from so that the axial and equatorial protons are constantly exchanged at lower temperatures (a solution of cyclohexane in carbondisulphide) beginning with 243 K, the signal is broadened and at 173 K, two distinct signals and their fine structure are observed, the fine structure being due to s - s interaction. The energy barriers for such conformational changes can be calculated from these studies. Let us now examine ^{19}F -NMR spectrum of 1,1-difluorocyclohexane at different temperatures indicated in Fig. (b). At 303 K, a single peak appears, which means that both fluorine atoms, the axial and the equatorial atoms are practically equivalent because of the rapid introversion of the two conformations (so that one fluorine atom becomes alternately axial and equatorial). At low temperatures the energy barrier between the two conformations becomes large due to which the lifetime of each conformation becomes longer. As the temperature decreases the signal widens

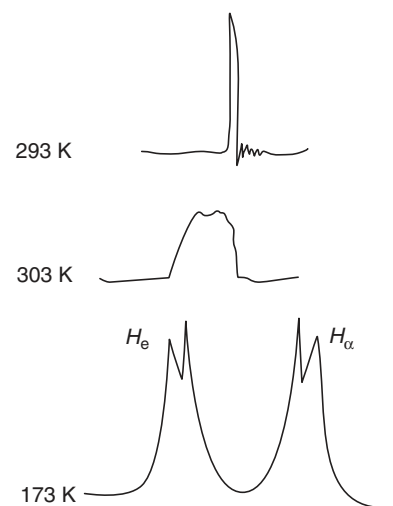


Fig. (a) PMR spectra of cyclohexane (operating frequency: 100 MHz).

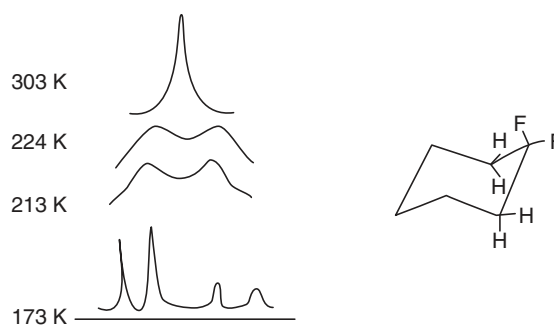


Fig. (b) ^{19}F -spectra of 1,1-difluorocyclohexane.

and splits into two maxima (peaks) and finally, at 173 K there appear two signals corresponding to the two different conformation of the molecules. The peaks of the axial fluorine atoms are somewhat widened on the right due to *s-s* interaction with the ring protons. From the spectral data we can calculate the lifetime τ of an individual conformer at each temperature by the formula

$$\frac{\delta_\tau}{\delta_\infty} = \left[1 - \frac{1}{2\pi^2 \tau^2 (\delta_\infty)^2} \right]^{1/2} \quad (7.108a)$$

where δ_τ is the chemical shift between the signals of fluorine atoms at a given temperature and δ_∞ is the chemical shift at 173 K (or at lower temperature) when the peaks are distinctly separated.

Thus the lifetime and rate constant (*k*) of a conformation at different temperatures is as follows:

Temperature (K)	τ (s)	k (s^{-1})
303	1.0×10^{-6}	$1 \times 10^{+6}$
224	6.5×10^{-4}	$0.15 \times 10^{+4}$
213	1.2×10^{-3}	$0.83 \times 10^{+3}$
173	2.0×10^{-2}	$0.50 \times 10^{+2}$

The energy barrier between the conformations can also be determined from this data.

7.32 NMR SPECTROMETERS

Two types of NMR instruments available in the market are wide-line and high-resolution spectrometers. Magnets in wide-line spectrometers have of a few tenths of tesla whereas the strengths of magnets lies in the range 1.4–14 tesla which corresponds to proton frequency of 60–1000 MHz in high-resolution instruments. CWNMR instruments are equipped with permanent or conventional electromagnets. These days conventional magnets are seldom used. Permanent magnets with field strengths of 0.7, 1.4 and 2.1 tesla corresponding to proton frequency of 30, 60 and 90 MHz are used in CWNMR spectrometers. In FTNMR instruments superconducting solenoids are the source of magnetic field. Computer is an integral part of FTNMR spectrometers. The role of a computer is to record spectrum in the time domain, i.e. the radiation emitted by the excited nuclei in the sample are collected as a function of time in the computer, perform FT on the FID signal stored, to obtain the frequency domain signal or spectrum. High resolution and sensitivity, both of which depend upon the strength and quality of magnets, are the two main characteristics of FTNMR instruments. Due to this, these instruments have made possible, the analysis of analytes containing (i) ^{13}C nuclei, (ii) protons in microgram quantity, and (iii) ^{19}F , ^{31}P and other such nuclei. These days, all the modern high-resolution NMR spectrometers are equipped with superconducting magnets. These magnets can attain magnetic field strength of 21 tesla, corresponding to a proton frequency of 900 MHz. Superconducting magnet system is obtained by winding superconducting niobium/tin or niobium/titanium wire on a solenoid. The wound solenoid is then bathed in liquid helium at 4 K. The helium dewar is kept in an outer liquid-nitrogen dewar. Such magnet systems must be filled with liquid nitrogen every 10 days and with liquid helium every 80–130 days. These types of superconducting magnets are highly stable, homogeneous and have high strengths as compared to conventional electromagnets.

7.32.1 Basic Principle of CWNMR Spectrometer

To obtain good NMR spectra, we should have maximum possible spins, i.e. NMR nuclei in the lower state. This can be achieved according to Boltzmann's law, i.e. either by lowering the temperature or increasing the field strength or both. There are, of course, practical limitations to these two variables. The flowsheet diagram of an NMR spectrometer is shown in Fig. 7.29. The sample tube which consists of a 5 mm ordinary glass tube containing 0.5 ml of liquid (neat or solution with a trace of reference, i.e. 5 per cent TMS; microtubes for smaller volumes are also available) is placed between the poles of a magnet which produces a uniform constant field of high strength, say *H*. A circularly polarised radio frequency field (H_{rf}) is applied by passing an AC through a coil wound around

the sample tube. Experimentally, it is arranged so that H_{rf} oscillates in a direction (say X) which is perpendicular to the direction of the applied magnetic field, H (say Z). The field H_{rf} induces transition between the magnetic levels, say n and m . The spectra can be obtained both by field-sweep method and frequency-sweep method. Frequency sweep method is more difficult but has advantages especially for some double resonance experiments. Both types of spectrometers are available in the market. When H is varied and ν , i.e. frequency of radio frequency field is kept constant, then at a certain value of H , the sample absorbs energy and current flow in the coil falls off. This variation is amplified and transmitted to the recorder or oscillograph. The spectra of neat liquids or solutions and sometimes of gases are recorded. However, in case of solids, the absorption bands are blurred, because in crystals the magnetic moments of nuclei are affected by the spatially fixed magnetic moments of the neighbouring nuclei. The influence of neighbouring nuclei is averaged out to zero by the random molecular motions in case of liquids. This type of effect also becomes operative if the applied field is not homogeneous. Under this condition, resonance will occur at apparently different magnetic fields, say $H \pm \delta H_1$, $H \pm \delta H_2$,... and the broadening will result due to overlapping of lines. This effect is minimised by spinning the sample tube with a frequency so that all nuclei senses an average magnetic field. The spinning frequency should be greater than the rate of fluctuation of the magnetic field. Spinning is done by passing a stream of air to drive the plastic turbine that slips over the sample tube at a rate of 20–50 revolutions per second. Sometimes, the magnetic field is modulated at the spinning frequency, consequently side bands also called spinning bands appear on each side of the absorption lines. Inhomogeneities in the applied field are also compensated by the skimming process and by locking the magnetic field. In the former case, controlled currents are passed through the pairs of wire loops called skim coils (not shown in Fig. 7.29) to produce small magnetic fields in order to compensate the inhomogeneities in the applied field. Skimming is done each time a new sample is introduced in the NMR spectrometer. The effect of field fluctuations can be compensated by a field frequency lock system. NMR absorption signal of a reference nucleus, i.e. deuterium in a solvent, is obtained by continuously irradiating the nuclei at a constant magnetic field of strength H and its behaviour is monitored along with that of the sample under study. Changes in intensity of the reference signal are given to a feedback network whose output is fed into the coils in such a way that drift in the magnetic field (positive or negative) is automatically taken care of or corrected. When stable superconducting magnets are used, the spectra can be obtained in an unlocked mode for a period of 1–20 minutes. Signal integrators (electronic or digital) are the essential components of modern spectrometers. They determine the areas under the absorption signals.

The solvents used in PMR spectroscopy should be such liquids which do not give NMR signals (CCl_4 , CS_2) or absorb in a different regions, e.g. CDCl_3 , $(\text{CD}_3)_2\text{SO}$; AsCl_3 and C_6D_6 .

The NMR instruments are characterised by three main parameters: the frequency (40, 60, 100 MHz) which depends upon the field strength, H ; sensitivity; and resolving power. The higher the sensitivity of the instrument, the more intensive the signals, will be observed with the same concentration of protons in the analyte. Current instruments allow us to distinguish between two lines which are only 0.2–0.5 cps apart from each other. The resolving power of the most efficient Instruments operating at a frequency of 100 MHz is $0.2 \text{ cps}/10^8 \text{ cps} = 2 \times 10^{-9}$. Since revolving power R_p is defined as the ratio of the maximum distance resolvable to the operating frequency of instruments expressed in cps. The R_p grows with growth in the operating frequency of the instrument. The resolution of spectra, however, depends upon, the resolving power of the instrument, the velocity of the spectrum scanning and on the properties of the sample, i.e. on the viscosity of the solution.

Thus, depending upon the purpose of NMR studies, we can obtain either low resolution (wideline) or high-resolution spectra of the analyte. In addition to the blurring of absorption band of a nucleus by the magnetic moments of the neighbouring nuclei in crystals, line broadening in solids is also caused by chemical shift anisotropy, i.e. changes in the chemical shift with the orientation of the molecule or part of the molecule with respect to an applied magnetic field cause line broadening. The chemical shift $\Delta\delta$ brought about by magnetic anisotropy is given by the equation

$$\Delta\delta = \Delta\chi (3 \cos^2\theta - 1)/r^3 \quad (7.114)$$

where θ is the angle between the double bond and the applied field, $\Delta\chi$ is the difference in magnetic susceptibilities between the parallel and perpendicular orientations of bond and r is the distance between the anisotropic functional group and the nucleus. For $\theta = 54.7^\circ$, $\Delta\delta = 0$. Experimentally, line broadening due to chemical shift

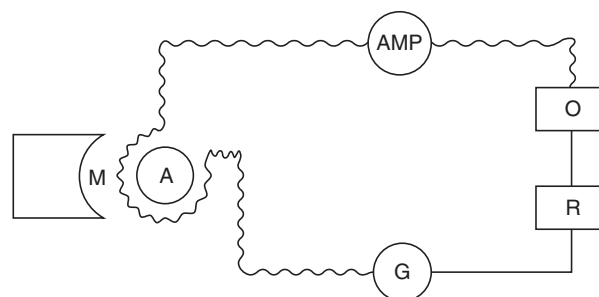


Fig. 7.29 Schematic representation of an NMR instrument—A: Ampule with sample, M: Magnet, G: Generator, AMP: Amplifier, O: Oscillograph, R: Recorder.

anisotropy is annihilated by Magic Angle Spinning (MAS). The solid samples are rotated rapidly at a frequency greater than 2 kHz in a special sample holder that is maintained at an angle of 54.7° with respect to the external field. Under such experimental conditions the solid behaves like a liquid being rotated in the external magnetic field. The ^{19}F spectrum of static and rotated (at 5.5 kHz) polycrystalline KAsF_6 is shown in Fig. 7.30. The spectrum of static sample shows the ordinary NMR signal, the width of which is governed by d - d interactions among the spins. On the other hand, magic angle rotation of the sample gives rise to a quartet structure. The structure is because of the electron coupled interaction between ^{19}F $\left(I = \frac{1}{2}\right)$ and ^{75}As $\left(I = \frac{3}{2}\right)$ nuclei. The coupling constant is $J = 905 \text{ Hz}$.

A good NMR spectrum is obtained in about 5 minutes when 20 mg of sample containing ^{31}P , ^{19}F or ^1H nuclei is dissolved in 0.5 ml of the solvent. 10 mg of sample takes about 20 minutes.

Problem 7.18: If the operating frequencies of NMR instruments are 30, 40 and 60 MHz, what will be their resolving powers if the maximum distance resolvable is 0.3 cps?

Solution We know that resolving power of

$$\text{NMR spectrometer } (R_p) = \frac{\text{Maximum distance resolvable in cps}}{\text{Operating frequency in cps}}$$

$$\text{Thus, } R_p (30 \text{ MHz}) = \frac{0.3 \text{ cps}}{30 \times 10^6 \text{ cps}} = 1 \times 10^{-8}$$

$$\text{Similarly, } R_p (40 \text{ MHz}) = 0.75 \times 10^{-8}$$

$$\text{And } R_p (60 \text{ MHz}) = 0.5 \times 10^{-8}$$

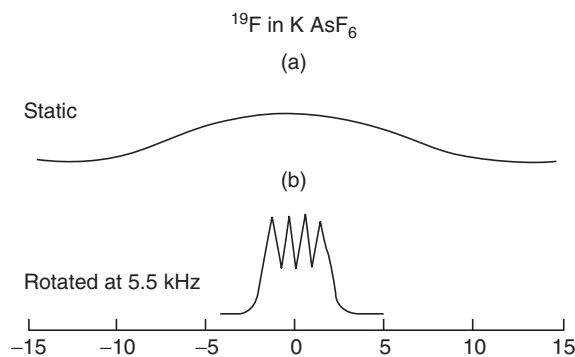


Fig. 7.30 ^{19}F spectrum of poly crystalline KAsF_6 : (a) without sample rotation, and (b) with magic angle rotation of the sample.

7.32.2 Basic Principle of a Fourier Transform NMR (FTNMR) Spectrometer

FTNMR spectrometer has higher sensitivity, and resolution as compared to conventional NMR instrument. A conceptual block diagram of one-dimensional FTNMR instrument is presented in Fig. 7.31. The sample in a static magnetic field undergoes bulk magnetisation, $\mathbf{M}$ which is the sum of the magnetisation of the individual spins and is aligned with the Z -axis, i.e. the direction of the external magnetic field, H . The bulk magnetisation vector $\mathbf{M}$ is stimulated with a single $\pi/2$ pulse along X -axis, covering a broad range in the radio frequency region. The pulse is generated by a transmitter/receiver coil (wound around the sample but not shown in Fig. 7.31) whose axis is aligned, perpendicular to the Z -axis, i.e. along the X -direction. The pulse rotates the vector $\mathbf{M}$ by 90° to an orientation perpendicular to the static field, i.e. Y -axis. The torque due to applied field after the termination of the pulse causes the bulk magnetisation to relax back to the Z -axis. The response, i.e. the relaxation of the pulsed system which is picked up by the same coil which now serves as a receiver coil is measured as a function of time using a digital computer. A separate receiver coil whose axis is aligned with the Y -direction may also be used. The signal due to relaxation process is called a Free Induction Decay (FID). The FID signal which is normally collected and analysed is the difference between the NMR signal and the excitation frequency. The FID is then converted to the normal frequency domain signal by a Fourier transformation with the aid of a digital computer and the signal is stored in the memory. With FT technique, it is possible to pulse or scan the entire resonance regions of a given type of nucleus repeatedly. The FIDS derived from each pulse are summed, thus greatly enhancing the signal-to-noise ratio, thereby making it possible to record the NMR spectrum of small quantities of sample or even containing a low abundant nucleus such as ^{13}C , ^2H , ^{15}N , ^{17}O .

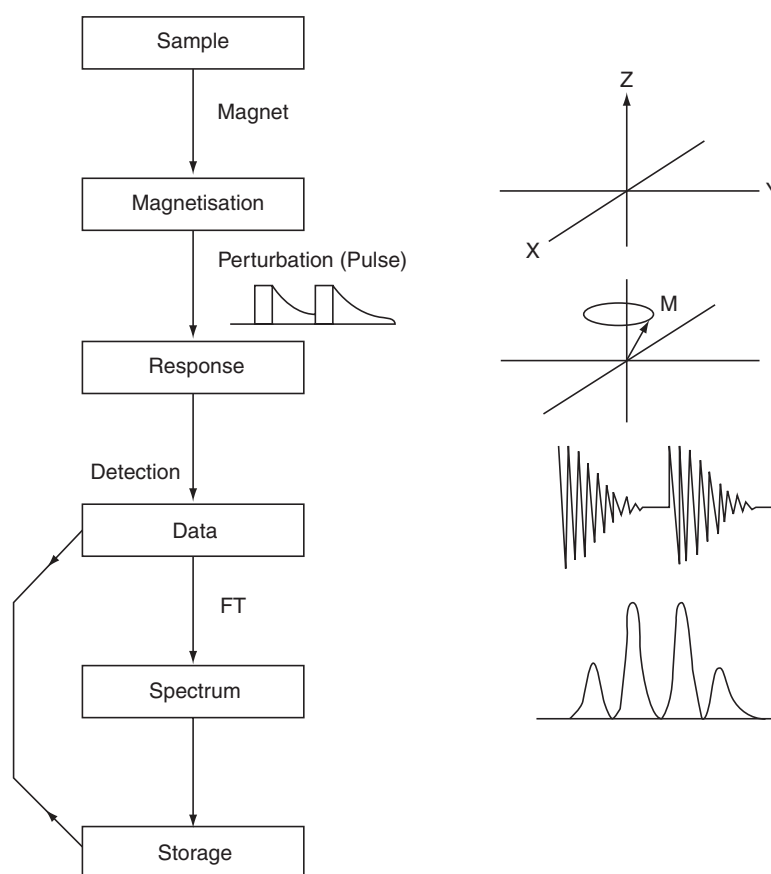


Fig. 7.31 Block diagram of a Fourier transform NMR spectrometer.

7.33 SIMPLIFICATION OF NMR SPECTRA

The complexity in NMR spectra of complex molecules arises due to the overlapping of several NMR bands with one another. It is removed by a number of methods such as shift reagents, superconducting magnets and, double resonance, i.e. spin decoupling, spin tickling, nuclear overhauser effect, internuclear double resonance, etc., so that the structural pattern in the spectra becomes easily recognisable and analysable.

7.33.1 Shift Reagents

Certain lanthanide chelates that cause a change in the chemical shift of nuclei when added to solutions of organic compounds that contain a Lewis basic functional group are known as *chemical shift reagents*. These reagents are used to spread out a spectrum when several NMR signals overlap with one another. The change in PMR shifts by such reagents is of the order of 0–200 ppm.

Chelates of the trivalent ions Tb, Dy, Ho and Tm have greater shifting abilities than those of Eu and Pr, still the latter are preferred firstly because they cause negligible line broadening and secondly they are complementary, i.e. a dipivalomethane (DPM) complex of Eu (III); (DPM)₃ Eu induces a chemical shift to lower field with a certain substrate whereas Pr(DPM)₃ causes a chemical shift to higher field with the same substrate. This is due to different reagent–substrate geometry. The parameter ($3 \cos^2 \theta - 1$) can have either positive or negative values. Here, θ is the angle between the principal symmetry or crystal field axis and the lanthanide proton direction. Lanthanide complex of 1, 1, 1, 2, 2, 3, 3-hepta fluoro-7, 7-dimethyl-4, 6-octane dione (FOD), i.e. Eu(FOD)₃ is preferred over DPM chelate, i.e. Eu(DPM)₃ because of its lower field shifts in the order Er < Eu < Yb < Tm while higher field shifts are produced by chelates of Dy, Sm, Nd, Pr, Ho in the order Ho > Pr > Nd > Sm > Dy.

The efficiency of a shift reagent depends upon the following:

- Ability of the organic compound (analyte) to form a Lewis-acid-base complex.* The order of induced shift is amines, alcohols > carbonyl compounds > ethers, sulphides and alkenes, alkynes and aromatics.
- Distance between the complexing functional group and lanthanide reagent.* It follows the $1/r^3$ law, i.e. as the distance increases, the induced chemical shift decreases. The line broadening of proton resonances by lanthanide ion follows approximately the $1/r^6$ law.
- Nature of the lanthanide metal and the ligands attached to it.* Eu(DPM)₃ produces large shifts than Eu(FOD)₃.

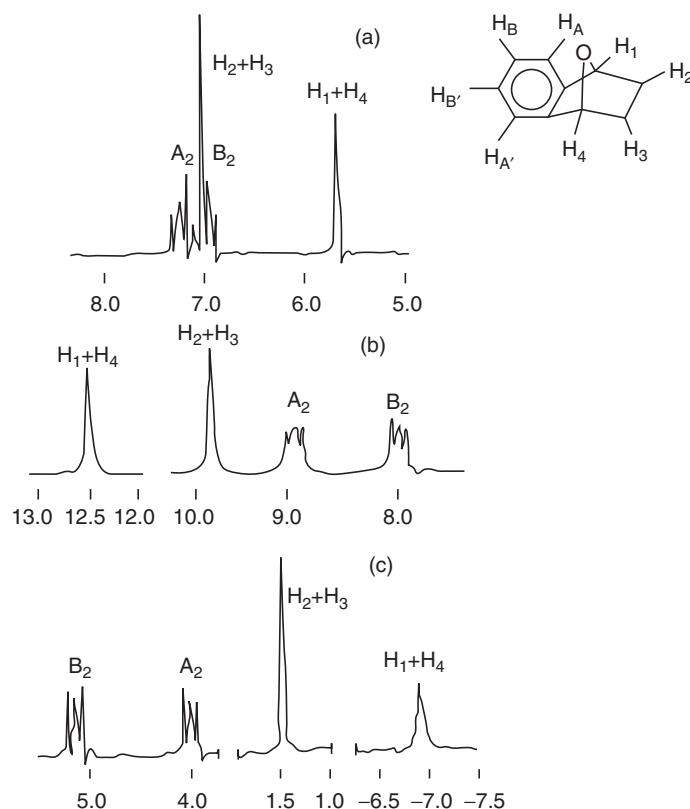


Fig. 7.32 PMR spectrum of 1,4-dihydronaphthalene-1,4-oxide on a 60 MHz instrument: (a) 0.5M in CDCl_3 , (b) 0.5M in CDCl_3 with 0.2 equivalent of $\text{Eu}(\text{FOD})_3$ added, (c) 0.5M in CDCl_3 with 0.2 equivalent of $\text{Pr}(\text{FOD})_3$ added; shifts used as δ values in ppm from internal TMS.

- (iv) *Amount of complex added to the sample.* The induced shift increases with the increase in the amount of the complex added.
- (v) *Type of functional group and structural features present in organic molecules.* The induced shift in amines [in ppm/mole of $\text{Eu}(\text{DPM})_3$ /mole of substrate] lies in the range 30–150 whereas in alcohols it is 20–100 ppm.

Shift reagents are also useful with ^{13}C -NMR spectra, e.g. $\text{Eu}(\text{DPM})_3$ is used for distinguishing the *cis* and *trans* isomers of 3-methylcyclopentanol and 1,3-dimethylcyclopentanol. $\text{Eu}(\text{DPM})_3$ produces down-field shifts in PMR while it induces up-field shift of ^{14}N resonance lines, the largest shifts observed in alkylamines and pyridine are around 1500 ppm, the corresponding Yb complex gives down-field shifts of up to 400 ppm. Chiral shift-reagents, i.e. β -diketoanion of 3-trifluoroacetyl-isobornane ($\text{C}_{12}\text{H}_{15}\text{O}_2\text{F}_3$) or 3-hepta fluoropropyl-isobornane ($\text{C}_{14}\text{H}_{15}\text{O}_2\text{F}_7$) are useful for the analysis of mixtures of enantiomers which have identical spectra. In the presence of a chiral shift reagent, complexes are formed that are diastereomeric and have non-equivalent NMR spectra in solutions (in chiral solvents) because the optically active solvent solvates the optically active solute, e.g. a chiral solvent and chiral shift reagent are used to distinguish the meso *d* and *l* stereoisomers of the pesticide dieldrin.

Figure 7.32 illustrates the value of shift reagents, i.e. $\text{Eu}(\text{FOD})_3$ and $\text{Pr}(\text{FOD})_3$, in the clarification of the spectrum of 1,4-dihydronaphthalene-1,4-oxide. The sizes of the induced shifts are such that the spectrum can be treated by a first-order analysis: the A_2B_2 pattern of the aromatic protons is clearly recognisable and J_{AB} and $J_{AB'}$ are readily measured. The induced shifts should be greatest for the protons closest to the coordination site. Indeed, the least shifted H_1 and H_4 protons in the uncomplexed spectrum [Fig. 7.32(a)] are strongly shifted in the shifted spectrum [Figs 7.32(b) and (c)].

7.33.2 Superconducting Magnets

Chemical shift is directly proportional to the strength of applied magnetic field while coupling constant is independent of it. These days superconducting magnets with field strength of 25 to 30 tesla, i.e. a million times stronger than the earth's magnetic field are available. Consequently, it is possible to obtain the proton spectra in the 60–1000 MHz region. Thus, the overlapping signals can be separated, using magnets of different field strengths. However, this method is not preferred over shift reagents since it is neither efficient nor economically viable.

7.33.3 Double Resonance

Double resonance implies that the spin system, i.e. sample is subjected to two or more radiofrequency fields simultaneously known as irradiation (secondary) and observation (primary) fields respectively. The observation field having amplitude H_1 and frequency ν_1 is usually weak while the irradiation field of amplitude H_2 and frequency ν_2 is strong enough to cause perturbation of one or more of the irradiated transitions. The effective width, i.e. $\gamma H_2/2\pi$ of the irradiation field, is maintained around its centre of frequency ν_2 so that the lines that differ from ν_2 by few multiples of $\gamma H_2/2\pi$ are not affected by the irradiation field. Some of the typical techniques based on double resonance used for the simplification of spectra are described here.

(a) Spin Decoupling Consider an AX spin system in which each of both the nuclei have spin = 1/2. Due to $s-s$ interaction, the first-order spectra ($\nu\delta_{AX} \gg J_{AX}$) of such a system consist of two doublets centred at resonance frequencies ν_A and ν_X respectively and each doublet is separated by J_{AX} as shown in Fig. 7.33(a).

For an ideal spin decoupling, the widths of the two basic groups involved are both small as compared with the difference in their centre frequencies. The $s-s$ splitting of signal of X nuclei by A nuclei is removed by irradiating the sample with a strong decoupling field of strength H_2 and frequency ν_2 centred at ν_A while the signal due to X nuclei is observed by the usual method. The doublet of X nuclei in the decoupled spectra appears as a singlet [Fig. 7.33(b)]. The decoupling of X doublet into a singlet arises because the decoupling frequency, ν_2 causes such a rapid transitions between the possible spin states of A that X nuclei are no more able to sense the spin state of A .

Further, if both the nuclei in the system are of same type, i.e. $^1\text{H}-^1\text{H}$, $^{19}\text{F}-^{19}\text{F}$, etc., the decoupling is termed as homonuclear spin decoupling and heteronuclear spin decoupling if both the nuclei are of different kind, i.e. $^1\text{H}-^{19}\text{F}$, $^1\text{H}-^{31}\text{P}$, $^1\text{H}-^{13}\text{C}$, etc. Figure 7.34 displays a highly resolved proton spectrum of ethanol using spin decoupling. While observing the methyl group signal, irradiation is performed on the methylene resonance and vice versa.

(b) Spin Tickling Double resonance in spin tickling involves a primary (H_1, ν_1) and a weak secondary (H_2, ν_2) rather than a strong, radio frequency fields. The effective width of $\gamma H_2/2\pi$ of the secondary field is made comparable to the smallest splitting, $\Delta\nu$ observable with the NMR instrument. Under these conditions, a partial decoupling of the NMR signal takes place and in some circumstances extra multiplet splitting may also be observed. Double resonance behaviour under spin tickling may be stated in the form of three rules: (i) When a nondegenerate connected 'a' transition is selectively irradiated, all connected transitions say 'b' and 'c' split into doublets. (ii) The doublets corresponding to regressive transitions are well resolved while those of progressive transitions are broad. (iii) The doublet splitting is not only proportional to the square root of the intensity of the irradiated signal but also to the amplitude H_2 of the secondary field.

These rules are valid only for symmetrical doublets when ν_2 , the radio frequency of the secondary field, H_2 is centred exactly on the connected 'a' transition. However, if the weak secondary field is applied in the neighbourhood of one single nondegenerate connected 'a' transition but slightly off resonance, all connected 'b' and 'c' transitions split into asymmetrical doublets. The intense line of such a doublet nearly coincides with the position of the corresponding single resonance line but weak satellite is

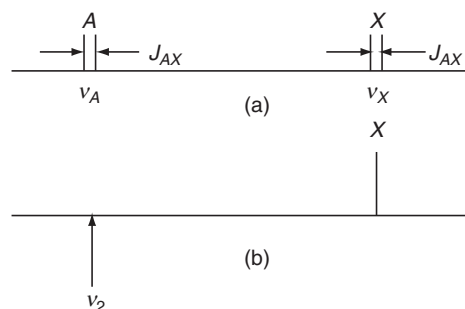


Fig. 7.33 (a) Highly resolved NMR spectrum of an AX spin system, and (b) NMR spectrum of AX spin system using spin decoupling. While recording the X nuclei line, irradiation is performed on the A nuclei resonance.

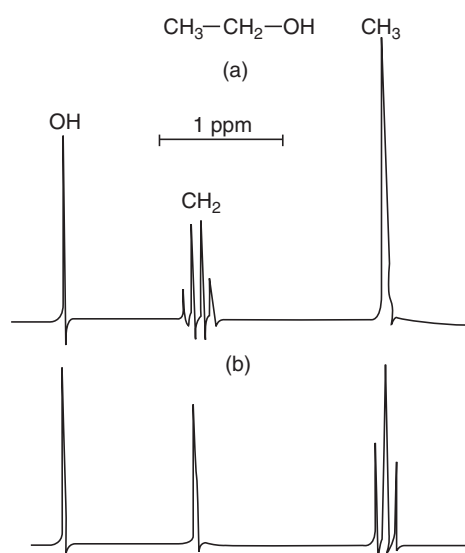


Fig. 7.34 Highly resolved spectrum of ethanol using spin decoupling: (a) while recording the methyl group line, irradiation is performed on the methylene resonance, and (b) while recording the methylene group line, irradiation is performed on the methyl group resonance.

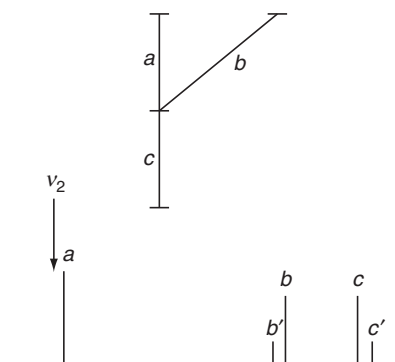


Fig. 7.35 Schematic diagram showing the splittings obtained in the b and c lines when the connected 'a' transition is perturbed by an irradiation field H_2 of frequency ν_2 .

displaced from that position to the left in the regression doublet and to the right in the progression doublet as shown in Fig. 7.35. Spin tickling leads to measurements of fundamental NMR constants, particularly the relative signs of coupling constants.

(c) Broadband Decoupling Broadband decoupling is a type of heteronuclear decoupling in which the ^{13}C nuclei are decoupled by hydrogen nuclei. The decoupling is carried out by a broadband radio frequency of the irradiation field H_2 , that covers the whole range of proton spectral region, while the spectrum of ^{13}C nuclei is simultaneously monitored. Area under the ^{13}C peaks is enhanced by a factor than that expected from the collapse of multiplets into singlets. The unexpected increase in intensity of the ^{13}C signals is because of Nuclear Overhauser Effect (NOE) that arises because of the $d-d$ interaction between a decoupled ^{13}C nuclei and neighbouring protons, e.g. broad band decoupled, ^{13}C -NMR spectrum of, $^{13}\text{CH}_3\text{CH}_2\text{Cl}$ consists of a singlet which is due to ^{13}C of CH_3 group.

(d) Off-spin Resonance Decoupling Despite the fact that the broadband decoupling simplifies the complex spectra but the disadvantage is that much of the information pertaining to structural elucidation contained in the uncoupled spectra is lost. So, instead of using broadband radio frequency field, the decoupling field is set at 1–2 kHz above the proton spectral region, which causes a partial decoupling because of which all but the largest $s-s$ shifts disappear in the off-spin resonance spectra. Under these conditions, CH_3 group gives a quartet pattern in the ^{13}C -NMR spectrum, CH_2 group appears as a triplet, CH exhibits a doublet and quarternary carbon yields a singlet. Figure 7.36 displays the broadband and off-spin proton decoupled, ^{13}C -NMR spectra of p-ethoxybenzaldehyde at 25.2 MHz.

(e) Nuclear Overhauser Effect (NOE) When an electron spin resonance in a metal is irradiated by a strong microwave frequency field of amplitude H_2 and frequency ν_2 , the electron spin resonance undergoes relaxation by transferring its spin energy to nuclear spin, thereby enhancing the intensity of the simultaneously monitored nuclear spin magnetic resonance signal by the usual method. The efficiency of the relaxation process depends upon the distance between the nucleus and the unpaired electrons. The relaxation of the unpaired electron spins and of the nuclei is coupled by $s-s$ /or $d-d$ interactions so that both spins flip simultaneously. For $d-d$ interactions, a downward

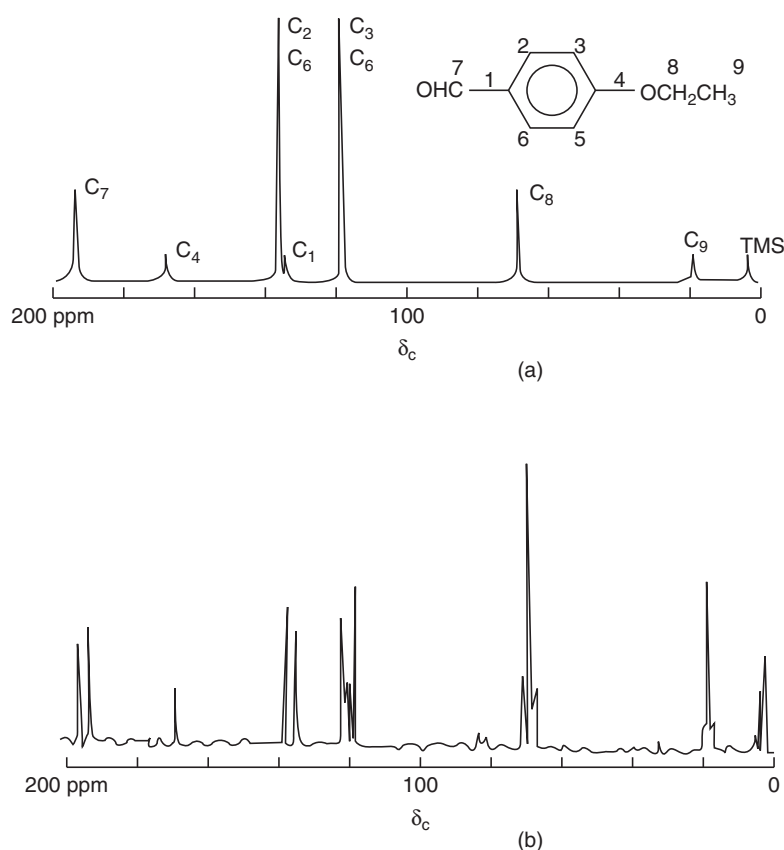


Fig. 7.36 Comparison of (a) broadband, and (b) off-resonance decoupling in ^{13}C spectra of p-ethoxybenzaldehyde.

flip of electron spin ($\downarrow$) is accompanied by an upward flip of nuclear spin ($\uparrow$) and vice versa. Here, the electron spin relaxation process leads to enhancement of nuclei population over that predicted from Boltzmann law in the upper nuclear magnetic levels. Consequently, the NMR signal becomes an emission signal with enhanced intensity. On the other hand, when s - s interactions dominate over the d - d interactions, the electron spin relaxation process causes an increase in population of nuclear spins in the lower levels. As a consequence, the NMR signal becomes an absorption signal with enhanced intensity. The phenomenon of increase in intensity of NMR signal in case of metals by such relaxation mechanism is known as Nuclear Electron Overhauser Effect (NEOE). An analogous effect has been observed in nuclear magnetic resonance also and is termed as Nuclear Overhauser Effect (NOE) and is also sometimes called *spin pumping*. The effect arises from direct magnetic coupling, between a saturated nucleus and a neighbouring simultaneously monitored decoupled nucleus that results in an increase in the population of lower energy level of the monitored nucleus over that predicted from Boltzmann law.

PMR measurements are carried out in solvents without protons such as CCl_4 , CDCl_3 and also solvents devoid of oxygen since it is paramagnetic, so that the intermolecular proton-proton and electron-proton spin interactions are minimised and the d - d interactions dominate over them. Thus the main mechanism left for the proton spin relaxation amongst the solute molecules is d - d interactions between the neighbouring protons on the same molecule. So when one particular proton is irradiated by a strong radio frequency field (H_2 , ν_2) at its resonance frequency, the relaxation rate of the neighbouring decoupled proton increases. Consequently, the intensity of the observed NMR signal from the decoupled proton enhances.

The fractional growth $f(I_1)(I_2)$ of the integrated intensity of spin I_1 , (when I_2 is saturated) compared to its equilibrium intensity, $\propto \frac{\gamma(I_2)}{\gamma(I_1)}$ where $\gamma(I_2)$ and $\gamma(I_1)$ are the gyromagnetic ratios of spins I_2 , and I_1 respectively. For small molecules, where only d - d relaxation mechanism is operative,

$$f(I_1)(I_2) = \frac{\gamma(I_2)}{\gamma(I_1)} = \frac{\gamma(\text{Saturated})}{\gamma(\text{Observed})} \quad (7.115)$$

For protons the maximum increase of intensity is of the order of 50 per cent, ^{13}C -nuclei are relaxed predominantly by d - d interactions with protons. Irradiation of proton resonances by strong broadband radio frequency field led to an increase in intensity of ^{13}C -NMR signal by ~ 2 from NOE but the disadvantage is that the proportionality between the areas under the peaks and number of ^{13}C nuclei is lost. The γ of an electron is larger than that of nucleus, so the saturation of electron spin can cause an increase in the intensity of NMR signal of the order of 1000.

For large molecules such as proteins and nucleic acids, negative NOE has been observed, i.e. $f(I_1)(I_2)$ is negative. The negative NOE may be due to (i) the presence of third *spin* proximate to the spins, (ii) the presence of nuclei with gyromagnetic ratios of opposite sign, (iii) the presence of scalar coupling modulated by chemical exchange or internal motion, and (iv) the dependence of NOE on frequency in case of macromolecules.

NOE and consequently the technique based upon it is useful to determine the stereochemical relationships in NMR active molecular systems that may be difficult by chemical shifts and coupling constants, e.g. the two methyl resonance signals in N, N-dimethylformamide (DMF) are not clearly distinguished by chemical shifts or coupling constants. Irradiation of low field (high δ value) methyl resonance in 8 per cent solution of DMF, enhance the intensity of the decoupled formyl proton signal by 18 per cent. On the other hand, saturation of the high-field methyl signal decreases the intensity of the formyl proton signal by 82 per cent. This led to suggest that low-field signal is because of the *cis*-methyl group rather than the *trans*-methyl group. The PMR of β , β -dimethyl acrylic acid $[(\text{CH}_3)_2\text{C} = \text{CHCOOH}]$ exhibits two doublets at $\delta = 1.97$ and 1.42 ppm ($J = 1.3$ Hz) from methyl groups and a septet because of olefinic proton at higher δ value. Saturation of *cis*-methyl group causes a 17 per cent increase in the intensity of formyl proton signal while no change in intensity of formyl proton resonance is observed when *trans*-methyl group is irradiated. On the other hand when formyl protons are irradiated, the intensities of resonance signals of either of the methyl groups remain unaffected because the methyl protons relax one another. The contribution of outside protons is little so that saturation causes no change in the observed methyl group line intensities.

7.34 TWO-DIMENSIONAL FOURIER TRANSFORM NMR (2DFTNMR)

2DFTNMR is the extension of 1DNMR spectroscopy. The FID signal in 1DFTNMR is recorded as a function of time t_2 for a fixed evolution time t_1 , and is represented by the function $S(t_2)$. However, when a large number of one-dimensional signals are recorded as a function of time t_1 , i.e. FID as a function of t_2 at various values of t_1 , these are represented by the functions $S_1(t_2)$, $S_2(t_2)$, $S_3(t_2)$, ..., $S_n(t_2)$, i.e. $S_i(t_2)$, where $i = 1, 2, 3, \dots, n$, or a two-dimensional array $S(t_1, t_2)$. Such an array of one-dimensional signals is collected and is Fourier transformed

twice to obtain a two-dimensional spectrum in terms of two frequency variables ν_1 and ν_2 or sometimes the chemical shift parameters δ_1 and δ_2 , i.e. $f(\nu_1, \nu_2)/f(\delta_1, \delta_2)$,

$$S(t_1, t_2), \dots \quad (7.116)$$

$$2 \times \text{FFT} \dots f(\nu_1, \nu_2)$$

where *FFT* refers to the fast Fourier transform algorithm.

Thus, 2DFTNMR is a technique to obtain two-dimensional NMR spectrum in terms of two frequency variables ν_1 and ν_2 by performing Fourier transformation twice on a large number of one-dimensional FID signals recorded at various values of evolution time, t_1 .

The structure of the array $S(t_1, t_2)$ depends on the chemical shift, coupling constants present at the periods during which they are expressed, the evolution periods (t_1) used and the nature of the applied pulses and the times during which decoupler is operating. Thus a large number of different types of two-dimensional techniques have been developed (more than 100) and some selected 2DFTNMR techniques are listed in Table 7.7. In heteronuclear J-resolved spectroscopy, the experimental conditions are adjusted such that only one parameter, say spin coupling, is expressed during the evolution period and the second parameter, say chemical shift, is expressed during the detection period. The pulse sequence used for a heteronuclear ^1H — ^{13}C 2D J-resolved NMR spectroscopy using the ^1H -decoupler method is shown in Fig. 7.37. In order to obtain the spectrum, the proton decoupler is turned off and a $\pi/2$ pulse is applied to the system and it is allowed to evolve for time t_1 . After time t_1 , the decoupler is turned on and a π pulse is applied and the system is allowed to evolve for time t_1 . The carbons, therefore, evolve for half of the time as singlets and for the remainder of the time as proton coupled multiplets. After the equilibrium is re-established, the process is repeated for other values of t_1 . The FID signals are digitised and Fourier transformed twice to obtain the 2DNMR spectrum. The 2DNMR spectrum is represented in the form

Table 7.7 Selected 2DFTNMR techniques.

Pulse Sequence	Experiment	f_1	f_2	Information
$\frac{\pi}{2} - \tau - \pi - \tau - t_2$	Heteronuclear J-resolved	J_{AX}	δ_X	Heteronuclear coupling constants
$\frac{\pi}{2} - \tau - \pi - \tau - t_2$	Homonuclear 2DJ	J_{AA}	δ_A	Homonuclear J and δ
	CHESY or HETCOR or HETEROCOSY	δ_A	δ_X	Correlation of δ_X and δ_A
$\frac{\pi}{2} - \tau - \frac{\pi}{2} - t_2$	2DCOSY or (HOMCOR) (2-D)	δ_A	δ_A	Identification of all scalar coupling interactions
$\frac{\pi}{2} - \tau - \frac{\pi}{2} - t_m - \frac{\pi}{2} - t_2$	NOESY EXSY	δ_H J_{HH}	δ_H J_{HH}	Spatial proximity and three-dimensional molecular structure
$\frac{\pi}{2} - t_D - \pi - t_D - \frac{\pi}{2} - t_2 (^1\text{H})$	2D-INADE-QUATE (Double quantum Coherence experiment)	$\delta_A + \delta_X$	δ_X	Homonuclear connectivities (coupling) $\text{H}^1\text{—H}^1$, $^{13}\text{C}\text{—C}^{13}$
$\frac{\pi}{2} - t_D - \pi - t_D - \frac{\pi}{2}$				
$-\tau - \frac{\pi}{2} - t_2 (^{13}\text{C})$				

τ —incremented delay;

t_m —mixing periods help in causing magnetisation transfers between the spins in the network,

HETCOR—Heteronuclear chemical shift correlation or HETEROCOSY—Heteronuclear correlated spectroscopy,

CHESY—Chemical shift heteronuclear spectroscopy,

COSY—Correlation spectroscopy or HOMCOR—Homonuclear correlated,

NOESY—Nuclear Overhauser effect spectroscopy, EXSY—Exchange spectroscopy,

2D-INADEQUATE—Incredible natural abundance double quantum transfer experiment.

of a map which contains two frequency axes, f_1 and f_2 . One of the two frequency axes, f_2 always represents the parameter, e.g. chemical shift, of the observed (acquired) nucleus and the other f_1 , axis may represent information, e.g. chemical shift, spin coupling or both, that depends on the pulse sequence and the evolution time, i.e. the behaviour of the spins during the evolution period appears along f_1 -dimension, e.g. in the ^{13}C -HET2DJ spectrum, the f_2 -axis gives the chemical shift of the observed ^{13}C nucleus and the f_1 -axis gives coupling constant for ^{13}C — ^1H . The position of the signal on the map tells us about both the chemical shift of that signal, and another piece of information which depends on the nature of f_1 .

The display mode of 2DNMR is either the contour plots or stack plots. Contour plots enable to see all the responses at once whereas the stack plots usually have most interesting peaks hidden behind another, less important signal. Contour plots are the excellent way of abolishing the noise in 2DNMR spectrum. Stack plots give a more realistic picture of signal-to-noise ratio, and line shape but are otherwise less convenient. The users of 2DNMR spectrum who do not themselves decide on the contour levels to be drawn and the readers of NMR literature should be careful about the contour plots they see before them. The plots might be disguising more than they reveal.

The power of 2DNMR technique to unravel the complex spectra has been demonstrated with the following examples.

^1H 2DCOSY Spectrum for *m*-dinitrobenzene The process of correlating scalar J couplings is called COSY. The basic COSY pulse is: $\pi/2 - \tau - \pi/2 - t_2$. The $\pi/2$ preparation pulse is applied to the sample. It excites the coherences (transitions) for an evolution time t_1 . During this period, the coherences are frequency labelled, i.e. these precess during t_1 . Subsequently, a $\pi/2$ mixing pulse is applied which performs a controlled transfer of coherence to different nuclear spin transitions where the coherences continue to precess with a new frequency during time t_2 . After the equilibrium is re-established, this process is repeated for other values of t_1 . The FID signals are digitised and Fourier transformed twice to obtain 2D spectrum correlating the frequencies during the evolution with the frequencies during the detection. The set of spectra will have normal shifts and coupling in f_2 , but each peak will contain coded information about the frequencies of all the other peaks to which it is coupled. The second Fourier transformation then gives a spectrum with ^1H chemical shifts in each axis. The normal spectrum will be found along the diagonal because the intensity of each transition oscillates at ν_1 during t_1 and because its detected frequency in t_2 is also ν_1 . The off-diagonal cross-peaks show which chemical shifts are spin coupled to one another, because the intensity of ν_1 transition is modulated during t_1 by all the transitions to which it is attached.

The basic 2DCOSY spectrum of *m*-dinitrobenzene is compared with its 1DNMR spectrum in Fig. 7.38. The three multiplets of the one-dimensional spectrum are along the diagonal line. The off-diagonal cross peaks are observed at the intersection of the chemical shifts of $\text{H}_{4,6}$ with H_2 and of $\text{H}_{4,6}$ with H_5 . H_5 is a triplet because it is coupled equally to H_4 and H_6 . H_2 is also a triplet because of its coupling with H_4 and H_6 . However, in the COSY spectrum, the central line expected in both the triplets is completely missing from the off-diagonal cross-peaks because the intensity distribution arising from population transfer from H_4 to H_6 is 1 : 0 : -1. Similarly, the central lines of quintets are often missing.

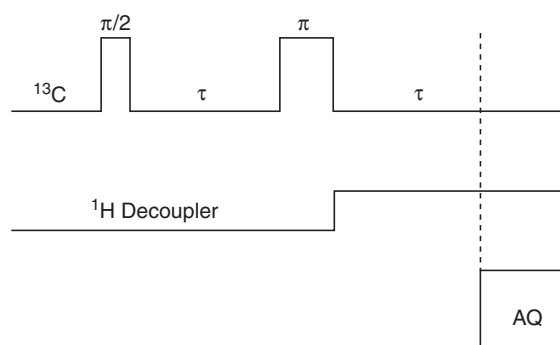


Fig. 7.37 Pulse sequence for ^1H — ^{13}C two-dimensional J -resolved Spectroscopy using the gated decoupler method.

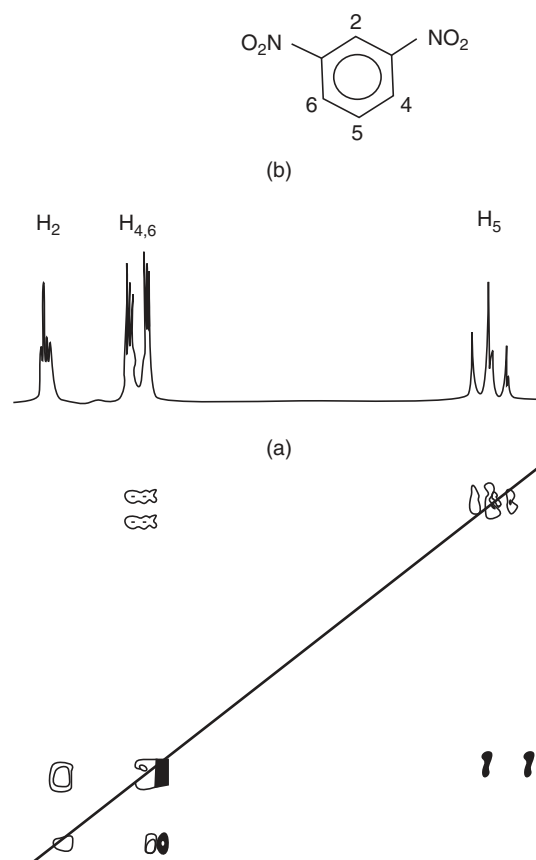


Fig. 7.38 (a) 250 MHz ^1H COSY- $\pi/2$ spectrum of *m*-dinitrobenzene, and (b) the one-dimensional spectrum.

Although ^1H COSY experiments are most common, the technique may be applied to observe nuclei having diverse natural abundance, i.e. ^{11}B , ^{19}F , ^{31}P and ^{51}V and to materials that are enriched in nuclei such as ^{13}C or ^{29}Si . Let us now examine the spectrum in which a proton decoupled spectrum appears in f_2 -dimension and proton coupled spectrum is obtained in f_1 -dimension. The 2DNMR spectrum of 1,3-butanediol is shown in Fig. 7.39 along with its 1DNMR spectrum. The 2D spectrum consists of a quartet ($-\text{CH}_3$), two triplets ($-\text{CH}_2$, $-\text{CH}_2\text{OH}$) and a doublet ($-\text{CHOH}$). These multiplets appear due to the interaction of protons (with ^{13}C) attached to each of the four ^{13}C nuclei in the molecule. On the other hand, this information is missing in 1DNMR spectrum. In conclusion, the 2DNMR spectrum can be used to identify ^{13}C -peaks in the 1DNMR spectrum.

3DNMR spectroscopy is an extension of 2DNMR spectroscopy and can be treated as a combination of two 2D experiments. Instead of a single mixing process which relates two frequency variables, two sequential mixing processes relate three frequencies: the original (first evolution) frequency, ν_1 ; the second evolution frequency, ν_2 ; and the detection frequency, ν_3 . Likewise, higher dimensional experiments can be conceived and generated in a similar manner. The schematic diagram for one-, two- and three-dimensional NMR pulse sequences is shown in Fig. 7.40. The time axis is segmented into various periods as indicated.

The preparation period is used to prepare the nuclear-spin system in a suitable equilibrium or a non-equilibrium state depending upon the purpose of the experiment. The mixing periods following the evolution periods help in causing magnetisation transfer between nuclei spins in the network which are frequency labelled during evolution and thus the detected signals carry information about the history of spin system evolutions. The data are actually collected only during the detection period.

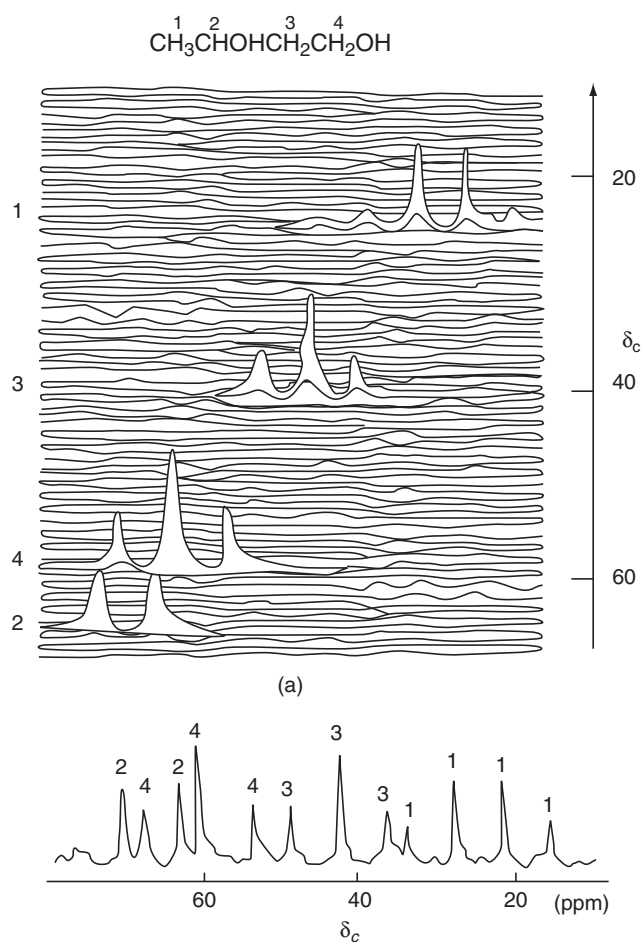


Fig. 7.39 Illustration of the use of the two-dimensional stack spectrum (a) to identify the ^{13}C peaks in a one-dimensional spectrum of 1,3-butanediol (b).

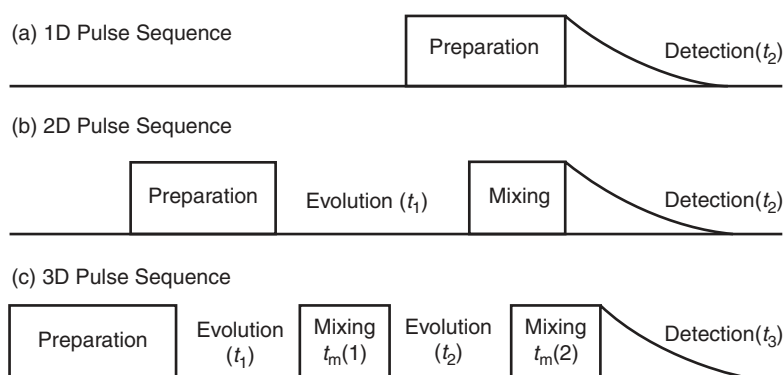


Fig. 7.40 Schematic diagram of (a) one-, (b) two- and (c) three-dimensional NMR pulse sequences.

7.35 ^{13}C -NMR SPECTROSCOPY

^{13}C -NMR was first studied in 1957. With the advent of superconducting magnets and Fourier transfer techniques, it has become a versatile tool for the structural elucidation of molecules.

^{13}C is the naturally occurring stable isotope of carbon and, therefore, is present in all carbon compounds. The ^{13}C nucleus resonates at 15.09 MHz in a magnetic field of 14092 G. Owing to low magnetic moment and low natural abundance (1.1 per cent), the sensitivity of ^{13}C resonance signal in natural abundance samples is only

$\left(\frac{\gamma_{^{13}\text{C}}}{\gamma_{\text{H}}}\right)^3 \times \frac{1}{100} = \frac{1}{6300}$ of that of equal number of proton nuclei. In order to overcome this problem, large sample tubes and strong radio frequency field H_{rf} are used to obtain ^{13}C resonance signals. Moreover, the s - I relaxation time (T_1) of ^{13}C nucleus is large as compared to that of proton and varies from few seconds to several minutes, e.g. relaxation time of ^{13}C nucleus in small highly symmetrical molecules lies in the range of 10–15 seconds at room temperature, in larger molecules with slower reorientation time in solution phase such as cholesteryl chloride, many of the ^{13}C nuclei have relaxation time less than 1 second and only side chain carbons linked to protons have relaxation times in the range of 2–8 seconds. Consequently, unless the scan of ^{13}C nuclear resonance is very fast, the ^{13}C multiplets show distorted peak intensities because of magnetisation.

The intensity of ^{13}C resonance signal depends upon the relaxation time and roughly it is inversely proportional to the relaxation time of the nucleus under consideration, e.g. the intensity of secondary carbon nuclei (two protons attached; 2–4 seconds) > primary carbon nuclei (three protons attached; 10–20 seconds) > quaternary carbon nuclei (no protons attached; 30 seconds). The low intensity of ^{13}C peak of CH_3 group is used to distinguish it from peaks of CH_2 or CH groups. Enhancement of ^{13}C -resonance signal can be obtained in the presence of free radicals (Overhauser effect). The ^{13}C spectrum usually exhibits normal intensity pattern after the addition of a solution of paramagnetic ion such as iron or chromium to the sample. Free electrons in such reagents are efficient relaxers and ^{13}C spectrum usually exhibits normal intensity pattern after the addition of such reagents. In case the reagent complexes with the sample, the relaxation becomes too efficient that the NMR signal becomes too broad to be observed.

Positive enhancement of ^{13}C signal is observed in compounds such as CH_3Cl , CH_2Cl_2 , CH_2Br_2 , CH_2I_2 and CCl_4 . Here, the lone pairs of electrons of halogen atoms participate in the transfer of electron density from the radical to the ^{13}C nucleus. This process facilitates scalar coupling which leads to positive increase in signal intensity. Negative enhancement has been observed for aromatic compounds, alcohols, ketones and CS_2 . On the other hand, positive Overhauser signal enhancements have been observed in aromatic polyfluorocarbons.

Intensities of ^{13}C resonances cannot be simply correlated with the number of atoms contributing to each resonance.

^{13}C -NMR has several advantages over PMR regarding the structure elucidation of molecules. It provides information about the backbone of molecules rather than about the periphery. Diamagnetic effect dominates in shielding the carbon nucleus whereas paramagnetic effect predominates in shielding the hydrogen nucleus. Long-range shielding effects are less important in ^{13}C -NMR, consequently ^{13}C chemical shifts do not parallel proton chemical shifts. ^{13}C -chemical shifts/coupling constants to protons, lie in the range 0–200 ppm/0–300 Hz in contrast to 0–20 ppm/0–20 Hz range for protons. Because of this large difference of chemical shifts, the overlapping of signals in ^{13}C spectra is less as compared to PMR spectra. The ^{13}C chemical shifts of some typical systems are listed in Table 7.8. Substituents affect the ^{13}C chemical shifts and shifts of polar molecules are solvent dependent. The effect of substituents on ^{13}C shifts is similar to that of ^1H chemical shifts. Heteronuclear s - s coupling between ^{13}C and ^{12}C does

Table 7.8 The approximate chemical shift ranges of some ^{13}C resonances relative to TMS.

System	Chemical Shift (in ppm)
CH_3-C	9–29
$\text{CH}-\text{C}$	31–59
$\text{C}-\text{C}$	28–52
$-\text{CH}_3-\text{Hal}$	3–25
$-\text{CH}_2-\text{Hal}$	4–40
CH_2-Hal	30–66
$\equiv \text{C}-\text{Hal}$	33–76
CH_3-N	12–40
$-\text{CH}_2-\text{N}$	42–58

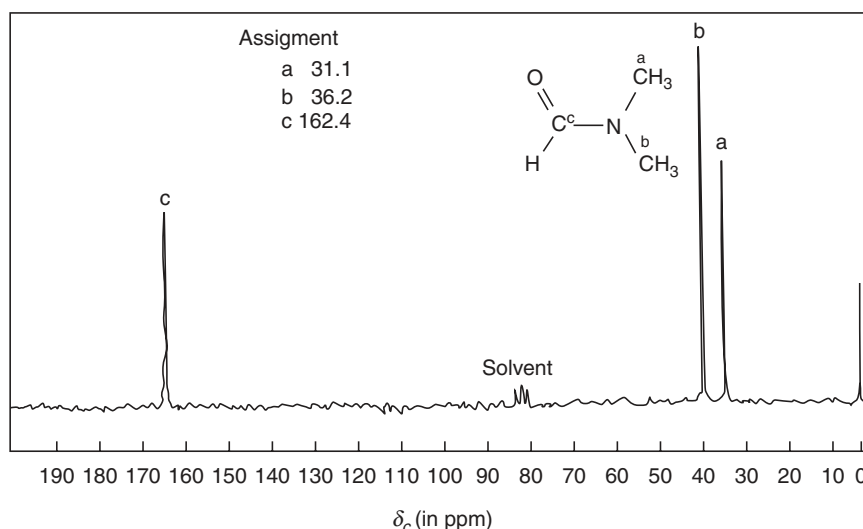
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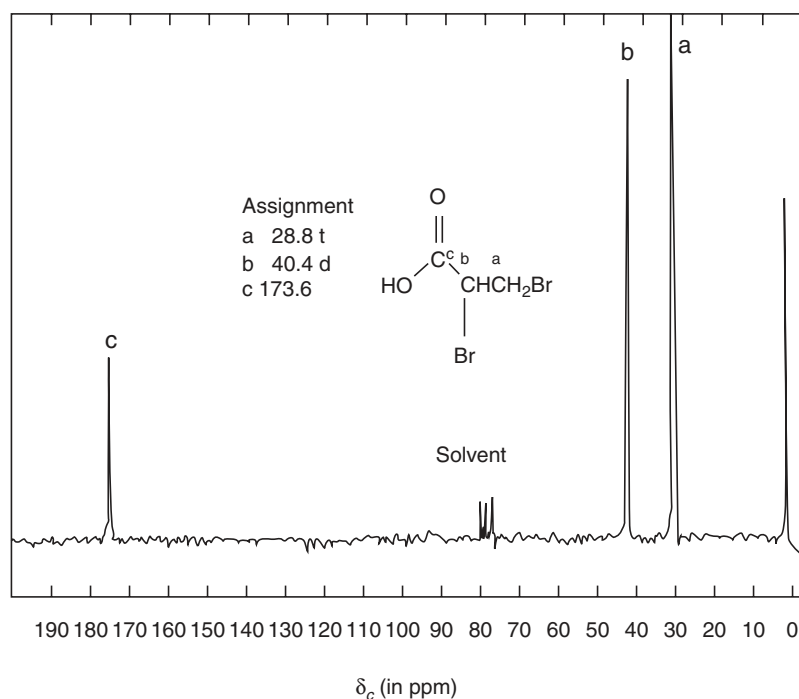
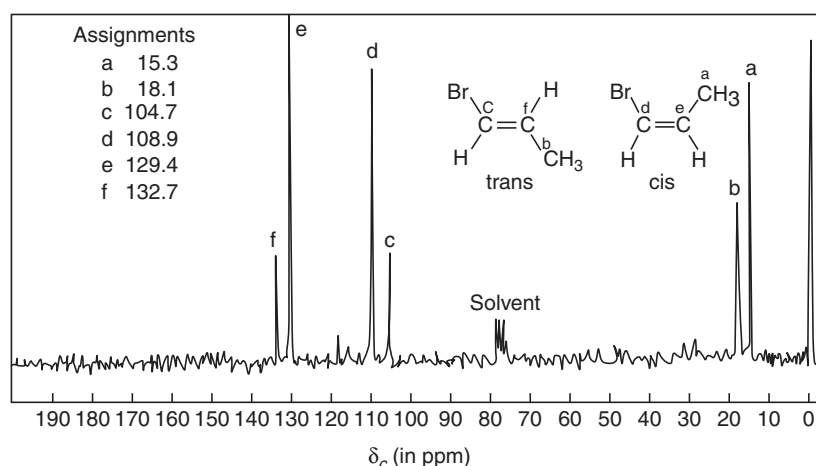
Table 7.8 The approximate chemical shift ranges of some ^{13}C resonances relative to TMS—Cont'd.

>CH—N<	53–68
>C—N<	59–74
$\text{CH}_3\text{—O}$	49–60
$\text{—CH}_2\text{—O}$	42–69
>CH—O	64–77
$\equiv\text{C—O}$	69–83
$\text{—C}\equiv\text{C—}$	72–96
$\text{C}=\text{C}$ (alkene)	105–145
$\text{C}=\text{C}$ (aromatic)	105–160
$\text{—C}\equiv\text{N}$	116–127
$\text{C}=\text{O}$ (ester, amide)	164–175
$\text{C}=\text{O}$ (acid)	168–179
$\text{C}=\text{O}$ (ketone)	196–213
$\text{C}=\text{O}$ (aldehyde)	193–205
$\text{C}=\text{O}$ (quinone)	179–190
$\text{—O—C}\equiv\text{N}$	103–120
$\text{—S—C}\equiv\text{N}$	97–118
$\text{—N}=\text{C}=\text{S}$	117–141

not take place since I for $^{12}\text{C} = 0$. Owing to low natural abundance of ^{13}C , the probability of occurring of ^{13}C atom adjacent to other ^{13}C atom in the molecule is remote, and consequently, the homonuclear s - s interaction between ^{13}C nuclei in molecules is not observed. Thus, the ^{13}C -NMR spectrum yields peak for individual carbon atoms. However, ^{13}C nuclei bound directly together in a molecule or separated from each other by two or three bonds give rise to the AX type spectrum. Protons attached directly to ^{13}C nuclei also exhibit AX type spectrum, e.g. primary carbon nucleus yields a quartet with intensity ratio 1 : 3 : 3 : 1, secondary carbon nucleus shows a triplet having intensity ratio 1 : 2 : 1, tertiary carbon yields a 1 : 1 doublet and quarternary carbon exhibits a singlet only. The coupling constants of primary, double bonded and triple bonded carbon to proton follows the order.

$$J\left(\text{>C—H}\right) = 125 \text{ Hz} < J\left(\text{>C}=\text{C—H}\right) = 170 \text{ Hz} \\ < J\left(\text{C}\equiv\text{C—H}\right) = 250 \text{ Hz}$$

**Fig. 7.41** ^{13}C -NMR spectrum of *N,N*-dimethylformamide.

Fig. 7.42 ^{13}C -NMR spectrum of 2,3-dibromopropionic acid.Fig. 7.43 ^{13}C -NMR spectrum of 1-bromo-2-methylene.

The large difference in chemical shifts of ^{13}C nuclei as well as in the J_{CH} coupling constants is helpful in assigning resonances to a particular ^{13}C nuclei in the molecule. However, it spreads out the intensity of the already weak ^{13}C resonance, signal. This is overcome by simplifying the ^{13}C spectrum by double resonance technique called the broad band decoupling. ^{13}C -NMR spectra of some typical molecules are shown in Figs 7.41 to 7.43.

^{13}C shifts are additive and constitutive. The chemical shifts of simple unsubstituted hydrocarbons may be predicted using additivity relations, although there are deviations from the constitutive additivity rule when the hydrocarbons are substituted by polar groupings. The additivity rule for polar and branched chain alkanes is given by

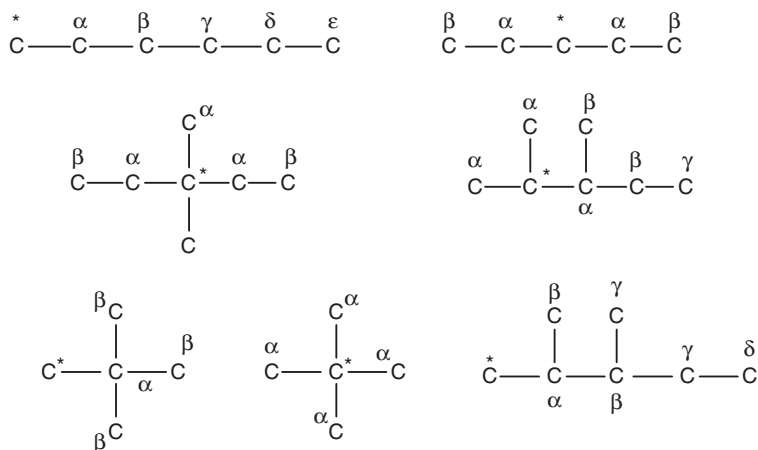
$$\delta = -2.5 + \sum nA \quad (7.117)$$

Here, δ is the predicted chemical shift for a carbon atom, A is the additive shift parameter whose values for ^{13}C atoms in linear and branched chain hydrocarbons have been reported in Table 7.9 and n is the number of carbon atoms for each shift parameter (-2.5 is the shift for the ^{13}C of methane). The effect of substituents on linear and branched alkanes is listed in Table 7.10.

Table 7.9 ^{13}C shift parameters in some linear and branched chain hydrocarbons.

^{13}C atoms	Shift (ppm) (Δ)
α	+ 9.1
β	+ 9.4
γ	-2.5
δ	+ 0.3
ϵ	+ 0.1
$1^0(3^\circ)^a$	-1.1
$1^0(4^\circ)^a$	-3.4
$2^\circ(3^\circ)^a$	-2.5
$2^\circ(4^\circ)$	-7.2
$3^\circ(2^\circ)$	-3.7
$3^\circ(3^\circ)$	-9.5
$4^\circ(1^\circ)$	-1.5
$4^\circ(2^\circ)$	-8.4

$1^\circ(\text{sp}^3\text{C}, -\text{CH}_3)$, $2^\circ(\text{sp}^2\text{C}, -\text{CH}_2)$, $3^\circ(\text{spC}, -\text{CH})$, $4^\circ(\text{quarternary C})$. a— The notations $1^0(3^\circ)$ and $1^0(4^\circ)$ denote a CH_3 group bound to a R_2CH and to a R_3C group, respectively. The notation $2^\circ(3^\circ)$ denotes a RCH_2 group bound to a R_2CH group and so on. Carbons α , β , γ , δ and ϵ are one bond, two bonds, three bonds, four bonds and five bonds apart from the carbon atom (C^*) where δ is to be estimated, i.e.



The deviation, D_X , from the constitutive rule, in ppm, for a given X in the series alkyl-X is given by

$$D_X = n(1.50 - d_x)22.6 \quad (7.118)$$

where n is the number of carbon atoms attached to the monosubstituted α -carbon atom and d_x is the $\text{C}-\text{X}$ bond distance. With the aid of this relationship, the chemical shifts of the α -carbon atoms in $\text{C}_2\text{H}_5\text{X}$, $i\text{-C}_3\text{H}_7\text{X}$, and $t\text{-C}_4\text{H}_9\text{X}$ can be estimated to an accuracy of ± 3 ppm for $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OH}, \text{NO}_2$ and COOH . The $\text{C}-\text{F}$, $\text{C}-\text{Cl}$, $\text{C}-\text{Br}$ and $\text{C}-\text{I}$ bond lengths are 1.38, 1.77, 1.94 and 2.12 Å respectively.

Empirical relations for the prediction of $^{13}\text{C}-^1\text{H}$ coupling constants are also available in the literature. The $J_{^{13}\text{C}-^1\text{H}}$ of monosubstituted methanes is given by

$$J_{^{13}\text{C}-^1\text{H}} = 3.25d\chi + 94.9 \quad (7.119)$$

Here, χ is the substituent Mulliken electronegativity.

For polysubstituted methanes,

$$J_{^{13}\text{C}-^1\text{H}} = \chi[3.25nd + 4.6(n-1)] - 68.74 + 163.6 \quad (7.120)$$

Table 7.10 Incremental substituent effects (ppm) on replacement of H by Y in alkanes. Y is terminal or internal (+ down-field, – up-field).

$\begin{array}{c} \gamma \quad \alpha \\ \quad \\ \beta \quad Y \\ \text{Terminal} \end{array}$ $\begin{array}{c} \gamma \quad Y \quad \gamma \\ \quad \quad \\ \beta \quad \alpha \quad \beta \\ \text{Internal} \end{array}$							
		α			β		γ
Y	Terminal		Internal	Terminal		Internal	
CH ₃	+ 9		+ 6	+ 10		+ 8	– 2
CH = CH ₂	+ 20			+ 6			– 0.5
C CH	+ 4.5			+ 5.5			– 3.5
COOH	+ 21		+ 16	+ 3		+ 2	– 2
CO $\overline{\text{O}}$	+ 25		+ 20	+ 5		+ 3	– 2
COOR	+ 20		+ 17	+ 3		+ 2	– 2
COOI	+ 33		+ 28			+ 2	
CONH ₂	+ 22			+ 2.5			– 0.5
COR	+ 30		+ 24	+ 1		+ 1	– 2
CHO	+ 31			0			– 2
Phenyl	+ 23		+ 17	+ 9		+ 7	– 2
OH	+ 48		+ 41	+ 10		+ 8	– 5
OR	+ 58		+ 51	+ 8		+ 5	– 4
OCOR	+ 51		+ 45	+ 6		+ 5	– 3
NH ₂	+ 29		+ 24	+ 11		+ 10	– 5
NH ₃ ⁺	+ 26		+ 24	+ 8		+ 6	– 5
NHR	+ 37		+ 31	+ 8		+ 6	– 4
NR ₂	+ 42			+ 6			– 3
NR ₃ ⁺	+ 31			+ 5			– 7
NO ₂	+ 63		+ 57	+ 4		+ 4	
CN	+ 4		+ 1	+ 3		+ 3	– 3
SH	+ 11		+ 11	+ 12		+ 11	– 4
SR	+ 20			+ 7			– 3
F	+ 68		+ 63	+ 9		+ 6	– 4
Cl	+ 31		+ 32	+ 11		+ 10	– 4
Br	+ 20		+ 25	+ 11		+ 10	– 3
I	– 6		+ 4	+ 11		+ 12	– 1

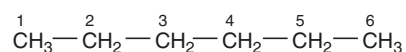
Add these increments to the shift values of the appropriate carbon atom of the alkanes calculated from Table 7.10.

Here, n is the number of substituents attached to the same carbon atom.

Problem 7.19: Calculate the chemical shifts (in ppm) of individual carbon atoms in (a) hexane, (b) neopentane (c) 2,2-dimethylbutane, (d) 2,2,3-trimethylbutane, (e) 3-chloropentane and (f) 3-iodopentane.

Solution

(a) The structural formula of hexane is



Carbon atom 1 has 1 α -, 1 β -, 1 γ -, 1 δ - and 1 ϵ -carbon atoms. So

$$\begin{aligned}\delta_1 &= -2.5 + 1\alpha + 1\beta + 1\gamma + 1\delta + 1\epsilon \\ &= -2.5 + (1 \times 9.1) + (1 \times 9.4) + (1 \times -2.5) + (1 \times 0.3) + (1 \times 0.1) \\ &= 13.9 \text{ (obs = 14.1)}\end{aligned}$$

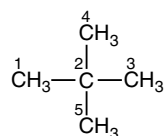
Carbon atom 2 has 2 α -, 1 β -, 1 γ -, and 1 δ -, carbon atoms.

$$\begin{aligned}\delta_2 &= -2.5 + (2 \times 9.1) + 9.4 - 2.5 + 0.3 \\ &= 22.9 \text{ (obs = 23.1)}\end{aligned}$$

The carbon atom 3 has 2 α -, 2 β -, 1 δ -, carbon atoms.

$$\begin{aligned}\delta_3 &= -2.5 + (2 \times 9.1) + (2 \times 9.4) + (1 \times -2.5) \\ &= 32.0 \text{ (obs = 32.2)}\end{aligned}$$

(b) The structural formula of neopentane is



Carbon atom 1 has 1 α - and 3 β -carbon atoms. It is a 1 $^\circ$ atom with one 4 $^\circ$ atom attached.

$$[1^\circ(4^\circ) = -3.4]$$

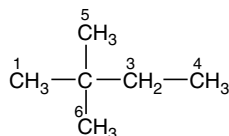
$$\begin{aligned}\delta_1 &= -2.5 + (1 \times 9.1) + (3 \times 9.4) - (1 \times 3.4) \\ &= 31.4 \text{ (obs = 31.7)}\end{aligned}$$

The carbon atom 2 has 4 α carbon atoms. Carbon 2 is a 4 $^\circ$ carbon with four 1 $^\circ$ atoms attached

$$[4^\circ(1^\circ) = -1.5]. \text{ So}$$

$$\begin{aligned}\delta_2 &= -2.5 + (4 \times 9.1) + (4 \times -1.5) \\ &= 27.9 \text{ (obs = 28.1)}\end{aligned}$$

(c) The structural formula of 2,2-dimethylbutane is



The carbon atom 1 has 1 α -, 3 β - and 1 γ -carbon atoms attached and is a 1 $^\circ$ carbon with one 4 $^\circ$ carbon attached. $[1^\circ(4^\circ) = -3.4]$

$$\begin{aligned}\delta_1 &= -2.5 + (1 \times 9.1) + (3 \times 9.4) - 2.5 - 3.4 \\ &= 28.9 \text{ (obs = 29.1)}\end{aligned}$$

The carbon atom 2 has 4 α -, and 1 β -carbon atoms attached. Carbon atom 2 is a 4 $^\circ$ carbon with three 1 $^\circ$ carbons and one 2 $^\circ$ carbon attached. $[4^\circ(1^\circ) = -1.5, 4^\circ(2^\circ) = -8.4]$

$$\begin{aligned}\delta_2 &= -2.5 + (4 \times 9.1) + 9.4 + (3 \times -1.5) - 8.4 \\ &= 30.4 \text{ (obs = 30.6)}\end{aligned}$$

The carbon atom 3 has 2 α -, and 3 β -carbon atoms attached. Carbon atom 3 is a 2 $^\circ$ with a 4 $^\circ$ carbon attached $[2^\circ(4^\circ) = -7.2]$

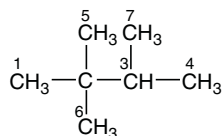
$$\delta_3 = -2.5 + (2 \times 9.1) + (3 \times 9.4) - 7.2$$

$$= 36.7 \text{ (obs = 36.9)}$$

The carbon atom 4 has 1 α -, 1 β - and 3 γ -carbon atoms attached.

$$\delta_4 = -2.5 + 9.1 + 9.4 + (3 \times -2.5) = 8.5 \text{ (obs = 8.9).}$$

(d) The structural formula of 2,2,3-trimethylbutane is



$$\delta_1 = -2.5 + 1\alpha + 3\beta + 2\gamma + 1^\circ(4^\circ)$$

$$= -2.5 + 9.1 + (3 \times 9.4) + (2 \times -2.5) - 3.4$$

$$= 26.4 \text{ (obs = 27.4)}$$

$$\delta_2 = -2.5 + 4\alpha + 1\beta + 3 \times 4^\circ(1^\circ)$$

$$= -2.5 + (4 \times 9.1) + 9.4 + (3 \times -1.5)$$

$$= 38.8 \text{ (obs = 38.3)}$$

$$\delta_3 = -2.5 + 3\alpha + 1\beta$$

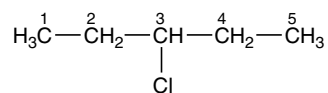
$$= -2.5 + (3 \times 9.1) + 9.4 = 34.2 \text{ (obs = 33.1)}$$

$$\delta_4 = -2.5 + 1\alpha + 2\beta + 3\gamma + 1^\circ(3^\circ)$$

$$= -2.5 + 9.1 + (9.4 \times 2) + (3 \times -2.5) - 1.1$$

$$= 16.8 \text{ (obs = 16.1)}$$

(e) The structural formula of 3-chloropentane is



The calculated values of chemical shifts for individual carbon atoms are

$$\delta_1 = 13.8 \text{ (obs = 13.9)}$$

$$\delta_2 = 22.6 \text{ (obs = 22.8)}$$

$$\delta_3 = 34.5 \text{ (obs = 34.7)}$$

The contribution of Cl atom at position '3' is + 31 (Table 7.10). So δ_3 in 3-chloropentane = 34.5 + 31 = 65.5

(f) Proceeding as above, δ_3 in 3-idopentane = 34.5 - 6 = 28.5.

7.36 ^{19}F -NMR SPECTROSCOPY

^{19}F possesses a spin quantum number of 1/2 and thus exhibits characteristic NMR absorptions. The sensitivity of ^{19}F ($\mu_I = 2.6273$) is close to that of ^1H ($\mu_I = 2.79270$). The energy level diagram for ^{19}F nucleus in terms of M_I is as follows.

$$-\frac{1}{2}$$

$$+\frac{1}{2}$$

Thus, a ^{19}F nucleus attached to another ^{19}F nucleus senses two different fields, all equally probable. Consequently, the ^{19}F -NMR spectrum of a ^{19}F nucleus attached to another ^{19}F nucleus will be a 1 : 1 doublet. The ^{19}F -NMR spectrum of HF involves coupling of the fluorine nucleus with a proton. Since the ^1H nucleus has a spin of 1/2, the ^{19}F nucleus can be in either of the two net fields ($+1/2$, $-1/2$) of protons. The ^1H spin may be parallel or antiparallel to the external field. Thus, ^{19}F -NMR signal of HF will be a symmetrical doublet. Similarly, the PMR spectrum of proton attached to ^{19}F will consist of a symmetrical doublet.

The Larmor frequency for ^{19}F appears at lower energies than that of the proton by a ratio of 1/1.063. Thus, on a 30 MHz proton spectrometer, ^{19}F is observed at 28.22 MHz, on a 60 MHz at 56.44 MHz, on a 100 MHz at 94.07 MHz and on a 200 MHz at 188.14 MHz.

The fluorine chemical shifts (δ_{F}) and coupling constants are much larger (10 fold more) than those of protons. Fluorine chemical shifts are sensitive to chemical environments and spread over a range of 300 ppm. $J(^{19}\text{F} - ^1\text{H})$ lies in the range of 0–90 Hz. ^{19}F chemical shifts of some selected compounds (in ppm) relative to CFCl_3 are CH_3F (278), HF(203), $\text{F}^-(\text{aq})$ (120), PF_5 (96, 62), CF_3H (88), $(\text{CF}_3)_2\text{CO}$ (82), CF_3COOH (77), CF_4 (70), PF_3 (68, 12), $(\text{CF}_3)_4\text{C}$ (61.5), CF_3Cl (32), CF_2Cl_2 (9), CF_3I (4), CFCI_3 (0), IF_5 (–4), SOF_2 (–70), ClF_3 (–80), ClF_3 (–116), BrF_3 (–132, –269), CF_3OF (–142), OF_2 (–250), F_2 (–422). The larger positive numbers show higher fields.

The difference between fluorine chemical shift in F_2 and in $\text{F}^-(\text{aq})$ is 542 ppm compared to the range of about 12 ppm for proton chemical shifts.

Because of high sensitivity, large chemical shift and small size of ^{19}F nucleus, it is used as a site specific probe for biochemical systems. ^{19}F -NMR has been successfully used to differentiate between amino acids (see biological applications).

^{19}F -NMR may also be used for structural elucidation of fluorine containing molecules, e.g. ^{19}F -NMR spectrum of PF_5 shows one resonance peak instead of two in the ratio 3 : 2, i.e. ratio of axial to equatorial sites. ClF_3 has two long $\text{Cl}-\text{F}$ bonds and one short $\text{Cl}-\text{F}$ bond giving rise to non-equivalent fluorines. 40 MHz ^{19}F -NMR spectrum of ClF_3 consists of a triplet and a doublet and the intensity of triplet is half that of doublet as expected. The spectrum is in accord with the interaction between non-equivalent fluorines.

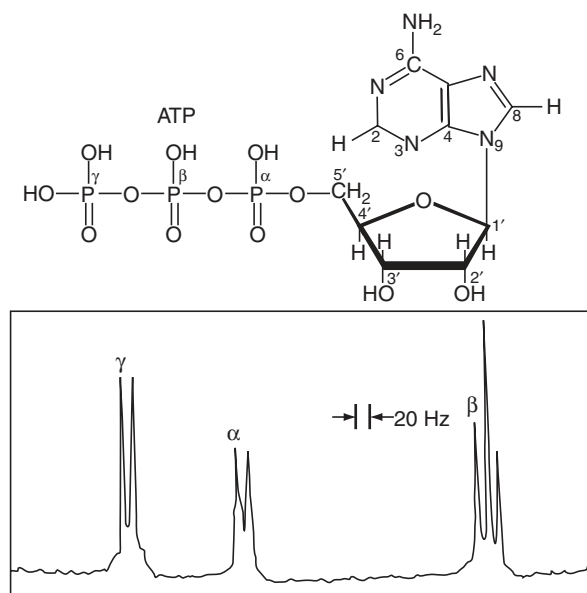
7.37 ^{31}P -NMR SPECTROSCOPY

The spin quantum number of ^{31}P nucleus is 1/2 ($I = 1/2$) and its sensitivity is $\approx 1/15$ of that of proton nucleus. In a homogeneous magnetic field, a given nucleus can assume any one of the $2I + 1$ possible orientations relative to the applied field. Thus, the energy level diagram for a ^{31}P nucleus in terms of M_I is as follows.

$$-\frac{1}{2}$$

$$+\frac{1}{2}$$

Thus, a proton attached to ^{31}P nucleus experiences two different fields of ^{31}P nucleus and the probability of coupling of proton nucleus with the ^{31}P nucleus fields will be the same; consequently, the PMR spectrum of proton coupled to ^{31}P nucleus will be a 1 : 1 doublet. We would expect one ^{31}P nucleus coupled to another ^{31}P nucleus to exhibit a 1 : 1 doublet assuming that the two nuclei are under identical chemical environments so that overlapping of peaks due to two ^{31}P nuclei takes place. ^{31}P -NMR spectrum of P_4O_6 conforms the expected behaviour of one ^{31}P nucleus towards another ^{31}P nucleus, it exhibits only a single peak at –113 ppm relative to 85 per cent H_3PO_4 . On the other hand, if the phosphorous nuclei in a system are in different chemical environments, the signals corresponding to these nuclei will be observed at different positions in the ^{31}P -NMR spectrum. ^{31}P -NMR spectrum of adenosine-5'-triphosphate (ATP) exhibits three signals corresponding to a α , β and γ phosphorous atoms as shown in Fig. 7.44. The peak (triplet) due to the β - ^{31}P nucleus in ATP is more isolated as compared to peaks (doublets) of α and γ - ^{31}P nuclei because its environment is unique, it alone is flanked by phosphate groups. Chemical shifts due to γ , α and β phosphorous atoms of ATP in its FT ^{31}P -NMR spectrum in aqueous environment are observed at –11, –14 and –22.5 ppm respectively.

Fig. 7.44 ^{31}P -FT NMR spectrum of adenosine-5'-triphosphate.Table 7.11 ^{31}P Chemical shifts and coupling constants of some phosphines.

Phosphine	δ_p ppm	J_{pH} Hz
PCl_3	-215	$J_{PH}(1) = (150-250)$
$\text{PCl}_2\text{C}_6\text{H}_5$	-164	$J_{PH}(2) = (-5- + 27)$
$\text{P}(\text{OCH}_3)$	-141	$\begin{array}{c} \text{C} \\ \\ \text{J}_P - \text{C} - \text{H}(2) = (46) \end{array}$
$\text{P}(\text{OC}_2\text{H}_5)$	-140	$J_{PCCH}(3) = (10-20)$
$\text{P}(\text{OC}_6\text{H}_5)$	-128	$J_{PC=CH}(3) \text{ trans} = (5-41) \text{ cis} = (6-20)$
PF_3	-97	$J_{PCCCH}(4) = (0-5)$
$\text{P}(\text{C}_6\text{H}_5)_3$	+ 6.6	Range of coupling constants in Phosphines: -5- + 250
$\text{P}(\text{C}_2\text{H}_5)_3$	+ 19.1	
$\text{P}(\text{CH}_3)_3$	+ 62	Phosphine oxides: 2-750
PH_3	+ 240	Phosphonium salts: 2-900
$[\text{CH}_3\text{PH}]^+$	+ 2.8	Phosphites: 5-20 Phosphates: 0-30

The numbers between brackets attached to J 's correspond to the number of intervening bonds.

The Larmor frequency for ^{31}P nucleus appears at lower energies than that for proton nucleus by a ratio of $17.235/42.577 = 1/2.470$. Thus, on a 60 MHz proton spectrometer, ^{31}P is observed at 24.29 MHz, on a 100 MHz proton spectrometer at 40.48 MHz and on a 200 MHz proton spectrometer at 80.98 MHz.

The drawback of ^{31}P -NMR owing to low sensitivity of ^{31}P as compared to ^1H and ^{19}F nuclei is off set because like ^1H and ^{19}F ; ^{31}P has also 100 per cent natural abundance, due to which no labelling technique, i.e. isotopic enrichment is required as in case of ^{13}C and ^{15}N nuclei. Moreover ^{31}P nuclei have large chemical shifts as compared to ^1H and spread over a range of 0-700 ppm due to which it is easy to handle the ^{31}P -NMR spectrum. The ^{31}P chemical shifts of some phosphines in ppm (δ_p), and coupling constants in Hz (J_{PH}) of some typical systems with respect to 85 per cent H_3PO_4 are given in Table 7.11.

The coupling constants $J(^{31}\text{P}-\text{O}-^{31}\text{P})$ in phosphites and phosphates lie in the range 0-20 and 0-30 Hz respectively.

7.38 NMR SPECTRA OF NUCLEI WITH $I > 1/2$

The NMR spectra of nuclei having $I > 1/2$ are usually intrinsically weak either due to low magnetic moment or low natural abundance or because of both, and are difficult to observe. However, the most common nuclei having $I > 1/2$ attached to hydrogen nuclei are ^{14}N , ^{35}Cl , ^{79}Br and ^{127}I ; they may affect the PMR spectra of molecules through s - s coupling. The spins of these nuclei are 1, 3/2, 3/2 and 5/2 respectively. The energy-level diagrams for these nuclei in terms of M_I are as follows.

Nuclei	^{14}N	$^{35}\text{Cl}, ^{79}\text{Br}$	^{127}I
I	1	$\frac{3}{2}$	$\frac{5}{2}$
M_I	-1, 0, +1	$-\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, \frac{3}{2}$	$-\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, +\frac{5}{2}$

Thus, a proton coupled to a ^{14}N nucleus 'sees' three different fields, all equally probable. All transitions are degenerate and the NMR spectrum of proton coupled to a ^{14}N nucleus will be a triplet with all the peaks of equal intensity. This happens only when nitrogen quadrupole effects do not operate as in symmetrical molecules, N-CH coupling may be observed, J values being commonly less than 1 Hz. The 31.65 MHz PMR spectrum of tetramethylammonium bromide $(\text{CH}_3)_4\text{N}^+\text{Br}^-$ in H_2O (Fig. 7.45) exhibits a triplet (1 : 1 : 1) due to $(\text{CH}_3)_4\text{N}^+$ ion, J is ~ 0.55 Hz. On the other hand, PMR spectrum of CH_3NH_2 in presence of mineral acid exhibits a quartet (1 : 3 : 3 : 1) for the protons of CH_3 group and a triplet with very broad resonance lines (1:1:1) due to protons of NH_3^+ group. The quartet due to protons of CH_3 group arises because of the interaction of CH_3 group protons with protons of NH_3^+ group. The sharp nature of the quartet indicates that the exchange rate between hydrogens attached to nitrogen is slowed down in the presence of the acid. The broadening of triplet is because of quadrupole relaxation which causes a rapid transition between the spin states.

PMR spectra of protons attached to $^{35}\text{Cl}/^{79}\text{Br}$ and ^{127}I should consist of a quartet (1:3:3:1) and a sextet (1 : 5 : 10 : 10 : 5 : 1), respectively. However, in practice these multiplets are not observed because the nuclear quadrupole relaxation causes line broadening.

The Larmor frequency for ^{14}N , ^{35}Cl , ^{79}Br , and ^{127}I will appear at lower energies than that for ^1H by a ratio of 1/13.841, 1/10.205, 1/3.991 and 1/4.998 respectively. Thus, on a 60 MHz proton spectrometer, ^{14}N is observed at 4.3 MHz, on a 100 MHz proton spectrometer, ^{14}N is observed at 7.2 MHz and on a 200 MHz proton spectrometer, ^{14}N is observed at 14.4 MHz.

The primary standards used are nitromethane and the nitrate ion for organic and aqueous solutions, respectively and tetranitromethane and dimethylformamide are used in cases where there are complications because of very small δ_N values (Table 7.12).

^{14}N chemical shifts of aliphatic nitro compounds, for aromatic nitro groups (from nitrate resonance); amides (from nitrate resonance) and thioamides (from nitrate resonance) lie in the range -2.5 – 30 ppm, 6 – 20 ppm, 235 – 283 ppm and 210 – 239 ppm, respectively. In NH_3 , $J_{\text{N(14)}-\text{H(1)}}$ = 43.6 Hz and $J_{\text{H-H}}$ = 10.35 Hz. In NH_4NO_3 in HNO_3 on successive deuteration, i.e. NH_4^+ , NH_3D^+ , NH_2D_2^+ , NHD_3^+ ; $J_{\text{N(14)}-\text{H(1)}}$ = 52.7 Hz. Thus deuterium substitution has little effect on ^{14}N — ^1H coupling constant. However, a down-field shift of the proton resonance on successive deuteration in ammonium nitrate–nitric acid system is observed and is attributed to electrostatic effects arising

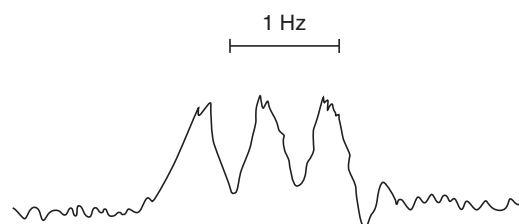
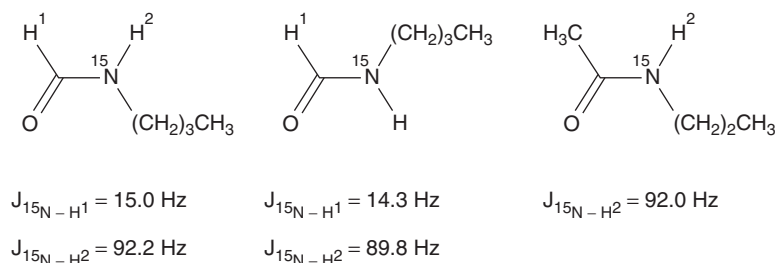


Fig. 7.45 31.65 MHz PMR signal of $(\text{CH}_3)_4\text{N}^+$ ion in water.

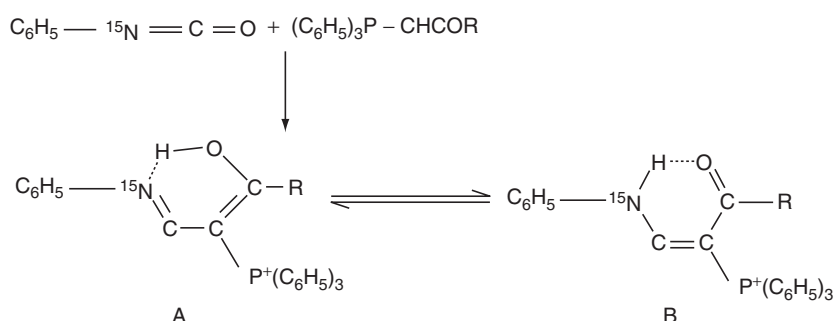
Table 7.12 Internal standards for ^{14}N measurements.

Standard	δ_N (ppm)	Application
MeNO_2	0	Primary: For general use with organic solvents and concentrated mineral acids
NO_3^-	0	Primary: For general use in aqueous solutions
$\text{C}(\text{NO}_2)_4$	+ 48	Secondary: For nitro compounds
Me_2NCHO	+ 276	Secondary: For aromatic nitro compounds and nitrogen heterocycles.

from hydrogen bonding with solvent molecules. The N^{15} nucleus ($I = 1/2$) resonates at 4.315 MHz in a magnetic field of 10 kG. Since this isotope has a low magnetic moment ($\mu_N = -0.28304$) and is present in only 0.365 per cent of natural nitrogen, the sensitivity of ^{15}N resonance signal in natural abundance samples is only about $1/2630 \times 10^4$ which in case of ^{14}N nucleus is $\approx 1/2650$ of that of an equal number of proton nuclei. However, ^{15}N has no quadrupole moment and s - s coupling is easily detected under suitable conditions. The ^{15}N chemical shifts (in ppm from nitrobenzene- ^{15}N) of aromatic nitro groups of nitrobenzene derivatives lie in the -3.85 – 4.38 region. The observation of ^{15}N coupling can be used for studying isomeric and tautomeric phenomenon which are very common in organic nitrogen-containing compounds. The nitrogen proton coupling constants for the separately observable *cis* and *trans* isomers of ^{15}N -*n*-butylformamide and ^{15}N -4-propylacetamide are shown in Fig(A).



The reaction of phenylisocyanate and acylmethylenetriphenylphosphoranes gives a product whose structure may be represented by the tautomeric equilibrium. The observed ^{15}N -H coupling constant $J_{^{15}\text{N}-\text{H}} = 85$ – 88 Hz indicates that tautomeric form B predominates over A irrespective of solvent or temperature.



7.39 APPLICATIONS OF NMR SPECTROSCOPY

The use of NMR spectroscopy makes it possible to investigate the structure of molecules, their conformation, electron density delocalisation, weak intermolecular interactions, i.e. complex formation, solvation, hydrogen bonding, hindered internal rotation, tautomeric equilibria, composition of multicomponent systems and sometimes also the kinetics of reactions. NMR technology is also widely recognised in the fields other than chemistry such as biology, agriculture, engineering, medicine and industrial quality control. The NMR parameters which are generally exploited to carry out these type of studies are chemical shift, integrated intensity or height of signal or peak areas when the signals have significant width, coupling constant and bandwidth.

7.39.1 Mole Fraction of a Non-ideal Solution from NMR Spectrum

The nature of NMR is such that for a homogeneous mixture, one obtains a spectrum whose integration peaks are proportional to the number of protons present at a given field producing that signal. So, if a particular proton in a molecule can be associated qualitatively with a given peak and then the area of that peak for each molecule can be related by an exact ratio to each other, the mole ratios as well as mole fractions of the components may be determined.

Let *A* and *B* be the two components of a homogeneous solution. To determine the mole fraction of *A* and *B* from a spectrum, the areas of specific protons of *A* and *B* are measured. These areas are then normalised by the number of protons resonating in each material. Thus,

$$\bar{I}_a = \frac{I_a}{n_a} \quad (7.121)$$

$$\bar{I}_b = \frac{I_b}{n_b} \quad (7.122)$$

where n_a and n_b are the number of protons associated with the signals having areas I_a and I_b respectively. Barred quantities indicate the areas per proton. The mole fractions of A and B are then given by

$$X_a = \frac{\bar{I}_a}{\bar{I}_a + \bar{I}_b} \quad (7.123)$$

$$X_b = \frac{\bar{I}_b}{\bar{I}_b + \bar{I}_a} = 1 - X_a \quad (7.124)$$

e.g. in case of chloroform–acetone system, the normalised areas of the peaks corresponding to protons of chloroform and acetone are given by

$$\bar{I}_{ch} = \frac{\bar{I}_{ch}}{1}$$

$$\bar{I}_{ac} = \frac{\bar{I}_{ac}}{6}$$

Here, the subscripts ch and ac stand for chloroform and acetone respectively.

This method is equally applicable to a three-component system, i.e. chloroform–acetic acid– H_2O . The integration peaks used are the methyl group for acetic acid (3 protons), the single hydrogen from chloroform and the hydrogens of water minus the one hydrogen from the O–H group of acetic acid which falls at the same chemical shift as H_2O , since the protons are in rapid exchange between the two molecules. Consequently, the normalised areas of the signals corresponding to protons of chloroform (ch) acetic acid (HOAC) and H_2O are given by

$$\bar{I}_{ch} = \frac{I_{ch}}{1}$$

$$\bar{I}_{HOAC} = \frac{I_{HOAC}}{3}$$

$$\bar{I}_{H_2O} = \frac{I_{H_2O}(2 \text{ water protons} + \text{HOAC acidic proton}) - I_{HOAC}}{2 \text{ protons/molecule of water}}$$

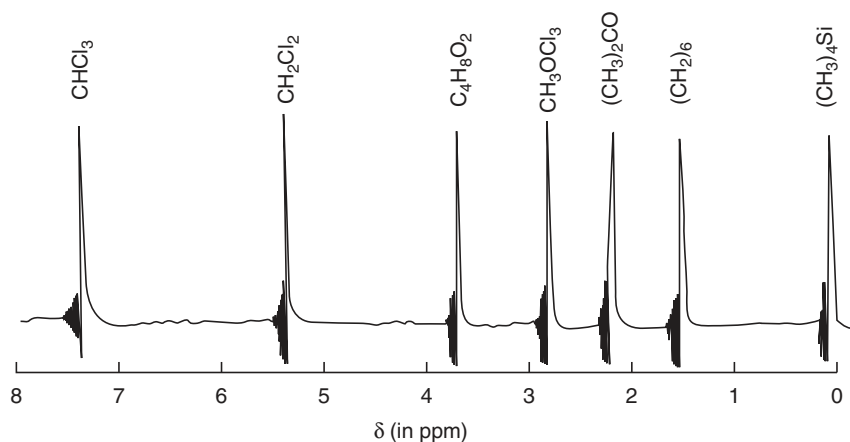
7.39.2 Analysis of Mixtures

The NMR spectra may be used for the quantitative analysis of mixtures provided the applied magnetic field is homogeneous. The residual hydrogen in D_2O may be determined as follows: standard samples containing known amounts of H_2O and D_2O are prepared. A calibration curve between intensity of proton signal and the amount of water in the standard sample is plotted. The intensity of the proton signal in the unknown sample of ($H_2O + D_2O$) is observed. The amount of water corresponding to this intensity can then be directly read from the calibrated graph.

The NMR spectra is also used for the analysis of multicomponent mixtures, e.g. a mixture of cyclohexane (C_6H_{12}), dimethylacetone ($(CH_3)_2CO$), 1,1,1-trichloroethane (CH_3CCl_3), dioxane ($C_4H_8O_2$), dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$) has been analysed by this technique. The amount of each component in the mixture is proportional to the number of equivalent protons contained in their molecules. So from the ratios of the normalised integrated intensities of all the signals, the concentration of each component can be determined. The NMR spectrum of the above-said mixture is presented in Fig. 7.46. Since the intensities of all the signals are identical, the concentrations of the components in the mixture are, therefore, inversely proportional to the number of equivalent protons contained in the molecules, i.e.

$$C_6H_{12} : C_3H_6O : CH_3CCl_3 : C_4H_8O_2 : CH_2Cl_2 : CHCl_3 :: 2 : 4 : 8 : 3 : 12 : 24,$$

Thus, the amounts of various components in the mixture are $C_6H_{12} = 3.77$; $C_3H_6O = 7.54$; $CH_3CCl_3 = 15.09$; $C_4H_8O_2 = 5.66$; $CH_2Cl_2 = 22.64$ and $CHCl_3 = 45.28$ per cent.

Fig. 7.46 ^1H -NMR spectrum of a mixture of compounds.

7.39.3 Study of Tautomeric Equilibria

The amount of tautomeric forms in any molecular system can be determined from the normalised integrated intensities of the NMR active nuclei responsible for tautomerism. The amount of keto and enol forms in a system exhibiting tautomeric equilibrium can be determined from the intensities of the olefinic proton ($-\text{CH}$) of enol form and of methylenic protons ($-\text{CH}_2$) of keto form. If I_{CH} is the intensity of $-\text{CH}$ proton and I_{CH_2} that of $-\text{CH}_2$ protons, then

$$\text{Percentage of enol form} = \frac{\bar{I}_{\text{CH}}}{I_{\text{CH}} + \bar{I}_{\text{CH}_2}} \times 100 \quad (7.125)$$

$$\text{Percentage of keto form} = \frac{\bar{I}_{\text{CH}_2}}{I_{\text{CH}} + \bar{I}_{\text{CH}_2}} \times 100 \quad (7.126)$$

Here, $\bar{I}_{\text{CH}} = \frac{I_{\text{CH}}}{1}$ and $\bar{I}_{\text{CH}_2} = \frac{I_{\text{CH}_2}}{2}$ are the normalised integrated intensities.

Problem 7.20: Determine the amount of keto and enol forms in acetylacetone if the integrated intensities of olefinic and methylenic protons are 5.2 and 2 units respectively.

Solution The tautomeric equilibrium in acetylacetone is



We know what, $I_{\text{CH}_2} = 2$ units and $I_{\text{CH}} = 5.2$ units.

Using Eqs (7.125) and (7.126) we obtain

$$\text{Percentage of enol form} = \frac{\frac{5.2}{1}}{\frac{5.2}{1} + \frac{2}{2}} \times 100 = 83.3$$

$$\text{Percentage of keto form} = \frac{\frac{2}{2}}{\frac{5.2}{1} + \frac{2}{2}} = 16.2$$

Keep in mind that this type of equilibrium is a function of temperature and solvent.

7.39.4 Determination of Hydration Number

None of the methods based on conductance, electromotive force or transference number provides a direct measure of the coordination number of an ion. Protons in water molecules occupying the first hydration sphere exhibit a proton magnetic resonance signal discernible from bulk water signal because of their different magnetic environments. At low temperatures (generally $\leq -20^\circ\text{C}$), the exchange of both protons and H_2O molecules is slowed to the extent that these two peaks may be resolved. The ratio of their areas then gives a direct measure of the primary hydration number.

$$\text{Hydration number} = \frac{\text{Area of the coordinated peak}}{\text{Area of coordinated peak} + \text{area of bulk peak}} \times \frac{[\text{H}_2\text{O}]}{\text{Moles of salt}} \quad (7.127)$$

Here, $[\text{H}_2\text{O}] = 55.5$ moles.

Incomplete resolution owing to overlap between bulk and complexed water peaks may pose a problem for accurate determination of areas. Complete resolution of peaks is hindered because of freezing, precipitation as well as increase in viscosity of solutions at low temperatures. Freezing may be prevented by using solvent systems containing low-freezing-point organic solvents or by use of solutions of high ionic strength. Solvent exchange in non-aqueous solutions is also slow enough to permit the observation of signals resulting from the protons of bulk molecules and molecules in the first coordination sphere of anions. All these factors cause large line broadening of water signals. The much greater line width of the signal of complexed water molecules may be because of s - s or quadrupole interaction with the metal ion.

The dependence of NMR signal shape on rate processes occurring in solutions may be demonstrated by spectra recorded at different temperatures. At room temperature when only one water proton signal is noticed, the lifetime of proton at a particular site is given by $\tau = \frac{1}{2\pi\Delta\nu}$. When the separate signals are observed (at low temperature), the proton (not water) exchange has been slowed down to such an extent that τ increases by 10^3 .

Problem 7.21: The PMR spectrum of 1.75 M AlCl_3 plus 1.65 M $\text{Ca}(\text{NO}_3)_2$ at -38°C on a 60 MHz instrument exhibits two bands corresponding to coordinated and bulk water molecules. The coordinated water peak is to the left (upfield = 124 Hz) of the bulk water peak. If the areas of the coordinated and bulk water peaks are 84 and 600 units respectively, determine the coordination number of $\text{Al}(\text{III})$.

Solution Concentration of $\text{AlCl}_3 = 1.75$ M

$$[\text{H}_2\text{O}] = 55.55 \text{ moles}$$

Area of coordinated water peak = 84 units

Area of the uncomplexed water peak = 600 units

Substituting these values into Eq. (7.127),

$$\text{Hydration number} = \frac{84}{600 + 84} \times \frac{55.55}{1.75} = 3.88$$

The low value of hydration number of $\text{Al}(\text{III})$ in the presence of Cl^- ions may be taken as evidence for contact ion pairing.

7.39.5 Determination of Optical Purity

A mixture of equal quantities of two enantiomers E_+ and E_- called racemic mixture does not rotate the plane of polarised light. However, another mixture of enantiomers will exhibit optical rotation. The percent optical purity (P) of a mixture of enantiomers is defined as

$$P(\%) = \frac{[\alpha]}{[A]} \times 100 \quad (7.128)$$

where $[\alpha]$ is the specific rotation of a mixture of enantiomers and $[A]$, is the specific rotation of the pure enantiomer and is also called the *absolute rotation*. The value of the per cent optical purity is equal to the per cent enantiometric purity; which is a measure of the excess of one enantiomer over another,

$$P(\text{percent}) = \text{enantiometric purity (percent)}$$

$$= \frac{|E_+ - E_-|}{|E_+ + E_-|} \times 100 \quad (7.129)$$

$$= (2E_+ - 1) \quad (7.130)$$

where, E_+ and E_- are the mole fractions of the enantiomers. E_+ is assumed to be the predominant isomer. The optical purity may be determined by polarimetry provided the absolute rotation of the pure enantiomer is known, which is always not possible.

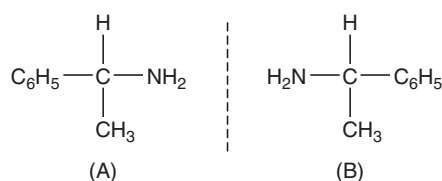
In order to resolve the racemic mixture, it is treated with a second chiral substance Z_+ , to produce a mixture of diastereomers Y_+Z_+ and Y_-Z_+ which have different physical properties, e.g. melting point, solubility, infrared and NMR spectra. The NMR method of optical purity is based on the difference in properties of diastereomers. The two enantiomers Y_+ and Y_- are completely converted into Y_+Z_+ and Y_-Z_+ by reaction with an excess of Z_+ . Under this condition, the ratio of mole fractions of enantiomers reacted equals the ratio of diastereomers formed, i.e.

$$\frac{E_+}{E_-} = \frac{E_{Y_+Z_+}}{E_{Y_-Z_+}} = R \quad (7.131)$$

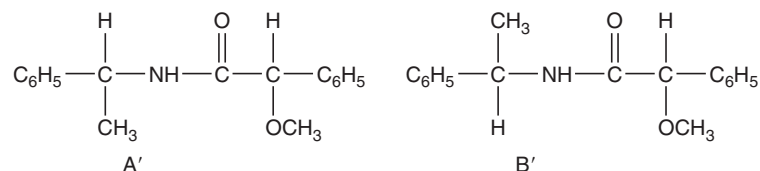
From Eqs (7.129) and (7.131), we obtain

$$P(\text{percent}) = \frac{R-1}{R+1} \times 100 \quad (7.132)$$

Thus, if R (the ratio of enantiomers) is known, the optical purity of the original mixture Y_+ and Y_- can be calculated, R is taken as the ratio of intensities of particular NMR signals corresponding to diastereomers formed from enantiomers, e.g. the optical purity of a partially resolved sample of α -phenylethylamine ($A + B$) is determined by converting,



into a mixture of diastereomeric amides ($A' + B'$) by reaction of optically pure *o*-methyl-mandelyl chloride.



The two C-methyl groups (as well as the other corresponding groups) in A and B though have same chemical shifts because of enantiomeric environments but have different chemical shifts in A' and B' due to diastereomeric environments. Thus from the ratio of integrated intensities (R) of any of the sets of signals in the PMR spectrum of a mixture of diastereomers, the optical purity of enantiomers can be determined from Eq. (7.132).

The NMR method for the determination of optical activity is not only limited to amines but is also applicable to alcohols, sulphinates, phosphinates and sulphinamides.

7.39.6 Determination of Molecular Mass

Molecular mass can be determined from the integration of proton signals. A certain integral is equated with the amount of protons by adding a known weight of standard in the NMR sample of the unknown. If I_{std} = integral of the standard, W_{std} = mass of standard, M_{std} = molecular mass of standard, and n_{std} number of protons in the standard peak, then

$$I_{\text{std}} = \frac{W_{\text{std}} n_{\text{std}}}{M_{\text{std}}} \text{ protons} \quad (7.133)$$

Therefore,

$$I = \frac{W_{\text{std}} n_{\text{std}}}{M_{\text{std}} I_{\text{std}}} \quad (7.134)$$

where, I is the integral of unknown signal from say n protons.

The $\frac{W_{std}n_{std}}{M_{std}I_{std}} \cdot I$ proton signal is because of W of unknown. Therefore, n protons correspond with

$$\frac{nW M_{std}I_{std}}{W_{std}n_{std}} = \text{molecular mass of unknown} \quad (7.135)$$

The standard used should not overlap any signals of the unknown and hexmethyldichlorosiloxane $[(CH_3)_2SiO]_3$ is recommended. It is a very soluble inert solid with a high field chemical shift a few cycles down-field from TMS. This method does not appear to have received much application in practice. Molecular mass of polymers may be determined by PMR spectroscopy. The OH resonance of the polyethylene glycol carbowax 600 $[HO(CH_2CH_2O)_nH]$ may be integrated separately from the $-OCH_2CH_2O-$ signal and the number average molecular mass (NAMM) is calculated as follows.

Let $I(OH)$ is the OH integral and $I(OCH_2CH_2O)$ is the OCH_2CH_2O integral.

$$I(OH) \text{ integral} \equiv 2 \text{ protons}$$

Therefore,
$$I(OCH_2CH_2O) \equiv \frac{2I(OCH_2CH_2O)}{I(OH)} \text{ protons}$$

$$\text{Since } I(OCH_2CH_2O) \equiv 4 \text{ protons} \equiv \text{mass } 44 (CH_2CH_2O).$$

Therefore,
$$\frac{2I(OCH_2CH_2O)}{I(OH)} \text{ protons} = \frac{\text{mass } 22I(OCH_2CH_2O)}{I(OH)}$$

i.e.
$$\text{NAMM} \equiv \frac{2I(OCH_2CH_2O)}{I(OH)} + 18$$

The PMR value of 422 is much lower than the cryoscopic value of 598. This method is not very reliable since it depends on the accurate integration of a very small area $I(OH)$ relative to a large area $I(OCH_2CH_2O)$ and upon the absence of water which may contribute to the OH signal. So it is better to exploit the terminal methylene signal $(HO-CH_2)$. This is not resolvable in the $CDC1_3$ spectrum. The PMR spectrum is recorded in pyridine- CF_3COOH containing a trace of hydrogen chloride to decouple HO from the adjacent CH_2 signal on a 60 MHz instrument. Polyethylene glycol 400 is $HOCH_2(CH_2OCH_2)_nCH_2OH$.

Let $I(HOCH_2)$ is the signal of CH_2 protons of $HOCH_2 \cdot I(HOCH_2) \equiv 4$ protons

If $I(CH_2OCH_2)$ is integral of CH_2OCH_2 protons.

Then,
$$I(CH_2OCH_2)_2 \equiv \frac{4I(CH_2OCH_2)}{I(OHCH_2)} \text{ protons.}$$

Now
$$I(CH_2OCH_2) \equiv 4 \text{ protons} \equiv \text{mass of } 44(CH_2OCH_2)$$

Therefore,

$$\frac{4I(CH_2OCH_2)}{I(HOCH_2)} \text{ protons} \equiv \frac{\text{mass } 44I(CH_2OCH_2)}{I(HOCH_2)}$$

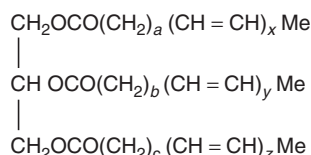
i.e.
$$\text{NAMM} \equiv \frac{44I(CH_2OCH_2)}{I(HOCH_2)} + 62$$

where
$$2 \times HOCH_2 = 62$$

The molecular mass determined by this method is 592.

7.39.7 Degree of Unsaturation in Natural Fats

A general formula for natural fats may be written as follows.



The molecular mass corresponding to this formula is

$$MM = 173 + 45 + 14(a + b + c) + 26(x + y + z) \quad (7.136)$$

where, 173 is the formula mass of the $\text{C}_6\text{H}_5\text{O}_6$ glyceryl triester radical, while 45 is the mass of three terminal methyl groups; 14 is the mass of CH_2 group and 26 is the mass of $\text{CH}=\text{CH}$ group. The total number of protons (T) is

$$T = 5 + 9 + 2(a + b + c) + 2(x + y + z) \quad (7.137)$$

The number of vinylic protons is

$$V = 2(x + y + z) \quad (7.138)$$

Lumping together Eqs (7.137) and (7.138), we obtain

$$(a + b + c) = \frac{(T - V - 14)}{2} \quad (7.139)$$

Thus, Eq. (7.136) may be expressed in terms of T and V as,

$$\begin{aligned} MM &= 218 + 7(T - V - 14) + 13V \\ &= 120 + 7T + 6V \end{aligned} \quad (7.140)$$

Knowing T and V from integral data, the molecular mass of the natural fats can be determined from Eq. (7.140). Once MM is known, the iodine value may be calculated from the expression

$$\begin{aligned} \text{Iodine value} &= \frac{126.9}{MM} \times \text{number of vinylic protons} \times 100 \\ &= \frac{12690V}{MM} \end{aligned} \quad (7.141)$$

Using this method, the iodine number, the molecular mass and the number of vinylic protons in a sample of pure trilinolein have been found to be 173.3, 879 and 6.00 respectively.

7.39.8 Study of Conformational Equilibria

The conformational studies by NMR technique are carried out using ^1H , ^{13}C and other nuclei. Consider a system exhibiting conformational equilibria, i.e.



where suffixes a and e stand for axial and equatorial, respectively.

$$K = \frac{[\text{A}_e]}{[\text{A}_a]} \quad (7.143)$$

By making use of Eq. (7.112), i.e

$$\delta = P_1\delta_1 + P_2\delta_2, \quad (7.144)$$

we write

$$\delta = P_e\delta_e + P_a\delta_a$$

Here, δ_a and δ_e are the chemical shifts of the NMR active nuclei responsible for the conformational equilibria. δ is the observed chemical shift of the identical NMR active nuclei rapidly equilibrating in the parent structure of the system exhibiting conformational equilibria.

Since, $P_a + P_e = 1$,

$$\therefore P_e = \frac{\delta_a - \delta}{\delta_a - \delta_e}; \quad (7.145)$$

$$P_a = \frac{\delta - \delta_e}{\delta_a - \delta_e} \quad (7.146)$$

From Eqs (7.145) and (7.146), we obtain

$$K_{a-e} = \frac{P_e}{P_a} = \frac{\delta_a - \delta}{\delta - \delta_e} \quad (7.147)$$

$$K_{e-a} = \frac{P_a}{P_e} = \frac{\delta - \delta_e}{\delta_a - \delta} \quad (7.148)$$

Thus, by monitoring the chemical shift of the system exhibiting conformational equilibria as a function of temperature, the value of K and hence ΔG at a particular temperature can be evaluated. The best approach to determine the conformational equilibrium constants is the examination of an equilibrating system at sufficiently low temperatures so that the rate of conformational inversion is slow on the NMR time scale. Consequently, resonance lines for each individual conformer will appear whose relative intensities will provide a direct measure of K at that very temperature. The results of conformational equilibria based on PMR spectroscopy may be supplemented by ^{13}C -NMR technique. However, the determination of K from ^{13}C -chemical shift data using Eqs (7.147) and (7.148) depends upon the availability of reliable values of δ_a and δ_e . In case it is difficult to obtain accurate values of δ_a and δ_e , the latter approach based on intensities of the conformers is appreciated.

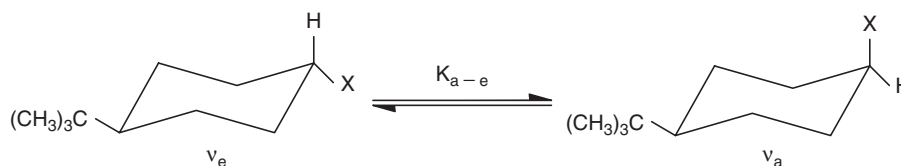
Problem 7.22: The NMR data on the conformational behaviour of 3- and 4-*t*-butyl-substituted cyclohexanes are listed in the tabular form as under. Determine the equilibrium constants of the systems.

C_1 -proton signals in 3- and 4-, *t*-butyl substituted cyclohexanes.

C_1 substituted		$-\nu_{\text{CHX}}^a$ (in cps)		
X	Axial H		Equatorial H	
	trans-4	cis-3	cis-4	trans-3
OH	202.0	206.0	236.0	244.0
F	281.1*	282.0*	304.6*	312.5*
Cl	221.5	225.5	262.5	269.8

$J = 49.4$ cps in all cases, a-down field from TMS in CCl_4 , * lower field signal of fluorine split doublet

Solution The general conformational equilibrium for these systems is



By Eq. (7.148),

$$K_{e-a} = \frac{\nu - \nu_e}{\nu_a - \nu} \quad (7.149)$$

Here, ν is the observed chemical shift for —CHX proton in the rapidly equilibrating cyclohexyl system. For hexanol system, $\nu = -211$ cps is the shift of —CHX proton in cyclohexyl chloride. The observed shift $\nu = -291.6$ cps to be used in fluoride system is the lower field component of the CHF doublet. In case of chloride system, $\nu = -234.4$ cps is the chemical shift of —CHX proton in the cyclohexyl chloride. Thus,

$$K_{\text{OH}}(4-t) = \frac{-211 + 236}{-202 + 211} = \frac{25}{9} = 2.77$$

$$K_{\text{OH}}(3-t) = \frac{-211 + 244}{-206 + 211} = \frac{33}{5} = 6.6$$

For other systems, the calculated values of K 's are

$$K_{\text{F}}(4-t) = 1.25; K_{\text{Cl}}(4-t) = 2.18$$

$$K_{\text{F}}(3-t) = 2.18; K_{\text{Cl}}(3-t) = 3.98$$

7.39.9 Study of H-bonded Equilibria

Proton-exchange processes are affected by temperature and are accelerated in the presence of strong acids and bases. The time of spin orientation in the magnetic field or the time required for the resonance measurement ($\approx 10^{-2} - 10^{-3}$ second) is long compared to the lifetimes of H-bonded moieties ($10^{-12} - 10^{-13}$ second). This is because of very rapid formation and breaking of hydrogen bonds in solution. Thus, the H of an AH group will participate in many H-bonds with the neighbouring molecules in a time of the order of 10^{-3} second. Hence, the H of an AH will experience at each concentration an averaged out environment which will depend on the number and kind of proton donor species present. This fact decreases the usefulness of PMR as a tool for studying the H-bonded dimers and n -mers and their equilibria in the case of self-associated H-bonded systems. However, the PMR technique proved to be very useful tool for the investigation of H-bonded 1:1 complex because there is only one type of proton donor H-bonded to acceptor molecules in such systems. In view of it, PMR differs from infrared spectroscopy in that only one PMR signal is observed for protons involving H-bonding. This signal is a weighted average of all protons in their environments, in the free as well as in the associated forms.

The measured chemical shift of such a nucleus is,

$$\delta = \sum P_i \delta_i$$

where, P_i is the population of the nucleus in the i th environment relative to the total population of the nucleus, i.e. $\sum P_i = 1$, and δ_i is the chemical shift of the nucleus purely in the i th environment. In the simple case of 1:1 complexes formed between donor and acceptor in which the rates of the forward and backward reactions are very fast, the measured chemical shift of nucleus in the acceptor or donor moiety will be

$$\delta = P_A \delta_A + P_{DA} \delta_{DA} \quad (\text{in acceptor moiety}) \quad (7.150)$$

$$\delta = P_D \delta_D + P_{DA} \delta_{DA} \quad (\text{in donor moiety})$$

Here, P_A/P_D is the fraction of uncomplexed acceptor/donor molecules and P_{DA} is the fraction of the acceptor/donor molecules complexed. Since $P_A + P_{DA}$ or $P_D + P_{DA} = 1$, the expression (7.150) may be written as

$$\delta = P_{DA} (\delta_{DA} - \delta_A) + \delta_A \quad (7.151)$$

$$\delta = P_{DA} (\delta_{DA} - \delta_D) + \delta_D$$

This equation can be used to evaluate the association constants of various types of complexes, viz., H-bonded and charge transfer.

(a) Case(i): Extent of Molecular Association due to H-Bonding Let us consider a system in which there is a rapid exchange of proton between free and H-bonded protons. The observed chemical shift δ of proton in such a system is

$$\delta = \frac{(\delta_1 C_1 + 2\delta_2 C_2 + 3\delta_3 C_3 + \dots + n\delta_n C_n)}{(C_1 + 2C_2 + 3C_3 + \dots + nC_n)} \quad (7.152)$$

Here, $C_1, C_2, C_3, \dots, C_n$ are the concentrations of monomer, dimer, trimer, ..., n -mer moieties respectively. If $K_1, K_2, K_3, \dots, K_n$ are the formation constants of the H-bonded species respectively, then we may write

$$K_n = \frac{C_n}{C_1^n} \quad (7.153)$$

Combining Eqs (7.152) and (7.153), we get

$$\delta = \frac{(\delta_1 C_1 + 2\delta_2 K_2 C_1^2 + \dots + n\delta_n K_n C_1^n)}{(C_1 + 2K_2 C_1^2 + \dots + nK_n C_1^n)} \quad (7.154)$$

The direct solution of Eq. (7.154) from experimental measurements of δ at several concentrations is not possible in H-bonded systems involving several equilibria. Therefore, in order to determine the extent of association, assume that only monomer and n -mer are present in the system. Under this assumption, Eq. (7.154) reduces to

$$\delta = \frac{(\delta_1 C_1 + n\delta_n K_n C_1^n)}{(C_1 + nK_n C_1^n)} \quad (7.155)$$

Let the stoichiometric (total) concentration, $C = (C_1 + nK_n C_1^n)$.

Then

$$\delta = \frac{(\delta_1 C_1 + n\delta_n K_n C_1^n)}{C} \quad (7.156)$$

An experimental curve is drawn between δ and C . A comparison is then made between the observed curve and the trial and error computed curves until the best fit is found. In case of *o*-cresol it is found that the theoretical curve (S-shaped) for $n = 3$ matches with the observed curve between δ of hydroxyl proton and $\log C$ (S-shaped). Thus in *o*-cresol, the major H-bonded moiety present is trimer.

(b) Case (ii): Formation Constant of 1 : 1 H-bonded/charge Transfer Complex Let us consider the equilibria



or

$$K = \frac{[A-H \cdots B]}{[A-H][B]} = \frac{(C_{AH}^0 - C_{AH})}{C_{AH} [C_B^0 - (C_{AH}^0 - C_{AH})]}$$

(a) If $C_B^0 \gg C_{AH}^0$
then

$$K = \frac{(C_{AH}^0 - C_{AH})}{[C_{AH}][C_B^0]} \quad (7.158)$$

Here, C_{AH}^0 and C_B^0 are the initial concentrations of A—H and the acceptor B respectively, and C_{AH} is the equilibrium concentration of free proton donor AH. The weighted average observed chemical shift δ in such a case is

$$\delta = \left(\frac{C_{AH}}{C_{AH}^0} \right) \delta_1 + \left(\frac{C_{AH}^0 - C_{AH}}{C_{AH}^0} \right) \delta_2 \quad (7.159)$$

Here δ_1 is the chemical shift of the monomer proton donor A—H and δ_2 is the chemical shift of the A—H proton in the H-bonded complex A—H $\cdots$ B.

From Eqs (7.158) and (7.159), the following relationship is obtained:

$$\frac{\delta - \delta_1}{KC_B^0} = \delta_2 - \delta = (\delta_2 - \delta_1) - (\delta - \delta_1)$$

$$(\delta - \delta_1) \left[\frac{1}{KC_B^0} + 1 \right] = \delta_2 - \delta_1$$

$$\frac{1}{\delta - \delta_1} = \frac{1}{KC_B^0 (\delta_2 - \delta_1)} + \frac{1}{\delta_2 - \delta_1} \quad (7.160)$$

$$\frac{1}{\Delta} = \frac{1}{KC_B^0 \Delta_0} + \frac{1}{\Delta_0} \quad (7.161)$$

where, $\Delta = \delta - \delta_1$ and $\Delta_0 = \delta_2 - \delta_1$.

The value of δ_1 is obtained by extrapolation of experimental results to infinite dilution.

(b) In case $C_{AH}^0 \gg C_B^0$, Eq. (7.161) will become

$$\frac{1}{\Delta} = \frac{1}{\Delta_0} + \frac{1}{KC_{AH}^0 \Delta_0} \quad (7.162)$$

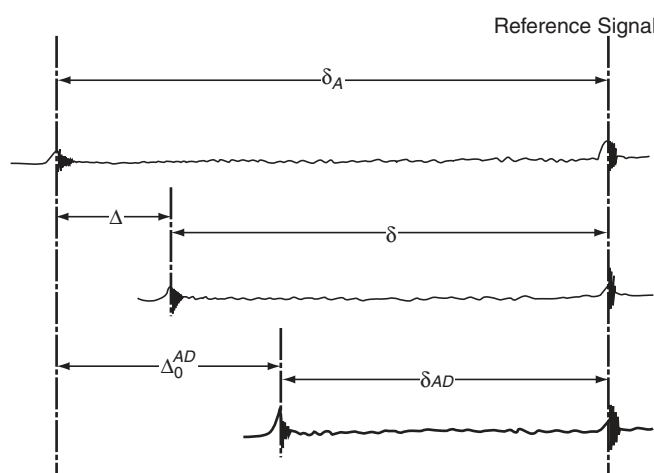
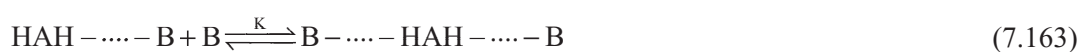


Fig. 7.47 The relationship between Δ , Δ_0^{AD} , δ , δ_A and δ_{AD} in a donor (D)-acceptor (A) system.

The relationship between various forms of δ 's in donor (D)-acceptor (A) system is shown in Fig. 7.47.

Thus, a plot between $\frac{1}{\Delta}$ and $\frac{1}{C_{AH}^0} \bigg/ \frac{1}{C_B^0}$ will be a straight line with slope $m = 1/K\Delta_0$ and intercept $= 1/\Delta_0$. From the slope and intercept, both K and Δ can be determined. The behaviour of K as a function of temperature may be employed to evaluate the thermodynamic parameters of the system. The values of association constant (K) for some charge-transfer complexes from PMR and ^{19}F chemical shifts measurements determined under the conditions $[D]_0 \gg [A]_0$ and $[D]_0 \ll [A]_0$ (all at 33.5°C) are listed in Table 7.13 while in Table 7.14 are the values of K of some 1:1 H-bonded complexes.

(c) Case (iii): Formation Constant of 1:2 H-bonded Complex Let us consider the equilibria of the type



$$K = \frac{[\text{B} \dots \text{HAH} \dots \text{B}]}{[\text{HAH} \dots \text{B}][\text{B}]} \quad (7.164)$$

Here, all HAH is H-bonded, $\text{HAH} \dots \text{B}$ is the 1:1 H-bonded complex formed between proton donor HAH and acceptor B, $\text{B} \dots \text{HAH} \dots \text{B}$ is the 1:2 H-bonded complex formed from 1:1 H-bonded complex and acceptor B.

Table 7.13 Values of association constant of some charge-transfer complexes determined by NMR technique under different experimental conditions (at 33.5°C).

System	Relative concentration	Nuclei Measured	$K(\text{kg mol}^{-1})$
1,3,5-trinitrobenzene-mesitylene in	$[A]_0 \gg [D]_0$	$\text{H}_{2,4,6}$ in D	0.2
1,2-dichloroethane	$[A]_0 \ll [D]_0$	$\text{H}_{2,4,6}$ in A	0.2
3,5-dinitrobenzene-trifluoride-hexamethylbenzene in CCl_4	$[A]_0 \gg [D]_0$	$\text{H}_{1,6}$ H_4 in A	1.73 1.76
		^{19}F	1.19
1,3,5-trinitrobenzene-indole in	$[D]_0 \gg [A]_0$	H_3 in D	0.9
$\text{CH}_2\text{ClCH}_2\text{Cl}$		$\text{H}^*_{\text{aromatic}}$	1.0
4-nitrobenzaldehyde-hexamethyl	$[A]_0 \gg [D]_0$	$\text{H}_{3,5}$ in A	0.5
benzene in CCl_4		$\text{H}_{2,6}$ in A	0.7
		H_{CHO}	0.9
N,N-dimethylaniline-	$[A]_0 \ll [D]_0$		0.4 [†]
1,3,5-trinitrobenzene in CHCl_3	$[A]_0 \gg [D]_0$	optical	1.0 [†]
	$[A]_0 \ll [D]_0$		0.6 [†]
	$[A]_0 \approx [D]_0$		0.4 [†]

* Band of maximum intensity in the aromatic multiplet Component containing measured nuclei, i.e. D or A.

† in lit mole^{-1} ,**Table 7.14** Values of K (at 33°C) for some 1:1 H-bonded complexes.

System	$K(\text{mole fraction})^{-1}$
Pyrrole-dimethyl sulfoxide(N-H....O)	8.69
Pyrrole-pyridine(N-H...N)	23.1
$\text{F}_{13}\text{C}_6\text{-CF}_2\text{-H-(CH}_3)_2\text{CO (C-H...O)*}$	2.0
$\text{F}_{13}\text{C}_6\text{-CF}_2\text{-H-(C}_2\text{H}_5)_3\text{N (C-H...N)*}$	1.5
$\text{F}_{13}\text{C}_6\text{-CF}_2\text{-H-(C}_2\text{H}_5)_2\text{O (C-H...O)*}$	0.6

*At 30°C

Let δ be the chemical shift of HAH proton in the system in a certain range of mole fractions n_{HAH} and B of mole fraction n_B in some suitable solvent. Let the value of δ extrapolated to zero HAH donor concentration be δ_0 . If δ_{11} and δ_{12} are the proton chemical shifts in 1:1 and 1:2 H-bonded complexes respectively and $\left(\frac{n_{11}}{n_{\text{HAH}}}\right)_0$ and $\left(\frac{n_{12}}{n_{\text{HAH}}}\right)_0$ are the fractions of HAH present as the 1:1 and 1:2 in the limit of zero HAH donor concentrations respectively then from Eq. (7.112), i.e. $\delta = P_1\delta_1 + P_2\delta_2$, we write

$$\delta_0 = \left(\frac{n_{11}}{n_{\text{HAH}}}\right)_0 \delta_{11} + \left(\frac{n_{12}}{n_{\text{HAH}}}\right)_0 \delta_{12} \quad (7.165)$$

Also, we know that

$$\left(\frac{n_{11}}{n_{\text{HAH}}}\right)_0 + \left(\frac{n_{12}}{n_{\text{HAH}}}\right)_0 = 1 \quad (7.166)$$

From Eqs (7.165) and (7.166), we write

$$\frac{1}{\delta_0 - \delta_{11}} = \left(\frac{n_{\text{HAH}}}{n_{12}}\right)_0 \left(\frac{1}{\delta_{12}} - \frac{1}{\delta_{11}}\right) \quad (7.167)$$

Eq. (7.164) may be expressed in terms of concentrations as

$$K = \frac{\left(\frac{n_{12}}{n_{\text{HAH}}}\right)_0}{\left(\frac{n_{11}}{n_{\text{HAH}}}\right)_0 \left[n_B - \left(\frac{n_{12}}{n_{\text{HAH}}}\right)_0\right]} \quad (7.168)$$

From Eqs (7.166) and (7.168), we get

$$K = \frac{\left(\frac{n_{12}}{n_{\text{HAH}}}\right)_0}{\left(1 - \frac{n_{12}}{n_{\text{HAH}}}\right)_0 \left[n_B - \left(\frac{n_{12}}{n_{\text{HAH}}}\right)_0\right]} \quad (7.169)$$

The square term $\left(\frac{n_{12}}{n_{\text{HAH}}}\right)_0^2$ in Eq. (7.169) being small, as compared to the other terms in the equation can be ignored. Hence Eq. (7.169) becomes

$$K = \frac{\left(\frac{n_{12}}{n_{\text{HAH}}}\right)_0}{\left[n_B - \left(\frac{n_{12}}{n_{\text{HAH}}}\right)_0 - n_B \left(\frac{n_{12}}{n_{\text{HAH}}}\right)_0\right]} \quad (7.170)$$

Lumping together Eqs (7.167) and (7.170), we obtain

$$\frac{1}{(\delta_0 - \delta_{11})} = \frac{1}{Kn_B(\delta_{12} - \delta_{11})} + \frac{1}{(\delta_{12} - \delta_{11})} \quad (7.171)$$

Let $(\delta_{12} - \delta_{11})$ be independent of temperature. Trial values of δ_{11} are selected and then plots of $\frac{1}{(\delta_0 - \delta_{11})}$ against $\frac{1}{n_B}$ will be a straight line with slope $m = 1/K(\delta_{12} - \delta_{11})$ and intercept $= 1/(\delta_{12} - \delta_{11})$. From the slope and intercept of various lines, different values of K and intercept corresponding to different trial values of δ_{11} will be obtained. The set of trial δ_{11} values which gives almost identical values of K is taken as the true value of δ_{11} . Based on this true value of δ_{11} then K and δ_{12} are evaluated from the curve. Thermodynamic functions may be determined from the effect of temperature on equilibrium constant.

7.39.10 Dissociation Constant of an Acid

The dissociation constant of an acid may be determined from proton chemical shifts as follows.

Let us consider that an acid HA dissociates into H^+ and A^- ions, i.e.



Here, the dissociation constant,

$$[K] = [\text{H}^+] \frac{[\text{A}^-]}{[\text{HA}]} \quad (1.173)$$

Let δ_{obs} , δ_{HA} and δ_{A^-} are the observed chemical shift at a given pH, the chemical shift of the protonated species, and the chemical shift of the unprotonated moiety, respectively.

By Eq. (7.112),

$$\delta = P_1 \delta_{\text{HA}} + P_2 \delta_{\text{A}^-}$$

Since, $P_1 + P_2 = 1$

Therefore,

$$P_2 = \frac{\delta - \delta_{\text{HA}}}{\delta_{\text{A}^-} - \delta_{\text{HA}}} \quad (7.174)$$

Comparing Eqs (7.173) and (7.174), we obtain

$$K = [H^+] \left[\frac{\delta - \delta_{HA}}{\delta_{A^-} - \delta_{HA}} \right]$$

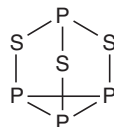
or

$$\log \frac{\delta - \delta_{HA}}{\delta_{A^-} - \delta_{HA}} = pH - pK_a \quad (7.175)$$

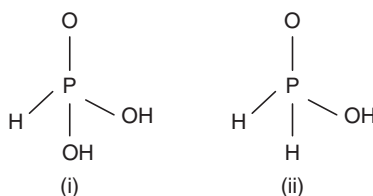
Trial values of δ_{A^-} are selected and then from the plot of $\log \left[(\delta - \delta_{HA}) / (\delta_{A^-} - \delta_{HA}) \right]$ against pH , the value of pK_a can be estimated. pK_a can also be obtained from the plot of δ (in Hz) versus pH . The shape of the curve is analogous to the potentiometric curve. This method can be extended for the determination of microscopic ionisation constants of various systems, e.g. amino acids and peptides. ^{13}C and ^{31}P chemical shifts are also employed to determine pK_a of nicotinamideadeninedinucleotide (NAD) and NAD phosphate (NADP). pK_a of imadizole obtained from chemical shifts of ^{13}C -2 and ^{13}C -4 have been found to be of the order of 7.2 and 7.15 respectively.

7.39.11 Structural Elucidation

The NMR spectroscopy alone or in conjunction with IR technique proved to be a very powerful tool for establishing the structure of molecules. The magnitude of J and pattern of s - s interaction are useful parameters for geometrical identification as is evident from the following examples. ^{31}P -NMR spectrum of P_4S_3 consists of two peaks (separation between two peaks is 185 ppm, $J = 70$ Hz) with intensity ratio 3 : 1 the more intense peak appears as a doublet (1 : 1) while the less intense as a quadruplet (1 : 3 : 3 : 1) to the right of the doublet. Since $I = 0$ for ^{32}S , both the s - s splitting and relative intensities of the signal reveal that there are three equivalent phosphorous atoms and one unique phosphorus atom in P_4S_3 . Consequently, the following structure is proposed for P_4S_3 .

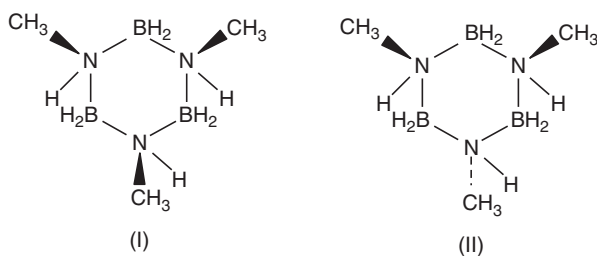


^{31}P -NMR spectra of phosphorous, $\text{HPO}(\text{OH})_2$ (I) and hypophosphorous, $\text{H}_2\text{PO}(\text{OH})$ (II) acids exhibit a doublet (1 : 1) and a triplet (1 : 2 : 1) respectively. The s - s splitting pattern indicates that the phosphorous atom interacts with protons in both the acids. Consequently, the following structures of the acids conform to the ^{31}P -NMR spectral data.



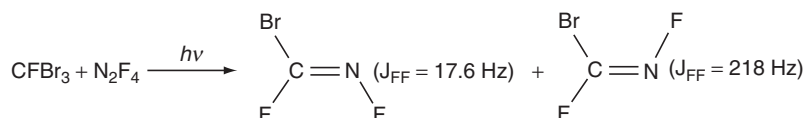
The simple nature of the spectra of both the acids is due to the following reasons: (i) the interaction between OH protons and phosphorous is too weak to be resolved since OH protons are at a distant apart from ^{31}P , and (ii) the OH protons do not couple with ^{31}P nucleus because of fast exchange of proton with the other acid molecule through H-bonding.

PMR spectrum of 1,3,5-trimethylcyclotriborazane (MeNHBH_2)₃ exhibits two types of doublets due to methyl protons, i.e. a single doublet and two such double doublets with relative intensity ratio 1 : 2 and $J = 5$ Hz. The doublet pattern may arise from the interaction of NH protons with the protons of the methyl group. The nature of two types of doublets suggests that the compound exists in two isomeric forms. By analogy with cyclohexanes, the most stable isomer should be a chair with all the methyl groups in the equatorial position (I) whereas the other less stable isomer should have one axial and two equatorial methyl groups (II) as shown here.



The barrier to internal conversion is large and both the structures are rigid (by NMR criterion) as compared to cyclohexanes.

The structure of two products of photochemical reaction given below is proposed simply from $J_{FF'}$.



These are rigid structures by NMR criterion.

Let us now examine how NMR in conjunction with infrared spectra could be useful in structural elucidation of molecules.

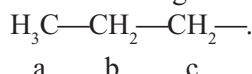
Molecular formula: $\text{C}_3\text{H}_7\text{O}_2\text{N}$.

NMR-triplet ($\delta = 1.03$ ppm; 1 : 2 : 1), triplet ($\delta = 4.38$ ppm; 1 : 2 : 1),

sextet ($\delta = 2.07$ ppm; 1 : 5 : 10 : 10 : 5 : 1)

IR: 1560 cm^{-1} (s), 1350 cm^{-1} (s).

The chemical shifts and splitting pattern of the NMR signals tentatively conforms to the skeleton structure



By empirical rules regarding the multiplicity of the NMR signal, the signal due to 'b' protons should appear as a twelve $(3 + 1)(2 + 1) = 12$ lines multiplet. However, the sextet nature of the 'b' protons arises because the *s-s* coupling between protons at 'a' and 'b' and 'b' and 'c' centres is almost the same, i.e. $J_{ab} \approx J_{bc}$. Actually the PMR spectrum of the compound when monitored on a moderate resolution NMR instrument shows a sextet pattern for the 'b' protons. Further, the two strong infrared bands at 1560 and 1350 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of NO_2 group. Thus the structure of the compound having molecular formula $\text{C}_3\text{H}_7\text{O}_2\text{N}$ is $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NO}_2$.

The structure of complex molecular systems can be established from infrared group frequencies and from chemical shifts and coupling constants by comparison methods. The IR group frequencies, chemical shifts and coupling constants of the system under study are matched with their respective literature values assigned to the standard structures.

NMR Evidence for Alkali Metal Anions The possibility that an alkali metal can exist as an anion has been explored as early as 1864 by W Weyl in Germany. The first-ever known anion of sodium, i.e. sodium ion (Na^-) in solid state was synthesised in 1974. The 'cryptand' 2, 2, 2 crypt [4, 7, 13, 16, 21, 25-hexaoxa-1, 10, diazabicyclic (8, 8, 8) hexacosane], was dissolved in ethylamine and allowed to react with metallic sodium. The blue colour formed was rapidly evaporated to leave behind a gold-coloured compound at -80°C . The experiment was carried out in moisture-free atmosphere and at a pressure of 10^{-5} Torr. The composition of the compound so formed is $[(\text{Na}^+\text{C})(\text{Na}^-)]$ where C is the cryptand. The nature of both Na^+ and Na^- in the solutions has been established by ^{23}Na -NMR technique. The crowned Na^+ shows a resonance at 10.4 ppm with a large line width while Na^- resonance occurs at 62.8 ppm with a narrow line width. The presence of well-separated signals shows that there is no exchange between Na^+ and Na^- and the solvent is excluded from their immediate spin-paired vicinity. ^{23}Na -NMR results point out to the fact that the added electron in Na^- resides in 3s orbital Spin paired.

The molecular structures determined by NMR are essentially motionally averaged. Therefore, it is important to note the motional properties of the molecule. The range of correlation times (τ_c) that can be measured by NMR is from picoseconds to greater than a second. While real-time monitoring after the pulse is possible for $\tau_c > 1$ second, T_1 can be measured for cases where τ_c is between 30 ps and $1\mu\text{s}$. The 2D-EXSY methods measure τ_c values between 10 ms – 1s.

7.39.12 Kinetic Studies

If two groups of chemically equivalent nuclei, say A and B, are exchanged by an intramolecular process, the NMR spectrum is a function of the difference in their resonance frequencies, $\nu_A - \nu_B = \Delta\nu$, and of the rate of exchange, k (a typical value of $\Delta\nu$ is about 10 cps). The effects of exchange at several temperatures on the width of NMR signals at ν_A and ν_B are exhibited in Figs 7.48(a) to (d). At low temperatures, the exchange is slow and $k \ll \Delta\nu$. The spectrum thus consists of two sharp singlets at ν_A and ν_B [Fig. 7.48(a)]. At high temperatures, the exchange is fast and $k \gg \Delta\nu$ and a single sharp peak is observed [Fig. 7.48(d)]. There is also an intermediate temperature range

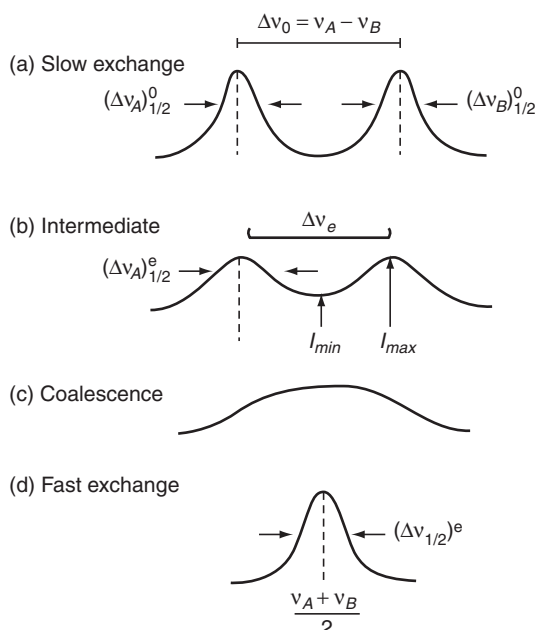


Fig. 7.48 Effect of exchange of chemically equivalent nuclei on NMR line shapes.

over which the spectrum consists of two significantly broadened overlapping lines [Fig. 7.48(b)].

We know that usually the s - s and s - l relaxations determine the width of an NMR absorption line. However, the exchange of two groups of chemically equivalent nuclei also causes additional line broadening of the NMR absorption line.

According to Heisenberg uncertainty principle,

$$\Delta\nu_{1/2} = \frac{\Delta E}{h} = \frac{\Delta E \Delta t}{h \Delta t} = \frac{1}{2\pi \Delta t} \quad (7.176)$$

where $\Delta\nu_{1/2}$ is the Heisenberg absorption linewidth for the transition, Δt is lifetime of the excited state.

The exact shape of the NMR signal in the case of two equivalent exchanging groups with no coupling is expressed by the function

$$I(\nu) = \frac{K_n \tau (\nu_A - \nu_B)^2}{\left[\frac{1}{2}(\nu_A - \nu_B) - \nu \right]^2 + 4\pi^2 \tau^2 (\nu_A - \nu)^2 (\nu_B - \nu)^2} \quad (7.177)$$

Here, $I(\nu)$ is the intensity at the frequency ' ν ', K_n is a normalisation constant for the exchange and $\tau = 1/2 k$, where k is the rate constant of the exchange; τ , ν_A and ν_B are functions of temperature and cannot be determined separately. These days computer programs are available in which estimated values for τ , ν_A and ν_B are used to determine $I(\nu)$ which is then compared to the observed spectrum, i.e. hit and trial values of τ , ν_A and ν_B are selected such that the difference between the theoretical and observed NMR peak is minimised.

Direct calculation of lifetime of a specific spin state from Eq. (7.177) can be made over a limited temperature range. Beyond a certain temperature, the rate of exchange is so fast that the magnetic environment of the two sets of nuclei are identical and hence cannot be discerned. Thus, we have only one set of spins with a lifetime determined by s - s and s - l relaxation processes.

In order to study the exchange rate over a wide range of temperature, a series of approximations are made in Eq. (7.177), though the approximate methods may give less accurate results as compared to Eq. (7.177).

(a) Slow and Intermediate Exchange When the exchange rate is very slow, the spectrum consists of two lines. In this region of temperature, $\tau \gg (\nu_A - \nu_B)^{-1}$, consequently Eq. (7.177) becomes

$$I(\nu)_A = I(\nu)_B = \frac{K_n T_{2A'}}{1 + T_{2A'}^2 (\nu_A - \nu)^2} \quad (7.178)$$

Here, $T_{2A'}$ is the s - s relaxation time. Comparing Eqs (7.177) and (7.178), we obtain the linewidth of line ν_A

$$(\Delta\nu_A)_{1/2} = \frac{1}{\pi} \left(\frac{1}{T_{2A'}} + \frac{1}{\tau_A} \right) \quad (7.179)$$

In the absence of exchange, the linewidth is

$$(\Delta\nu_0)_{1/2} = \frac{1}{\pi T_{2A}'} \quad (7.180)$$

The line broadening due to exchange is equal to $1/\pi\tau_A$. A value of k ($=1/2\tau$) is determined by comparing linewidths of exchange peaks to those of peaks observed at temperatures where the rate of exchange is very small.

$$k = \pi[(\Delta\nu_e)_{1/2} - (\Delta\nu_0)_{1/2}] \quad (7.181)$$

For slow exchange, the rate is related to peak separation by the expression

$$k = \frac{\pi}{\sqrt{2}} (\Delta\nu_0^2 - \Delta\nu_e^2)^{1/2} \quad (7.182)$$

where $\Delta\nu_i$ is the peak separation in cps ($i = e$ or 0). Equation (7.182) is obeyed over a limited temperature range where there is extensive overlapping between the two separate peaks but not too close to coalescence.

A third method based on the intensity measurements called ratio method may also be applied in the slow exchange region. k is determined from the ratio of the intensities of the peaks, $I_{\max}$ to the intensity midway between the peaks, $I_{\min}$:

$$r = \frac{I_{\max}}{I_{\min}}$$

and

$$k = \frac{\pi \Delta\nu_0}{\sqrt{2}} [r - (r^2 - r)^{1/2}]^{-1/2} \quad (7.183)$$

(b) Coalescence Temperature (T_c) The temperature at which the appearance of the spectrum changes from that of two separate peaks to that of a single, flat-topped peak is called coalescence temperature [Fig. 7.48(c)]. At this temperature,

$$k = \frac{\pi \Delta\nu_0}{\sqrt{2}} \quad (7.184)$$

(c) Fast Exchange NMR may be used to study fast exchange rates where the mean lifetime is in the region of one second to one millisecond. Above the coalescence temperature, the spectrum consists of a single peak. In this region, $\tau \ll (\nu_A - \nu_B)^{-1}$ and Eq. (7.177) reduces to

$$I(\nu) = \frac{K_n T_2'}{1 + \pi T_2' (\nu_A + \nu_B - 2\nu)^2} \quad (\text{Eq. 7.178a})$$

If the signal is not completely collapsed, i.e. the process is slow enough to contribute to its width but is still well beyond the rate corresponding to separate signals, then the following expression results.

$$k = \frac{\pi \Delta\nu_0^2}{2} [(\Delta\nu_e)_{1/2} - (\Delta\nu_0)_{1/2}]^{-1} \quad (7.185)$$

Problem 7.23: The PMR spectra of N, N-dimethylacetamide; N, N DMA (in CCl_4 containing 2 per cent TMS) in the temperature range 279–368 K on 50 MHz instrument is presented in Fig 7.49. Calculate the rotational barrier from the PMR spectral data.

Solution The study of barrier to internal rotation is an example of dynamic nuclear magnetic resonance spectroscopy. Reaction rates and rotational barriers in the range 10^{-1} – 10^{-5} s^{-1} and 3–20 kcal mole $^{-1}$ respectively can be studied by this method, e.g. N, N DMA (16.8 kcal mole $^{-1}$), nitrosoamine (23 kcal mole $^{-1}$).

cis-trans isomerisation of N, N DMA in which reactants and products are chemically and hence magnetically identical is shown as

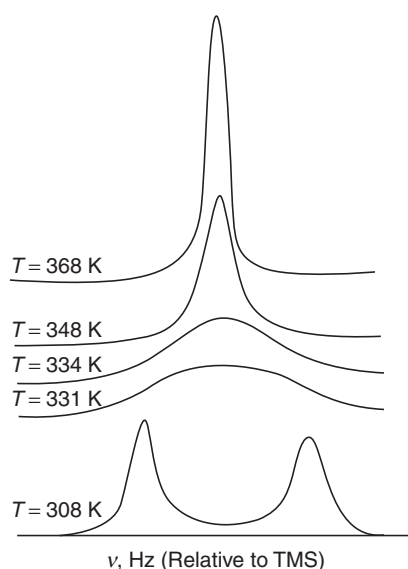
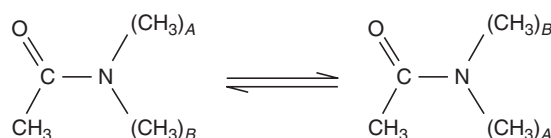


Fig. 7.49 Effect of temperature on the shapes in the NMR spectrum of *N,N*-dimethylacetamide.



In order to determine the barrier to internal rotation, the value of rate constants at different temperatures need be estimated from the PMR spectra at different temperatures (Fig. 7.49). The data deduced from the spectra are

T, K	$(\Delta\nu_e)_{1/2}$
368	2.8193
348	3.9427
334	9.1337
331	10.1778
308	$r = 8.46$
$\Delta\nu_0 = 10.844$	$(\Delta\nu_0)_{1/2} = 2.5103$

Using this data and employing the Eqs (7.181–7.185), the values of k , the rate constant, are

T, K	368	348	334	331	308
k, s^{-1}	598.0	129.0	27.8	24.1	5.95

From the plot of $\ln k$ versus $1/T$, the value of barrier to internal rotation about C—N bond has been found to be around 17 kcal mole⁻¹.

Problem 7.24: The behaviour of PMR spectra of 1-ethylaziridine (C_4H_9N) and 1-ethyl-2-methyleneaziridine (C_5H_9N) has been observed as a function of temperature on a 40 MHz instrument. The coalescence peak due to ring protons for the former has been observed at $108 \pm 5^\circ C$ whereas for the latter at $-65 \pm 10^\circ C$. If the bandwidths of the respective peaks are 29.9 and 26.4 cps, determine the rate of inversion of nitrogen in the two systems.

Solution We know that sufficiently rapid exchange of nuclei between two individual chemical environments, is capable of collapsing a complex NMR pattern into a simpler one. So the time of inversion of nitrogen is related to the bandwidth of the coalescence peak by the expression

$$\tau = \frac{\sqrt{2}}{\pi(\Delta\nu_0)} \quad (7.186)$$

Since the rate constant $k = 1/\tau$

$$k = \frac{\pi(\Delta\nu_0)}{\sqrt{2}}$$

For 1-ethylaziridine,

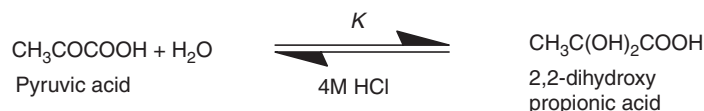
$$k = \frac{22}{7\sqrt{2}} \times 29.9 = 66.45 \text{ s}^{-1}$$

For 1-ethyl-2-methyleneaziridine,

$$k = \frac{22}{7\sqrt{2}} \times 26.4 = 58.67 \text{ s}^{-1}$$

Problem 7.25: The hydration of pyruvic acid ($\text{C}_3\text{H}_4\text{O}_3$) in presence of HCl was carried out by NMR technique. The spectrum of pure pyruvic acid consists of two signals at 10.70 and 2.60 ppm relative to an internal reference TMS. The integrated intensities of these bands are in the ratio 1 : 3. The NMR spectrum of 4M solution of pyruvic acid in heavy water at 34.5°C exhibits three bands at 5.48, 2.60 and 1.75 ppm respectively. Assign the bands to the different functional groups present in the system. Calculate the equilibrium constant of hydration process of pyruvic acid if the intensities ratio of methyl protons of pyruvic acid and hydrate of pyruvic acid is 1:1.4.

Solution On the basis of intensities ratio of the signals of pyruvic acid, the band at 2.60 ppm may be assigned to methyl protons while at 10.70 ppm to carboxyl proton. The hydration of pyruvic acid in the presence of HCl takes place according to the scheme



The proton exchange process in presence of 4M HCl becomes so fast that the carboxyl, hydroxyl and water protons may exhibit only one signal. Thus, the signal at 5.48 ppm may be assigned to these protons. The signals at 2.60 and 1.75 ppm may be assigned to the methyl protons of pyruvic acid and 2,2-dihydroxy propionic acid respectively. We know that

$$\begin{aligned} K_{\text{eq}} &= \frac{\text{Intensity of hydrated methyl resonance}}{\text{Intensity of pyruvic acid methyl resonance}} \\ &= \frac{1}{1.4} = 0.71 \end{aligned}$$

Problem 7.26: The kinetics of hydration of pyruvic acid



in presence of HCl at 34.5°C to form 2,2-dihydroxy propionic acid has been investigated by NMR technique. As the exchange is increased by the addition of HCl, the methyl proton resonances of pyruvic acid and its hydrate are observed to broaden. With further increase in HCl, the methyl proton resonance coalesces and finally a single narrow line is observed at very fast exchange. The exchange broadened resonance bandwidth of the methyl proton resonances of pyruvic acid and its hydrate at different concentrations of HCl are given in Table 7.15. Calculate the hydrogen-ion catalytic rate constant.

Solution We know that

$$\pi\Delta\nu_{1/2} = \frac{1}{T_2} + \frac{1}{\tau}$$

Table 7.15 Methyl proton resonances of pyruvic acid and its hydrate.

Bandwidths (cps)		
HCl Molar concentration	Pyruvic Acid	Hydrate of Pyruvic Acid
0.250	0.318	0.374
0.450	0.949	1.413
0.900	1.817	2.193
1.00	1.590	2.446

(Continued)

Table 7.15 Methyl proton resonances of pyruvic acid and its hydrate. —Cont'd.

1.50	2.446	3.975
1.80	3.180	4.542
2.25	3.975	6.360
3.00	5.300	—
4.00	7.950	—

T_2 is mainly responsible for the natural width of the resonance of a nonviscous liquid, τ the mean lifetime, a proton spends at a particular site in the exchange process contributes to the natural width of the signal. Thus, by measuring the bandwidth in the absence of exchange, the transverse relaxation time may be found. The mean lifetime may now be found by measuring the bandwidth of the exchange broadened resonance, i.e.

$$\tau = \frac{1}{\pi \Delta \nu_{1/2}}$$

The specific rate constant, k of the exchange process is given by

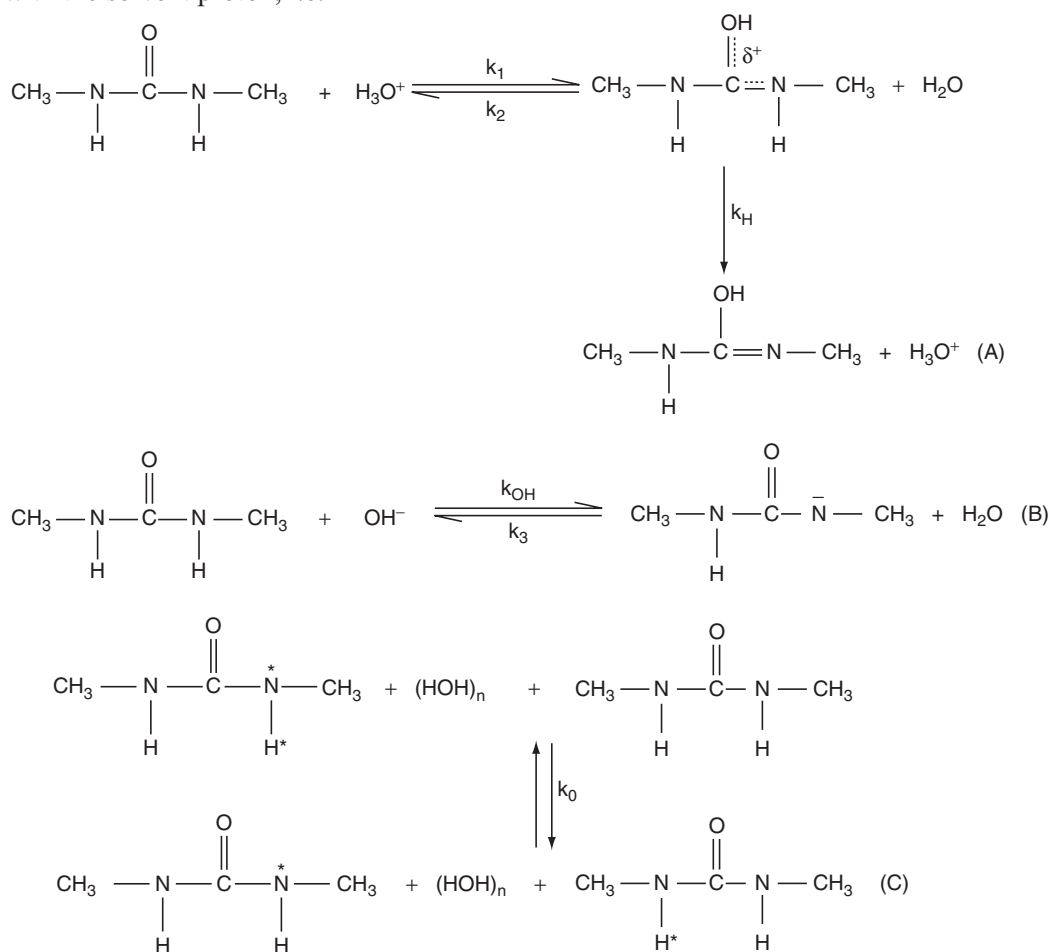
$$k = k_{H^+} [H^+]$$

where, k_{H^+} is the hydrogen ion catalytic rate constant. We know that $k = 1/\tau$. Consequently, $1/\tau = k_{H^+} [H^+]$.

The reciprocals of the mean lifetimes of pyruvic acid and its hydrate are plotted against the hydrochloric acid concentration to obtain k_{H^+} . The value of k_{H^+} is equal to the slope of the lines for pyruvic and its hydrate, and are found to be 5.55 and 16.32 s⁻¹ respectively.

(d) Proton Exchange Rate Constant of *N,N*-Dimethyl Urea (DMU) The rates of exchange of protons in proteins have been postulated to reflect the structure and conformation of these molecules. The proton-exchange rate of model amides has been observed to be both acid and base catalysed by H^+ and OH^- ions. The acid-catalysed exchange occurs through a mechanism involving protonation of the $C=O$ groups with subsequent release of the $N-H$ proton to the solvent. The proton-exchange rate of DMU can also be determined from the effect of pH on the width of the NMR signal.

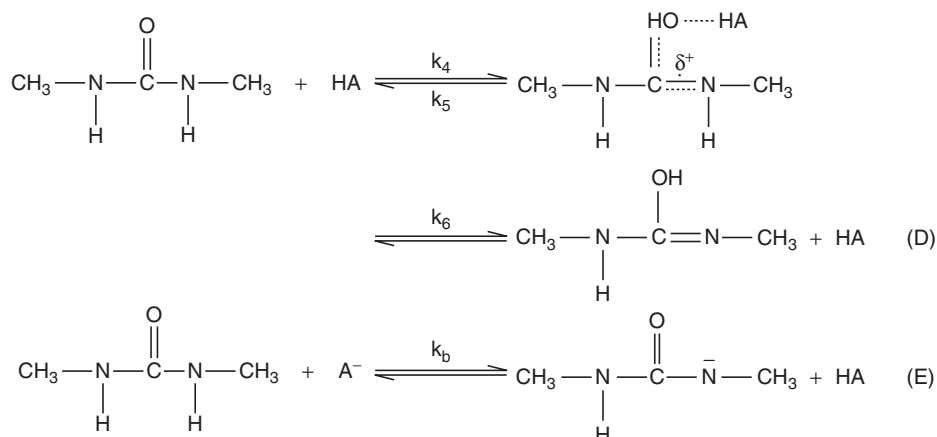
Several mechanisms of the general acid catalysis type may be proposed by which an $N-H$ proton can be exchanged with the solvent proton, i.e.



Scheme (A) describes the acid-catalysed exchange in which hydronium ion protonates the oxygen atom causing the N—H proton to become more acidic. The N—H proton is then abstracted by the solvent molecule (H_2O) affecting an observable exchange. The reproduction of $\bar{\text{N}}$ site is considered diffusion controlled and is not important in describing an effective NMR proton exchange.

The mechanism (B) indicates the direct abstraction of proton by a base which in H_2O solution is the hydroxide ion. There also exists a self-catalysed exchange through water bridge as shown in scheme (C). For DMU, this contribution to the overall exchange rate is too small to be measured by high-resolution NMR line-broadening techniques.

In presence of acetic acid (HA), chloroacetic acid (CA), trifluoroacetic acid (TFA) and phosphoric acid (H_3PO_4), two additional mechanisms, i.e. (D) and (E) are possible:



Scheme (D) gives the contribution due to HA, the unionised acid in solution whereas scheme (E) gives the contribution from the conjugate base.

In the absence of added acetic acid, substituted acetic acids or phosphoric acid, the net equations describing proton exchange in the acid and base catalysed regions as obtained from schemes (A) and (B) are

$$\frac{1}{\tau} = k_1 k_H [\text{H}^+] / (k_2 + k_H) \quad (\text{acid catalysed}) \quad (7.187)$$

and
$$\frac{1}{\tau} = k_{\text{OH}} [\text{OH}^-] \quad (\text{base catalysed}) \quad (7.188)$$

In Eq. (7.187), k_2 may be assumed to be diffusion controlled and the assumption $k_2 \gg k_H$ is made, Consequently,

$$\frac{1}{\tau} = k_1 k_H [\text{H}^+] / k_2 \quad (7.189)$$

The terms k_1, k_H and k_2 may be combined to yield $k_{\text{ex}} = \frac{k_1 k_H}{k_2}$, producing the acid catalysed rate equation,

$$\frac{1}{\tau} = k_{\text{ex}} [\text{H}^+] \quad (7.190)$$

The reverse reaction in the k_H step is not considered since a net observable NMR exchange occurs with completion of k_H .

Considering mechanisms (D) and (E) for the effect of acetic acid, substituted acids or phosphoric acid, we obtain

$$\frac{1}{\tau} = k_a [\text{HA}] + k_b [\text{A}^-] + k_{\text{ex}} [\text{H}^+] + k_{\text{OH}} [\text{OH}^-] \quad (7.191)$$

The effect of addition of acetate ions is due to the second term i.e. $k_b [\text{A}^-]$ of Eq. (7.191) since in all cases except acetic acid, the concentration of undissociated acid HA is negligible. For phosphoric acid, the pH range of

interest is 6-8, thus the important species are H_2PO_4^- and HPO_4^{2-} . In such a case, Eq. (7.191) in the acid catalysed region reduces to

$$\frac{1}{\tau} = k_b [A^-] + k_{ex} [H^+] \quad (7.192)$$

In order to obtain proton-exchange rate constant under different conditions, T_2 at different pH values are obtained from the line width of the CH_3 doublet under conditions of slow exchange and are limited by field homogeneity. Thus, by making use of Eqs (7.190) and (7.188), to acid and base catalysed regions, respectively, one can determine k_{ex} and k_{OH} . The plot between $\log(1/\tau)$ and pH for DMU in aqueous solution and in the presence of acetic acid, monochloroacetic acid and trichloroacetic acid has been shown in Fig. 7.50. In order to obtain k_b , use is made of Eq. (7.192). From the slope of the curve describing $1/\tau$ as a function of $[A^-]$ at constant pH, k_b can be calculated.

The proton-exchange rate constants for N,N-DMU determined by NMR technique are listed in Table 7.16.

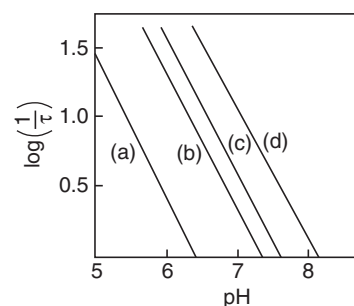


Fig. 7.50 Log of the exchange rate ($1/\tau$) of N,N-dimethyl urea against pH for (a) 1M dimethylurea, (b) 1M dimethyl urea + 1M trichloroacetic acid, (c) 1M dimethyl urea + 1M monochloroacetic acid, (d) 1M dimethyl urea + 1M acetic acid.

Table 7.16 Kinetic results for N,N-dimethylurea (Temp = 39°C, Operating frequency = 56.4 MHz).

System	k_{ex} ($\text{mole}^{-1} \text{s}^{-1}$)	k_{OH} ($\text{mole}^{-1} \text{s}^{-1}$)	k_b ($\text{mole}^{-1} \text{s}^{-1}$)
1 M DMU	2.5×10^6 (x)	1.0×10^6	NA
DMU + 1 M(HA)	1.48×10^8 (x)	1.1×10^6	73.0
DMU + 1 M(MCA)	4.2×10^7 (x)	1.0×10^6	15.0
DMU + 1 M(DCA)	2.09×10^7	1.0×10^6	11.6
DMU + 1 M(TCA)	2.4×10^7 (x)	1.3×10^6	6.5
DMU + 1 M(TFA)	2.5×10^7	0.8×10^6	6.5
DMU + 1 M(NaCl)	1.1×10^6	1.6×10^6	NA
DMU + H_3PO_4	NA	NA	205(pH 7.0)

(x)-values for the observed rate constant obtained from the intercepts in Fig. 7.50.

7.40 BIOLOGICAL APPLICATIONS

NMR technique being rapid and non-invasive is widely used in studies related to biology, e.g. human, animal and plant subjects. It has been extensively used in studies related to agricultural plants and their products. The principle of FID of low-field NMR is used for rapid and nondestructive determination of oil and moisture in oil seeds. Both $s-l$ and $s-s$ relaxation times T_1 , and T_2 , have been exploited to obtain degree of unsaturation of oil in oilseeds and dry rubber content in natural rubber latex. ^{31}P -NMR is used to elucidate the mechanism of uptake of phosphorous by plants. The fatty acid composition of oil in a single intact seed can be obtained using ^{13}C -NMR. Analysis of mixtures of amino acids and of peptides can be carried out using ^{19}F -NMR.

7.40.1 Determination of Oil Contents in Oilseeds

The oil contents in oilseeds, i.e. groundnut, mustard, til, cotton, sunflower, soyabean, safflower, etc., can be determined by the liquid FID signal and solid-liquid FID signal methods.

(a) Liquid FID Signal Method Hydrogen nuclei which show strong NMR peaks in oilseeds exist mainly in four forms: oil, moisture, carbohydrates and proteins. The $s-s$ relaxation times for protons of oils, moisture

and carbohydrates—proteins are of the order of 10^{-1} , 10^{-3} and 10^{-6} second respectively. Thus, the decay of NMR signal in oilseeds will follow the order: [Solid (carbohydrates—proteins)] (fast) > [moisture and oil] (slow). Based on the order of decay of NMR signal, the oil contents in oil seeds can be determined as follows. The dried and weighed seeds are subjected to a $\pi/2$ pulse and FID corresponding to the oil content in seeds is monitored. The oil content is then noted from the standard linear graph between the FID NMR signal and the amount of pure oil.

The major factors which affect the efficiency of this method are s - l relaxation time T_1 and field inhomogeneity. The effect of s - l relaxation time on the NMR signal is eliminated by selecting the pulse repetition time long enough to attain the full equilibrium magnetisation. T_1 for most of the oilseeds is < 200 milliseconds, so pulse repetition time of the order of one second is sufficient, i.e. $5 \times T_1$. Magnetic field inhomogeneity is eliminated by proper selection of delay times t_D 's so as to measure T_2 rather than T_2^* which is governed by magnetic field inhomogeneity of the spectrometer.

(b) Solid-liquid (S-L) FID and Spin Echo Signal Method The liquid-signal method is slow and not truly nondestructive since the seeds are to be weighed and dried. In the S-L method, the system is subjected to a $\pi/2$ - t_D - π - A_Q sequence and the response is monitored. The FID and spin echo signals of protons corresponding to the solid and liquid constituents measured by the $\pi/2$ - t_D - π - A_Q pulse are displayed in Fig. 7.51.

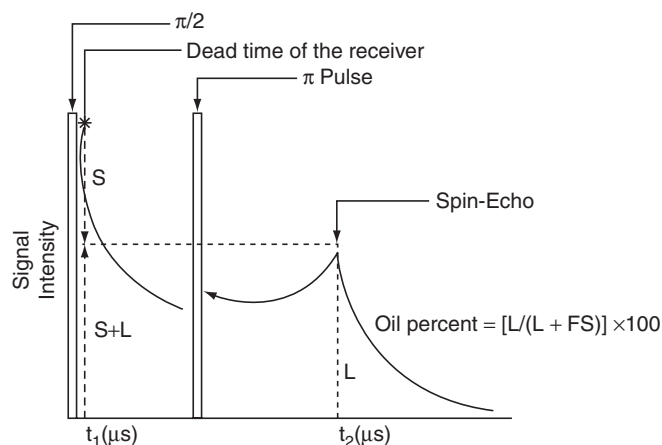


Fig. 7.51 FID signal of dried seeds.

The signal intensity at $t_1 \mu s$ (immediately after the dead time of the receiver) will have full contribution from the liquid phase signal (L) and partly decayed solid phase signal (S) in the seeds. The spin echo signal measured after the application of π -pulse, at $t_2 \mu s$ represents nearly full liquid phase signal only as solid-phase signal has almost completely decayed by then. The oil content is then determined by the formula.

$$\text{Seed oil content} = \frac{L}{L + FS} \times 100 \quad (7.193)$$

This formula holds good for samples having similar moisture and solid phase, T_2 . The correction factor, F accounts for the decay of solid signal during the dead time of the receiver, and proton density difference in solid and liquid phases of oilseeds and the residual moisture signal at $t_2 \mu s$. Using Eq. (7.193), mean values of F are estimated from some dried samples of seeds of known oil contents. Once F is established, Eq. (7.193) can be readily used for the estimation of oil in oilseeds.

7.40.2 Dry Rubber Content in Natural Rubber Latex

s - s relaxation rate constants of solid and aqueous phases of latex are markedly different. The signals due to rubber particles (mostly solid) and the aqueous phase of latex are resolved by spin echo technique. The signals cannot be resolved by FID method where both the phases decay with T_2^* .

7.40.3 Study of Fate of Inorganic Phosphates (Pi) in Developing Seeds

^{31}P -NMR spectra of perchloric acid extract of seeds collected at different periods of flowering showed a decrease in intensity of the signal due to Pi accompanied by an increase in intensity of signals corresponding to phytates (Fig. 7.52). A similar behaviour of Pi and phytate signals have been observed in the ^{31}P -NMR spectra of intact seeds (*in vivo*) at similar period of flowering. Thus, ^{31}P -NMR study of seeds supplements the already established fact that phytate acts as a store of phosphorus which may be utilised during the seed development.

7.40.4 Analysis of Mixtures of Amino Acids and of Peptides

The mixture to be analysed is treated with trifluoroacetic anhydride and the ^{19}F -NMR spectrum of the resultant N-trifluoroacetylated (N-TFA) product is recorded with acetone as solvent. The fluorine chemical shift is very sensitive to small differences in shielding, hence, most N-TFA derivatives of amino acids have distinctive ^{19}F chemical shifts as shown in Fig. 7.53. The relative proportions of components of the mixture of amino acids may be judged from the peak heights of each COCF_3 signal. Dipeptides may also be differentiated in this manner even when two peptides differ only in their second amino acid units, e.g. the ^{19}F resonances of methyl esters of N-TFA-glycyl-L-Leucine and N-TFA-glycyl-L-alanine are resolved at 84.6 MHz.

7.40.5 Optical Purity of Dipeptides and Configuration of Diketopiperazines Isolated from Natural Sources

Dipeptides may be converted to corresponding cycloforms (diketopiperazines) without change of configuration (See A) and the cyclodiastereoisomers also differ in their PMR characteristics especially if aromatic groups are present. Thus the methyl resonances of DL (*trans*) and LL (*cis*) cyclo-alanyl phenylalanine differ by 34 Hz. The higher field position of the *cis* signal is attributed to aromatic shielding which arises as a result of preferred conformation in which benzene ring faces a piperazine ring (see C), equatorial methyl as in (B) is too far removed to be affected in this way. These PMR differences serve as a further check of the optical purity of dipeptides and also are of potential value in establishing the configuration of diketopiperazines isolated from natural sources.

In addition to various parts of plants, NMR technique is also used to investigate small animals or parts of large animals, e.g. a human leg or arm still attached to its living host. The concentration of intracellular adenosine-5'-triphosphate (ATP) in some cases approaches 1 mM or more, so ^{31}P -NMR method has been exploited to study the behaviour of phosphate compounds within cells. ^{31}P -NMR spectrum of the contents of mouse tumor cells displayed in Fig. 7.54 reveals that inorganic phosphate (Pi) combines with adenosine diphosphate (ADP) to form ATP, a molecule in which living cells store chemical energy. The interconversion of ATP into ADP and Pi in the cell is coupled to passage of protons through the membrane of the cell. The reaction that generates chemical energy by splitting ATP into ADP and Pi serves to expel protons from the cell, thereby creating a proton gradient that stores both electrical and chemical energy. Conversely, the re-entry of protons into the cell provides energy required by the reaction that combines Pi and ADP into ATP. A change in the concentration of protons inside the cell constitutes a change in the intracellular pH. At an intracellular pH of 6.7 the populations of the singly protonated Pi form and the doubly protonated Pi form are equal. At higher pHs (a more basic environment), the singly protonated form dominates and at lower pHs (a more acidic environment),

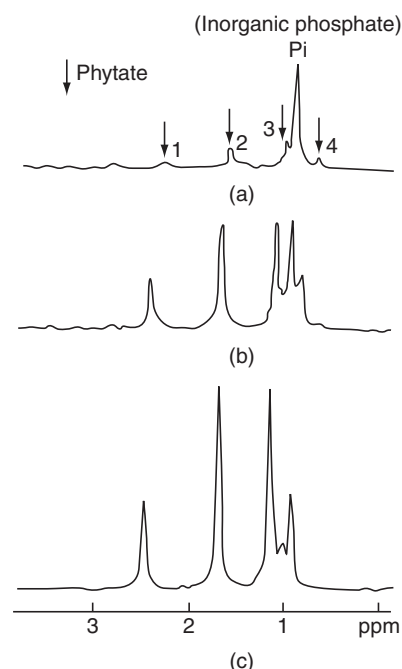


Fig. 7.52 ^{31}P -NMR spectrum of perchloric extract of oilseeds after different periods: (a) < (b) < (c) of flowering. The numbered peaks correspond to phytate and the signal labelled Pi corresponds to inorganic phosphate.

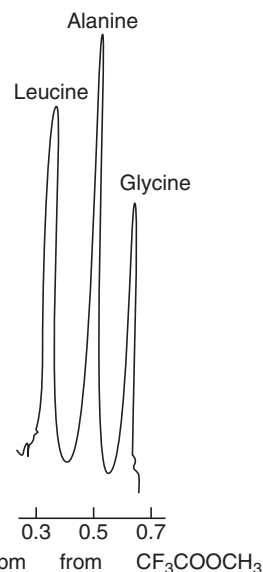
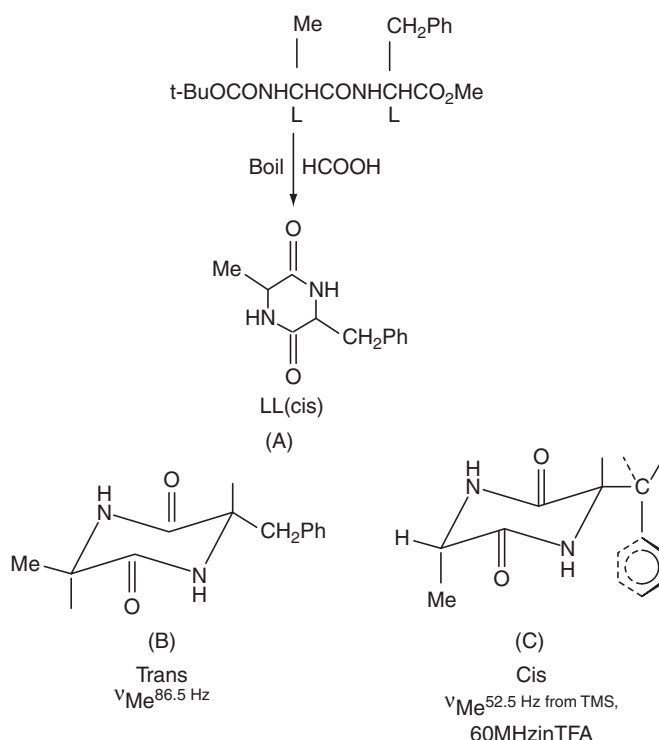


Fig. 7.53 ^{19}F -84.6 MHz NMR spectrum of a mixture of N-TFA-L-leucine, N-TFA-L-alanine and N-TFA-glycine in acetone.



the doubly protonated form dominates. Each form has a distinctive chemical shift, but the inorganic phosphate peak in a NMR spectrum of cells will be found in some intermediate position depending on the average degree of protonation of all the P_i in the cells. Thus the position of P_i peaks yields an accurate measure of the degree of protonation of the P_i , which in turn yields an accurate measure of the intracellular pH. ^{31}P -NMR spectrum of living muscle from the frog exhibits phosphorous peaks from P_i , from ATP and from phosphocreatine (Pcr), a molecule that muscle cells draw on to convert ADP to ATP. When external energy is not available to the muscle, the intensity of the signal corresponding to Pcr decreases whereas the intensity of the ATP signals is maintained

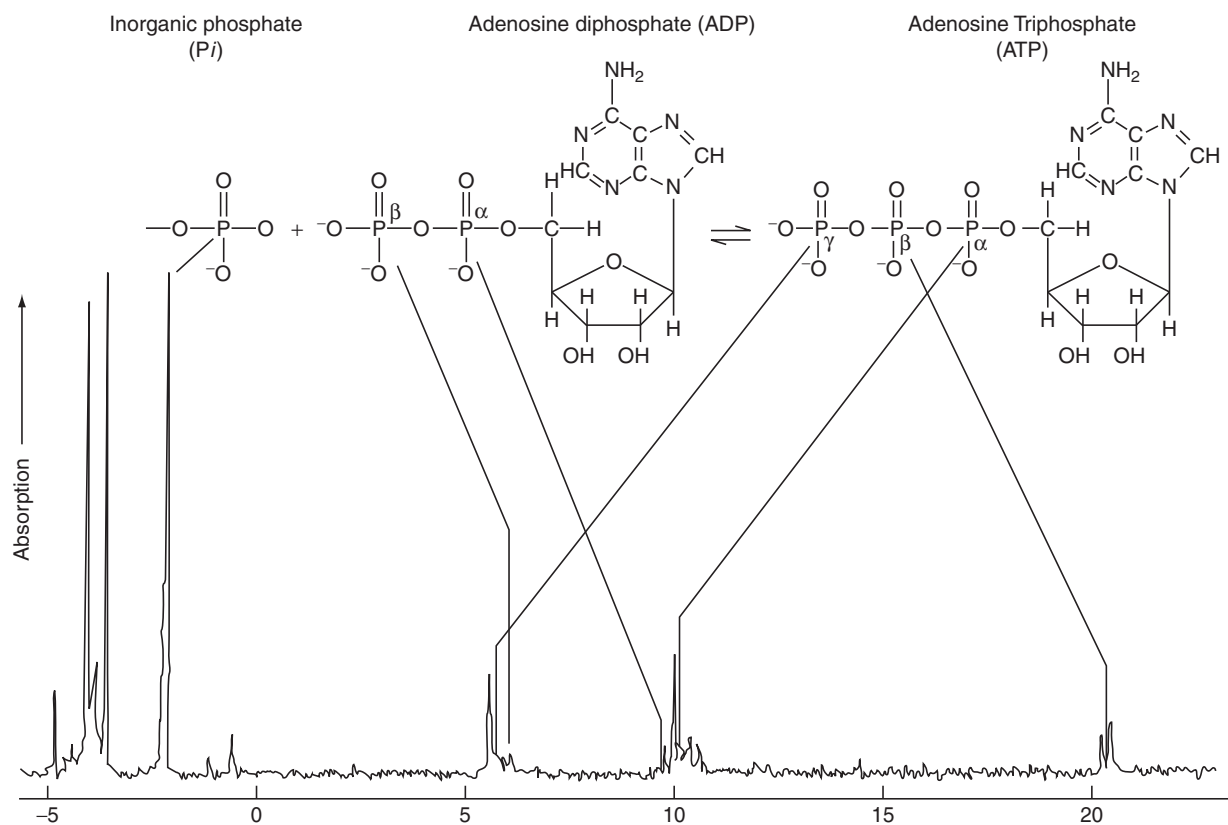
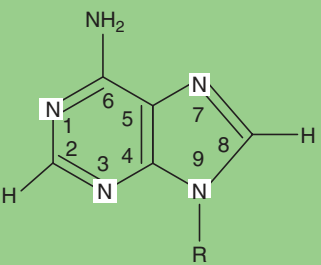


Fig. 7.54 ^{31}P -NMR spectrum of the contents of mouse tumor cells. Change in magnetic field strength (ppm of base value).

Table 7.17 ^{15}N shifts (in ppm from $H^{15}\text{NO}_3$) of nitrogen atoms in ATP and in equimolar metal ion-ATP solutions.

 $J_{15\text{N}-7-\text{H}-8} = 10 \text{ Hz}$ $J_{15\text{N}-1-\text{H}-2} = 16 \text{ Hz}$					
	N-1	N-3	N-7	N-9	NH ₂ -6
ATP	144.7	135.6	129.5	191.6	282.8
Mg ²⁺ -ATP	144.9	135.0	129.5	191.6	282.3
Zn ²⁺ -ATP	144.9	135.0	132.5	190.1	279.7

constant by the reservoir of Pcr. When Pi is completely utilised, the intensity of ATP signal decreases leaving ADP and Pi. The position of ATP signal indicates that all the ATP in the cells are complexed with magnesium ions. FT ^{31}P -NMR spectra of ATP in presence of Mg^{2+} in an aqueous medium reveal that phosphorous chemical shifts corresponding to α , β , and γ phosphorous atoms move down-field as the Mg^{2+} concentration is increased. For a 1 : 1 composition of Mg^{2+} and ATP, β - ^{31}P shifts from -22.5 to -20.5 ppm, α - ^{31}P moves slightly, i.e. from -14 to ≈ -13.7 ppm and γ - ^{31}P moves from -11 to ≈ -10 ppm.

The metabolism throughout the animal's body can be investigated with NMR spectra. ^{13}C -NMR spectra of rats fed on glucose labelled with ^{13}C revealed that the intensity of glucose peaks decreases and ultimately disappears from the stomach of the living animal. After some hours, the level of glycogen in the animal's liver increases, the glucose is stored as glycogen there. Finally, the glycogen signal disappears as the labelled glycogen is consumed. The nitrogen-15 resonance spectra have been used to ascertain the extent and type of complexing of alkaline earth metals (Mg^{2+} and Zn^{2+}) to adenosine triphosphate (ATP). The ^{15}N chemical shift values given in Table 7.17 indicate that although Mg^{2+} does not bind to the adenosine ring nitrogens in the ATP- Mg^{2+} complexes, the shifts for the Zn^{2+} case are consistent with a model in which Zn^{2+} interacts at both the 6-amino and the N-7 positions.

7.40.6 Protein–Drug Interactions

NMR is used in pharmaceutical industrial research including screening studies when a particularly important protein is being considered as a target for new drugs. The protein is exposed to a variety of small molecules; the potential candidates for a new drug. When a particular small molecule interacts with the macromolecule, the NMR spectrum of the macromolecule will change. If the resonances of the macromolecule have been assigned, it is possible to determine which residues are involved in the interaction, and the potential use of the small molecule in further drug development can be assessed.

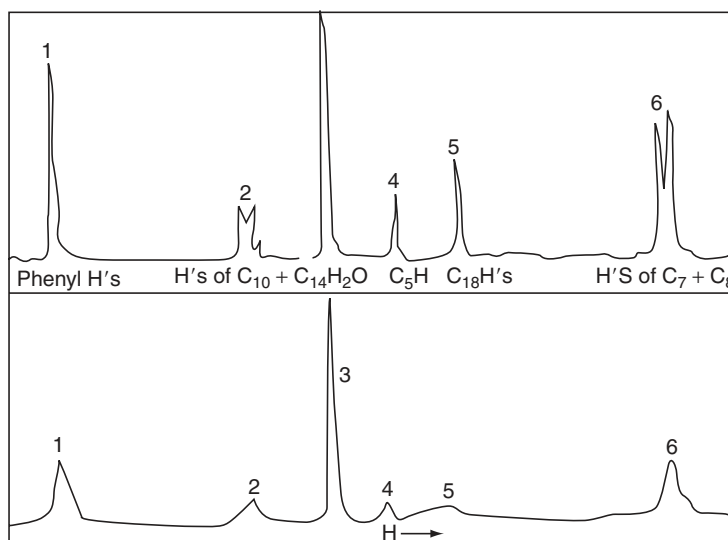
**Fig. 7.55** Proton magnetic resonance spectrum of penicillin G (a) D_2O and (b) in D_2O in the presence of 10% w/v bovine serum albumin.

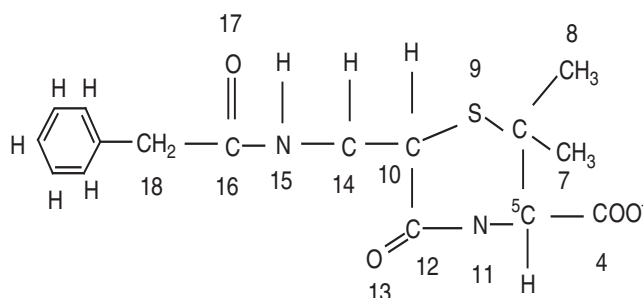
Table 7.18 Effect of bovine serum albumin on the NMR of penicillin G.

Peak	$\frac{1}{T_2^*} (s^{-1})$	Stabilisation ratio
1 (phenyl protons)	3400	5200
4 (C ₅ proton)	1430	1700
5 (C ₁₈ proton)	5975	2060

In general, it has been found that PMR spectra of proteins consist of a few very broad peaks which form a rather uninformative background on which the high resolution spectrum of small molecules is superimposed. Differential broadening of one peak as compared to others gives some indication that the portion of small molecule from which that peak originates is more affected by the interaction with the protein than the remainder of the molecule. For example, the peak arising from the benzyl methylene group of penicillin G broadens much more than the other peaks when antibiotic is bound to bovine serum albumin (Fig. 7.55). This effect is clearly specific, in that it is not observed in the presence of other proteins, e.g. ribonuclease.

The s - I relaxation time T_1 can be determined by saturating PMR signal then measuring its intensity (A_t) as a function of time (t_D). T_1 can then be calculated from the equation.

$$A_t = A_0 [1 - \exp(-t_D / T_1)] \quad (\text{Eq. 7.31})$$



by plotting $\ln[(A_0 - A_t)/A_0]$ versus t_D . The s - s relaxation time T_2^* can be obtained from the line width of high resolution spectrum using the relationship.

$$\Delta\nu_{\frac{1}{2}} = \frac{1}{\pi T_2^*} \quad (\text{Eq. 7.27})$$

where $\Delta\nu_{\frac{1}{2}}$ is the line width at half-height.

The relaxation rates for three of the peaks of bound penicillin G are listed in Table 7.18.

While the methylene peak has the fastest relaxation rate, it can be seen that the phenyl group has the highest stabilisation ratio R , where

$$R = \frac{T_2^* \text{ for free penicillin G}}{T_2^* \text{ for bound penicillin G}} \quad (7.194)$$

Since the stabilisation ratio is a more significant indicator of an effect on molecular motion, it would appear that the binding of penicillin G to bovine serum albumin involves mainly hydrophobic interactions between the phenyl group of the antibiotic and the protein binding site.

7.40.7 Nuclear Magnetic Resonance Imaging (NMRI)

NMRI is one of the most important and promising applications of FTNMR. In NMRI, the map of density of the NMR nuclei, say ^1H , ^2H , ^{13}C , ^{31}P , ^{23}Na , in various regions of the solid and semisolid objects is produced rather than the NMR spectrum. Basically, the FIDs are Fourier transformed and converted to three-dimensional images of the interior of the objects. NMRI enjoys advantage over x-ray CAT scans or other methods in that it is non-invasive, i.e. there is little or no potential danger of radiation injury or other damage to human, or animal or plant subjects.

In 1DFTNMR, the magnetic resonance signal of a sample placed in a uniform magnetic field (1 part in 10^8) of strength H is given by

$$\nu = \frac{\gamma}{2\pi} \cdot H \quad (7.195)$$

Being a waveform, the FID corresponding to each resonating species is a composite of three parameters, viz., the signal amplitude, frequency (ν) and phase (ϕ). Amplitude is a measure of the number of resonating nuclei (proton density), ν and ϕ may be used together to code the resonance signal at each time-domain point.

The fundamental principle of NMRI is that the signal frequency is made to vary deliberately in a linear manner with the spatial location of the group of nuclei producing the signal by applying moderate (up to 20 mT m⁻¹) linear magnetic field gradients. Thus, for imaging experiments, Eq. (7.195) modifies to

$$\nu_i = \frac{\gamma}{2\pi} (H + \bar{G} \cdot r_i) \quad (7.196)$$

where, ν_i is the frequency of the proton at position r_i and $\bar{G}$ is the vector representing the magnetic gradient amplitude and direction, i.e. intensity at different spatial locations of the proton.

$$\bar{G} = \hat{i} \left(\frac{\partial H}{\partial x} \right)_{y,z} + \hat{j} \left(\frac{\partial H}{\partial y} \right)_{z,x} + \hat{k} \left(\frac{\partial H}{\partial z} \right)_{x,y} \quad (7.197)$$

Thus, in order to obtain ID image projection, the signal is obtained in the simultaneous presence of field gradient G_z and radio frequency pulse and the intensity is plotted against the frequency, with the frequency axis being coded. Consider, for example, the situation as shown in Fig. 7.56 where the field gradient in H , G_z is created by auxiliary coils in the magnetic bore that is under the control of the computer of the magnetic resonance instrument. Protons in different positions in the sample experience different magnetic fields H_1 and H_2 for two of the regions shown in Fig. 7.56 and will have different frequencies $\nu_1 = \frac{\gamma H_1}{2\pi}$ and $\nu_2 = \gamma H_2 / 2\pi$. The frequency ν_2 will be higher than the frequency ν_1 , and the frequency difference $\Delta \nu = \nu_2 - \nu_1$. Thus by changing the centre frequency of the NMR probe pulse in increments of $\Delta \nu$, it is possible to probe successive r_i positions in the direction of the applied magnetic field gradient. Each consecutive radio frequency pulse produces an FID signal that encodes the concentration of protons at each r_i position along the direction of the field gradient. By performing the Fourier transformation on the FIDs, concentration information can be produced as indicated by the heights of the peaks. Images in three directions can be made by an extension of this coding concept using additional magnetic field gradients along the Y and X axes. The precessing spin will experience a gradient pulse of duration Δt along either of these axes and will accumulate an additional phase, e.g. $\phi_y = \gamma G_y y \Delta t$. Thus phase and frequency encoding of the three spatial dimensions can be achieved by linear magnetic field gradient applied successively along three orthogonal directions for the duration t_1 , t_2 and t_3 respectively in a pulsed FT experiment. The recorded FID signal is Fourier transformed to produce $S(\nu_1, \nu_2, \nu_3)$ which is equivalent to three-dimensional spatial image when spatial information is decoded using the relations; $x = \nu_1 / G_x$, $y = \nu_2 / G_y$ and $z = \nu_3 / G_z$ with three field gradients G_x , G_y and G_z , i.e. the concentration of protons in a volume element or voxel corresponding to each set of coordinates x , y and z is contained in $S(\nu_1, \nu_2, \nu_3)$. The ability to generate high-resolution (millimetre) images from 'three-dimensional data is a unique strength of the NMRI technique. Note that three orthogonal gradients are produced by employing three sets of orthogonal gradient coils. Further, the direction of gradient may be changed at will by suitable linear combination of currents in the three sets of coils.

Abnormalities due to different diseases in different parts of humans or animals or plant subjects are imaged routinely these days. Tumours in the human brain, spine, etc., and perfusion (a microcirculation process which measures nutrient delivery to tissues) are being imaged routinely. In food industry, NMRI has been used for the determination of fat and muscle distribution in meats, the determination of water and lipid contents in sunflower oil, composition of foods such as biscuits during processing, investigation of hydration of foods, to measure water movement in heterogeneous systems, i.e. plants, etc., the determination of NMR relaxation parameters in cured pork.

Problem 7.27: A biological sample is placed along the bore (or Z-axis) of a NMRI magnet. What would be the difference between the resonance frequencies of the two successive protons

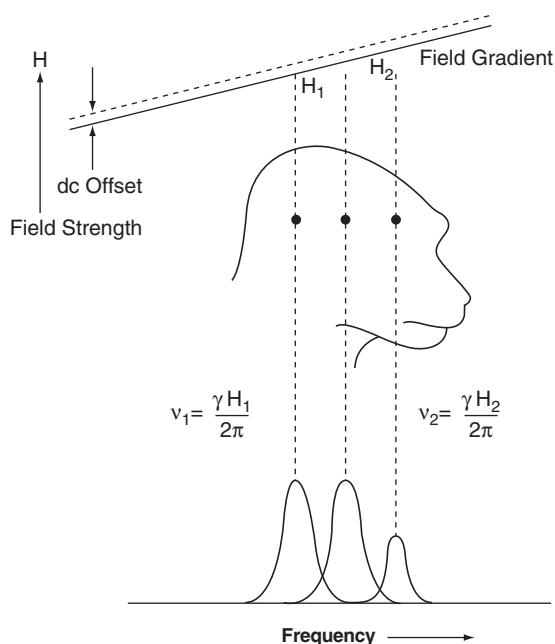


Fig. 7.56 Fundamental concept of nuclear magnetic resonance imaging.

1 mm apart in the sample if a magnetic field gradient of $10^{-4} \text{ T(mm)}^{-1}$ is applied along the bore of the NMRI magnet? ($\gamma_H = 2.68 \times 10^8 \text{ radians s}^{-1} \text{ T}^{-1}$)

Solution According to Eq. (7.196), the frequency of proton in the sample in a magnetic field gradient G_z is given by

$$\nu_i = \frac{\gamma}{2\pi} (H + G_z r_i) \quad (7.198)$$

Let ν_1 and ν_2 be the frequencies of the protons at positions r_1 and r_2 respectively in the sample. Accordingly, we write

$$\nu_1 = \frac{\gamma}{2\pi} (H + G_z r_1) \quad (7.199)$$

$$\nu_2 = \frac{\gamma}{2\pi} (H + G_z r_2) \quad (7.200)$$

Thus, the difference between the two frequencies is

$$\Delta\nu = \nu_2 - \nu_1 = \frac{\gamma}{2\pi} (r_2 - r_1) G_z$$

or

$$\Delta\nu = \frac{\gamma}{2\pi} \Delta r G_z \quad (7.201)$$

Here $\Delta r = r_2 - r_1$, is the distance between two successive protons.

Substituting the values of the respective parameters, we obtain

$$\begin{aligned} \Delta\nu &= \frac{2.68 \times 10^8 (\text{radians s}^{-1} \text{ T}^{-1}) \cdot 1 (\text{mm}) \cdot 10^{-5} (\text{T (mm)}^{-1})}{2\pi (\text{radians})} \\ &= 426 \text{ Hz} \end{aligned}$$

Problem 7.28: A biological sample having ^{31}P nuclei is placed in the bore of a NMRI magnet. A magnetic field gradient of strength $10^{-5} \text{ T cm}^{-1}$ is applied along the bore of the magnet and the frequency difference between the two consecutive phosphorous nuclei has been found to be 10 Hz. Determine the distance between the two consecutive ^{31}P nuclei. ($\gamma(^{31}\text{P}) = 1.08 \times 10^8 \text{ radians s}^{-1} \text{ T}^{-1}$).

Solution Here, $\Delta\nu = 10 \text{ Hz}$, $\gamma = 1.08 \times 10^8 \text{ radians s}^{-1} \text{ T}^{-1}$, $G_z = 10^{-5} \text{ T cm}^{-1}$,

From Eq. (7.201), we write

$$\Delta r = \frac{2\pi \Delta\nu}{\gamma \cdot G_z}$$

Substituting the values of the respective parameters into the above expression, we obtain

$$\begin{aligned} \Delta r &= \frac{2\pi (\text{radians}) \cdot 10 (\text{Hz})}{1.08 \times 10^8 (\text{radians s}^{-1} \text{ T}^{-1}) 10^{-5} (\text{T cm}^{-1})} \\ &= \frac{2 \times 22 \times 10}{7 \times 1.08 \times 10^8 \times 10^{-5}} \text{ cm} = 0.058 \text{ cm} = 0.58 \text{ mm}. \end{aligned}$$

The distance between the two consecutive P^{31} nuclei in the biological sample is 0.58 mm.

7.40.8 Liquid Crystals in High Resolution NMR Spectroscopy

The NMR spectra of organic molecules in isotropic liquids are not caused by direct ‘through space’ interactions of the individual dipoles because this interaction, i.e. d - d interaction averages out to zero through rapid reorientation of internuclear axes. However, there remains a small isotropic interaction between nuclear spins mediated by

the electron-nuclear and electron-electron interactions in a molecule. Thus, the high-resolution NMR spectra of organic molecules in isotropic liquids are determined (i) by isotropic chemical shifts (δ_{AB}), and (ii) by the isotropic indirect s - s coupling (J_{AB}) acting between nuclei (A , B) of a molecule. As stated above the third basic magnetic interaction, the direct dipole-dipole interaction between the nuclear magnetic moments is completely averaged out. Moreover, the solute tumbling motion averages out the anisotropic contributions to J_{AB} and δ_{AB} . The anisotropic magnetic interactions affect the NMR spectra in isotropic media only through their influence of the relaxation times (or the line widths). The isotropic molecular tumbling in ordinary liquids leads to a loss of most valuable information. However, NMR spectra obtained in liquid crystals are primarily determined by the direct intramolecular spin-spin coupling whereas isotropic and anisotropic contributions to chemical shift and the indirect nuclear spin coupling respectively, appear as second-order effects.

The isotropic part of internuclear interaction is identical to indirect coupling constant. The anisotropic nuclear coupling D_{AB} contains both the direct d - d interaction (D_{AB}^{dir}) and the anisotropic part of the indirect nuclear coupling, D_{AB}^{ind} i.e. $D_{AB} = D_{AB}^{\text{dir}} + D_{AB}^{\text{ind}}$ has the same orientational dependence with respect to $\vec{H}$ as D_{AB}^{dir} and is therefore, called pseudodipolar coupling. $D_{AB}^{\text{ind}} \ll D_{AB}^{\text{dir}}$ at least for H-H and C-H interactions. D_{AB}^{ind} amounts to about 10 percent of the corresponding D_{AB}^{dir} in C_6F_6 . D_{AB}^{ind} can be estimated from the deviations between the observed D_{AB} values and the values of D_{AB}^{dir} calculated from the known geometry of the molecule.

D_{AB}^{dir} is a function (i) of the time average over the anisotropic solute tumbling motion, and (ii) of the internuclear distances. The NMR spectroscopy in liquid crystals may, therefore, provide information on both the average solute orientation and molecular geometry. Moreover, information on the absolute signs of indirect coupling constants and on the anisotropic contribution to chemical shift and indirect coupling constant respectively may be obtained from NMR spectra of partially oriented molecules.

The interpretation of NMR spectra in isotropic media is simplified by the rule that the indirect s - s coupling between the so-called equivalent nuclei (nuclei with identical chemical shifts) does not lead to observable line splitting. However, this rule does not hold good for direct nuclear coupling. The proton resonance spectrum of acetylene is split up in doublet by the dipolar coupling between two equivalent nuclei. The spectrum of partially aligned benzene exhibits about fifty lines. The spectrum of n interacting nuclei yields $n(n-1)/2$ interaction parameters D_{AB} from which the geometry of the molecules can be established. The direct d - d coupling (derivable from the observed NMR spectra) between two nuclei A and B of molecules performing a rapid tumbling motion (isotropic or anisotropic) is given by

$$D_{AB}^{\text{dir}} = -K_{AB} \left\langle \frac{3 \cos^2 \theta_{AB} - 1}{r_{AB}^3} \right\rangle; \quad (7.202)$$

where,

$$K_{AB} = \frac{\gamma_A \gamma_B \hbar}{4\pi^2} \quad (7.203)$$

θ_{AB} is the angle between the vector connecting the coupling nuclei and the applied field H_z and r_{AB} is the internuclear distance. The angle brackets $\langle \rangle$ denote the time average both over the molecular tumbling motion and over the internuclear motions (vibrations, internal conversions). When r_{AB} is expressed in Å and D_{AB}^{dir} in MHz, then for protons

$$K_{AB} = \frac{\gamma_H^2 \hbar}{4\pi^2} = 120067 \text{ Hz } \text{\AA}^3. \quad (7.204)$$

For a cylindrical molecule (such as acetylene) whose long axis Z coincides with the internuclear vector $\vec{r}_{AB}$, D_{AB}^{dir} is given by

$$D_{AB}^{\text{dir}} = 2K_{AB} \left\langle \frac{1}{r_{AB}^3} \right\rangle S_{zz} \quad (7.205)$$

provided the magnetic field is parallel to the liquid crystal optical axis $\vec{L}$. $\vec{L} \cdot \vec{S}_{zz}$ is the average orientation of the long molecular axis (of acetylene) with respect to $\vec{L}$.

For simple molecules, the line positions and the intensities can be expressed in terms of chemical shifts (isotropic and anisotropic) and coupling constants D_{AB} and J_{AB} . A system of equations may be derived which allows the determination of the coupling constants (D_{AB} and J_{AB}) from the experimental line positions. However, for complex molecules, the spectra are only analysed by computer techniques either by a simulation or an iterative method. In the simulation method, the input parameters used are molecular structural parameters and motional constants. The theoretical spectra predicted from the input parameters (bond distances and motional constants)

are compared with experimental spectra. The trial and error procedure is carried out till both the spectra overlap. Thus, the geometry of the molecular system under study is obtained.

The nematic phase has proved most useful as a solvent for NMR studies. Two kinds of nematogens are used as NMR solvents. Organic, thermotropic nematogens are most widely applicable solvents (See Table 1.5). Lyotropic liquid crystals may also be used as NMR solvents and have important property of dissolving both ionic and neutral species. A mixture of caesium decyl-sulphate, *n*-decanol and water will accept a wide range of solutes to form nematic phases. The applicability of nematogens as anisotropic solvents in NMR spectroscopy is limited to relatively simple and symmetric molecules which do not have more than eight protons since overlapping of lines occurs. Note that pure liquid crystals are formed from molecules having typically at least 12 protons, and the number and magnitude of interproton dipolar coupling results in unresolved proton spectra covering about 30 kHz, e.g. 220 MHz proton spectrum of tropone (C_7H_6O) dissolved in nematogen Merck Phase IV exhibits sharp intense lines from the six protons whereas the protons of the liquid crystal exhibit broad bands. The NMR intensities are much lower in nematic solvents than in isotropic liquids, due to the large number of lines caused by partially aligned molecules. So, concentration of the solute is kept in the order of 20 mole per cent. The quite complicated and large molecules could, in principle, be studied and analysed with this technique if species that are deuterated at specific sites could be prepared.

The ratios of nuclear distances can be obtained from NMR spectra of molecules in an isotropic solvent. Absolute values of order parameters can only be determined for molecules with known internuclear distances. The order parameter $S = 1/2 \langle 3 \cos^2 \theta - 1 \rangle$ is a measure of the efficiency of the molecular orientation along the optic axis $\vec{L}$. Here, θ is the angle between the long molecular axis and optic axis. For $\theta = 0$, $S = 1$, i.e. all molecular axes are parallel. Such a nematic order is possible near the absolute zero point of temperature provided the material would not freeze. For isotropic liquids $S = 0$. Depending on temperature, $S = 0.4$ – 0.7 for real nematic liquid crystals. S is not substantially changed by applied magnetic or electric fields.

(a) Geometry of Molecules The relative bond lengths of molecules can be obtained from the NMR spectra in anisotropic solvents. However, the geometry can be obtained in anisotropic media if the internuclear distances from other techniques, namely *x*-ray diffraction, microwave spectroscopy are available, e.g. the proton resonance spectra of $X-CH_3$ ($X = CN, I, OH$, etc.) is characterised by one direct $H-H$ coupling constant D_{HH} . The spectrum consists of a triplet with relative intensity ratios 1 : 2 : 1. The splitting between two adjacent lines is $3D_{HH}$. For molecules containing ^{13}C -isotope (I , the spin quantum number = $\frac{1}{2}$) in CH_3 group, each of the triplet lines splits in doublets of separation D_{CH} . The orientation of these molecules is described by only one order parameter (if X is an atom or a cylindrical symmetric group). Thus, we may write

$$\frac{D_{HH}}{D_{CH}} = \frac{\gamma_H}{\gamma_C} \cdot \frac{r_{CH}^3}{r_{HH}^3} \quad (7.206)$$

The angle $H-C-H$ can directly be determined from the expression (7.206).

The internuclear distances determined from D_{AB}^{dir} are averages over the vibrational motions of the molecules. In order to get accurate geometry of the molecules, the influence of molecular vibrations on D_{AB}^{dir} be estimated. Due to this reason, the structural parameters determined from NMR differs from microwave and electron diffraction methods, e.g. HCH bond angle in CH_3OH determined by liquid crystal NMR technique is $110^\circ 3' \pm 8'$ as compared to $109^\circ 2'$ from microwave spectroscopy. In case of CH_3I , $\angle HCH = 111^\circ 42' \pm 2'$ from liquid crystal NMR and $111^\circ 25'$ from microwave spectroscopy.

(b) Shape of Molecules In favourable circumstances, we can predict theoretically the ratios of the dipolar couplings to be expected for regular hexagon, pentagon and square and then by comparison with the experimentally determined ratios, we can determine whether the rings really are regular in shape, e.g. data in Table 7.19 indicate that benzene and the cyclopentadiene ring in the nickel compound have regular polygon shapes, whereas the ratios of D_{AB} values for other two compounds indicate a lower symmetry. However, it is not possible to determine the nature of the distortion. Note that the internal rotation about the metal-ring bonds is giving an averaged ratio of the dipolar coupling.

(c) Optical Active Molecules The order parameters are very sensitive to small changes in molecular geometry. This makes the difference between the NMR spectra of *d*- and *l*-isomers of optically active molecules, e.g. the two isomers of racemic mixture of trichloropropyleneoxide ($C_3H_3Cl_3O$) yield different NMR spectra in a compensated

Table 7.19 Comparison of ratios of experimental interproton dipolar couplings for various molecules, with theoretical values for regular polygons.

Molecule	Experiment	Theory
 Benzene	1.000 : 0.192 : 0.125	1.000 : 0.192 : 0.125(0.125)
 Mn(CO) ₃ Cyclopentadiene manganese tricarboxyl	4.11 ± 0.01	4.216(4.236)
 Ni-NO Cyclopentadienyl nickel nitrosyl	4.211 ± 0.003	4.216(4.236)
 Fe(CO) ₃ Cyclobutadiene iron tricarboxyl	2.67 ± 0.04	2.768(2.828)

The quantities within brackets are without averaging.

nematic mixture of cholesteryl derivatives, i.e. cholesteryl chloride or cholesteryl bromide with cholesteryl esters in appropriate amounts. Such a compensated mixture provides an environment which exhibits both anisotropy and helicity. The two isomers have somewhat different order parameters in a solvent with a local screw sense and correspondingly exhibit different values of the direct coupling constants. However, in an ordinary nematic solvent such as *n*-hexyloxyazoxybenzene, the two isomers give identical spectra.

(d) Barrier to Internal Rotation: The sensitivity of D_{AB}^{dir} to small changes in molecular geometry has been exploited for determining barrier to internal rotation or conversion, e.g. 3,5-dichloroanisole, 3,3-bithienyl, tetrafluoroanisole, etc., *o*-chlorotoluene assumes a staggered conformation with a barrier height of 1.2 kcal mole⁻¹.

The magnitude of the barrier in this case has been estimated by comparing the motional constants and the relative molecular geometry obtained from the NMR spectrum with the corresponding values calculated by assuming different models for the form of the rotational barrier.

7.40.9 RECENT DEVELOPMENTS

The 2002 Nobel prize for Chemistry was shared among John B Fenn, of Virginia Commonwealth University, USA; K Tanaka of Nishinkokyo Kuwabaracho Nakagyou Ku, Kyoto, Japan; and K Wuthrich of Swiss Federal Institute of Technology, Zurich, Switzerland; in the areas of mass spectrometry and NMR as applied to biological macromolecules. These laureates have contributed in different ways to the development of these methods to embrace biological macromolecules.

Fenn and Tanaka shared the Nobel prize for developing soft desorption ionisation methods for mass spectrometric analysis of biological macromolecules in relation to their identification and structure. The method due to Fenn is called *hovering through spraying*, whereas the one due to Tanaka is called *hovering through blasting*. In the former method, the sample is sprayed using a strong electric field to produce small, charged, free hovering ions whereas in the latter the free ions are produced using an intense laser pulse.

Wuthrich, on the other hand, shared the prize for his development of NMR spectroscopy for determining the three-dimensional structure of biological macromolecules in solution. He showed that NMR is possible for proteins and has invented a systematic method of pairing each NMR signal with the right hydrogen nucleus (proton) in the macromolecule. This method is called *sequential assignment* and is today a cornerstone of all NMR structural investigations. He also showed how it is subsequently possible to determine pairwise distance between a large number of nuclei and used this information with a mathematical method based on distance geometry to calculate three-dimensional structure for the molecule.

Presently, scientists can see the proteins and understand how they function in the cell. The ³He NMR has been proved to be a powerful new tool for following fullerene chemistry. The soccer-ball shaped, sixty-carbon molecule, Buckminster fullerene and its larger relatives (the fullerenes) all have the intriguing feature of possessing cavities surrounded by cages of carbon atoms. The rare isotope helium-3 can be imprisoned within the hollow cavities in quantities sufficient for its observation by NMR. The electrons on the fullerene cage partially shield the

magnetic field, and so the resonance line of trapped ^3He appears at a higher field (lower frequency) than for ^3He outside the fullerene. Each type of fullerene and each derivative of fullerene has a different shielding and hence a different resolvable, NMR line, i.e. the sharp helium NMR peaks in different chemically substituted fullerenes cover a wide range of NMR shifts; they have given us valuable information about the aromatic character of fullerenes and the isomers of higher fullerenes. They are also useful in following the many addition reactions which attach groups to the outside of the fullerene and in following processes which open windows in the cage to release atoms, e.g. release of noble gas atoms from inside fullerenes.

PROBLEMS

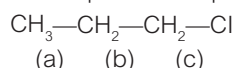
1. Calculate the gyromagnetic ratio and Lande g' factor for ^{17}O , ^{25}Mg , ^{39}K , ^{43}Ca , ^{63}Cu , ^{65}Cu , ^{67}Zn , ^{107}Ag and ^{109}Ag nuclei if their NMR frequencies are observed at 5.772, 2.606, 1.987, 2.865, 11.285, 12.090, 2.635, 1.722 and 1.981 MHz respectively in a magnetic field of strength 10 kG. μ_I 's for ^{17}O , ^{43}Ca , ^{107}Ag and ^{109}Ag nuclei are negative.

[Ans: $\gamma(^{17}\text{O}) = 3.628 \times 10^3 \text{ G}^{-1} \text{ s}^{-1}$; $g_N(^{39}\text{K}) = 0.2605$]

2. A high resolution 100 MHz NMR instrument is capable of differentiating between frequency differences of 0.01 ppm. What will be the resolving power of the instrument?

[Ans: 1×10^{-8}]

3. Predict the spin decoupled PMR spectra of



if the secondary field is centred on the resonances of (a), (b) and (c) protons respectively. Given $J_{ab} = J_{bc}$.

[Ans: (i) a—triplet; b—triplet; c—triplet (ii) a—singlet; c—singlet; b—twelve line multiplet (sextet under moderate resolution, $J_{ab} \approx J_{bc}$); (iii) a—triplet; b—quartet; c—triplet]

4. (a) Predict the number of signals and their multiplicities in the FT ^{13}C -NMR spectra of CH_3^*COOH and $^*\text{CH}_3\text{CH}_2\text{COOH}$.

[Ans: quartet in both the systems]

(b) Predict the high-resolution PMR spectrum of (i) acetic acid (ii) 1, 2-dimethoxyethane, (iii) ethyl benzene (iv) methyl formate (v) methyl ethyl ketone (vi) formaldehyde (vii) thiopropionic acid (viii) acetaldehyde.

(c) Predict the high-resolution ^1H , ^{13}C , ^{19}F and ^{31}P -NMR spectra of (i) $^{13}\text{CH}_4$, (ii) $^{13}\text{CF}_4$, (iii) $^{31}\text{PH}_3$.

5. How many major sets of peaks would you expect in the PMR spectra of (a) isopropyl alcohol in presence of acid or base, (b) toluene, (c) propionamide, (d) *n*-propyl alcohol, (e) biphenyl (f) methanol? Indicate the relative areas under the major sets of peaks for each compound. What will be the multiplicity of the signals in (c), (e) and (f)?

6. The resonance frequencies of ^{13}C , ^1H , ^{19}F and ^{31}P nuclei for 10 kG field are observed at 10.705, 42.577, 40.055 and 17.235 MHz respectively. What will be their resonance frequencies for a magnetic field of 2.3487 T?

[Ans: $^{13}\text{C} = 25.142 \text{ MHz}$; $^1\text{H} = 100.000 \text{ MHz}$; $^{19}\text{F} = 94.077 \text{ MHz}$; $^{31}\text{P} = 40.479 \text{ MHz}$]

7. A special sample of petrol prepared from tetralin, naphthalene and *n*-hexane, exhibits three sets of PMR signals in the regions of aliphatic, alicyclic and aromatic protons respectively. If the areas of the respective sets are of the order of 6.6, 1.6 and 3.6 units, determine the composition of the petrol sample

Hint: Let x , y and z be the number of moles of tetralin, naphthalene and *n*-hexane respectively. Then the areas under the bands will be $4x = 1.6$; $4x + 8y = 3.6$ and $4x + 14z = 6.6$.

8. FT ^{13}C -NMR signals for some of the molecular systems are listed below. Assign the ^{13}C -resonances to the different carbon atoms present in the molecules.

System	Molecular Formula	δ_c (in ppm)
Methyl methacrylate	$\text{C}_5\text{H}_8\text{O}_2 [\text{H}_2\text{C} = \text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3]$	18.3, 51.5, 124.7, 136.9, 167.3
1, 1, 2-tribromoethane	$\text{C}_2\text{H}_3\text{Br}_3$	38.7t, 40.3d
Thiazole	$\text{C}_3\text{H}_3\text{NS}$	118.6, 143.2, 152.7
1, 2-dibromopropane	$\text{C}_3\text{H}_6\text{Br}_2$	24.1q, 37.6t, 45.7d
1, 2-dibromo-2-methyl propane	$\text{C}_4\text{H}_8\text{Br}_2$	31.8, 44.6
tert-butylalcohol	$\text{C}_4\text{H}_{10}\text{O}$	31.2, 68.9
<i>p</i> -quinone	$\text{C}_6\text{H}_4\text{O}_2$	136.4, 187.1
Bromobenzene	$\text{C}_6\text{H}_5\text{Br}$	122.4, 126.7, 129.8, 131.4

9. CW- ^{13}C -NMR spectrum of crotononitrile ($\text{C}_4\text{H}_5\text{N}$) exhibits a set of four lines at (17.3, 18.8), (100.9, 101.2), (116.0, 117.6), and (150.2, 151.6) ppm. How do you interpret this spectrum? Also assign these bands to the carbon atoms involved in the spectrum.

Hint: *cis* and *trans*.

10. The operating frequency of a NMR spectrometer is 60 MHz; what magnetic fields are required to bring ^{31}P and ^{19}F nuclei to resonance at this operating frequency if the resonance frequencies of ^{19}F and ^{31}P nuclei are observed at 40.055 and 17.235 MHz respectively in an external magnetic field of 10 kG strength?

[Ans: $^{19}\text{F} = 1.4979 \text{ T}$; $^{31}\text{P} = 3.4812 \text{ T}$]

11. Sketch the PMR spectrum of 1,1,2-trichloroethane given the chemical shifts of $-\text{CH}_2$ and $-\text{CH}$ protons as 3.95 and 5.77 ppm (on δ scale) respectively and the spin coupling constant between the $-\text{CH}_2$ and $-\text{CH}$ protons as 6 Hz. Indicate the relative intensity of the lines in the first-order approximation.

12. Predict the structure (s) consistent with each of the following sets of PMR spectral data:

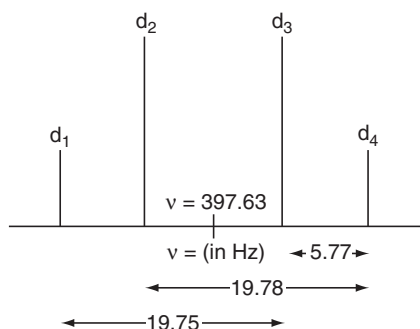
(a) $\text{C}_3\text{H}_5\text{Cl}_3$: singlet, δ (2.20 ppm), 3H; singlet, δ (4.02 ppm), 2H

- (b) $C_{10}H_{13}Cl$: singlet, δ (1.57 ppm), 6H; singlet, δ (3.07 ppm), 2H; singlet, δ (7.27 ppm), 5H.
- (c) $C_{10}H_{14}$: singlet, δ (1.30 ppm), 9H; singlet (7.28 ppm), 5H.
- (d) $C_9H_{11}Br$: quintet, δ (2.15 ppm), 2H; triplet, δ (2.75 ppm), 2H; triplet, δ (3.38 ppm), 2H; singlet, δ (7.22 ppm), 5H.
- (e) C_4H_9NO : Two peaks at 2.85 and 3.0 ppm and one peak at 2 ppm. $C_4H_8D_3NO$: Two peaks at 2.95 and 3.1 ppm.

Intensities of peaks in both the cases are equal. NMR data is in 15 per cent CCl_4 (2 per cent TMS) IR: 1655 cm^{-1}

- (f) C_7H_8O : δ (2.43 ppm) 1H; δ (4.58 ppm) 2H, δ (7.28 ppm) 5H.

13. The protons of 2,3-dibromothiophene are consistent with an AB spin system. The PMR spectrum of the compound is shown in the following illustration.



- (a) Calculate the frequencies of the lines.
 (b) Compute the values of J_{AB} , ν_A and ν_B .
 (c) Calculate the intensity ratio of the inner to outer lines in the spectrum.
 (d) Determine the δ values of A and B.
 (e) Calculate the positions of the lines that will be expected if the spectrum is recorded on a 100 MHz instrument.

[Ans: (a) 410.39, 404.65, 390.64 and 384.87 Hz.
 (b) $J_{AB} = 5.70$ Hz]

14. (a) The two signals due to complexed and uncomplexed water in the PMR spectrum of 2M $AlCl_3$ solution in a 10 : 1 mole ratio mixture of water to DMSO (at -20°C) are 252 cps apart (operating frequency of instrument = 60 MHz). The areas of the complexed and bulk water peaks are 52.5 and 390 units respectively. Calculate the hydration number of Al (III) and comment on the value so obtained.

[Ans: 3.27]

- (b) The PMR spectrum of 1.75M $AlCl_3$ in H_2O at -49°C on a 60 MHz instrument exhibits a coordinated water peak to the left (up-field ≈ 124 Hz) of the bulk water peaks. If the areas of the coordinated and uncomplexed water peaks are 24 and 480 units respectively determine the hydration number of Al (III).

[Ans: 1.5]

15. The hydrogen bonding of water to acetone, tetrahydrofuran and N,N-dimethyl acetamide, present in large excess in cyclohexane was investigated by PMR spectroscopy. The chemical shift of the water proton signal ν , in ternary systems containing water in the range of mole fractions $n_w = 0.003$ to 0.02 and acetone of mole fraction n_A in cyclohexane, were determined at several temperatures. The values of ν extrapolated to zero water concentration, ν_0 , are given in Table 7.19. Assume that all the water is H-bonded and the process under consideration is



Table 7.19

n_A	$\nu_0(\text{Hz relative to TMS})$			
	36°C	19°C	2°C	-14°C
0.99	163.0	169.7	178.0	184.3
0.85	157.0	164.4	173.0	179.7
0.68	150.2	157.8	165.3	174.5
0.59	147.5	163.5	163.5	174.7

- (a) Calculate K , ν_{11} and ν_{12} .
 (b) Calculate ΔG° at 19°C , ΔH° and ΔS° .

[Ans: (a) $\nu_{11} = 100$, $\nu_{12} = 230$; $K = 0.9$ at 36°C ; 1.2 at 19°C ; 1.5 at 2°C , and 2.0 at -14°C , (b) $\Delta H^\circ = -2.4\text{ kcal mole}^{-1}$, $\Delta S^\circ = -6.4\text{ e.u.}$; $\Delta G^\circ_{292} = +0.061\text{ kcal mole}^{-1}$]

16. How many times is the sensitivity of ^2H relative to ^1H if $\gamma_{^2\text{H}} = 4.106 \times 10^{-3}\text{ G}^{-1}\text{ s}^{-1}$; $\gamma_{^1\text{H}} = 26.7519\text{ G}^{-1}\text{ s}^{-1}$? Relative natural abundance: $H^1 = 100$, $^2\text{H} = 0.0156$.

[Ans: 5.6×10^{-7}]

17. Calculate the inherent bandwidth of a spectral line in a liquid and a solid provided the relaxation time of a nucleus in the former is one second and in the latter is 10^{-4} second.

[Ans: For liquid: = 0.1 Hz; For solid = 100 Hz].

18. Calculate the chemical shifts of individual ^{13}C atoms in (a) propane, (b) decane, (c) isobutane, (d) isohexane, (e) 3-methyl pentane, (f) 2,3-dimethyl butane, and (g) 2,3-dimethyl pentane.

[Ans: (a) obs: δ_1 (15.8), δ_2 (16.3), δ_3 (15.8)

(b) obs: δ_1 (14.2), δ_2 (23.2), δ_3 (32.6), δ_4 (31.1), δ_5 (30.5)

(c) obs: δ_1 (24.5), δ_2 (25.4)

(d) obs: δ_1 (22.7), δ_2 (28.0), δ_3 (42.0), δ_4 (20.9), δ_5 (14.3)

(e) obs: δ_1 (11.5), δ_2 (29.5), δ_3 (36.9), δ_4 (18.8, 3- CH_3)
 calc: δ_1 (11.3), δ_2 (29.5), δ_3 (36.2), δ_4 (19.3, 3- CH_3);

(f) obs: δ_1 (19.5), δ_2 (34.3);

(g) obs: δ_1 (7.0), δ_2 (25.3), δ_3 (36.3), δ_4 (14.6, 3- CH_3).

19. Calculate the s - l relaxation time if the time taken for some hypothetical NMR peak to decay to zero intensity is ≈ 7 seconds.

[Ans: $\approx 10\text{ s}$]

20. Systox is a mixture of $(\text{EtO})_2\text{PSO}-\text{C}_2\text{H}_4\text{SET}$, A (thiono); $(\text{EtO})_2\text{POS}-\text{C}_2\text{H}_4\text{SET}$ and $(\text{EtO})_2\text{PO}-\text{PO}(\text{OEt})_2$.

B (thiol)

C (Sulfotep)

60 MHz PMR spectrum of 20 per cent systox sample in CCl_4 exhibits three distinct multiplets, the low field signal due to the OCH_2 protons ($\delta = 3.8-4.3$ ppm) the mid-field to SCH_2 (2.3-3.1 ppm) and the high field to $\text{C}-\text{Me}$ (1.1-1.5 ppm) and the areas of each are measured by integration. If the areas of the respective peaks are I_{OCH_2} , I_{SCH_2} and I_{CH_3} and n_A , n_B and n_C are the relative mole fractions of compounds A, B and C respectively, show that

$$n_A = \frac{3}{8}I_{\text{OCH}_2} + \frac{1}{8}I_{\text{SCH}_2} - \frac{1}{4}I_{\text{Me}}$$

$$n_B = \frac{1}{6}I_{\text{Me}} - \frac{1}{4}I_{\text{OCH}_2}$$

$$n_C = \frac{5}{48}I_{\text{Me}} - \frac{3}{32}I_{\text{SCH}_2} - \frac{3}{32}I_{\text{OCH}_2}$$

Hint: Component A has

3 × OCH₃ (6 protons)

3 × SCH₂ (4 protons)

3 × C—Me (9 protons)

Component B has 2 × OCH₂ (4)

3 × SCH₂ (6)

3 × C—Me (9)

Component C has 4 × OCH₂ (8)

4 × CMe (12)

Thus, $I_{\text{OCH}_2} = 6n_A + 4n_B + 8n_C$.

21. Predict the number of signals and their multiplicities and assign these to the protons causing them in (a) *n*-propyl alcohol in presence of acid or base, (b) isopropyl alcohol (pure), and (c) tert-butyl alcohol (pure).

[Ans: (a) 4; triplet, 12 line multiplet, triplet, singlet, (b) 3, doublet; 14 line multiplet, doublet, (c) 2; singlet (strong), singlet (weak)]

22. Compute the reduced coupling constants for Cl and Br in PCl₃ and PBr₃

$\left(\begin{matrix} J_{^{31}\text{P}^{35}\text{Cl}} = 120 \\ J_{^{31}\text{P}^{37}\text{Cl}} = 100 \end{matrix} \right)$ and $\text{PBr}_3 \left(\begin{matrix} J_{^{31}\text{P}^{79}\text{Br}} = 350 \pm 17 \\ J_{^{31}\text{P}^{81}\text{Br}} = 380 \pm 19 \end{matrix} \right)$ respectively.

[Ans: 252×10^{20} and $288 \pm 14 \times 10^{20} \text{ cm}^{-3}$]

23. Predict the spectrum of a two-spin system for $\nu = 60$ MHz and $\nu = 270$ MHz provided $\sigma_A - \sigma_B = 24 \times 10^{-8}$ and $J = 8.0$ Hz. Sketch the spectrum in each case and comment. **[Ans:**

$$\nu_{\substack{1 \rightarrow 2 \\ (3 \rightarrow 4)}} = 60 \text{ MHz} \mp 12.2 \text{ Hz}$$

$$= 270 \text{ MHz} \mp 36.6 \text{ Hz}$$

$$\nu_{\substack{1 \rightarrow 3 \\ (3 \rightarrow 4)}} = 60 \text{ MHz} \pm 4.2 \text{ Hz}$$

$$= 270 \text{ MHz} \pm 28.6 \text{ Hz}$$

Relative intensities: 0.35 to 1 at 60 MHz and 0.78 to 1 at 270 MHz. The 270 MHz spectrum looks like a first-order spectrum with $J = 8.0$ Hz. While the 60 MHz spectrum looks like a second-order spectrum. The $(n + 1)$ rule holds good for the 270 MHz spectrum but not for the 60 Hz spectrum.]

24. Which of the following groups of elements are most suitable, depending on their atomic number, mass number and nuclear spin, for studies by NMR method?

[Ans: (c), (e)]

	(a)	(b)	(c)	(d)	(e)	(f)	(g)
Mass number	$2n$	$2n$	$2n + 1$	$2n$	$2n + 1$	$2n + 1$	$2n$
Atomic number	$2n$	$2n + 1$	$2n$	$2n + 1$	$2n + 1$	$2n + 1$	$2n + 1$
Spin	0	An integer	$\frac{1}{2}(2n - 1)$	$\frac{1}{2}(2n + 1)$	$\frac{1}{2}(2n - 1)$	0	0

CHAPTER 8

NUCLEAR QUADRUPOLE
RESONANCE SPECTROSCOPY

“Only God knows the profound and original things. Among men, only those he loves.”

—Plato *Timaeus*

8.1 INTRODUCTION

Nuclear Quadrupole Resonance (NQR) spectroscopy is a branch of NMR spectroscopy and deals with the absorption of radio waves by molecules containing quadrupole nuclei, i.e. ^2H and ^{14}N ($I = 1$); ^{75}As , ^{35}Cl , ^{37}Cl , ^{79}Br , ^{81}Br , ^{33}S , ^{63}Cu , ^{65}Cu and ^{11}B ($3/2$); ^{10}B (3); ^{17}O and ^{127}I ($5/2$); ^{59}Co ($7/2$), etc., in zero magnetic field. Other isotopes like ^{57}Fe are inaccessible in their nuclear ground states since $I = \frac{1}{2}$, but have a nuclear quadrupole moment in one or more of their nuclear excited states and so can be studied by Mossbauer Spectroscopy (MB) (Chapter 10).

Before describing the basic principles and applications of NQR spectroscopy, the origin of two main terms, namely nuclear quadrupole moment and electric field gradient involved in it needs to be discussed.

8.2 NUCLEAR ELECTRIC QUADRUPOLE MOMENT

The quadrupole moment ‘ Q ’ or in multiple of e , i.e. ‘ eQ ’ is a measure of deviation from spherical symmetry of the rotating nuclear charge and is generally expressed as

$$eQ = \int \rho_n r^2 (3\cos^2\theta - 1) d\tau \quad (8.1)$$

where, e is the charge on the electron ($= 4.8 \times 10^{-10}$ esu), ρ_n is the nuclear charge density in the volume element $d\tau_n$ (i.e. $dx dy dz$) at a distance ‘ r ’ from the centre of the nucleus and at an angle ‘ θ ’ to the nuclear spin axis. Q is expressed in barns ($1 \text{ barn} = 10^{-28} \text{ m}^2$) and can be either positive or negative.

For a sphere, this integral will be zero since the average value of $r^2 \cos^2\theta$ equals $\frac{r^2 \cos^2\theta}{3}$ but for a prolate spheroid the integral is finite and positive, and negative for an oblate spheroid, because of the presence of the fundamental unit of charge on both sides of Eq. (8. 1), itself has the dimensions of r^2 , viz. cm^2 . Thus, for an elongated (i.e. prolate rotational ellipsoid) nucleus along the axis of the nuclear spin, the sign of ‘ eQ ’ is positive [Fig. 8.1(a)] whereas negative for a flattened (i.e. oblate rotational ellipsoid) nucleus along the axis of the spin [Fig. 8.1(b)].

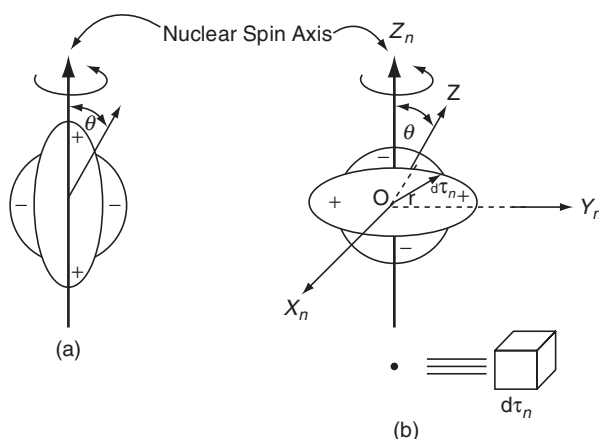


Fig. 8.1 The origin of nuclear electric quadrupole moments through deformation of a (rotating) charged spherical nucleus (a) elongated nucleus with positive ‘ eQ ’, and (b) flattened nucleus with negative ‘ eQ ’.

Further, atomic beam as well as proton scattering experiments show the existence of electric hexadipole moment also. However, the magnitude of a hexadipole moment is 10^{-8} of the electric quadrupole moment.

8.3 ELECTRIC FIELD GRADIENT (EFG)

A point charge ' q ' at a distance $r = (x^2 + y^2 + z^2)^{1/2}$ (in the arbitrarily chosen X , Y and Z axes which are different from the coordinate axes for Q ; Fig 8.2) from the nucleus gives rise to a potential $U(r) = \frac{q}{r}$ at the nucleus. The electric field gradient at the nucleus is given by

$$EFG = \nabla E = \nabla^2 U = - \begin{vmatrix} U_{xx} & U_{xy} & U_{xz} \\ U_{yx} & U_{yy} & U_{yz} \\ U_{zx} & U_{zy} & U_{zz} \end{vmatrix} \quad (8.2)$$

where E is the electric field gradient at the nucleus ($E = \nabla U$), ∇ is the Laplacian operator

$$U_{ij} = \frac{\partial^2 U}{\partial i \partial j} (i, j = x, y, z) \quad (8.3)$$

Since electric field gradient is symmetrical, so

$$U_{xy} = U_{yx}; U_{xz} = U_{zx}; U_{yz} = U_{zy} \quad (8.4)$$

The principal axis of MB nucleus is selected in such a way that the off-diagonal elements are zero i.e.,

$$U_{xy} = U_{yx} = U_{zx} = 0$$

and the diagonal elements are ordered as

$$|U_{zz}| \geq |U_{yy}| \geq |U_{xx}| \quad (8.5)$$

With respect to principal axis, EFG is described by two independent parameters choosen as $U_{zz} = eq$ and the symmetry parameter η , defined by

$$\eta = \frac{(U_{xx} - U_{yy})}{U_{zz}} \quad (8.6)$$

and is a measure of the departure from the axial symmetry. ' eq ' can theoretically be obtained from the equation

$$eq = \int \varphi^* \left[(3 \cos^2 \theta - 1) / r^3 \right] \varphi d\tau$$

where φ is the appropriate wave function.

With the above ordering of the diagonal elements, the asymmetry parameter is restricted to $0 \leq \eta \leq 1$. For a four-fold or three-fold axis (120° rotation) passing through the nucleus (i.e. choosing these axes as Z -axis) $U_{xx} = U_{yy}$ and therefore $\eta = 0$ and the field is called axially symmetric. Moreover, it can be shown that two mutually perpendicular axes of three-fold or higher symmetry give rise to a vanishing EFG. In general, the following three factors contribute to the total EFG: (i) noncubic charges on electrons belonging to the MB atom, i.e. noncubic electron distribution in partially filled valence orbitals of the atom, e.g. in transition metal ions, the inner d or f shells are not completely filled and produce EFG at the nucleus. The effective contribution due to this phenomenon is given by $(U_{zz})_{val} (1 - R)$ where R is called the *Sternheimer shielding factor* and has been estimated to be $0.2 - 0.3$

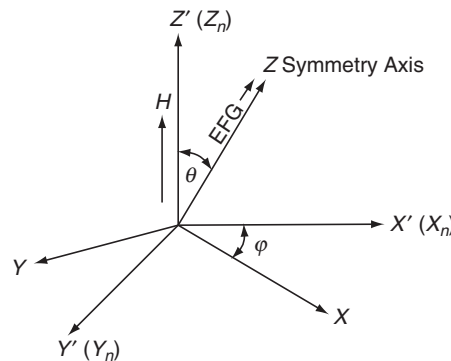


Fig. 8.2 Coordinate axes with respect to magnetic field axis and electric field gradient axis.

for iron and tin (ii) charges external to the MB atom or non-MB atom in noncubic symmetry. Such a contribution is termed ligand/lattice contribution. The effective contribution is given by $(U_{zz})_L (1 - \gamma_\infty)$; where

$$(U_{zz})_L = \sum_i^n q_i r_i^{-3} (3 \cos^2 \theta_i - 1),$$

$$\eta = 1 / (U_{zz})_L \sum_i^n q_i r_i^{-3} 3 \sin^2 \theta_i \cos 2\phi_i,$$

If the distances r_i and the angles ϕ_i and θ_i of all n ions i with respect to an atom are known from crystal-structure determination, and if effective charges q_i can be assigned to the parent ion then $(U_{zz})_L$ and η_L can be computed. γ_∞ is called the *Sternheimer anti-shielding factor*; $(1 - \gamma_\infty)$ has been estimated to be in the order of 10 for iron compounds. However, $(U_{zz})_L$ is not the EFG contribution felt by the nucleus, and (iii) polarisation of the filled inner shells of the atom. The filled inner shells being spherically symmetrical normally do not contribute to the EFG, However, charges because of ligand/lattice and valence electrons cause polarisation of filled inner shells which then contribute to the EFG at the nucleus and is known as *polarisation contribution*, i.e. $(U_{zz})_{\text{pol}}$.

In general, the Z-component of the total effective EFG at the nucleus may be written as

$$U_{zz} = (1 - R)(U_{zz})_{\text{val}} + (1 - \gamma_\infty)(U_{zz})_L + (U_{zz})_{\text{pol}} \quad (8.7)$$

and the asymmetry parameter is given by

$$\eta U_{zz} = U_{xx} - U_{yy} = (1 - R)(U_{zz})_{\text{val}} \eta_{\text{val}} + (1 - \gamma_\infty)(U_{zz})_L \eta_L + (U_{zz})_{\text{pol}} \eta_{\text{pol}} \quad (8.8)$$

For all practical purposes, polarisation contribution being small is ignored. Similar expressions are also there for the other two diagonal EFG elements.

The relative contribution of these factors depends upon the type of solid, e.g. the lattice contribution will predominate in ionic crystals or nontransition elements whereas the valence electron contribution will be dominant in transition elements. In molecular solids, the asymmetric π -electrons or the presence of π -bonding contribute mainly to the EFG.

The EFG elements and η , for electrons of different angular momenta, can be worked out from the above typed expressions. Since in most chemical applications only d - and p -electrons are considered, the contributions to $(U_{zz})_{\text{val}}$ from these electrons expressed in the units of expectation value of $\frac{1}{r^3}$, i.e. $\langle r^{-3} \rangle$ have been reported in Table 8.1 where $\langle \rangle$ refers to integral over all space. For some cases $\eta > 1$ the ordering (8.5) is not obeyed. In

Table 8.1 The magnitude of $(EFG)_{\text{val}}$ and η for the p - and d -electron orbitals.

Orbital	$(U_{xx})_{\text{val}}$ $e \langle r^{-3} \rangle$	$(U_{yy})_{\text{val}}$ $e \langle r^{-3} \rangle$	$(U_{zz})_{\text{val}}$ $e \langle r^{-3} \rangle$	η
p_x	$-\frac{4}{5}$	$+\frac{2}{5}$	$+\frac{2}{5}$	-3
p_y	$+\frac{2}{5}$	$-\frac{4}{5}$	$+\frac{2}{5}$	+3
p_z	$+\frac{2}{5}$	$+\frac{2}{5}$	$-\frac{4}{5}$	0
d_{xy}	$-\frac{2}{7}$	$-\frac{2}{7}$	$+\frac{4}{7}$	0
d_{xz}	$-\frac{2}{7}$	$+\frac{4}{7}$	$-\frac{2}{7}$	+3
d_{yz}	$+\frac{4}{7}$	$-\frac{2}{7}$	$-\frac{2}{7}$	-3
$d_{x^2-y^2}$	$-\frac{2}{7}$	$-\frac{2}{7}$	$+\frac{4}{7}$	0
d_z^2	$+\frac{2}{7}$	$+\frac{2}{7}$	$-\frac{4}{7}$	0

order that (8.5) is followed, the principal axis system should be chosen properly. The expectation value, $\frac{1}{r^3}$, i.e. $\langle r^{-3} \rangle = \int R(r)r^{-3} R(r)r^2 dr$ cannot be calculated precisely but may be obtained from experiments. The order of expectation value, $\langle r^{-3} \rangle$ for various orbitals is $4p < 3p$ and $3d, 3d < 3p$. This is because of the greater radial extent of the former orbitals relative to the latter. Similarly, we can interpret the sign of q in the X - and Y -directions also. The total value of q for a completely filled or half-filled shell of electrons is zero. An excess of electrons in the Z -axis (occupying p_z, d_{z^2}, d_{xz} or d_{yz}) gives a positive value of q whereas an excess in the XY plane (p_x, p_y, d_{xy} or $d_{x^2-y^2}$) results in negative value of q .

It is to be noted that spherically symmetric s -electron gives no EFG. f electrons being closer to nucleus than d -, p - and s -valence electrons of a particular complex ion are shielded by them from the influence of the ligand hence rarely participate in chemical bonding. Consequently, f orbitals do not undergo ligand field splitting and, therefore, electrons in the degenerate f -orbitals set do not contribute towards EFG.

8.4 NUCLEAR ELECTRIC QUADRUPOLE COUPLING

Nuclear quadrupole coupling constants in atoms were first observed in 1935 by Z Schmidt and H Schuler and for the first time in molecules (HD and D_2) by JMB Kellogg, I Rabi, NF Ramsey and JH Zacharias in 1940 by atomic and molecular beam spectroscopy. However, with the discovery of pure nuclear quadrupole resonance by H G Dehmelt and H Kruger in 1951, the nuclear quadrupole coupling constants of molecules became readily accessible experimentally.

In 1934, Harold Clayton Urey (USA) received the Nobel Prize in chemistry for the discovery of deuterium and in 1944 Isidor Isaac Rabi (USA) got the Nobel Prize in physics for resonance method for recording the magnetic properties of atomic nuclei.

The interaction between nuclear electric quadrupole moment ' eQ ' and electric field gradient ' eq ' (i.e. U_{zz}) is termed as nuclear quadrupole coupling and is measured in terms of a quantity ' ν_Q ' called nuclear quadrupole coupling constant. It is expressed as

$$\nu_Q = \frac{e^2 q Q}{h} \quad (8.9)$$

ν_Q which contains the product of q and Q is measured experimentally. From a reliable theoretical value of q for an atom, we can derive from Eq. (8.9), the value of Q for the nucleus of that atom. We may then use this value to derive ' q ' in compounds of the atom and compare with values calculated quantum mechanically.

8.5 ORIGIN OF NUCLEAR ELECTRIC QUADRUPOLE COUPLING

In quadrupole nuclei, there are two antiparallel dipoles. In an electric field, each of these dipoles senses a torque tending to align them with the field. However, since the two turning torques are equal and opposite, there is no net effect. On the other hand in an electric field gradient which is assumed to be axially symmetric about Z -axis, the torques on two dipoles are not equal and the net turning torque exists and is proportional to EFG ($= -eq$, along Z axis) and quadrupole moment ' eQ ' i.e. to the magnitude $|e^2 q Q|$.

The nuclear electric quadrupole coupling causes a splitting of the Zeeman energy levels. Further depending on the magnitude of the nuclear quadrupole interactions relative to Zeeman energy, the field of nuclear quadrupole interactions has been roughly divided into two areas, viz., combined magnetic and quadrupole interactions, and pure quadrupole resonance.

8.6 COMBINED MAGNETIC AND QUADRUPOLE INTERACTIONS

When both magnetic and quadrupole interactions (both are directional effects) exist simultaneously, their respective principal axes may or may not be in the same direction because of which the resulting behaviour may be complex. Consequently, the general interpretation of the spectrum can be quite complex. The combined effects may cause a change in line positions and/or in the relative line intensities or width of the hyperfine pattern. The combined effects can operate in two ways, either the magnetic hyperfine interaction, i.e. Zeeman splitting is perturbed by an electric quadrupole interaction or the quadrupole interaction is perturbed by magnetic dipole interaction, for instance by an applied external magnetic field. In case the quadrupole interaction is very weak relative to magnetic hyperfine interaction (i.e. $e^2 q Q \ll \mu H$), the quadrupole coupling in such a

situation is taken as perturbation and causes a splitting in the NMR resonance signal into several components. Quadrupole interactions in such systems are studied by NMR techniques.

The Hamiltonian operator of a nucleus with quadrupole moment ' eQ ' in the presence of applied magnetic field and nuclear quadrupole coupling is given by

$$\begin{aligned} H_{QM} &= H_M + H_Q \\ &= -g_N \beta_N H I + \frac{e^2 Q U_{zz}}{4I(2I-1)} [(3\hat{I}_z^2 - \hat{I}^2) + \eta(\hat{I}_+^2 + \hat{I}_-^2)/2] \end{aligned} \quad (8.10)$$

where, $\hat{I}_z$ is the z -component of the nuclear spin operator $\hat{I}$ and $\hat{I}_+$ and $\hat{I}_-$ are the raising and lowering operators defined as

$$\hat{I}_\pm = \hat{I}_x \pm i\hat{I}_y \quad (8.11)$$

The eigen value of the operator $\hat{I}^2$ is $I(I+1)$.

It is to be noted that in a high magnetic field the spin is quantised in the direction of the field. Let Z' -axis be the direction of the applied magnetic field (Fig. 8.2). If EFG has cylindrical symmetry, i.e. $\eta = 0$, the symmetry axis of the EFG, i.e. Z -axis differs from Z' -axis (Fig 8.2). If X' -axis is in the plane containing Z and Z' then

$$I_z = I_{z'} \cos \theta + I_{x'} \sin \theta \quad (8.12)$$

The Hamiltonian operator with $\eta = 0$ will then appear as

$$H_{QM} = -g_N \beta_N H I + \frac{e^2 q Q}{4I(2I-1)} (3\hat{I}_z^2 - \hat{I}^2) \quad (8.13)$$

Squaring Eq. (8.12), we obtain

$$I_z^2 = I_{z'}^2 \cos^2 \theta + I_{x'}^2 \sin^2 \theta + (I_{z'} I_{x'} + I_{x'} I_{z'}) \sin \theta \cos \theta$$

Substituting the value of I_z^2 into Eq. (8.13), we get

$$\begin{aligned} H_{QM} &= -g_N \beta_N H I + \frac{e^2 q Q}{4I(2I-1)} \cdot \\ &\quad \left[3I_{z'}^2 - I^2 \left(\frac{3 \cos^2 \theta - 1}{2} \right) + \frac{3}{2} \sin \theta \cos \theta \{ I_{z'} (I_+ + I_-) + (I_+ + I_-) I_{z'} \} + \frac{3}{4} \sin^2 \theta (I_+^2 + I_-^2) \right] \end{aligned} \quad (8.14)$$

Here, $I_{x'}$ is expressed in terms of I_+ and I_- .

The eigen values of the operator H_{QM} , i.e. the energy of the sublevels as deduced from the standard perturbation theory are given by

$$E_{QM} = -g_N \beta_N H M_I + \frac{3e^2 q Q}{4I(2I-1)} \left[M_I^2 - \frac{1}{3} I(I+1) \right] \cdot \left[\frac{3 \cos^2 \theta - 1}{2} \right] + \dots \quad (8.15)$$

where first and second terms represent the zeroth, and first-order contributions to the energy. The second and higher-order contributions to the energy have been ignored. The terms and symbols in Eq. (8.15) have their usual meanings. θ is the angle between magnetic spin axis and the major axis (Z -axis) of EFG.

8.6.1 Shift in Zeeman Energy Levels Due to First-order Nuclear Quadrupole Coupling

Let us now work out the shift in Zeeman energy levels due to first-order quadrupole interactions, for quadrupole nuclei with different spins.

(a) For nuclei with $I = \frac{1}{2}$, the number of substates due to Zeeman effect/first term of Eq. (8.15) is two according to $(2I+1)$ rule. These substates are characterised by $M_I = \pm \frac{1}{2}$. The second term of Eq. (8.15) which is because of

first-order nuclear quadrupole interaction is zero for $M_I = \pm \frac{1}{2}$. Therefore, for a nucleus with $I = \frac{1}{2}$, the first order quadrupole interaction is zero. Consequently, the Zeeman substates are not affected due to first order nuclear quadrupole coupling [Fig. 8.3 (a)].

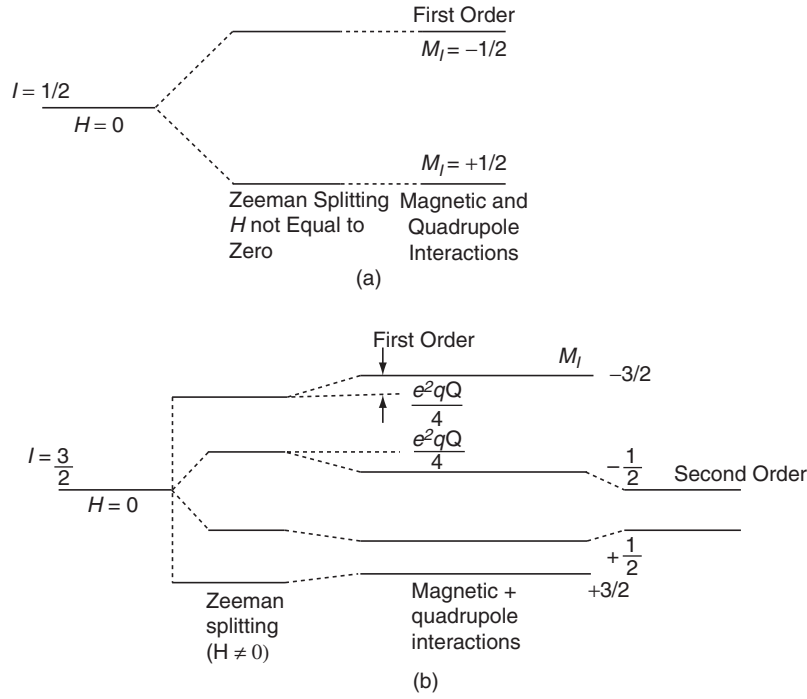


Fig. 8.3 Perturbation of Zeeman levels by the first-order quadrupole interaction in a nuclear system with symmetry axis parallel to spin axis for (a) $I = 1/2$ (b) $I = 3/2$.

(b) For nuclei with $I = \frac{3}{2}$, the number of equally spaced sublevels due to Zeeman energy is four according to $(2I + 1)$ rule. These four substates are characterised by $M_I = \pm \frac{3}{2}, \pm \frac{1}{2}$

Since, $I = \frac{3}{2}$, so Eq. (8.15) reduces to

$$E_{QM} = -g_N \beta_N H M_I + \frac{e^2 q Q}{4} \left[M_I^2 - \frac{5}{4} \right] \{3 \cos^2 \theta - 1\}$$

For $M_I = \pm \frac{1}{2}$, the term $\left(M_I^2 - \frac{5}{4} \right) = -1$ and $+1$ for $M_I = \pm \frac{3}{2}$. Therefore, Eq. (8.15) for $I = \frac{3}{2}$ can be expressed as

$$E_{QM} = -g_N \beta_N H M_I + (-1)^{|M_I| + \frac{1}{2}} \left(\frac{e^2 q Q}{4} \right) \left(\frac{3 \cos^2 \theta - 1}{2} \right) \quad (8.16)$$

For $M_I = \pm \frac{3}{2}$

$$E_{QM} \left(\pm \frac{3}{2} \right) = \mp \frac{3}{2} g_N \beta_N H + \left(\frac{e^2 q Q}{4} \right) \left(\frac{3 \cos^2 \theta - 1}{2} \right) \quad (8.17a)$$

and for $M_I = \pm \frac{1}{2}$

$$E_{QM} \left(\pm \frac{1}{2} \right) = \mp \frac{1}{2} g_N \beta_N H - \left(\frac{e^2 q Q}{4} \right) \left(\frac{3 \cos^2 \theta - 1}{2} \right) \quad (8.17b)$$

Equations. (8.17a) and (8.17b) reveal that the substates with $M_I = \pm \frac{3}{2}$ will be raised by an amount $\left(\frac{e^2 q Q}{4} \right) \left(\frac{3 \cos^2 \theta - 1}{2} \right)$ while those with $M_I = \pm \frac{1}{2}$ will be lowered with the same amount as shown in Fig (8.3 b).

Further, for $\cos \theta = \frac{1}{\sqrt{3}}$, there is no shift in Zeeman substates due to first-order nuclear quadrupole coupling whereas the quadrupole coupling term will be in error by a factor of $\frac{-1}{2}$ for $\theta = \frac{\pi}{2}$. Therefore, without the independent knowledge of the direction of the magnetic field relative to the symmetry axis of the field, the quadrupole moment can't be defined by the hyperfine field alone.

If the symmetry axis is parallel to the magnetic field H , i.e. $\theta = 0$, Eq. (8.16) becomes

$$E_{QM} = -g_N \beta_N H M_I + (-1)^{|M_I|+\frac{1}{2}} \left(\frac{e^2 q Q}{4} \right)$$

Consequently, the Zeeman level corresponding to $M_I = \pm \frac{3}{2}$ will be raised whereas lowered corresponding to $M_I = \pm \frac{1}{2}$ by an amount $\left(\frac{e^2 q Q}{4} \right)$ rather than $\left(\frac{e^2 q Q}{4} \right) \left(\frac{3 \cos^2 \theta - 1}{2} \right)$ Fig. (8.3b).

It is to be noted that the treatment of second-order perturbation is beyond the scope of this book. However the influence of second-order perturbation on the Zeeman levels has been shown in Fig. 8.3 b.

Further it is evident from Fig. (8.3 b) that in the presence of quadrupole interaction, the energy levels are no longer symmetrical about the centroid.

8.6.2 Transition between Zeeman Energy Levels Perturbed by First-order Quadrupole Interaction

We know that the energy of Zeeman levels perturbed by first-order quadrupole interaction is given by

$$E_{QM} = -g_N \beta_N H M_I + \frac{3e^2 q Q}{4I(2I-1)} \left[M_I^2 - \frac{1}{3} I(I+1) \right] \quad (8.18)$$

provided the angle between the symmetry axis (i.e. Z-axis) and spin axis is zero.

(a) For nuclei with $I = \frac{1}{2}$, the number of magnetic substates is two according to the $(2I+1)$ rule. These states are characterised by $M_I = \pm \frac{1}{2}$. Further for $I = \frac{1}{2}$ the second term in Eq. (8.15) vanishes, consequently the energy expression resembles with that of an unperturbed Zeeman energy, i.e.

$$E_{QM} = -g_N \beta_N H M_I \quad (8.19)$$

Since,

$$M_I = \pm \frac{1}{2}$$

Therefore,

$$E_{QM} \left(-\frac{1}{2} \right) = \frac{1}{2} g_N \beta_N H \quad (8.20)$$

$$E_{QM} \left(+\frac{1}{2} \right) = -\frac{1}{2} g_N \beta_N H \quad (8.21)$$

Thus, according to the selection rule $\Delta M_I = \pm 1$, the transition frequency between the two states characterised by $M_I = \pm \frac{1}{2}$ is given by

$$\begin{aligned} \Delta E \left(\frac{+1}{2} \rightarrow \frac{-1}{2} \right) &= E_{QM} \left(\frac{-1}{2} \right) - E_{QM} \left(\frac{+1}{2} \right) \\ &= g_N \beta_N H = h \nu_0 \end{aligned} \quad (8.22a)$$

or

$$\nu_0 = \frac{g_N \beta_N H}{h} \quad (8.22b)$$

Thus, the NMR spectrum of quadrupole nuclei with $I = \frac{1}{2}$ consists of a single line having frequency $\nu_0 = \frac{g_N \beta_N H}{h}$ and is independent of the first order nuclear quadrupole coupling. The zeroth order spectrum is shown in Fig 8.4 (a).

(b) For quadrupole nuclei with $I = \frac{3}{2}$, the energy of Zeeman levels perturbed by first order nuclear quadrupole interaction has been expressed as

$$E_{QM} = -g_N \beta_N H M_I + (-1)^{|M_I|+\frac{1}{2}} \cdot \frac{e^2 q Q}{4} \quad (\text{Eq. 8.18})$$

The energy of four substates characterised by $M_I = \pm \frac{3}{2}, \pm \frac{1}{2}$ can be expressed as

$$E_{QM} \left(\pm \frac{3}{2} \right) = \mp \frac{3}{2} g_N \beta_N H + \frac{e^2 q Q}{4} \quad (8.23)$$

$$E_{QM} \left(\pm \frac{1}{2} \right) = \mp \frac{1}{2} g_N \beta_N H - \frac{e^2 q Q}{4} \quad (8.24)$$

The frequencies of NMR lines corresponding to the permissible transitions by the selection rule $\Delta M_I = \pm 1$ as deduced from Eqs. (8.23) and (8.24) are given by

$$\left. \begin{aligned} \nu_0 \left(\frac{+1}{2} \rightarrow \frac{-1}{2} \right) &= \frac{g_N \beta_N H}{h} \\ \nu_1 \left(\frac{-1}{2} \rightarrow \frac{-3}{2} \right) &= \nu_0 + \frac{e^2 q Q}{4h} \\ \nu_2 \left(\frac{+3}{2} \rightarrow \frac{+1}{2} \right) &= \nu_0 - \frac{e^2 q Q}{4h} \end{aligned} \right\} \quad (8.25)$$

The frequency separation between two adjacent peaks, i.e. quadrupole splitting, Δ , is given by

$$\Delta = \frac{e^2 q Q}{4h} \quad (8.26)$$

Intensities of various lines are proportional to $\langle M_I | I_x | M_I - 1 \rangle^2$ and are in the ratio 3 : 4 : 3 for $I = \frac{3}{2}$.

The set of Eqs. (8.25), shows that the NMR spectrum consists of three resonance lines with frequencies ν_0 , ν_1 and ν_2 . The lines with frequencies ν_1 and ν_2 are termed as satellite lines and are on the opposite side and equidistant from the central line. The spectrum is shown in Fig. 8.4 (b).

(c) For quadrupole nuclei with $I = 5/2$, the number of substates are six by $(2I + 1)$ rule. The six substates are characterised by $M_I = \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2}$.

Further, for $I = 5/2$, the Eq. (8.15) can be expressed as

$$E_{QM} = -g_N \beta_N H M_I + \frac{3e^2 q Q}{40} \left[M_I^2 - \frac{35}{12} \right] \quad (8.27)$$

The energies of six substates characterised by $M_I = \pm 5/2, \pm 3/2, \pm 1/2$ can then be deduced from Eq. (8.27) and are given by

$$\begin{aligned} E_{QM} \left(\pm \frac{5}{2} \right) &= \mp \frac{5}{2} g_N \beta_N H + \frac{5e^2 q Q}{20} \\ E_{QM} \left(\pm \frac{3}{2} \right) &= \mp \frac{3}{2} g_N \beta_N H - \frac{e^2 q Q}{20} \\ E_{QM} \left(\pm \frac{1}{2} \right) &= \mp \frac{1}{2} g_N \beta_N H - \frac{4e^2 q Q}{20} \end{aligned} \quad (8.28)$$

The frequencies of NMR lines corresponding to the allowed transitions by the selection rule $M_I = \pm 1$ can be deduced from the set of Eqs. (8.28) and are given by

$$\begin{aligned} \nu_2 \left(\frac{-3}{2} \rightarrow \frac{-5}{2} \right) &= \nu_0 + \frac{3e^2 q Q}{10h} \\ \nu_1 \left(\frac{-1}{2} \rightarrow \frac{-3}{2} \right) &= \nu_0 + \frac{3e^2 q Q}{20h} \\ \nu_0 \left(\frac{+1}{2} \rightarrow \frac{-1}{2} \right) &= \frac{g_N \beta_N H}{h} \end{aligned} \quad (8.29)$$

$$\nu_3 \left(\frac{+3}{2} \rightarrow \frac{+1}{2} \right) = \nu_0 - \frac{3e^2qQ}{20h}$$

$$\nu_4 \left(\frac{+5}{2} \rightarrow \frac{+3}{2} \right) = \nu_0 - \frac{3e^2qQ}{10h}$$

The set of Eqs. (8.29), shows that the NMR spectrum consists of five resonance lines with frequencies ν_2 , ν_1 , ν_0 , ν_3 and ν_4 . The lines with frequencies ν_2 and ν_1 and ν_3 and ν_4 are on the opposite side and equidistant from the central line. The quadrupole splitting for $I = 5/2$ is $3e^2qQ/20$.

The NMR lines with frequencies ν_2 , ν_1 , ν_0 , ν_3 , and ν_4 are in the intensity ratio 5 : 8 : 9 : 8 : 5. The NMR spectrum for nuclei $I = 5/2$ is shown in Fig. 8.4 (c). The second-order perturbation shifts the central line in the spectrum.

Further, it is evident from Fig. 8.4 that the numbers of NMR lines in the spectra of nuclei with $\left[I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots \right]$ are given by $2I$. Thus the spin of a nucleus can be obtained from the number of lines in the NMR spectrum, e.g. if the number of lines in the NMR spectrum is only one, the spin of the nucleus will be $\frac{1}{2}$.

The energy expression for the cylindrically asymmetric systems is given by

$$E_{QM} = -g_N \beta_N H M_I + \frac{3e^2qQ}{8I(2I-1)} (3\cos^2\theta - 1 + \eta \sin^2\theta \cos^2\phi) \left[M_I^2 - \frac{1}{3}I(I+1) \right] \quad (8.30)$$

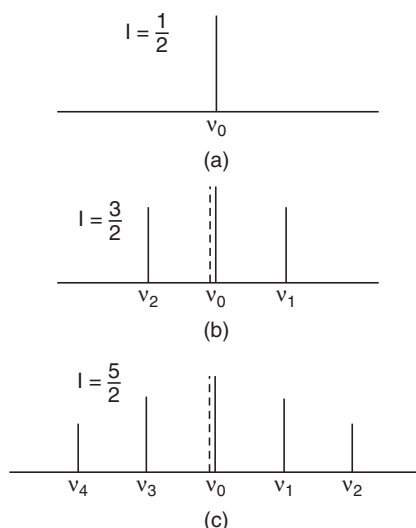


Fig. 8.4 Schematic NMR spectra for nuclei with (a) $I = \frac{1}{2}$ (b) $I = \frac{3}{2}$ and (c) $I = \frac{5}{2}$ in the presence of zeroth, first and second-order quadrupole effects. The central line is not affected by the first-order quadrupole coupling. The dashed line shows the second-order shift of the central line.

If we use single crystals that can be rotated with respect to the applied field, it is possible from the spectral shapes for different orientations to determine the positions of the principal axes of the EFG in the crystal and the values of the parameters η and e^2qQ .

Problem 8.1: If the EFG is axially symmetric, prove that for $I = 3/2$ the frequency separation between two adjacent lines, Δ , in an NMR spectrum showing first order quadrupole effects is given by

$$\Delta = \Delta(\theta) = \left| \frac{3e^2qQ(3\cos^2\theta - 1)}{4hI(2I-1)} \right|$$

Solution From Eq. (8.15), we can easily deduce the required result as follows.

$$\nu_1 = \frac{g_N \beta_N H}{h} + \frac{3e^2qQ}{4hI(2I-1)} \cdot (3\cos^2\theta - 1)$$

$$\nu_0 = \frac{g_N \beta_N H}{h}$$

$$\nu_2 = \frac{g_N \beta_N H}{h} - \frac{3e^2 q Q}{4Ih(2I-1)} \cdot (3\cos^2 \theta - 1)$$

Thus,

$$\Delta = \Delta(\theta) = \nu_1 - \nu_0 = \nu_2 - \nu_0 = \left| \frac{3e^2 q Q (3\cos^2 \theta - 1)}{4hI(2I-1)} \right| \quad (8.31)$$

For a crystalline or powder sample where all directions of the EFG are equally probable, NMR absorption occurs over a wide range, i.e. $3\cos^2 \theta - 1 = 1$, $\cos \theta = \sqrt{\frac{2}{3}}$ or $\theta = 35.3^\circ$ or 144.7° , the powder sample behaves like NMR liquid.

The quadrupole splitting between adjacent peaks is given by

$$\Delta_p = \left| \frac{3e^2 q Q}{4hI(2I-1)} \right| \quad (8.32)$$

8.7 QUADRUPOLE SPLITTINGS IN LIQUID CRYSTALS

NMR studies of quadrupole ions or molecules in liquid crystals are used to obtain information pertaining to molecular geometry and EFGs. Order parameter (S) using known value of ν_Q and observed value of quadrupole splitting can also be determined.

In quadrupole nuclei, all directions of the EFG with respect to the applied magnetic field are considered to be equally probable. However, a slight anisotropy in the EFG may turn simple natured NMR signal into a complex pattern, which is analogous to that observed in all solids. In liquid crystalline systems, a rapid molecular motion also tends to average out the quadrupole interaction. However, for an anisotropic mesophase, complete averaging out does not result. The residual interaction gives rise to NMR effects analogous to those obtained for rigid lattices except that quadrupole splittings are generally much smaller for liquid crystals, because of the rapid molecular motion.

For uniaxial liquid crystals like nematic mesophases, lamellar and hexagonal amphiphilic phases, the system is cylindrically symmetric with respect to an axis called *director*. It is convenient to perform the transformation from the molecular coordinate system (M) to the laboratory frame (L) via the director coordinate system. The M - D - L (Z) transformation in the mesomorphous structure in the lamellar phase is shown in Fig. 8.5.

For a sample, (with $I = 3/2$) with uniform director orientation, the quadrupole splitting is given by

$$\Delta(\theta) = \left| \frac{3e^2 q Q S}{4hI(2I-1)} \cdot (3\cos^2 \theta_{LD} - 1) \right| \quad (8.33)$$

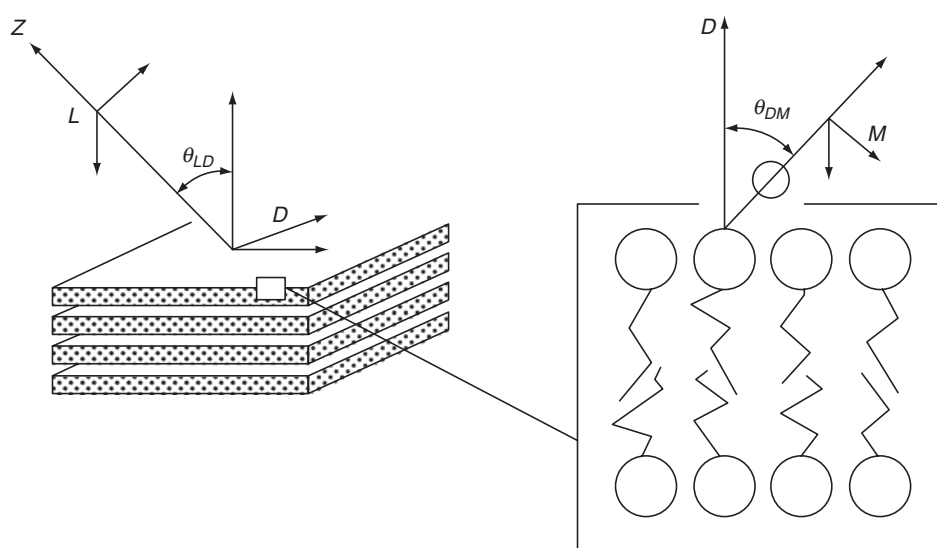


Fig. 8.5 The outline of the transformation of coordinates from the molecular to laboratory via the director coordinate system. θ_{LD} and θ_{DM} are angles between Z -axis in the laboratory-director and director-molecular systems respectively.

For a powder sample, all values of θ_{LD} are equally probable and for $\theta_{LD} = 90^\circ$, the quadrupole splitting, Δ_p , is given by

$$\Delta_p = \left| \frac{3e^2qQS}{4hI(2I-1)} \right| \quad (8.34)$$

Further, the study of liquid crystalline phases is built up of amphiphilic compounds, e.g. surfactants and water is important since phases of this type are important building stones in biological systems, i.e. membranes. The counter cations in amphiphilic water mesophases can reside in different binding sites which are characterised by different quadrupole splittings. In most cases, it is assumed that the rate of exchange of counter cations between different positions is rapid than the difference between the quadrupole splittings between the different sites.

However, if the exchange is slow, the first-order quadrupole splittings are given by

$$\Delta(\theta) = \left| (3\cos^2\theta_{LD} - 1) \sum \frac{3P_i v_{Q(i)} S_i}{4I(2I-1)} \right|; v_{Q(i)} = \frac{e^2 q_i Q}{h} \quad (8.35)$$

and

$$\Delta_p = \left| \sum \frac{3P_i v_{Q(i)} S_i}{4I(2I-1)} \right| \quad (8.36)$$

where, P_i is the probability for occupation of site i characterised by the field gradient q_i , and the order parameter S_i .

The observed quadrupole splitting, Δ_p , of Cl^{35} in the hexagonal mesophase of the dodecyltrimethyl ammonium chloride ($\text{C}_{12}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$) water system decreases as the concentration of surfactant is increased whereas the reverse has been observed for ^{37}Cl and ^{35}Cl in the lamellar mesophases of the $\text{C}_8^+\text{NH}_3\text{Cl}^-$ — H_2O and ($\text{C}_8^+\text{NH}_3\text{Cl}^-$ — C_{10}OH — H_2O) systems respectively. The hexagonal mesophase is built up of rod-shaped amphiphilic aggregates arranged in a hexagonal array whereas the lamellar phase is built up of alternating amphiphilic bilayers and water layers. The latter gives rise to an asymmetric splitting of the ^{35}Cl and ^{37}Cl NMR signals. It is to be noted that these substances behave as electrolytes in dilute aqueous solutions rather than mesophases.

Problem 8.2: Concentrated solutions of poly- γ -benzyl- L -glutamate behave as liquid crystal of cholesteric type and when placed in a magnetic or electric field, the cholesteric structure breaks up to give nematic phase. ^{35}Cl —NMR spectrum of CH_2Cl_2 in poly- γ -benzyl- L -glutamate (10 CH_2Cl_2 molecules/monomer residue) at 24°C shows quadrupole splitting of 56 kHz. Calculate the order parameter provided $v_Q(\text{CH}_2\text{Cl}_2) = 72 \text{ MHz}$.

Solution We know that

$$\begin{aligned} \Delta(\theta) &= \left| \frac{3e^2qQS(3\cos^2\theta_{LD} - 1)}{4hI(2I-1)} \right| \quad (\text{Eq. 8.33}) \\ &= \frac{3(3\cos^2\theta_{LD} - 1)S.v_Q}{4I(2I-1)} \end{aligned}$$

Rearrangement of Eq. (8.33) gives

$$S = \frac{4\Delta(\theta)I(2I-1)}{3v_Q(3\cos^2\theta_{LD} - 1)}$$

Since the sample is under the influence of magnetic field, so $\theta_{LD} = 0$. Thus,

$$S_{11} = \frac{4\Delta I(2I-1)}{6v_Q}$$

Substituting the values $I = \frac{3}{2}$, $\Delta = 56 \text{ kHz}$ and $v_Q = 72 \text{ MHz}$, we get

$$\begin{aligned} S_{11} &= \frac{4(56 \times 10^3 \text{ Hz}) \frac{3}{2} (2 \times \frac{3}{2} - 1)}{6(72 \times 10^6 \text{ Hz})} \\ &= 1.55 \times 10^{-3} \end{aligned}$$

8.8 NUCLEAR QUADRUPOLE RELAXATION

Nuclear quadrupole relaxation occurs through time dependent s - s and s - I interaction whereas quadrupole relaxation is due to time dependent electric field gradients at the nucleus. Both the magnitude and direction of EFG play an important role in the quadrupole relaxation process, e.g. the changes in magnitude of EFG contributes to the relaxation rate in halide ions whereas in covalent bonded halogens, the contribution to relaxation rate is due to changes in direction of EFG caused by molecular tumbling.

The relaxation of quadrupole nucleus is in general expressed in terms of two (for ^{35}Cl , ^{37}Cl , ^{79}Br , ^{81}Br) and three (for ^{127}I) exponentials. However, if the frequency of modulation of quadrupole interaction is rapid relative to Larmour frequency of the nucleus, the relaxation mechanism may be expressed by a single exponential, e.g. in halogens. In such cases, the longitudinal and transverse relaxation rates, i.e. R_1 and R_2 respectively, become equal and are given by

$$R_1 = R_2 = \frac{3\pi^2}{10} \frac{(2I+3)}{I^2(2I-1)} \cdot \left[\frac{e^2 q Q}{h} \right]^2 \left(1 + \frac{\eta^2}{3} \right) \tau_c \quad (8.37a)$$

Here, τ_c is the correlation time characterising the reorientation of the field gradient, i.e. molecular reorientation around symmetry (i.e. EFG) axis. In terms of coupling constant, $\nu_Q = \frac{e^2 q Q}{h}$,

$$R_1 = R_2 = \frac{3\pi^2}{10} \frac{(2I+3)}{I^2(2I-1)} \cdot \nu_Q^2 \left(1 + \frac{\eta^2}{3} \right) \tau_c \quad (8.37b)$$

The above expression is obeyed provided $\nu_Q \tau_c \geq \frac{1}{2\pi}$ otherwise fails for quadrupole halogen nuclei as well as for any magnetic nuclei with $I > 1$.

The above expression can be used to determine ' τ ' provided η , ν_Q and R_1 or R_2 are known. For axial symmetric molecules, $\eta = 0$. However, if the halogen is attached to an unsaturated carbon, the partial double bond character leads to loss of symmetry about the carbon halogen bond and $\eta \neq 0$. For ^{35}Cl , $\eta = 0.25$.

For Lorentzian shape NMR signals the values of the spin relaxation rates are expressed as:

$$\Delta\nu_{\frac{1}{2}} \text{ (Full width at half height)} = \frac{R_2}{\pi} = \frac{1}{\pi T_2} \quad (8.38a)$$

$$\Delta\nu_{pp} \text{ (peak-to-peak line width of the derivative absorption curve)} = \frac{R_2}{\sqrt{3}\pi} = \frac{1}{\sqrt{3}\pi T_2} \quad (8.38b)$$

The line broadening may also be either due to the dominance of correlation time or of ion exchange effects over the quadrupole relaxation on broadening due to T_1 or T_2 .

Equation (8.37) holds good only for rigid molecules. On the other hand, if the nucleus resides in a group which undergoes internal rotation relative to the rest of the molecule, the rate of relaxation may depend on both the internal rotation and on the rate of the rotation of the whole molecule. For isotropic motion of the whole molecule

$$R_1 = \frac{3\pi^2(2I+3)}{10I^2(2I-1)} \nu_Q^2 \cdot \left[\frac{1}{4}(3\cos^2\beta - 1)^2 \tau_{\text{rot}} + \left\{ 1 - \frac{1}{4}(3\cos^2\beta - 1)^2 \right\} \left(\frac{1}{\tau_{\text{rot}}} + \frac{1}{\tau_{\text{introt}}} \right)^{-1} \right] \quad (8.39)$$

Here, β is the angle between the largest component of the field gradient and the axis about which the internal rotation takes place

If $\tau_{\text{introt}} \ll \tau_{\text{rot}}$, (8.39) reduces to

$$R_1 = \frac{3\pi^2(2I+3)\nu_Q^2}{10I^2(2I-1)} \cdot \frac{1}{4}(3\cos^2\beta - 1)^2 \tau_{\text{rot}} \quad (8.40)$$

Therefore, the effect of fast internal rotation is to average out components of field gradient which are perpendicular to the axis of internal rotation.

The relaxation rates depend on temperature and increase with the increase of temperature. The effect is because of increase in the acceleration of molecular reorientation with the growth of temperature and is given by

$$R_{1,2} \propto e^{+E_a/RT} \quad (8.41)$$

The relaxation rate of ^{127}I in aqueous solution of MI ($M = \text{Li, Na, K}$) varies with temperature approximately as η/T (η denotes viscosity).

In general, the effect of temperature on quadrupole coupling constant is negligible. Therefore, the parameter τ_c , i.e. correlation time is used to determine E_a .

$$\frac{1}{\tau_c} \propto e^{+E_a/RT} \quad (8.42)$$

8.8.1 Quadrupole Relaxation Models

The two mathematical models to predict the quadrupole relaxation times are the following:

(a) Electrostatic Model This model is due to H G Hertz. The model is based on the assumption that the EFGs at the nucleus arise because of the distribution of charges set up by the surrounding species. For infinite dilute aqueous solutions, the expression for the randomly oriented water molecules around the relaxing monoatomic ion is

$$R_1 = R_2 = \frac{24\pi^3 (2I+3)}{5I^2 (2I-1)} \left(\frac{eQ}{h} \right)^2 \left[M_{H_2O} (1 + \gamma_\infty) P \right]^2 \left(\frac{C_{H_2O} \tau_{H_2O}}{r_0^5} \right) \quad (8.43)$$

where, P (polarisation factor) = $\frac{2D+3}{5D}$ is assumed to be 0.5 (D is the dielectric constant of the medium), $e = 4.8 \times 10^{-10}$ e.s.u. M_{H_2O} is the dipole moment of water molecule and its value in the gas phase ($M = 1.84$ D = 1.84×10^{-18} e.s.u cm) is used, C_{H_2O} is the water concentration in molecules/cm³. $(1 + \gamma_\infty)$ is the Sternheimer antishielding factor and r_0 is the distance between the relaxing nucleus and the water molecules in the first hydration sphere. It is taken as the sum of the ionic radius and radius of the water molecule.

$\frac{1}{\tau_{H_2O}} = \frac{1}{\tau_r} + \frac{1}{\tau_c^*}$, τ_r is the time constant for the reorientation of water dipoles relative to the ion–water molecule vector direction and τ_c^* is the time constant for the reorientation of water dipoles relative to the rotational motion axis of the ion–water molecule. The time variation of field gradient is either because of τ_r or τ_c^* .

Further according to simple electrostatic model, in case of amphiphilic liquid crystals, the EFGs are assumed to be due to charges of the amphiphilic ions and to the water dipoles. The quadrupole coupling constant arising from point charge Z at a distance r from a nucleus with spin $I = \frac{3}{2}$ with quadrupole moment Q is given by

$$v_Q = \frac{e^2 q Q}{h} = \frac{0.69 \times 10^6 (Hzm)(1 + \gamma_\infty) QZ}{r^3} \left[\frac{2D+3}{5D} \right] \quad (8.44a)$$

Here, v_Q will be in Hz if Z is expressed in atomic units, r in cm, Q in m². It can be assumed that $D \gg 1$.

Further if we assume that the field gradient experienced by the bound chloride ion is solely to a positively charged group on the protein, then the quadrupole coupling constant based on the simple electrostatic model is given by

$$v_Q (\text{in MHz}) = \frac{0.52(1 + \gamma_\infty)}{I(2I-1)} \cdot \left(\frac{2D+3}{5D} \right) \frac{QZ}{r^3} \quad (8.44b)$$

Here, Z is the point charge on the protein in atomic units, Q (in m²), r (in m) is the distance between the nucleus and the point charge. For Cl[−] ion binding to an arginine group, the estimated value of v_Q equals 1.4 MHz.

(b) Electronic Distortion Model This model is due to C Deverell. The model is based on the assumption that the field gradients are produced at the halide ion nucleus by deformation in the electron cloud resulting from collisions with other species in solution. Accordingly,

$$v_Q = \frac{1}{10} \cdot \frac{e^2 Q \sigma_p \Delta E}{h \alpha^2} \quad (8.45)$$

where, ΔE is the mean electron excitation energy and α is the fine structure constant $\left(\alpha = \frac{2\pi e^2}{hc} \right)$ and

$$R_1 = \frac{3\pi^2}{1000} \cdot \frac{2I+3}{I^2(2I-1)} \left(\frac{e^2 Q}{h} \right)^2 \left(\frac{\sigma_p \Delta E}{\alpha^2} \right)^2 \tau_c \quad (8.46)$$

Here, τ_c for ion–water interactions is the reorientational correlation time of water molecules adjacent to the relaxing ion. σ_p is the paramagnetic shielding constant $\sigma_p(\text{ClCl}) = \frac{-65.5 \times 10^{-4}}{\Delta E}$; ΔE lies in the range of 10–12 eV.

The modified version of electronic distortion model is due to Hertz. According to this version the distance between the relaxing ion and the water molecules is assumed to vary with time.

$$R_1 = R_2 = \frac{3\pi^2}{10} \cdot \frac{2I+3}{I^2(2I-1)} \cdot \left(\frac{eQ}{h} \right)^2 N_{\text{H}_2\text{O}} P(a) \tau_a \cdot U_a^2 \quad (8.47)$$

where, $N_{\text{H}_2\text{O}}$ is the total number of water molecules in the system. $P(a) = \frac{\tau_a}{\tau_a + \tau_b}$ is the probability of finding the water molecule in the position A . The contribution to relaxation rate from one water molecule is $\propto (U_a)^2$. U_a is the field gradient in the position A . This model is obeyed by only weakly hydrated ion.

Problem 8.3: Calculate the correlation times of ^{35}Cl -nuclei in (a) CH_3Cl , and (b) $\text{C}_6\text{H}_5\text{Cl}$ from the NQR data (at 298 K) given below:

Molecule	$T_2(\mu\text{s})$	$\nu_Q(\text{MHz})$
CH_3Cl	24.5	76.6
$\text{C}_6\text{H}_5\text{Cl}$	13	69.2

Solution From Eq. (8.37), we write

$$\tau_c = \frac{1}{3.94384 \times T_2 \times \nu_Q^2 \left(1 + \frac{\eta^2}{3} \right)}$$

$$\left[\text{For } I = \frac{3}{2} \right]$$

(a) For CH_3Cl , $\eta = 0$

Therefore,

$$\begin{aligned} \tau_c &= \frac{1}{3.94384 \times 24.5 \times 10^{-6} (\text{s}) \times (76.6 \times 10^6 \text{ Hz})^2} \\ &= 1.76 \times 10^{-12} \text{ s} = 1.76 \text{ ps.} \end{aligned}$$

(b) For $\text{C}_6\text{H}_5\text{Cl}$, $\eta = 0.25$

Therefore,

$$\begin{aligned} \tau_c &= \frac{1}{3.94384 \times 13 \times 10^{-6} (\text{s}) \times (69.2 \times 10^6 \text{ Hz})^2 \left[1 + \frac{(0.25)^2}{3} \right]} \\ &= \frac{10^{-6}}{3.94384 \times 13 \times (69.2)^2 \times 1.0208} \text{ s} \\ &= 3.99 \times 10^{-6} \times 10^{-6} \text{ s} \\ &= 3.99 \times 10^{-12} \text{ s} = 3.99 \text{ ps} \end{aligned}$$

Problem 8.4: Calculate the quadrupole relaxation time of $^{35}\text{Cl}^-$ ion in an infinite dilute solution of water if Q (cm^2) = -0.079×10^{-24} , $1 + \gamma_\infty = 57.6$, $r_0(\text{\AA}) = 3.21$, $\tau_{\text{H}_2\text{O}} (\text{s}) = 2.5 \times 10^{-12}$, $P = 0.5$.

Solution The negative sign of Q indicates that the charge distribution is flattened relative to the spin axis. We know that the relaxation rate R_1 is given by

$$R_1 = \frac{24\pi^3(2I+3)}{5I^2(2I-1)} \cdot \left(\frac{eQ}{h} \right)^2 \left[M_{\text{H}_2\text{O}}(1+\gamma_\infty)P \right]^2 \left(\frac{C_{\text{H}_2\text{O}}\tau_{\text{H}_2\text{O}}}{r_0^5} \right) \quad (\text{Eq. 8.43})$$

(A) (B) (C) (D)

In order to determine R_1 the values of four factors (A), (B), (C) and (D) need to be determined individually.

For Cl^- , $I = \frac{3}{2}$

Therefore,
$$(A) = \frac{24\pi^3(2I+3)}{5I^2(2I-1)} = \frac{24(3.14)^3 \left(2 \times \frac{3}{2} + 3\right)}{5 \times \frac{9}{4} \left(2 \times \frac{3}{2} - 1\right)}$$

$$= \frac{24(3.14)^3 6 \times 4}{5 \times 9 \times 2} = \frac{32 \times (3.14)^3}{5} = 198.1385$$

$$(B) = \left(\frac{eQ}{h}\right)^2 = \left(\frac{4.8 \times 10^{-10} \times 0.079 \times 10^{-24}}{6.62 \times 10^{-27}}\right)^2$$

$$[e = 4.8 \times 10^{-10} \text{ esu}, h = 6.62 \times 10^{-27} \text{ erg s}]$$

$$= (0.0572)^2 \times 10^{-14} = 3.2811 \times 10^{-17}$$

$$M_{\text{H}_2\text{O}} = 1.84 D = 1.84 \times 10^{-18} \text{ esu cm.}$$

$$C_{\text{H}_2\text{O}} = 55.5 \text{ moles/lit} = 55.5 \times 6.023 \times 10^{23} \text{ molecule}/10^3 \text{ cm}^3 =$$

$$334.2765 \times 10^{20} \text{ molecule/cm}^3 = 3.342 \times 10^{22} \text{ molecule/cm}^3$$

$$P = 0.5$$

$$(C) = [M_{\text{H}_2\text{O}}(1 + \gamma_\infty)P]^2 = [1.84 \times 10^{-18} \times 57.6 \times 0.5]^2 = 2.808 \times 10^{-33}$$

$$(D) = \frac{C_{\text{H}_2\text{O}} \tau_{\text{H}_2\text{O}}}{r_0^5} = \frac{3.342 \times 10^{22} \times 2.5 \times 10^{-12}}{(3.21 \times 10^{-8})^5} =$$

$$\frac{8.355}{340.820} \times 10^{50} = 0.02451 \times 10^{50} = 2.451 \times 10^{48}$$

Thus, $R_1 = (A) (B) (C) (D)$

$$= (198.1385) \times (3.2811 \times 10^{-17}) \times (2.808 \times 10^{-33}) \times (2.451 \times 10^{48}) \text{ s}^{-1}$$

$$= 4474.3 \times 10^{-2} \text{ s}^{-1} = 44.7 \text{ s}^{-1}$$

The quadrupole relaxation time of $^{35}\text{Cl}^-$ ion in an infinite dilute solution of water will be $\frac{1}{44.7} \text{ s} = 0.0223 \text{ s}$.

Problem 8.5: Compute the ^{35}Cl -quadrupole coupling constant for Cl^- counter ion bound to $\text{N}^+ (\text{CH}_3)_3$ group in the amphiphilic $[\text{C}_{12} \text{N}^+ (\text{CH}_3)_3 \text{Cl}^-] - \text{H}_2\text{O}$ system from the following data, γ_∞ (for chlorine) = 59, $D \gg 1$, r (the distance between Cl^- counter ion bound to amphiphilic surfaces and amphiphilic positive charge, i. e. $\text{N}^+ (\text{CH}_3)_3$ end group) = $7.3 \times 10^{-10} \text{ m}$. Q (for $^{35}\text{chlorine}$) = $-0.0802 \times 10^{-24} \text{ cm}^2$. The Cl^- counter ions are assumed to be hydrated.

Solution We know that for the amphiphilic $-\text{H}_2\text{O}$ mesophases,

$$\nu_Q = \frac{0.69 \times 10^6 (\text{Hzm})(1 + \gamma_\infty) Q Z \left(\frac{2D + 3}{5D}\right)}{r^3}$$

Substituting the values of respective parameters, we get

$$\nu_Q = \frac{0.69 \times 10^6 \text{ Hzm} \times 60 \times (0.0802 \times 10^{-28} \text{ m}^2) \left(\frac{2}{5} + \frac{3}{5D}\right)}{(7.3 \times 10^{-10} \text{ m})^3}$$

Further, $\left(\frac{2}{5} + \frac{3}{5D}\right) = 0.4$ [since $D \gg 1$] and $Z = 1$

$$\begin{aligned}\text{Therefore, } \nu_Q &= \frac{0.69 \times 10^6 \text{ Hzm} \times 60 \times (0.0802 \times 10^{-28} \text{ m}^2) \times 0.4}{(7.3 \times 10^{-10} \text{ m})^3} \\ &= 0.853 \times 10^6 \times 0.4 \text{ Hz} \\ &= 0.34 \times 10^6 \text{ Hz} = 0.34 \text{ MHz}\end{aligned}$$

8.9 PURE QUADRUPOLE RESONANCE

The field gradient responsible for large quadrupole interactions occur often in molecules with covalent bonding in which valence electrons produce large asymmetric electric fields close to the nucleus. In such molecular systems, the quadrupole interactions are very strong relative to Zeeman energy (i.e. $e^2qQ \gg \mu H$) and hence the Zeeman hyperfine interaction is merely taken as perturbation. Therefore, in the limit of zero magnetic field, the quadrupole interactions in such molecular systems are studied by pure nuclear quadrupole resonance (NQR) technique, which deals with radio frequency transitions within the hyperfine multiplet of a nucleus in the ground state. Further it is to be noted that in NQR, quadrupole moment is a probe to study the behaviour of electric field gradient in molecular systems.

In order to deduce theoretically the pure NQR spectra of systems with quadrupole nuclei we are to proceed as follows:

The classical expression for the quadrupole coupling Hamiltonian operator is given by

$$H_Q = \frac{e^2qQ}{6} \left[1 - \frac{1}{2} \frac{U_{xx} + U_{yy}}{U_{zz}} \right] \quad (8.48)$$

where terms independent of nuclear orientation have been ignored.

The quantum mechanical analogue of the classical quadrupole Hamiltonian is

$$H_Q = \frac{eQU_{zz}}{4I(2I-1)} \left[3I_z^2 - I^2 + \eta(I_+^2 + I_-^2)/2 \right] \quad (8.49)$$

where terms and symbols have their usual meanings. The asymmetry parameter η which is a measure of the departure from the axial symmetry has already been defined earlier and is expressed as

$$\eta = \frac{(U_{xx} - U_{yy})}{U_{zz}} \quad (8.50)$$

and is restricted to $0 \leq \eta \leq 1$.

The eigen values of the Hamiltonian operator H_Q i.e. the energy of the substates caused by pure nuclear quadrupole interaction is given by

$$E_Q = \frac{eQU_{zz}}{4I(2I-1)} \left[3M_I^2 - I(I+1) \right] f(\eta) \quad (8.51)$$

where $f(\eta)$ is a function of η .

Here, the substates are not discernible by the sign of M_I , since Eq. (8.51) contains only the second power of M_I . Therefore, the nuclear substates arising from nuclear quadrupole splitting remain doubly degenerate. The two-fold degeneracy of substates can only be lifted by magnetic perturbation.

For spherical symmetrical fields, (i.e. $U_{xx} = U_{yy} = U_{zz}$), all the quadrupole levels are degenerate, i.e. they have the same energy. Consequently the degeneracy corresponding to M_I cannot be lifted, and no resonance can take place, e.g. systems with closed shell structure, i.e. Cl^- ion, whereas for axial symmetrical fields, (i.e. $U_{xx} = U_{yy} \neq U_{zz}$ e.g., the EFG at the chlorine nucleus along the F-Cl bond in FCl molecule is defined as Z-axis), $I = 3/2, 5/2, 7/2 \dots$, the number of substates $= 2I + 1$. The substates split into a series of Kramer's doublet, i.e. the degenerate levels lie very close to each other. The energy level splitting due to pure quadrupole interaction only for nuclei with $I = 1/2, 3/2$ and $5/2$ has been shown in Fig. 8.6.

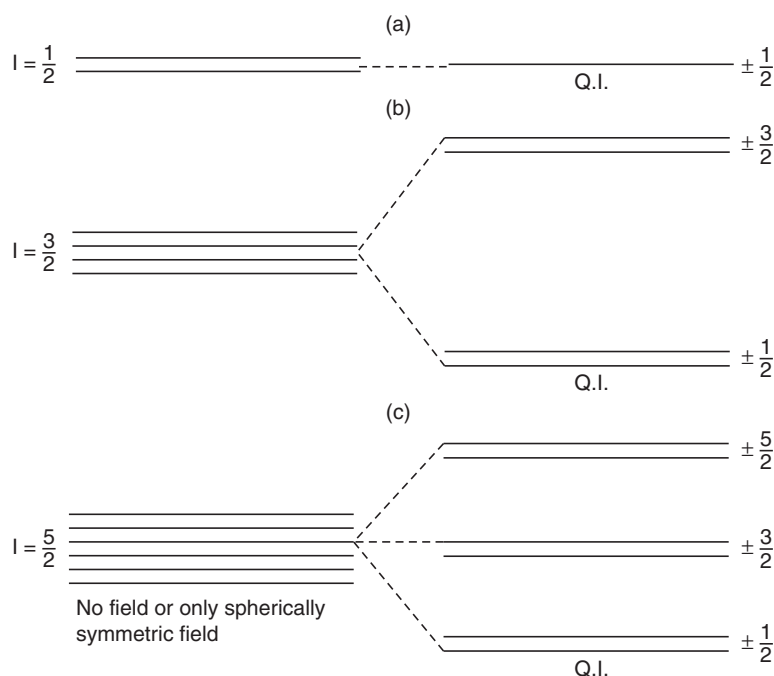


Fig. 8.6 Energy-level splitting under pure quadrupole interactions ($Q = I$) only for nuclei with (a) $I = \frac{1}{2}$, (b) $I = \frac{3}{2}$, (c) $I = \frac{5}{2}$.

Further, since $\eta = 0$ for spherical symmetric and axil symmetrical fields, so for such systems, Eq. (8.51) becomes

$$E_Q = \frac{eQU_z}{4I(2I-1)} [3M_I^2 - I(I+1)] \quad (8.52)$$

With the aid of this equation, let us deduce the pure NQR spectra of nuclei with $I = 1, \frac{3}{2}, 2$ and $\frac{5}{2}$.

(a) For nuclei with $I = 1, M_I = -1, 0, +1$. The two allowed transitions are: $0 \rightarrow -1, +1 \rightarrow 0$. From Eq. (8.52), it can be proved that the frequencies corresponding to these transitions have the same frequencies, i.e.

$$\nu_1(0 \rightarrow -1) = \nu_2(+1 \rightarrow 0) = \frac{3}{4} \frac{e^2 q Q}{h}$$

The quadrupole energy levels and transitions for $I = 1$ are shown in Fig. 8.7 (a).

(b) For nucleus with $I = \frac{3}{2}, M_I = \pm\frac{3}{2}, \pm\frac{1}{2}$. The allowed transitions are $\frac{-1}{2} \rightarrow \frac{-3}{2}, \frac{+1}{2} \rightarrow \frac{-1}{2}, \frac{+3}{2} \rightarrow \frac{+1}{2}$

The frequency corresponding to transition $\frac{+1}{2} \rightarrow \frac{-1}{2}$ is zero whereas the other two transitions have the same frequency, i.e.

$$\nu_1\left(\frac{-1}{2} \rightarrow \frac{-3}{2}\right) = \nu_2\left(\frac{+3}{2} \rightarrow \frac{+1}{2}\right) = \frac{e^2 q Q}{2h}$$

The quadrupole energy levels and transitions for $I = 3/2$ are shown in Fig. 8.7 (b).

(c) For nucleus with $I = 2, M_I = \pm 2, \pm 1, 0$. The allowed transitions are: $-1 \rightarrow -2, 0 \rightarrow -1, +1 \rightarrow 0, +2 \rightarrow +1$. The frequencies of transitions $-1 \rightarrow -2, +2 \rightarrow +1$ and $0 \rightarrow -1, +1 \rightarrow 0$ are the same, i.e.

$$\nu_1(-1 \rightarrow -2) = \nu_2(+2 \rightarrow +1) = \frac{3}{8} \frac{e^2 q Q}{h}$$

and

$$\nu_3(0 \rightarrow -1) = \nu_4(+1 \rightarrow 0) = \frac{1}{8} \frac{e^2 q Q}{h}$$

The quadrupole levels and transitions for $I = 2$ are shown in Fig. 8.7 (c). Thus for $I = 2$, the NQR spectrum consists of two lines and $\nu_1/\nu_2 = 3 [\nu_3/\nu_4]$.

(d) For a nucleus with $I = \frac{5}{2}, M_I = \pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$, the allowed transitions are $\frac{-3}{2} \rightarrow \frac{-5}{2}, \frac{-1}{2} \rightarrow \frac{-3}{2}, \frac{+1}{2} \rightarrow \frac{-1}{2}, \frac{+3}{2} \rightarrow \frac{+1}{2}, \frac{+5}{2} \rightarrow \frac{+3}{2}$. The frequency corresponding to transition $\frac{+1}{2} \rightarrow \frac{-1}{2}$

is zero whereas the transitions $\frac{-1}{2} \rightarrow \frac{-3}{2}$, $\frac{+3}{2} \rightarrow \frac{+1}{2}$ and $\frac{-3}{2} \rightarrow \frac{-5}{2}$, $\frac{+5}{2} \rightarrow \frac{+3}{2}$ have the same frequency, i.e.

$$\nu_1 \left(\frac{-1}{2} \rightarrow \frac{-3}{2} \right) = \nu_2 \left(\frac{+3}{2} \rightarrow \frac{+1}{2} \right) = \frac{3}{20} \frac{e^2 q Q}{h}$$

$$\nu_3 \left(\frac{-3}{2} \rightarrow \frac{-5}{2} \right) = \nu_4 \left(\frac{+5}{2} \rightarrow \frac{+3}{2} \right) = \frac{3}{10} \frac{e^2 q Q}{h}$$

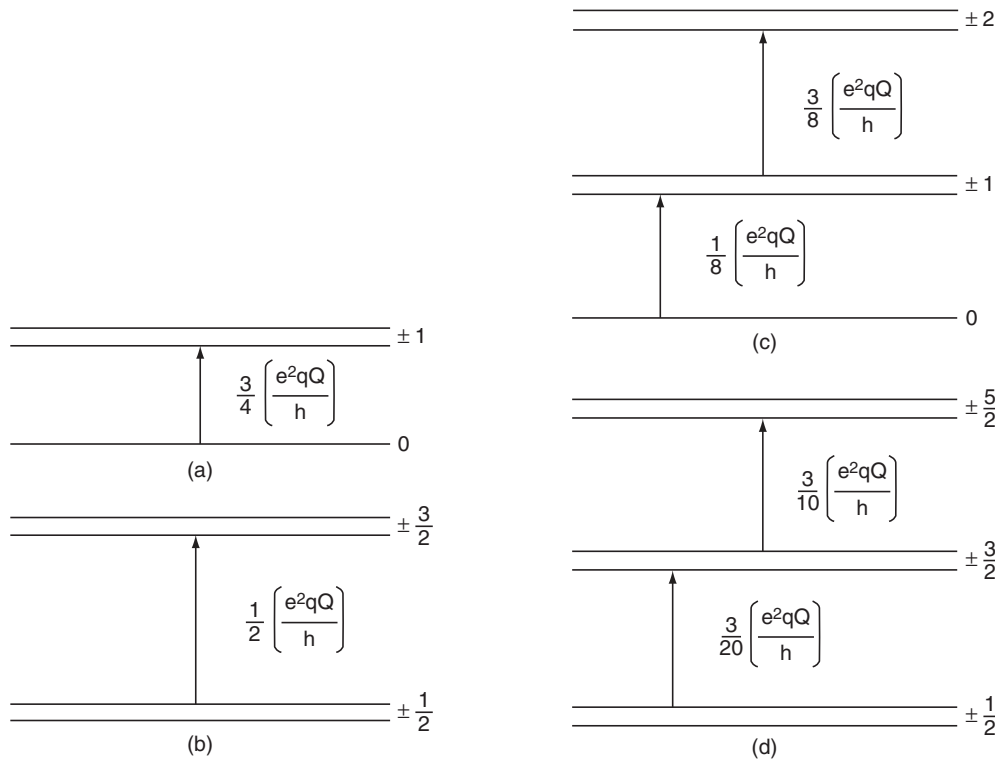


Fig. 8.7 Quadrupole energy levels and transitions for (a) $I=1$, (b) $I=\frac{3}{2}$, (c) $I=2$, and (d) $I=\frac{5}{2}$.

The quadrupole energy levels and transitions for $I=5/2$ are shown in Fig. 8.7 (d). Thus, for $I=5/2$, the NQR spectrum consists of two lines and the ratio between two frequencies is $\nu_3/\nu_4 = 2\nu_1/\nu_2$. Consequently, one can write

$$\nu_{M_I \rightarrow M_I - 1}^{(I)} = \frac{3e^2 q Q}{4I(2I-1)h} [2|M_I| - 1] \quad (8.53a)$$

and

$$\nu_{M'_I \rightarrow M'_I - 1}^{(I)} = \frac{3e^2 q Q}{4I(2I-1)h} [2|M'_I| - 1] \quad (8.53b)$$

The ratio of these frequencies is

$$\frac{\nu_{M \rightarrow M_I - 1}^{(I)}}{\nu_{M' \rightarrow M'_I - 1}^{(I)}} = \frac{2|M'_I| - 1}{2|M_I| - 1} \quad (8.54)$$

The above examples, i.e. (a)–(d), reveal that the pure NQR transition frequency depends on the magnitude of the magnetic quantum number M_I . The frequencies vary within very large limits that depend on the magnitude of quadrupole moment and nature of the system under study.

Uptil now we have predicted the NQR spectra of integral and half-integral spin systems assuming η to be zero, i.e. axially symmetrical fields. Let us now consider the case for nucleus with $I=3/2$ when $\eta \neq 0$, i.e.

$$U_{xx} \neq U_{yy} \neq U_{zz} \quad (\text{asymmetrical field})$$

This is the most complex case. The energy of pure NQR is given by

$$E_Q = \frac{e^2 q Q}{4I(2I-1)} [3M_I^2 - I(I+1)] \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \left[\text{From Eq. (8.51), } f(\eta) = \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \right] \quad (8.55)$$

The energy difference ΔE_Q between the two substates $\left|\frac{3}{2}, \pm\frac{3}{2}\right\rangle$ and $\left|\frac{3}{2}, \pm\frac{1}{2}\right\rangle$ can be worked out as follows. From Eq. (8.55), we write

$$E_Q \left(\pm\frac{3}{2}\right) = \frac{3e^2 q Q}{12} \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \text{ for } I = \frac{3}{2}, M_I = \pm\frac{3}{2}$$

$$E_Q \left(\pm\frac{1}{2}\right) = \frac{-3e^2 q Q}{12} \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \text{ for } I = \frac{3}{2}, M_I = \pm\frac{1}{2}$$

Thus, the quadrupole transition frequency is given by

$$\nu = \frac{\Delta E_Q}{h} = \frac{E_Q \left(\pm\frac{3}{2}\right) - E_Q \left(\pm\frac{1}{2}\right)}{h} = \frac{e^2 q Q}{2h} \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \quad (8.56)$$

Since there are two unknowns, i.e. η and Q , the values of both $e^2 q Q$ and η cannot be obtained from the measured frequency. In such cases, the results from NQR experiments on a sample in a weak magnetic field are necessary to obtain η .

For other half-integral spin systems with $I = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$, the secular quadrupole energy equations are very complex and cannot be solved exactly. However, for $I = \frac{5}{2}$ and $\eta^2 \leq 0.25$, the energy-level expressions are

$$E_Q \left(\pm\frac{5}{2}\right) = A \left[10 + \frac{5}{9}\eta^2 + \frac{85}{2916}\eta^4 - \frac{715}{472392}\eta^6 - \frac{62935}{306110016}\eta^8 + \dots \right] \quad (8.57)$$

$$E_Q \left(\pm\frac{3}{2}\right) = A \left[-2 + 3\eta^2 - \frac{23}{12}\eta^4 + \frac{449}{216}\eta^6 - \frac{44675}{15552}\eta^8 \right] \quad (8.58)$$

$$E_Q \left(\pm\frac{1}{2}\right) = A \left[-8 - \frac{32}{9}\eta^2 + \frac{1376}{729}\eta^4 - \frac{122656}{59049}\eta^6 + \frac{13740640}{4782969}\eta^8 + \dots \right] \quad (8.59)$$

where, $A = \frac{e^2 q Q}{4I(2I-1)}$

For $\eta \leq 0.1$, the second term in the brackets is significant. Therefore, for $I = 5/2$, it can easily be shown that

$$\nu \left(+\frac{3}{2} \rightarrow +\frac{1}{2} \right) = \frac{3e^2 q Q}{20h} \left[1 + \frac{59}{54}\eta^2 \right] \quad (8.60)$$

$$\nu \left(+\frac{5}{2} \rightarrow +\frac{3}{2} \right) = \frac{3e^2 q Q}{10h} \left[1 - \frac{11}{54}\eta^2 \right] \quad (8.61)$$

Thus, for a small value of η , we can compute both $\frac{e^2 q Q}{h}$ and η with the aid of Eqs. (8.60) and (8.61) provided both the frequencies are measured experimentally.

The ratio of frequencies for these two transitions is;

$$\frac{\nu \left(+\frac{5}{2} \rightarrow +\frac{3}{2} \right)}{\nu \left(+\frac{3}{2} \rightarrow +\frac{1}{2} \right)} = 2 \left[1 - \frac{35}{27}\eta^2 \right] \quad (8.62)$$

For a small value of η , Eq. (8.62) reduces to:

$$\frac{\nu\left(+\frac{5}{2} \rightarrow +\frac{3}{2}\right)}{\nu\left(+\frac{5}{2} \rightarrow +\frac{1}{2}\right)} = 2 \quad (8.63)$$

Therefore, any deviation from the observed ratio of these two frequencies from the value of 2 suggests that η is finite.

For low η (say < 0.25) and $I = \frac{5}{2}$, we also have

$$\nu_1 = \frac{3}{20} \left(\frac{e^2 q Q}{h} \right) (1 + 0.09259\eta^2 - 0.63403\eta^4) \quad (8.60a)$$

$$\nu_2 = \frac{3}{10} \left(\frac{e^2 q Q}{h} \right) (1 - 0.20370\eta^2 + 0.16215\eta^4) \quad (8.61a)$$

and, for

$$I = \frac{7}{2}, \eta < 0.25$$

$$\nu_1 = \frac{1}{14} \left(\frac{e^2 q Q}{h} \right) [1 + 3.63333\eta^2 - 7.26070\eta^4]$$

$$\nu_2 = \frac{2}{14} \left(\frac{e^2 q Q}{h} \right) [1 - 0.56667\eta^2 + 1.85952\eta^4] \quad (8.64)$$

$$\nu_3 = \frac{3}{14} \left(\frac{e^2 q Q}{h} \right) [1 - 0.1001\eta^2 - 0.01804\eta^4]$$

Here, also the harmonic ratio of the frequencies ν_1 , ν_2 and ν_3 is no longer observed due to the asymmetry parameter η . However, both η and $\frac{e^2 q Q}{h}$ can be separately derived provided the theoretical equations. (8.64) can be fitted to the observed frequencies.

For integral spins $I = 1, 2, 3 \dots$, etc., with nonzero η , the secular quadrupole energy equations except $I = 1$ are also complex and cannot be solved exactly. The behaviour of the energy levels and transition frequencies for $\eta = 0$ and finite η is shown in Fig. 8.8.

When, $\eta \neq 0$, we observe three transition frequencies of

$$\begin{aligned} \nu_1 &= \frac{1}{2} \left(\frac{e^2 q Q}{h} \right) \eta \\ \nu_2 &= \frac{3}{4} \left(\frac{e^2 q Q}{h} \right) \left(1 - \frac{\eta}{3} \right) \\ \nu_3 &= \frac{3}{4} \left(\frac{e^2 q Q}{h} \right) \left(1 + \frac{\eta}{3} \right) \end{aligned} \quad (8.65)$$

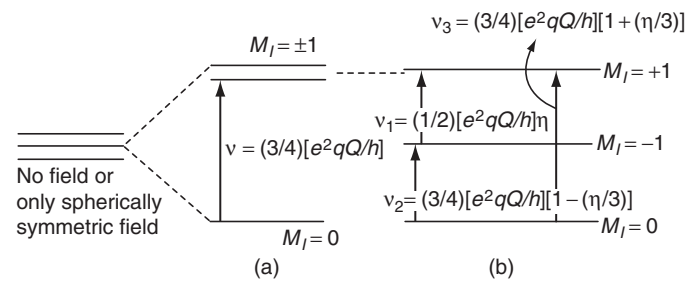


Fig. 8.8 Quadrupole energy levels and transitions for nuclei with $I = 1$ (a) $\eta = 0$ (axially symmetric field) (b) $\eta \neq 0$ (axially nonsymmetric field).

When, $\eta \rightarrow 0$, a single transition is observed at $\frac{3}{4} \left(\frac{e^2 q Q}{h} \right)$. Thus η and ν_Q can once again be deter-

mined from the NQR spectrum of the powder sample. ^{14}N -quadrupole spectra mostly consist of two lines corresponding to frequencies ν_2 and ν_3 .

Note that the M_I degeneracy of the energy levels is removed for nuclei with integral spins if $\eta \neq 0$. For half-integral spins, the M_I degeneracy is unaffected whether η is zero or not.

The sign of the coupling constant in a pure quadrupole resonance experiment (a) have been compared with the sign of the coupling constant in a nuclear magnetic resonance experiment in which the magnetic field lies along the field gradient principal axis is depicted in the schematic diagrams in Fig. 8.9.

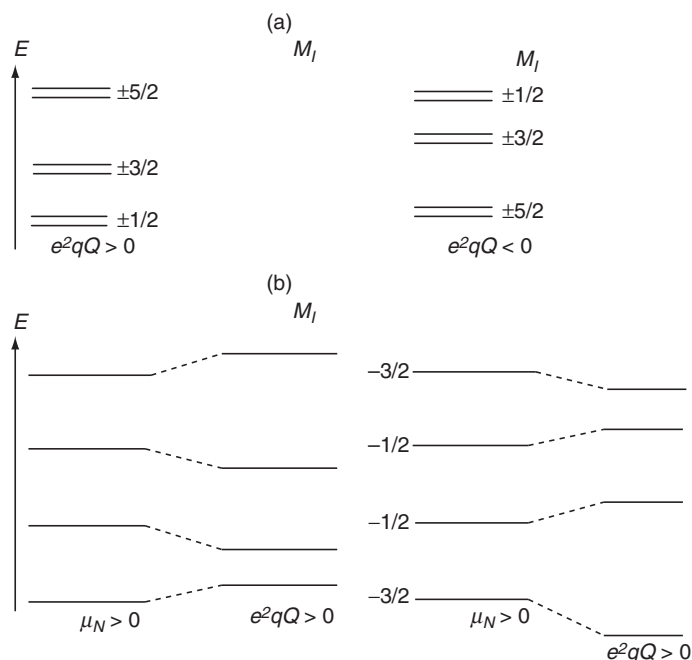


Fig. 8.9 Schematic diagram of the coupling constants (a) in pure quadrupole resonance experiment and (b) in a nuclear magnetic resonance experiment in the presence of magnetic field along the field gradient axis.

Problem 8.6: Two groups of transitions at 198.736, 199.999 and 397.430, 399.993 MHz have been observed in the ^{127}I -quadrupole spectrum of SiI_4 at 77 K. Determine the values of asymmetry parameter and coupling constants.

Solution The two groups of frequencies are in harmonic ratio. Therefore, $\eta = 0$.

For ^{127}I ($I = 5/2$), we observe two transitions of

$$\nu_1 = \frac{3}{20} \left(\frac{e^2qQ}{h} \right)$$

$$\nu_2 = \frac{3}{10} \left(\frac{e^2qQ}{h} \right)$$

Thus, the values of coupling constants corresponding to each of the frequencies in the group will be

$$\left(\frac{e^2qQ}{h} \right)_{198.736} = 198.736 \times \frac{20}{3} = 1324.90 \text{ MHz}$$

$$\left(\frac{e^2qQ}{h} \right)_{199.999} = 199.999 \times \frac{20}{3} = 1333.32 \text{ MHz}$$

The two coupling constants may be attributed to the lower point symmetry of the molecule in the crystal compared to the vapour.

Problem 8.7: ^{59}Co ($I = 7/2$) quadrupole spectrum of cobalticinium perchlorate $[\text{Co}(\text{C}_6\text{H}_5)_2^+ \text{ClO}_4^-]$ exhibits three groups of frequencies near 12, 24, and 36 MHz. Calculate the values of η and nuclear quadrupole coupling constants.

Solution The three groups of frequencies are in harmonic ratio. Therefore, $\eta = 0$. For $I = \frac{7}{2}$, the three transitions as worked out from Eq. (8.64) are

$$\nu_1 = \frac{1}{14} \left(\frac{e^2qQ}{h} \right)$$

$$\nu_2 = \frac{2}{14} \left(\frac{e^2 q Q}{h} \right)$$

$$\nu_3 = \frac{3}{10} \left(\frac{e^2 q Q}{h} \right)$$

Thus, $\left(\frac{e^2 q Q}{h} \right) = 14 \times \nu_1 = 14 \times 12 = 168 \text{ MHz}.$

Problem 8.8: ^{127}I -quadrupole spectra of BI_3 show two frequencies at 212.6 and 340.1 MHz. Find the values of quadrupole coupling constant and asymmetry parameter.

Solution For ^{127}I , $I = \frac{5}{2}$. The frequencies are not in harmonic ratio, so $\eta \neq 0$

From Eq. (8.62), we write

$$\frac{340.1}{212.6} = 2 \left[1 - \frac{35}{27} \eta^2 \right].$$

$$1 - \frac{35}{27} \eta^2 = \frac{340.1}{212.6 \times 2} = 0.7998$$

$$\frac{35}{27} \eta^2 = 0.20$$

$$\eta^2 = \frac{0.20 \times 27}{35} = 0.1543$$

or

$$\eta = 0.392$$

Substituting $\eta = 0.392$ into Eq. (8.61), we get

$$340.1 = \frac{3e^2 q Q}{10h} \left[1 - \frac{11}{54} \times (0.392)^2 \right]$$

or

$$\nu_Q = \frac{e^2 q Q}{h} = \frac{10 \times 340.1}{3 \left[1 - \frac{11}{54} (0.392)^2 \right]} = \frac{3401}{3 \times 0.969} = 1169.93 \text{ MHz}$$

8.10 EQUIVALENCE OF LARMOR'S THEOREM OF NMR IN NQR SPECTROSCOPY

In the quadrupole case, the precessional frequencies are different in different orientations whereas in magnetic case the frequency is independent of orientations. If nuclear spin axis is 'set' at one or more fixed orientations defined by I_z , the component of nuclear angular momentum along Z-axis, then at one of these positions, there will be one precessional frequency. This precession of the nucleus carries with it nuclear magnetic moment, thereby producing a small magnetic field at right angles to Z-axis rotating in phase with nuclear quadrupole at the same frequency.

Now a linearly oscillating field

$$H = 2 H_1 \cos \omega t \quad (8.66)$$

can be resolved into two rotating, i.e. clockwise (cW) and counter clockwise (ccW) fields.

$$\left. \begin{aligned} H(\text{cW}) &= H_1 \cos \omega t + i H_1 \sin \omega t \\ H(\text{ccW}) &= H_1 \cos \omega t - i H_1 \sin \omega t \end{aligned} \right\} \quad (8.67)$$

where, $H = H(\text{cW}) + H(\text{ccW})$.

Such a field is obtained by enclosing the sample in a small induction coil through which an alternating current is passed. The component of Eq. (8.67), which rotates in phase with the precessing nucleus exchange energy with it, resulting into resonance process occurring at a specific quadrupole frequency ν .

8.11 NQR SPECTROMETER

M_I degeneracy in NMR is lifted by external magnetic field whereas in pure NQR, it is removed by EFGs which are due to the electrons in the molecules. Since the transitions between the energy states in NQR are fixed by the electronic structure of the molecules, they are studied by the radio frequency (R_f) sweep method rather than the field sweep method. The frequency range that can be studied by NQR is a few MHz to 1000 MHz.

The NQR spectrum which is a plot between intensity (on the vertical axis) and frequency (on the horizontal axis) is obtained by a device called NQR spectrometer. A block diagram of an NQR spectrometer is shown in Fig. 8.10. The five basic elements of the spectrometer are (i) radio frequency (R_f) oscillator, (ii) bridge circuit, (iii) amplifier, and (iv) oscillator detector which is usually a single-tube arrangement employing frequency modulation. Conventional phase-sensitive detector arrangement is used for weak outputs and (v) recorder. The sample is placed in the induction coil of the bridge circuit. For better results, the coil is surrounded by the sample.

Power from the R_f oscillator is supplied to a pre-balanced bridge circuit where it is resonantly absorbed by the sample causing an unbalance in the circuit also. The resulting output is amplified, fed to the detector and then recorded.

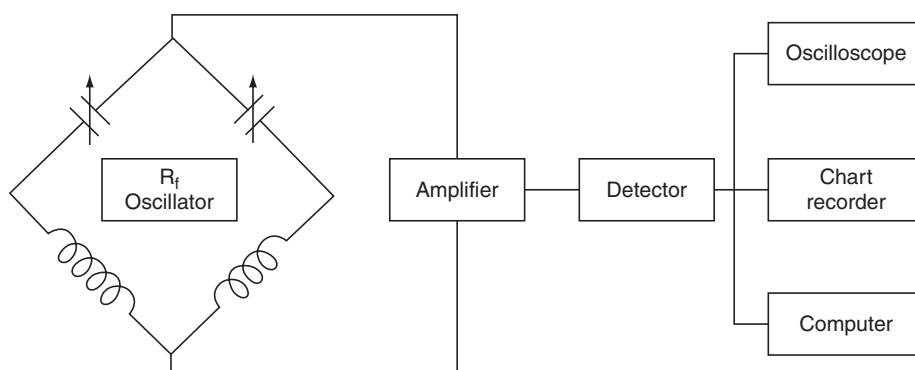


Fig. 8.10 Schematic diagram of NQR spectrometer.

Radio-frequency pulse techniques (spin-echo) are used in limited cases. The frequency shifts under the influence of external applied electric field (10 kV/cm) are also studied. This type of electric field effect may be of use in the study of noncentrosymmetric crystals by NQR. Measurements have been made on single crystals of sodium chlorate and on *p*-dichlorobenzene to verify the Stark effect in pure nuclear quadrupole resonance.

Only solids can be studied and samples may be in the form of crystals or crystalline powder but not amorphous powder. Gases and liquids cannot be studied by NQR method since at normal pressure, due to molecular collisions the axis of rotation changes continuously because of which the net EFGs at the nucleus averages to zero. This factor limits the applications of NQR compared to NMR. e^2qQ of gases is obtained from the fine structure of rotational spectrum arising from the interaction of EFGs with rotational motion of the molecules and has already been reported in Chapter 2.

Moderately large samples are required in NQR studies, e.g. a 50 mg sample of *p*-dichlorobenzene produces observable ^{35}Cl resonances and several grams of hexamethylene tetra-amine are needed to produce observable ^{14}N -resonances. Moreover, the liquid samples need to be cooled to 77 K in order to obtain a crystalline solid. The sample should be pure otherwise the impurities present in it will broaden the spectrum. The broadening may be due to charge as well as size of the impurities. The extra charge due to impurities generates additional EFGs at the nucleus. Since the foreign nuclei are asymmetrically distributed around the sample nuclei, the EFGs contribution due to foreign nuclei to different sample nuclei will vary, and consequently the asymmetric distribution of EFGs due to foreign nuclei over the sample nuclei will cause spectrum broadening. The size effect due to foreign nuclei will become appreciable provided the size of the foreign nuclei is comparable to that of the parent nuclei. The foreign nuclei will distort the electron cloud of the parent nuclei and consequently, the EFGs at the parent nuclei. It is to be noted that broadening not only depends on the charge and size of the impurity nuclei but also on the composition of the impurity since intermolecular interactions between foreign nuclei and neighbouring molecules depend on the quadrupole moments of nuclei in both the molecules, i.e. sample and impurity.

8.12 EFFECTS OF VARIOUS FACTORS ON NUCLEAR QUADRUPOLE RESONANCE FREQUENCY

The main parameters which affect the NQR resonance frequencies are temperature, pressure, internal rotation, substituents in the molecule, etc.

8.12.1 Effect of Temperature and Pressure

Frequency variation with temperature and pressure is interpreted on the basis of lattice and torsional oscillations and due to restricted rotation around C–C bond in some chloroethanes is interpreted in terms of torsional oscillations.

8.12.2 Conjugative Effects

The electron releasing and attracting groups in substituted halobenzenes affect the nuclear quadrupole coupling constants. The electron-releasing groups have negative Hammett- σ values and give rise to smaller ν_Q values. This may be attributed to increase of ionic character in the C–X (X=Cl, Br, I) bond which makes the X-atom more negatively charged.

In case of substituted halobenzenes, linear relationships exist between σ -constant and nuclear quadrupole resonance frequencies, i.e.

$$\nu(^{35}\text{Cl}) = 34.826 (1 + 0.0287 \sigma) \text{ MHz} \quad (8.68)$$

$$\nu(^{81}\text{Br}) = 226.932 (1 + 0.0336 \sigma) \pm 2.98 \text{ MHz} \quad (8.69)$$

$$\nu(^{127}\text{I}) = (267.0 + 1.424 \sigma) \text{ MHz} \quad (8.70)$$

Here, $\nu(^{127}\text{I})$ corresponds to the $M_I = \pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$ transitions only.

For multichlorobenzenes, the resonance frequency of a particular chlorine atom is well represented by an equation of the form

$$\nu(^{35}\text{Cl}) = \nu (= 34.622 \text{ MHz; chlorobenzene}) + \alpha \Delta\nu_{\text{ortho}} + \beta \Delta\nu_{\text{meta}} + \gamma \Delta\nu_{\text{para}} \quad (8.71)$$

where, $\Delta\nu_{\text{ortho}} = 1.30 \text{ MHz}$, $\Delta\nu_{\text{meta}} = 0.45 \text{ MHz}$, $\Delta\nu_{\text{para}} = 0.25 \text{ MHz}$ and α , β and γ are the numbers of chloro atoms ortho, meta and para respectively to the chlorine atom whose frequency is being calculated.

The theoretical ratios of $\Delta\nu$ s obtained from simple electrostatics combined with the known geometries of the chlorobenzenes are

$$\Delta\nu_{\text{ortho}} : \Delta\nu_{\text{meta}} : \Delta\nu_{\text{para}} :: 1 : 0.27 : 0.20$$

The experimental ratios are 1 : 0.35 : 0.19.

It is to be noted that for chloro and bromo benzenes, η is not much different from 0.1, so $\nu_Q = 2\nu$.

Problem 8.9: Calculate ^{35}Cl -pure quadrupole resonance frequencies of (a) m-dichlorobenzene, (b) p-dichlorobenzene, (c) o-dichlorobenzene, (d) 1, 2, 3-trichlorobenzene, and (e) 1, 2, 3, 4-tetrachloro benzene.

Solution From Eq. (8.71), we obtain

- (a) $\nu(^{35}\text{Cl}) = 34.622 + 0.45$
 $= 35.072 \text{ MHz}$ (observed (average) = 34.904 MHz; 34.809, 34.875, 35.030 MHz)
- (b) $\nu(^{35}\text{Cl}) = 34.622 + 0.25 = 34.875$ (observed (average) = 34.799 MHz)
- (c) $\nu(^{35}\text{Cl}) = 34.622 + 1.30 = 35.922$ (observed (average) = 35.719 MHz; 35.580, 35.755, 35.824 MHz)
- (d) $\nu(^{35}\text{Cl}) = 34.622 + 1.30 + 0.45 = 36.372 \text{ MHz}$ (observed (average) = 36.547 MHz; 36.214, 36.238, 36.268, 36.563, 36.973, 37.031 MHz).
- (e) $\nu(^{35}\text{Cl}) = 34.622 + 1.30 + 0.45 + 0.25$
 $= 36.622 \text{ MHz}$ (observed (average) = 37.34 MHz; 37.013, 37.455, 37.557 MHz).

Problem 8.10: (i) Predict the numbers of chloro atoms ortho, meta and para respectively to the chlorine atom whose frequency is being measured experimentally for the following chlorobenzenes (provided $\nu_{1,2,3,4} > \nu_{1,2,3,5} > \nu_{1,2,4,5}$)

(ii) Assign also the names to the tetrachlorobenzenes.

Chlorobenzene	$^{35}\text{Cl-NQR}$ frequencies (MHz)
Tetrachlorobenzene (a)	37.013, 37.455, 37.557
Tetrachlorobenzene (b)	36.185, 36.386, 36.816, 36.872, 37.020, 37.289, 37.483, 37.657
Tetrachlorobenzene (c)	36.702, 36.738, 36.843, 36.898

Solution The average values of frequencies for (a), (b) and (c) are 37.3416, 36.9635 and 36.7952 respectively. Thus

- (i) For tetrachlorobenzene (a), the average value of $\nu(^{35}\text{Cl})$ is 37.3416 MHz.

From Eq. (8.71), $37.3416 = 34.622 + 1.30 \alpha + 0.45 \beta + 0.25 \gamma$

Choose different numbers for α , β and γ so that the above expression is mathematically balanced.

The best fit is obtained for $\alpha = 1$, $\beta = 1$ and $\gamma = 1$, i.e. the right-hand side becomes equal to 36.622 MHz.

- (ii) The name of the tetrachlorobenzene (a) will be 1, 2, 3, 4-tetrachlorobenzene.

- (i) For tetrachlorobenzene (b), the average value of observed $\nu(^{35}\text{Cl})$ is 36.9635 MHz.

From Eq. (8.71), we write $36.9635 = 34.622 + 1.30 \alpha + 0.45 \beta + 0.25 \gamma$

The best fit is obtained for $\alpha = 1$, $\beta = 2$ and $\gamma = 0$, i.e. the right-hand side of the above expression becomes equal to 36.822 MHz.

- (ii) The tetrachlorobenzene (b) is 1, 2, 3, 5-tetrachlorobenzene.

- (i) For tetrachlorobenzene (c), the average value of observed $\nu(^{35}\text{Cl})$ equals 36.7952 MHz. From Eq. (8.71), we write

$$36.7952 = 34.622 + 1.30 \alpha + 0.45 \beta + 0.25 \gamma$$

The best fit is obtained for $\alpha = 1$, $\beta = 1$ and $\gamma = 1$, i.e. the right-hand side of the above expression becomes equal to 36.62 MHz.

- (ii) The tetrachlorobenzene is 1, 2, 4, 5-tetrachlorobenzene.

8.12.3 Inductive Effects

The coupling constants of the substituted chloroalkanes, i.e. series RCH_2Cl is a measure of the inductive effect of the substituent R, since the presence of the methylene ($-\text{CH}_2$) group prevents conjugation with the chlorine atom. The linear relationship between the Taft's σ^* parameter and the NQR frequency of the ^{35}Cl atom under measurement is given by

$$\nu(^{35}\text{Cl}) = 32.70 + 1.715 |\sigma^*| \quad (\text{MHz}) \quad (8.72)$$

where 32.70 MHz is the ^{35}Cl – NQR frequency of $\text{CH}_3\text{CH}_2\text{Cl}$. σ^* values of some typical groups are given in Table 8.2.

Table 8.2 σ^* values of some typical groups.

R	σ^*
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	-0.130
$\text{CH}_3\text{CH}_2\text{CH}_2-$	-0.115
CH_3CH_2-	-0.110
CH_3-	0.0
$\text{CH}_3\text{CH}=\text{CH}-$	0.36
$\text{ClCH}_2\text{CH}_2-$	0.385
$\text{CH}_2=\text{CH}-$	0.41
$\text{H}-$	0.49
CH_3OCH_2-	0.52
C_6H_5-	0.60
$\text{C}_6\text{H}_5\text{OCH}_2-$	0.85
HO CO CH_2-	1.05
ClCH_2-	1.05
$\text{CH}_3\text{CO}-$	1.65
$\text{HN}^+(\text{CH}_3)_2\text{CH}_2-$	1.90
$\text{CH}_3\text{OCO}-$	2.00
CF_3-	3.1

^{35}Cl -NQR frequency of a substituted methylchloride $R_1R_2R_3\text{CCl}$ is related to Taft σ^* parameter of the substituents by the expression.

$$\nu(^{35}\text{Cl}) = 32.05 \left(1 + 0.0317 \sum_i \sigma_i^* \right) \pm 0.35 \text{ MHz} \quad (8.73)$$

Problem 8.11: Calculate the ^{35}Cl -NQR frequency of (i) $\text{CF}_3\text{CH}_2\text{Cl}$ (ii) $\text{CH}_3\text{COCH}_2\text{Cl}$ (iii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$

Solution We know that

$$\nu(^{35}\text{Cl}) = 32.70 + 1.715 |\sigma^*| \text{ MHz} \quad (\text{Eq. 8.72})$$

Thus, for

(i) $\text{CF}_3\text{CH}_2\text{Cl}$

$$\begin{aligned} \nu(^{35}\text{Cl}) &= 32.70 + 1.715 \times 3.1 = 32.70 + 5.316 \\ &= 38.016 \text{ MHz} \quad (\text{obs: } 37.98 \text{ MHz, the average of two transitions}) \end{aligned}$$

(ii) $\text{CH}_3\text{COCH}_2\text{Cl}$

$$\begin{aligned} \nu(^{35}\text{Cl}) &= 32.70 + 1.715 \times 1.65 = 32.70 + 2.829 \\ &= 35.529 \text{ MHz} \quad (\text{obs: } 35.28 \text{ MHz, the average of two transitions}) \end{aligned}$$

(iii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$

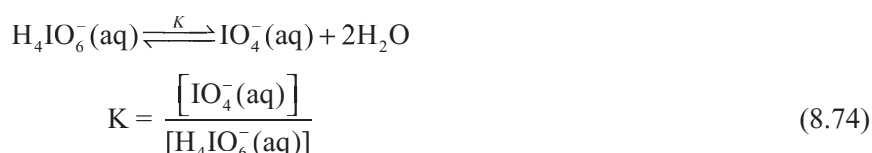
$$\begin{aligned} \nu(^{35}\text{Cl}) &= 32.70 + 1.715 \times 0.110 = 32.70 + 0.188 \\ &= 32.888 \text{ MHz} \quad (\text{Obs: } 32.968 \text{ MHz}). \end{aligned}$$

8.13 APPLICATIONS OF NQR SPECTROSCOPY

As already pointed out that when quadrupole interaction is small relative to Zeeman energy, the NQR is studied by NMR spectroscopy whereas in the reverse case, the splitting of energy levels is due to EFGs only. In such a case, the NQR is studied by pure NQR techniques. The applications of NQR in the former case are based mainly on the intensity and width of NMR lines whereas in the latter case are based mainly on three NQR parameters, viz., quadrupole splitting, EFG's and quadrupole coupling constant. Applications are being described here under two subtitles, namely NQR through NMR and pure NQR.

8.13.1 Applications of NQR through NMR

(a) Study of Chemical Equilibria The intensity of ^{127}I NMR signal can be used to study to equilibrium

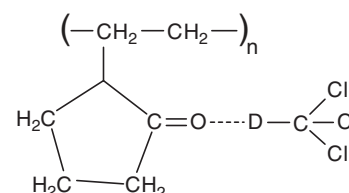


Thus, K can be obtained from Eq. (8.74) provided concentrations of the products and reactants are known.

The exchange between two iodine sites in the system is assumed to be slow. The signal of ^{127}I corresponding to $\text{H}_4\text{IO}_6^-(\text{aq})$ in the NMR spectrum is too broad to be detected. The signal of ^{127}I of $\text{IO}_4^-(\text{aq})$ gives directly the concentration of IO_4^- . Thus, the values of K can be obtained from Eq. (8.74).

(b) Study of Contact Ion-Pairs Formation in Non-aqueous Media The rapid increase in the ^{35}Cl relaxation rate (i.e. line width) with the increase in the concentration of electrolyte in an organic solvent is attributed to the formation of contact ion pairs, e.g. LiClO_4 in methanol, propanol, butanol, acetonitrile, nitro methane, ethyl acetate, etc.; $\text{Mg}(\text{ClO}_4)_2$ and NaClO_4 in propanol, butanol and ethyl acetate.

(c) Study of Interaction of ^{35}Cl Nuclei with the Electron Spins The addition of Mn^{2+} to an aqueous solution of ClO_4^- causes an increase of ^{35}Cl relaxation rate (i.e. line broadening). The decrease of ^{35}Cl line broadening in the presence of Mn^{2+} with the rise in temperature suggests that the relaxation results from the interaction of ^{35}Cl nuclei with the electron spins. This interpretation finds support from the ratio of the ^{35}Cl and ^{37}Cl relaxation rates which is found to be 1.35.



(d) Study of Molecular Interactions The NQR relaxation tool is most suited to study the molecular interaction of a small molecule with a macromolecule provided there is a marked difference between correlation times of the free and bound states of the small molecule, e.g. binding of CDCl_3 to polyvinylpyrrolidone. ^{35}Cl relaxation rate is less affected relative to ^1H relaxation rate on binding of CDCl_3 to the polymer. This suggests that chloroform reorientation is slowed down around the symmetry axis than around the perpendicular axis due to hydrogen bonding as shown below:

(e) Kinetics of Quadrupole Nuclei Chemical Exchange Process Recall from Chapter 7 on NMR that if magnetic nuclei reside in two chemically different environments say A and B , they will show two distinct NMR signals provided no exchange of nuclei occurs between the two sites. However, after the onset of exchange process, the signals will begin to broaden and at high exchange rates will merge together into a one narrow signal. If P_A and P_B are the mole fractions of nuclei at sites A and B respectively then $P_A + P_B = 1$. If $P_A \gg P_B$, then we can write $P_A \approx 1$. In the halide ion-exchange process, environment A corresponds to 'free' halide ions in solution and environment B corresponds to a halide ion coordinated to metal ion. Let us now consider the following exchange system.



where, M stands for metal.

In the absence of chemical exchange, the transverse relaxation rates $\frac{1}{T_{2A}}$ and $\frac{1}{T_{2B}}$ in the two environments will be different for quadrupole nuclei and $\frac{1}{T_{2B}} \gg \frac{1}{T_{2A}}$.

Under these conditions, the signal near or at A with frequency ν_A will be observable whereas the signal at B with frequency ν_B will be too broad to be easily observed. The NMR spectrum in the absence and after onset of exchange process, have been illustrated in Fig. 8.11. The line width of the major signal may be expressed as

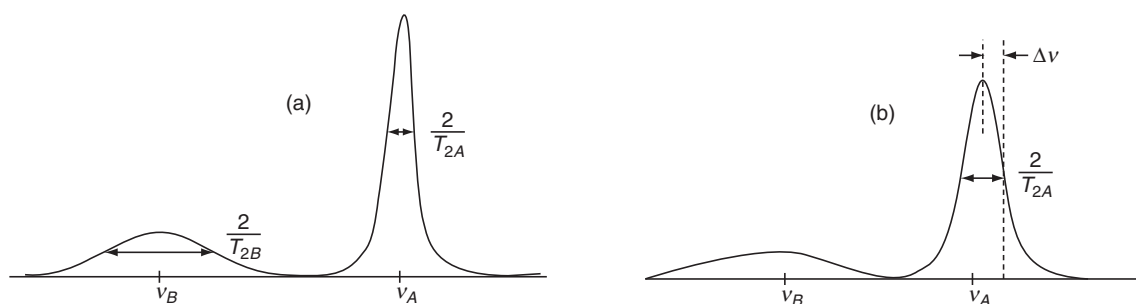


Fig. 8.11 Schematic NMR spectrum of nucleus which resides at two chemically different environments A and B with frequencies ν_A and ν_B respectively (a) in the absence of exchange, and (b) after onset of exchange process.

$$\frac{1}{T_2} = \frac{1}{T_{2A}} + \frac{\frac{P_B}{\tau_B} \left[\frac{1}{T_{2B}} \left(\frac{1}{T_{2B}} + \frac{1}{\tau_B} \right) + 4\pi^2 (\Delta\nu_{AB})^2 \right]}{\left(\frac{1}{T_{2B}} + \frac{1}{\tau_B} \right)^2 + 4\pi^2 (\Delta\nu_{AB})^2} \quad (8.76)$$

where, $\frac{1}{\tau_B}$ is the rate of chemical exchange of nuclei from environment B , and $\Delta\nu_{AB} = \nu_A - \nu_B$. The position of the observed signal near ν_A will be shifted from its original position by an amount $\Delta\nu$ and the following expression holds good:

$$\Delta\nu = \frac{2\pi\Delta\nu_{AB} \times \frac{1}{\tau_A} \times \frac{1}{\tau_B}}{\left[\frac{1}{T_{2B}} + \frac{1}{\tau_B} \right]^2 + 4\pi^2 (\Delta\nu_{AB})^2} \quad (8.77)$$

Here, $\frac{1}{\tau_A}$ is the chemical exchange rate of nuclei from environment A .

In the steady state,

$$\frac{\tau_A}{\tau_B} = \frac{P_A}{P_B} = \frac{1}{P_B}, \text{ so Eq. (8.77) may be written as}$$

$$\Delta\nu = \frac{2\pi \Delta\nu_{AB} \left(\frac{1}{\tau_B} \right)^2 P_B}{\left[\frac{1}{T_{2B}} + \frac{1}{\tau_B} \right]^2 + 4\pi^2 (\Delta\nu_{AB})^2} \quad (8.78)$$

According to Eqs (8.77) and (8.78), the appearance of a spectrum depends on the values of $\frac{1}{\tau_B}$, $\frac{1}{T_{2B}}$, P_B and $\Delta\nu_{AB}$. Parameter P_B is considered to be only a multiplicative constant and can be altered by changing the composition of the solution. All the four parameters depend on temperature but the most temperature-dependent parameter is the rate of chemical exchange, $\frac{1}{\tau_B}$. Thus, if the temperature dependence of the other three parameters is ignored then the influence of the exchange rate on the observed NMR spectrum can be conveniently discussed in terms of two dimensionless parameters defined as

$$\xi = \frac{\left(\frac{1}{\tau_B} \right)}{\left(\frac{1}{T_{2B}} \right)} = \frac{T_{2B}}{\tau_B} \quad (8.79)$$

and

$$\eta = \frac{2\pi \Delta\nu_{AB}}{\left(\frac{1}{T_{2B}} \right)} \quad (8.80)$$

Thus, Eq. (8.77) may be rewritten as

$$\Delta\left(\frac{1}{T_2} \right) = \frac{1}{T_2} - \frac{1}{T_{2A}} = \frac{P_B}{T_{2B}} \left[\frac{\xi(1 + \xi + \eta^2)}{(1 + \xi)^2 + \eta^2} \right] \quad (8.81)$$

where, $\Delta\left(\frac{1}{T_2} \right)$ is the excess relaxation rate of the observed signal. The excess line broadening, $\Delta\nu_e$, of a signal is then defined as

$$\Delta\nu_e = \frac{1}{\pi} \left[\Delta\left(\frac{1}{T_2} \right) \right] \quad (8.82)$$

Similarly, Eq. (8.77) in terms of dimensionless parameters ξ and η will appear as

$$\frac{\Delta\nu}{\Delta\nu_{AB}} = P_B \left[\frac{\xi^2}{(1 + \xi)^2 + \eta^2} \right] \quad (8.83)$$

Let us now discuss the effect of temperature of the system on $\Delta\left(\frac{1}{T_2} \right)$ and $\Delta\nu$ in terms of ξ which is a measure of exchange rate relative to the relaxation rate.

(i) When $\xi \ll 1$, the exchange rate will be very slow relative to the relaxation rate in site B . Therefore, in this region, Eq. (8.81) may be written as

$$\Delta\left(\frac{1}{T_2} \right) = \frac{\xi P_B}{T_{2B}} = \frac{P_B}{\tau_B} \quad (8.84)$$

Accordingly, the excess line broadening is very small and is independent of η . It will increase linearly with the chemical exchange rate. The relative chemical shift displacement, $\frac{\Delta\nu}{\Delta\nu_{AB}}$ in this region will be small.

For $\eta^2 \ll 1$, Eq. (8.83) reduces to

$$\frac{\Delta\nu}{\Delta\nu_{AB}} = \frac{P_B \xi^2}{(1 + \xi)^2} \quad (8.85)$$

i.e.

$$\frac{\Delta\nu}{\Delta\nu_{AB}} \propto P_B \xi^2$$

For larger values of η ,

$$\frac{\Delta\nu}{\Delta\nu_{AB}} < \frac{P_B \xi^2}{(1 + \xi)^2} \quad (8.86)$$

(ii) When $\xi = 1$, the exchange rate will be comparable in magnitude to the relaxation rate at the site B . Therefore, in this region, Eq. (8.81) may be written as

$$\Delta\left(\frac{1}{T_2}\right) = \frac{P_B}{T_{2B}} \left[\frac{\eta^2 + 2}{\eta^2 + 4} \right] \quad (8.87)$$

i.e. the observed excess line broadening in this region depends on η . Further, if (a) $\eta \ll 1$, we obtain

$$\Delta\left(\frac{1}{T_2}\right) = \frac{P_B}{T_{2B}} \left[\frac{\xi}{1 + \xi} \right] \quad (8.88)$$

or

$$\Delta\left(\frac{1}{T_2}\right) = \frac{P_B}{\tau_B + T_{2B}} \quad (8.89)$$

i.e. the excess relaxation rate becomes appreciable and its value is about half its limiting value (P_B/T_{2B}) at a very rapid chemical exchange ($\xi \gg 1$).

The corresponding relative chemical shift change $\frac{\Delta\nu}{\Delta\nu_{AB}}$ in this case is expressed as

$$\frac{\Delta\nu}{\Delta\nu_{AB}} = P_B \left[\frac{\xi^2}{(1 + \xi)^2} \right] \quad (8.90)$$

From this it can easily be shown that

$$\frac{\Delta\nu}{\Delta\nu_{AB}} = 0.25 P_B, \text{ i.e. it has reached about 25 per cent of its maximum value } (= P_B).$$

(b) For $\eta \gg 1$, we obtain

$$\Delta\left(\frac{1}{T_2}\right) = \frac{P_B \xi}{T_{2B}} \quad (8.91)$$

i.e. in this subcase, the excess relaxation rate or width is independent of η . The broadening may exceed the limiting excess relaxation rate at very rapid chemical exchange.

The relative chemical shift change $\frac{\Delta\nu}{\Delta\nu_{AB}}$, in this subcase will be given by

$$\frac{\Delta\nu}{\Delta\nu_{AB}} = P_B \left[\frac{\xi^2}{\eta^2} \right] \quad (8.92)$$

i.e. the relative chemical shift change in this subcase will be very small.

(c) For $\xi \simeq 1$ and $\eta \simeq 1$, the expressions (8.81) and (8.83) reduce to

$$\Delta\left(\frac{1}{T_2}\right) = \frac{3}{5} \frac{P_B}{T_{2B}} \quad (8.93)$$

and

$$\frac{\Delta\nu}{\Delta\nu_{AB}} = \frac{1}{5} P_B \quad (8.94)$$

In this subcase, both the excess relaxation rate and the relative chemical shift change will depend on η .

The excess relaxation rate is about 60 per cent of its maximum value $= \frac{P_B}{T_{2B}}$ whereas, the relative chemical shift change has reached 20 per cent of its maximum value ($= P_B$). Studies of NMR spectra at different frequencies may show frequency-dependent line broadenings and shift changes.

(iii) When $\xi \gg 1$, the chemical exchange rate at the site B will be very fast relative to the relaxation rate in this site. Assuming $\xi \gg \eta^2$, Eqs (8.81) and (8.83) reduce to

$$\Delta \left(\frac{1}{T_2} \right) = \frac{P_B}{T_{2B}} \quad (8.95)$$

and

$$\frac{\Delta \nu}{\Delta \nu_{AB}} = P_B \quad (8.96)$$

Thus, the maximum observable values of excess relaxation rate and relative shift change are $\frac{P_B}{T_{2B}}$ and P_B respectively. The signal now simply occurs at a weighted mean of the frequencies in environments A and B .

Further, when $\eta \approx \xi$ (i.e. $\Delta \nu_{AB} = \frac{1}{2\pi\tau_B}$), we obtain

$$\Delta \left(\frac{1}{T_2} \right) = \frac{P_B \xi}{T_{2B}} \left[\frac{1 + \xi(\xi + 1)}{1 + 2\xi(\xi + 1)} \right] \quad (8.97)$$

and

$$\left(\frac{\Delta \nu}{\Delta \nu_{AB}} \right) = P_B \left[\frac{\xi^2}{(1 + \xi)^2 + \xi^2} \right] \quad (8.98)$$

The excess relaxation rate as well as the relative chemical shift change will now depend on η but will never exceed their respective limiting values, i.e. $\frac{P_B}{T_{2B}}$ and P_B . The above results are summarised in the form of plots of $\Delta \left(\frac{1}{T_2} \right) \frac{T_{2B}}{P_B}$ and $\left[\frac{\Delta \nu}{P_B \Delta \nu_{AB}} \right]$ as a function of $\log \xi$ for different values of η (Figs 8.11 and 8.12). It is to be noted that the effect of chemical exchange rate on excess line width is small when η lies between 0 and 1 (Fig. 8.11), whereas the effect on relative chemical shift displacement is independent of η (Fig. 8.12).

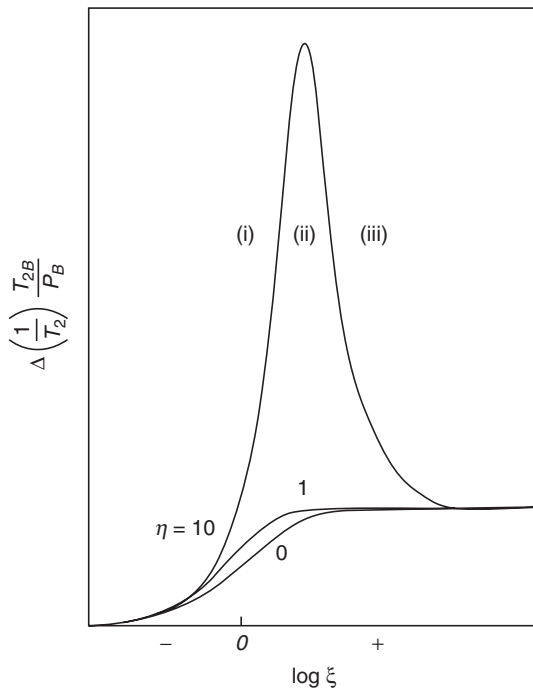


Fig 8.12 The behaviour of excess relaxation rate $\Delta \left(\frac{1}{T_2} \right)$ of the dominant NMR signal with the dimensionless exchange parameter ξ in a chemical exchange process for different values of η .

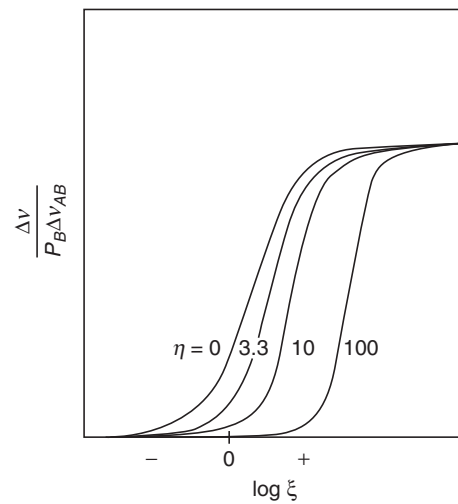


Fig 8.13 The behaviour of relative chemical shift displacement $\frac{\Delta \nu}{\Delta \nu_{AB}}$ of the dominant NMR signal with ξ in chemical exchange process for different values of η .

(f) Effects of Different Isotopes on Relaxation Rate In the limit of fast exchange, the relaxation rates of different isotopes in diamagnetic halogen compounds are proportional to the square of the respective nuclear quadrupole moments provided the effects of isotopes on EFGs' are ignored.

Thus, for chlorine isotopes

$$\begin{aligned} & {}^{35}\text{Cl}\left(\frac{1}{T_i}\right) / {}^{37}\text{Cl}\left(\frac{1}{T_i}\right) \\ &= [Q(^{35}\text{Cl}) / Q(^{37}\text{Cl})]^2 = 1.610 \end{aligned} \quad (8.99)$$

and for bromine isotopes

$$\begin{aligned} & {}^{79}\text{Br}\left(\frac{1}{T_i}\right) / {}^{81}\text{Br}\left(\frac{1}{T_i}\right) = [Q(^{79}\text{Br}) / Q(^{81}\text{Br})]^2 \\ &= 1.433 \end{aligned} \quad (8.100)$$

where, $i = 1$ or 2 .

The experimentally observable line widths for the two isotopes may be calculated from Eq. (8.101) as

$$\frac{\frac{1}{T_{2B(I)}}}{\frac{1}{T_{2B(II)}}} = k(k > 1) \quad (8.101)$$

where, I and II stand for two isotopes and $k = 1.61$ for chlorine and $k = 1.433$ for bromine.

The ratio of the observed excess line broadening when $\eta \ll 1$ is obtained from Eq. (8.81) and is given by

$$\frac{\Delta\left(\frac{1}{T_{2(I)}}\right)}{\Delta\left(\frac{1}{T_{2(II)}}\right)} = \frac{1 + k\xi(I)}{1 + \xi(I)} \quad (8.102)$$

where, the dimensionless parameter $\xi(I)$ refers to the relaxation rate, $\frac{1}{T_{2B(I)}}$.

For $\eta \gg 1$, the above ratio equals unity and for $\eta \approx 1$, the ratio becomes a function of η .

In general, we can state that for fast exchange rates, the isotope ratio of relaxation rates equals 1.610 for chlorine and 1.433 for bromine. For slow exchange rates, this ratio becomes equal to unity.

Further, since the nuclear quadrupole moments and hence the relaxation rates in the halide complexes increase in the order $\text{I} > \text{Br} > \text{Cl}$, the fastest exchange reactions which can be studied are iodine-exchange reactions.

The typical chemical exchange systems in which quadrupole relaxation is measured as a function of concentration and temperature by NMR technique in relation to chemical kinetics are halide ion exchange in metal halide complexes, e.g. exchange rate of Br^- and I^- in the complexes with Hg^{2+} and halide-ion exchange in systems involving halogen molecules, e.g. iodide-triiodide exchange.

(g) Biological Applications NQR spectroscopy has also entered the homeland of biological sciences. The biological applications of quadrupole nuclei-NMR roughly deals with studies of halide ion binding to metal free and metal containing proteins or to other molecules and proteins where an artificial metal label is attached. The parameters that may be obtained from halide probe techniques are stoichiometry and binding constants of halide ions, stoichiometry of metal reactive groups on a protein, rotational correlation times (s) of the macromolecule, quadrupole coupling constant (s) of halide ion (s) in different molecular binding sites, binding constants rates and activation parameters of halide ion exchange, and stoichiometry of other ions or molecules through competition experiments. However, before describing the applications, the definition and the role of proteins in biological systems demands a little attention.

Proteins, the keystones of life, are the most complex substances known to man. Thousands of different proteins which are composed of thousands of amino acids go into the make up of a living cell. They perform thousands of different acts in the exact sequence that causes the cell to live.

Many amino acids are linked together side by side to form a long protein chain. This linear chain then folds in a globular fashion.

The linkage between amino acids in a protein chain is cleavable, therefore, protein can be dis-assembled in its building blocks. The assembly of amino acids for the genesis of proteins and dis-assembly of proteins into amino acids as shown in Fig. 8.14, and are among the most crucial processes during the cell cycle. Therefore, any foreign material may cause disturbances in the cell cycle which ultimately leads to abnormal functioning of the cell in the biological systems.

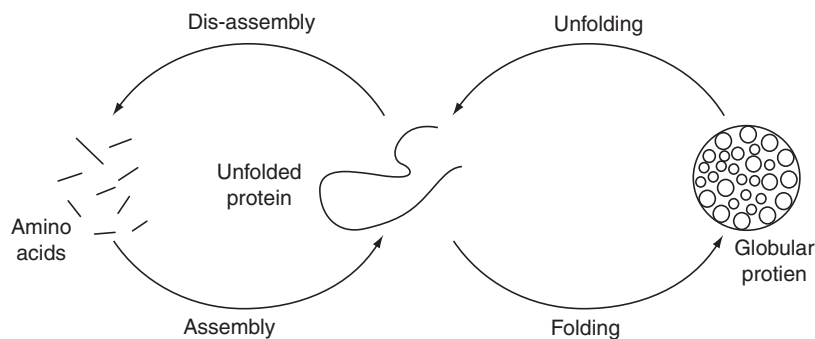


Fig. 8.14 Genesis and dis-assembly of proteins.

Combined magnetic field and NQR effects where NQR nearly acts as a perturbation is a useful tool to study small NQR nuclei binding to native metal-containing or metal-free proteins or other molecules and to proteins or other molecules where an artificial metal label is attached. This has been demonstrated with the help of halide ion probe method in which the relaxation of NQR nucleus in the biological system occurs either via chemical exchange process or correlation times, NQR relaxation times.

When the exchange rate of halide ions between a macromolecule binding site and the bulk exceeds the NMR relaxation rate in the binding site, then τ_s , the correlation time at the site, say 's', is neglected. The exchange rates $\frac{1}{\tau_s}$ increase usually rapidly with the increase in temperature. This suggests a low free energy of activation for the exchange process at room temperature. The fraction of ions bound in different sites, P_s , could increase as well as decrease with temperature. The latter is more probable since the binding of small ions to macromolecules at least to proteins is accompanied by an enthalpy decrease. However, at elevated temperatures, a conformational change of macromolecule may occur resulting in new binding sites being accessible for binding. If the latter possibility is ignored then the halide ion NMR line width decreases with temperature for fast-exchange conditions whereas increases with temperature for slow exchange conditions.

The exchange processes are usually studied using either $\frac{1}{T_1(s)}$ or $\frac{1}{T_2(s)}$ or in reality usually the halide signal line width as a function of temperature. $\frac{1}{T_1(A)}$ and $\frac{1}{T_2(A)}$ become smaller with increasing temperature, the same tendency is usually assumed also for $\frac{1}{T_1(s)}$ and $\frac{1}{T_2(s)}$.

Isotope effects on excess relaxation rates can also be fixed a criterion for the halide ion exchange rates in biological systems.

For fast exchange processes,

$$^{33}\text{Cl}\left(\frac{1}{T_i}\right) / ^{37}\text{Cl}\left(\frac{1}{T_i}\right) = \left[Q(^{35}\text{Cl}) / Q(^{37}\text{Cl}) \right]^2 \quad (\text{Eq. 8.99})$$

$$\text{and} \quad = 1.610 \quad (\text{Eq. 8.100})$$

$$^{79}\text{Br}\left(\frac{1}{T_i}\right) / ^{81}\text{Br}\left(\frac{1}{T_i}\right) = \left[Q(^{79}\text{Br}) / Q(^{81}\text{Br}) \right]^2$$

$$= 1.433$$

where, $i = 1 \text{ or } 2$.

For slow exchange processes, the isotope ratio of excess relaxation rates is equal to unity.

The parameter 'molar relaxivity', i.e. $\bar{\nu}_i (\text{Hz mole}^{-1})$ is defined as

$$\Delta \nu_e = \sum_i \bar{\nu}_i [(M - L)_i] \quad (8.103)$$

for fast exchange processes, may be fixed a criterion for the halide ions interaction with metal binding sites on macromolecule and also to fix the geometry of complexes so formed. Here, $\Delta \nu_e$ is the excess line width of ^{35}Cl

signal. $(M - L)_i$ stands for a particular complex between M^{2+} and a ligand L . $\bar{\nu}_i$ is proportional to the product of correlation time (τ_c), square of quadrupole constant, $(e^2qQ/h)^2$ and fraction of halide ions bound to a particular M complex (i).

The importance of molar relaxivities to gain understanding of the interaction of halide ions with metal binding sites on macromolecules can be realised from the following example. The molar relaxivities of the Cl^- ion interactions with Zn complexes having different bi- tri- and quadridentate ligands as obtained from ^{35}Cl line width at different pH in 0.5 NaCl, containing Zn^{2+} and a ligand in appropriate proportions are given in Table 8.3.

Table 8.3 ^{35}Cl -molar relaxivities ($\bar{\nu}_i$ in kHz) for Zn-complexes with different bi- tri- and quadridentate ligands.

Ligand	$\bar{\nu}$ (ZnL)	$\bar{\nu}$ (ZnL ₂)	$\bar{\nu}$ (ZnHL)
Bidentate			
Cysteine	19.06	0	20.35
Glycine	1.72	0.69	—
Glutamic acid	2.65	3.82	3.82
Tridentate			
Aspartic acid	0.54	0	4.26
Iminodiacetic acid	1.64	0	—
Citric acid	0.63	—	1.15
Quadridentate			
Nitrilotriacetic acid	2.21	—	—

For $Zn^{2+}(aq)$: $\bar{\nu}_i = 2.0 \text{ kHz mole}^{-1}$, ZnL, ZnL₂, Zn (HL) are the concentrations of the different liganded species. HL denotes a protonated ligand.

The following inferences can be drawn from the data in Table 8.3. (i) Except glycine, $\bar{\nu}_i$ values for 1:1 bidentate ligand complexes are higher than that of $Zn^{2+}(aq)$. This suggests that the increase of the product $\nu_0^2 \tau_c$ is more than sufficient to compensate the expected decrease in the number of bound Cl^- ions on chelation. The exceptionally high value of cysteine is because of high value of ν_0 for this complex. (ii) For tridentate ligands, the variation in $\bar{\nu}$ suggests that changes in the effective charge of metal ion depend on the nature of the tridentate ligand bound to the metal ion. (iii) The complexes of quadridentate and bidentate (for 1:2 complex) ligands may have either tetrahedral or octahedral geometry. In case of octahedral geometry, two water molecules enter into the first coordination sphere. The large $\bar{\nu}$ values for tetracoordinated chelates, Zn (glycinate)₂, Zn (glutamate)₂ and Zn (nitrilotriacetate) suggest that the geometry of these complexes is not of coordinately saturated tetrahedral type. On the other hand, $\bar{\nu}$ value of zero for Zn (cysteine)₂ complex suggests that it has a tetrahedral type of geometry (binding of Cl^- ion is not included).

The interaction of halide ion with proteins can be obtained from the halogen-NMR excess relaxation rates or excess line width $\Delta\nu_e$. It has been demonstrated by the following examples: (i) Carbonic anhydrase is a metalloenzyme. It has one zinc atom per protein molecule of a molecular mass of about 30,000. It catalyses the reversible hydration of carbon dioxide to form bicarbonate in the biological systems. ^{35}Cl -NMR studies on the zinc free solutions of bovine carbonic anhydrase (in aqueous NaCl) and on the enzyme containing zinc shows that line broadening is observed in the latter relative to the former. This is attributed to the coordination of Cl^- ion to zinc of the enzyme. Further, line narrowing takes place when the enzyme solution is titrated with acetazoleamide (a strong inhibitor of enzyme) and cyanide and the equivalence point is observed at stoichiometric ratio of acetazoleamide : carbonic anhydrase :: 1 : 1. This indicates that these ligands completely eliminate the Cl^- ions bound to the enzyme molecule. The pH dependence of line width also shows that at high pH, the Cl^- ions gets eliminated.

The —S—S— cross linkages of blood serum albumin (molecular mass = 65000) are responsible for resistance towards perturbations from environments. ^{35}Cl -NMR studies on excess line width ($\Delta\nu_e$) of NMR signal reveal that the anion binding follows the sequence

$SO_4^{2-} < F^- < CH_3COO^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < SCN^- < Pt(CN)_4^{2-} < Au(CN)_2^- < CH_3(CH_2)_{11}OSO_3^-$.
for high as well as low affinity binding sites of the protein.

^{35}Cl -NMR excess line width ($\Delta\nu_e$) as a function of pH (4.8–10.5) in solutions of human oxy and carbonmonoxide haemoglobin in 0.5 M NaCl indicates that the line width increases with the decrease in pH as expected since the number of positively charged groups on the protein molecule increase at lower pH. At about neutral pH, the consistently larger line width for carbon monoxide haemoglobin (HbCO) relative to deoxyhaemoglobin (Hb) is interpreted in terms of the finding that in oxyhaemoglobin (HbO₂) conformation a number of interchain and inter-chain salt links are broken and subsequently more charged residues will be available for the interaction with other ions. Further ^{35}Cl -NMR line width in 0.2 M NaCl decreases markedly as the concentration of ATP in the solution is increased at a pH about 6.0 to 6.3. This suggests that ATP and Cl[−] compete for some of the high-affinity binding sites. The binding constant is about $6 \times 10^3 \text{ mole}^{-1}$ for ATP-Hb and $4 \times 10^2 \text{ mole}^{-1}$ for ATP-HbO₂ systems, the order of binding constant being higher than for Cl[−].

Horse liver alcohol dehydrogenase (LADH), a zinc metalloenzyme, catalyses the reversible interconversion of several alcohols and the corresponding aldehydes in the presence of a coenzyme which is reduced (NADH) or oxidised (NAD⁺) nicotinamide adenine dinucleotide. The titration of solution containing LADH (in aqueous NaCl or NaBr) with NADH has been followed by ^{35}Cl or ^{79}Br longitudinal relaxation rates $\left(\frac{1}{T_1}\right)$. The decrease in excess

bandwidth on gradual addition of NADH suggests the elimination of Cl[−] or Br[−] ions bound to Zn of LADH. The complete elimination of halide ion occurs at a molar ratio of NADH : LADH :: 2 : 1.

The interaction of a mercury-labelled hapten (I), with antidinitrophenyl antibody can be studied by the ^{35}Cl -probe method. The increase in ^{35}Cl -NMR line width with the increase in the concentration of hapten is due to rapid relaxation of $^{35}\text{Cl}^-$ interacting with Hg in the hapten-antibody complex. ^{35}Cl -NMR line width as a function of the molar ratio of hapten (2, 4-dinitro-4'-(chloromercuri) diphenylamine) to antidinitrophenyl antibody suggests the stoichiometric ratio to be 2 : 1 (Hapten : antibody). Note that the line broadening may be dominated by Cl[−] exchange instead of relaxation.

Further it is to be kept in mind that when halide ion is liganded to an Hg-label attached to a macromolecule, the halide ion at the binding site may experience internal motion with respect to the overall motion of the macromolecule. This is illustrated schematically in Fig. 8.15.

When the rate of internal rotation $\left(\frac{1}{\tau_{\text{introt}}}\right) \gg$ overall motion of the macromolecule τ_R (i.e. $\tau_{\text{introt}} \ll \tau_R$), the effective quadrupole interaction in the Hg–X bond is reduced by a factor of

$\frac{1}{4}(3\cos^2\theta_i - 1)^2$ for each mode of internal rotation, θ_1 is the angle between the Hg–X bond (assuming $\eta = 0$) and the first internal rotation axis, θ_2 is the angle between the first and second rotational axes, etc. When θ equals the tetrahedral angle ($109^\circ 28'$), the above factor becomes 0.11. This result is valid for either unrestricted rotational diffusion around the axis of internal rotation or of random jumps between three equally deep potential minima around the C₃-axis. In practice, steric interactions between the halide label and neighbouring group of atoms may restrict the internal rotation and give rise to potential minima of appreciably different depths around the axis of internal rotation. Thus, in such a case, the effects of internal rotation on the quadrupole coupling constant may be partly quenched.

8.14 APPLICATIONS OF PURE NQR

The transition frequency in the pure quadrupole spectrum of spin 3/2 particles like chlorine and bromine nuclei is given by

$$\nu = \frac{e^2 Qq}{2h} \left(1 + \frac{\eta^2}{3} \right)^{1/2} \quad (\text{Eq. 8.56})$$

for a polycrystalline powder. For spin $I = 3/2$, η must be obtained from studies on single crystals, whereas for ^{127}I with $I = 5/2$ both ν_0 and η may be obtained from the spectrum of polycrystalline powder. For gases, the most important method for obtaining ν_0 's is microwave spectroscopy. However, only a small number of halogen quadrupole coupling constants are known for the gaseous state.

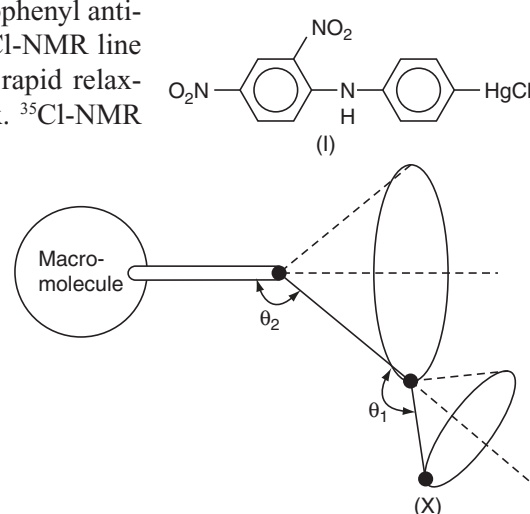


Fig. 8.15 Schematic diagram of halide nucleus (X) attached to a binding site on a macromolecule with the possibility of rotation around two axes.

8.14.1 Study of Chemically Inequivalent Quadrupole Nuclei in the Unit Cell

Chemically inequivalent quadrupole nuclei in solids may be attributed to interaction between the neighbouring molecules or the presence of different conformers of the same molecule in the unit cell. Chemical inequivalence may also arise when an atom containing the quadrupole nucleus is present at chemically different sites in the free molecule. Thus, the chemically inequivalent NQR active nuclei in solids should give rise to multiple lines in the NQR spectrum and the same has been observed indeed, e.g. the ^{35}Cl -NQR spectrum of trichloroacetyl chloride exhibits four lines at 33.721, 40.132, 40.474 and 40.613 MHz. The appearance of four lines suggests that four chlorine atoms of the molecule are inequivalent. The first line is attributed to chlorine atom of the $-\text{COCl}$ group whereas the last three lines are attributed to inequivalence of three chlorine atoms of $-\text{CCl}_3$ group caused by intermolecular interactions. The expected numbers of lines in the ^{35}Cl -NQR spectrum of dichloroacetylchloride is three but the observed spectrum contains six lines at 32.147, 32.962, 38.353, 38.521, 39.189 and 39.386 MHz. The two low-frequency and four high-frequency lines suggest that there are at least two types of chemically inequivalent conformers in the unit cell. Similarly, the two high and low frequencies (30.437 and 37.517 MHz) of monochloroacetylchloride are interpreted in terms of two chemically inequivalent conformers in the unit cell. Oxalylchloride ($\text{ClCO}-\text{COCl}$) shows only one line (at 33.621 MHz) in its ^{35}Cl -NQR spectrum suggesting that the two NQR active Cl nuclei in the unit cell are chemically equivalent. The four-line multiplet in the halogen quadrupole spectrum of each SiBr_4 , GeCl_4 , GeBr_4 , SnCl_4 , SnBr_4 , SnI_4 , etc., is attributed to the chemical inequivalence of nuclear sites in the free molecule.

8.14.2 Nature of Chemical Bond

Pure NQR tool is frequently used to study the electronic configuration of molecules. The extent of hybridisation and the ionic character in the covalent bond is obtained from the comparison of the quadrupole coupling constants of the nucleus under consideration in the molecule and the isolated atom. A number of relationships between the molecular and atomic quadrupole constants of the same nucleus to describe the covalent bond involving quadrupole nucleus are expressed as

$$\left(\frac{e^2 Qq}{h}\right)_{\text{molecule}} = (1 - \alpha^2)(1 - i) \left(\frac{e^2 q_0 Q}{h}\right)_{\text{atom}} \quad (8.104)$$

where, α is the fractional s -character of the bonding hybrid orbital on the quadrupole atom and ' i ' is a measure of the ionic character of the covalent linkage.

For halogen nucleus in the molecule and a free halogen atom, the relation is,

$$\left(\frac{e^2 qQ}{h}\right)_{\text{molecule}} = [1 - s + d - i(1 - s - d)] \left(\frac{e^2 q_0 Q}{h}\right)_{\text{atom}} \quad (8.105)$$

Here, d stands for the d -character of the bonding orbital. ν_Q for $^{35}\text{Cl}(3p) = +109.746$, $^{37}\text{Cl}(3p) = +86.510$, $^{79}\text{Br}(4p) = -769.76$, $\text{Br}^{81}(4p) = -643.032$ and $^{127}\text{I}(5p) = +2292.712$ MHz.

For an electropositive atom, ' i ' changes sign so Eq. (8.105) is written as

$$\left(\frac{e^2 qQ}{h}\right)_{\text{molecule}} = [1 - s + d + i(1 - s - d)] \left(\frac{e^2 q_0 Q}{h}\right)_{\text{atom}} \quad (8.106)$$

Note that for a molecule AB , $\psi = a\psi_A + b\psi_B$ and $i = a^2 - b^2$ if A is more electronegative than B and ψ is the bonding orbital for the molecule AB .

If π -bond is present in the molecule, Eq. (8.105) becomes

$$\left(\frac{e^2 qQ}{h}\right)_{\text{molecule}} = (1 - s + d - i - \pi) \left(\frac{e^2 q_0 Q}{h}\right)_{\text{atom}} \quad (8.107)$$

The exact nature of chemical bond cannot be deduced from NQR data since a large number of unknowns are involved in the above expressions. As the ionic character in a molecule increases, the electronic environment tends towards spherical symmetry, i.e. $q \rightarrow 0$, consequently the molecular quadrupole coupling constant decreases. sp hybridisation also causes a decrease in the value of molecular quadrupole coupling constant.

The contribution of d orbital to the bonding orbital increases the electric field gradient and hence molecular quadrupole coupling constant. In such a case, the asymmetry parameter η also becomes appreciable and cannot be ignored.

Let us now see how NQR data are utilised to study the nature of chemical bond in H_2S . The electronic configuration of sulphur is $[\text{Ne}] 3s^2 3p^4$ and the bond angle in H_2S is about 90° .

Prior to the ^{33}S -NQR studies on H_2S , it was assumed that in H_2S only p -orbitals of sulphur participate in bonding. However, NQR studies reveal that H_2S has a large value of asymmetry parameter, i.e. $\eta = -0.60$. Theoretically, η can be expressed in terms of electron population in the p_x , p_y and p_z orbitals of the atom. The components of molecular electric field gradient along the three axes in terms of electron population are given by

$$\begin{aligned} \left(\frac{e^2 U_{xx} Q}{h} \right)_{\text{molecule}} &= - \left(\frac{N_y + N_z}{2} - N_x \right) \left(\frac{e^2 q_0 Q}{h} \right)_{\text{atom}} \\ \left(\frac{e^2 U_{yy} Q}{h} \right)_{\text{molecule}} &= - \left(\frac{N_x + N_z}{2} - N_y \right) \left(\frac{e^2 q_0 Q}{h} \right)_{\text{atom}} \\ \left(\frac{e^2 U_{zz} Q}{h} \right)_{\text{molecule}} &= - \left(\frac{N_x + N_y}{2} - N_z \right) \left(\frac{e^2 q_0 Q}{h} \right)_{\text{atom}} \end{aligned} \quad (8.108)$$

where, N_x , N_y , and N_z are the effective electron populations in the p_x , p_y and p_z orbitals of the atom in the molecule.

The set of Eqs (8.108) yields

$$\begin{aligned} \eta &= (U_{xx} - U_{yy}) / U_{zz} \\ &= \frac{3(N_y - N_x)}{N_x + N_y - 2N_z} \end{aligned}$$

If p_z contains the lone pair, we have $N_z = 2$ and $1.50 N_y = N_x + 1$.

This suggests that N_x cannot be equal to N_y , otherwise η will become zero. Therefore, pure p -orbitals of sulphur are not involved in bonding. The large value of η is interpreted in terms of 15 per cent d character in the bonding orbitals. Thus, $p^{3.40} d^{0.60}$ hybridised orbitals rather than pure p -orbitals of sulphur are involved in bonding in the H_2S molecule.

8.14.3 Structural Information from NQR Spectrum

The similarity in the number and pattern of lines in the NQR spectra of different molecules having the same anions but different cationic part can be taken as a criterion to obtain information about their crystal structure, e.g. NQR spectrum of each AlBr_3 (97.497; 113.790, 115.450 MHz) and GaBr_3 (120.602, 120.635; 168.375, 168.430 MHz) has three lines, at 77 K two of which are closely spaced whereas the third one is far apart from the doublet. According to the principle of similarity in the NQR spectra, they must have similar structure. The same has indeed been observed on the basis of x -ray diffraction studies on these molecules. They exist as bridged dimers rather than monomers. Thus, the two closely spaced lines correspond to bromine atoms attached at the end positions of the bridge and the third line is due to bromine atoms in the bridge sites.

The doublet in the ^{14}N -NQR spectrum of solid BrCN may be attributed either to two inequivalent nitrogen atoms in the crystal lattice or to splitting of the nitrogen resonance signal. The former possibility is ruled out since single crystal x -ray diffraction studies suggests a linear chain structure of the type $\text{Br}-\text{C}\equiv\text{N} \mid \dots \text{Br}-\text{C}\equiv\text{N} \mid \dots \text{Br}-\text{C}\equiv\text{N}$. Accordingly, nitrogen has axial symmetry and only one line is expected. Therefore, the only alternative left to explain the doublet in the spectrum is in terms of induced asymmetry at the nitrogen nucleus arising because of interactions between the chains.

8.14.4 Study of Charge-Transfer Complexes

The advantage of nuclear quadrupole resonance spectroscopy in the study of charge transfer complexes, particularly when the crystal structure is known, is that the changes in NQR frequency produced by complex formation can provide evidence of the direction and extent of electron transfer.

Electronic absorption spectroscopy shows the formation of charge-transfer complexes in CCl_4 - p -xylene and CBr_4 - p -xylene systems. However, the NQR($^{35}\text{Cl}/\text{Br}^{79}, \text{Br}^{81}$) spectra of frozen equimolar solution of these

systems show that the resonance frequencies of the halogens in the mixture (CCl_4 —*p*-xylene: 40.472, 40.689 MHz, CBr_4 —*p*-xylene: 264.95, 269.18 MHz) are not appreciatively different from the halogenated component CCl_4 : ^{35}Cl : 40.465 to 40.817 MHz (15 lines); CBr_4 : ^{79}Br : 317.00, 322.09, ^{81}Br : 265.45, 266.06, 266.4, 267.06, 267.97, 268.30, 269.25 MHz, suggesting thereby that charge transfer complexation does not occur in the ground state.

The crystal structure of $\text{SnCl}_4 \cdot 2\text{POCl}_3$ complex, measured at room temperature shows that the tin atom has octahedral configuration with the POCl_3 groups occupying cis positions and bonded to the tin by oxygen (i.e. $(\text{Cl}_3\text{P}=\text{O})_2 \rightarrow \text{SnCl}_4$). ^{35}Cl -NQR frequencies (in MHz at 77 K) of SnCl_4 and POCl_3 are observed at 24.294, 24.226, 24.140, 23.719 and 28.9835, 28.9378 respectively. The ^{35}Cl -NQR frequencies in the $\text{SnCl}_4 \cdot 2\text{POCl}_3$ complex appear at 30.213, 30.117, 21.146, 19.807, 19.035 MHz at 77 K. If possible π -bonding in the P—Cl and Sn—Cl bonds is neglected, both the magnitude and sign in the shifts of the resonance of the chlorine atom attached to tin (−3 to −4 MHz) are in accordance with the structure $(\text{Cl}_3\text{P}=\text{O})_2 \rightarrow \text{SnCl}_4$, which leads to greater ionicity of the Sn—Cl bond. The positive shift (+1 MHz) in the POCl_3 ^{35}Cl resonance frequency is also in accordance with the above hypothesis. The smaller magnitude in the shift is because of the fact that chlorine atom is one bond further removed from the site of the complex formation, i.e. Cl—P—O ... Sn—Cl.

8.14.5 Study of Phase Transitions

NQR frequencies undergo abrupt changes at the transition temperature. These changes in the number and pattern of frequencies occur because the electron distributions within the molecules are affected by intermolecular interaction and depend upon the environment around each molecule, e.g. ^{79}Br -NQR spectrum of K_2SeBr_6 exhibits a single line at room temperature and two lines at dry ice temperature. This difference in the number of lines is attributed to crystalline phase change in going from room temperature to dry-ice temperature. At dry-ice temperature, there are at least two different bromide environments in the unit cell. The clearly visible ^{35}Cl -NQR resonance frequencies (30.213, 30.117, 21.146, 19.807, 19.035 MHz) of $\text{SnCl}_4 \cdot 2\text{POCl}_3$ complex at 77 K suddenly disappear at 183 K. This is attributed to the phase change in going from 77 to 183 K.

8.14.6 Study of Ionic Character of Chemical Bonds in the Gaseous and Solid States

A comparison of halogen (^{35}Cl , ^{79}Br , ^{127}I)-nuclear quadrupole coupling constants in halomethanes in relation to ionic character of chemical bonds both in the gaseous and solid states met with great success, e.g. the ^{35}Cl -quadrupole coupling constants of CH_3Cl in the solid state (−68.4 MHz) is large relative to in the gaseous state (−74.74 MHz). The decrease of quadrupole coupling constant on vaporization suggests that the ionic character of C—Cl (C^+Cl^-) bond is more in the solid state as compared to in the gaseous state. This increase of ionic character in going from gaseous to solid state is attributed to enhancement in the Madelung constant (M) in the binding or cohesive energy (U) of an ionic crystal.

$$U = \left[\frac{-N_A M e^2}{a} \right] + A \exp(-a/\rho) \quad (8.109)$$

where, A and ρ are constants, a is the equilibrium lattice parameter and $M = \sum_i \pm \frac{1}{r_i}$ where r_i 's are the distances from the origin to the points of a lattice with unit lattice parameter. The same has been observed in ICl ($^+\text{ICl}^-$).

Further, it is observed that in CFCl_3 the difference between quadrupole coupling constants in the gaseous and solid states (−78.05 − (−77.58) = −0.47 MHz) is small as compared to that in CH_3Cl (−6.34 MHz). This indicates that C—Cl bond in CH_3Cl becomes more ionic on solidification relative to the C—Cl bond of CF_3Cl in the solid state, the reason being carbon is more electropositive in CFCl_3 relative to CHCl_3 where it is slightly electronegative with respect to hydrogen. Moreover, on solidification, both the C—Cl and C—F bonds of CFCl_3 tend to acquire more ionic character since F and Cl atoms compete to remove electrons from the carbon atom. F being more electronegative than Cl, the C—F bond will have less ionic character relative to C—Cl bond.

8.14.7 Partial Double-Bond Character and Sigma Electron Population for Chlorine Atom Bonded to an sp^2 Hybridised Carbon Atom

The partial double-bond character of the C—Cl bond, and sigma electron population for chlorine atom in conjugated organochlorine compounds, namely substituted chloroethylenes, chlorobenzenes, chloropyridines, chloranil, etc. can be estimated from their nuclear quadrupole coupling constants.

The fractional π -bond character ρ_π is related to the molecular nuclear quadrupole coupling constant by

$$\rho_\pi = \frac{2}{3} \left| \frac{e^2 Qq}{e^2 Qq_0} \right| \eta \text{ per cent} \quad (8.110)$$

where, $e^2 Qq_0$ for ^{35}Cl (atom) = -109.74 MHz.

The total p -electron population on the chlorine atoms in substituted chlorobenzenes is given by

$$\sum \rho_p = 6 - \left| \frac{e^2 Qq}{e^2 Qq_0} \right| [\eta + 1] \quad (8.111)$$

The sigma electron population ρ_σ for chlorine atom bonded to an sp^2 hybridised carbon atom in organochlorine compounds is given by

$$\rho_\sigma = 2 - \left| \frac{e^2 Qq}{e^2 Qq_0} \right| \left(1 + \frac{\eta}{3} \right) \quad (8.112)$$

Problem 8.12: (A), Calculate the partial double-bond character of C—Cl bond and sigma electron population for chlorine atom bonded to an sp^2 hybridised carbon atom in (a) $\text{H}_2\text{C}=\text{CHCl}$ (b) $\text{O}=\text{CCl}_2$ (c) 1, 2, 4, 5- $\text{Cl}_4\text{C}_6\text{H}_2$ (d) 2, 4, 6-trichloro-*s*-triazene; from the following data.

Compound	ν (MHz)	η
(a)	36.0	0.14
(b)	36.23	0.25
(c)	36.283	0.116
(d)	36.30	0.23

(B) Calculate the total p -electron population on chlorine atoms in (a) p -dichlorobenzene, (b) p -hydroxychlorobenzene, and (c) p -aminochlorobenzene from the data given below:

Compound	ν (MHz)	η
(a)	34.25	0.067
(b)	34.367	0.058
	34.145	0.223
(c)	33.767	0.0489

Solution (A) From Eqs (8.110) and (8.112), we obtain for

(a) $\text{H}_2\text{C}=\text{CHCl}$

$$\rho_\pi = \frac{2}{3} \left| \frac{72}{109.74} \right| 0.14 \times 100 = 6.12$$

$$\rho_\sigma = 2 - \left| \frac{72}{109.74} \right| \left(1 + \frac{0.14}{3} \right) = 1.313$$

(b) $\text{O}=\text{CCl}_2$

$$\rho_\pi = \frac{2}{3} \left| \frac{72.46}{109.74} \right| 0.25 \times 100 = 11.00$$

$$\rho_\sigma = 2 - \left| \frac{72.46}{109.74} \right| \left(1 + \frac{0.25}{3} \right) = 1.284$$

(c)

$$\rho_\pi = \frac{2}{3} \left| \frac{72.566}{109.74} \right| 0.116 \times 100 = 5.11$$

$$\rho_\sigma = 2 - \left| \frac{72.566}{109.74} \right| \left(1 + \frac{0.116}{3} \right) = 1.313$$

$$(d) \quad \rho_{\pi} = \frac{2}{3} \left| \frac{72.60}{109.74} \right| 0.23 \times 100 = 10.14$$

$$\rho_{\sigma} = 2 - \left| \frac{72.60}{109.74} \right| \left(1 + \frac{0.23}{3} \right) = 1.287$$

(B) From Eq. (8.111), we obtain for

(a) *p*-dichlorobenzene

$$\sum \rho_p = 6 - \left| \frac{68.50}{109.74} \right| (1.067) = 5.333$$

(b) *p*-hydroxychlorobenzene

$$\sum \rho_{p1} = 6 - \left| \frac{68.734}{109.74} \right| (1.058) = 5.337$$

$$\sum \rho_{p2} = 6 - \left| \frac{68.290}{109.74} \right| (1.223) = 5.238$$

$$(c) \quad \sum \rho_p = 6 - \left| \frac{67.534}{109.74} \right| (1.0489) = 5.354$$

PROBLEMS

- Determine the spin of the quadrupole nuclei if the number of NMR lines in their respective spectra is (a) four, (b) five, and (c) seven,
- Calculate the quadrupole relaxation times for (a) $^{81}\text{Br}^-$, and (b) $^{127}\text{I}^-$ ions at infinite dilution in water from the following data.

Nucleus	$Q \times 10^{24} (\text{cm}^2)$	$1+\gamma_{\infty}$	$r_0 (\text{\AA})$	$^t\text{H}_2\text{O} \times 10^{12} (\text{s})$
$^{81}\text{Br}^-$	0.28	100	3.36	2.5
$^{127}\text{I}^-$	-0.75	180	3.56	2.5

Hint: Assume $P = 0.5$

[Ans: (a) $7.4 \times 10^{-4} \text{ s}$ (b) $1.77 \times 10^{-4} \text{ s}$]

- Compute the values of correlation times of ^{35}Cl nuclei from the NQR data of the systems given below. What inference can be drawn from the correlation times so obtained?

System	$T_2 (\mu \text{s})$	$\nu_Q (\text{MHz})$	Temperature (K)
CHCl_3	24.5	76.6	298
$\text{CHCl}_3\text{—C}_6\text{H}_6$	16	79	298
complex			
CHCl_3 bound to	3.3	77	300
polyvinyl pyrrolidone			

[Ans: 1.76, 2.53 and 12.9 p s]

- PbCl_4 , SnCl_4 and TiCl_4 , exhibit four lines in their respective ^{35}Cl -NQR spectra. The values of ν_a in the respective systems are 45.4, 48.2 and 12.2 MHz. Comment on the number of lines in the spectra and what inference can be drawn regarding the structure of these molecules?

- x-ray diffraction studies on the halides of group three, i.e. MX_3 ($M = \text{In}$; $X = \text{Cl}, \text{Br}, \text{I}$) show that these halides exist as bridged dimers in which there are two types of halogen atoms corresponding to the bridge and end sites. The ^{35}Cl -NQR spectrum of InCl_3 consists of three lines (at 104.112, 128.110 and 128.608 MHz at 77 K) two of which lie very close to each other whereas the third line is far away from the doublet. Interpret the NQR spectra in the light of x-ray studies on MX_3 systems.

- Calculate the paramagnetic shielding term in Cl_2 molecule if the mean excitation energy ΔE for the $^1\Sigma - ^1\Pi$ transition in Cl_2 is (a) 3.76 eV, and (b) 10 eV.

[Ans: (a) $\sigma_p(\text{Cl}) = -17.4 \times 10^{-4}$ [b] -6.55×10^{-4} is more reasonable]

- ^{19}F -NMR spectrum (58.3 MHz, 26°C , CFCl_3) of BrF_6^+ in HF solution consists of two overlapping 1 : 1 : 1 : 1 quartets at very low field. Splittings within the quadruplets have also been observed. The values of two coupling constants $J_{79\text{Br}-^{19}\text{F}}$ and $J_{81\text{Br}-^{19}\text{F}}$ have been found to be 1575 and 1679 ppm respectively. Interpret the spectral data.

[Ans: $^{79}\text{BrF}_6^+$ and $^{81}\text{BrF}_6^+$; Large coupling constants means

Br has long relaxation times, hence BrF_6^+ has octahedral symmetry. Splitting between the quadruplets is because of bromine ($I = 3/2$) spin coupling to equivalent fluorines].

- The coupling constants of halomethane series are tabulated as follows.

Halomethane	$\nu_Q (\text{MHz})$
CH_3Cl	68.0
CH_2Cl_2	72.0
CHCl_3	76.6
CCl_4	81.2

Calculate the average value of the increase in quadrupole coupling constant of chlorine atom in the halomethane series and comment. [Ans: ≈ 4 MHz]

9. Predict and explain the ionic character of C—X(X = Br, I) bond of each of the following pairs of halogenated methanes both in the gaseous and solid states from their respective quadrupole coupling constants.

Pair	Nucleus	ν_Q (MHz)	
		Gas	Solid
CH ₃ Br	⁷⁹ Br	577.15	529
CF ₃ Br	⁷⁹ Br	619	604
CH ₃ I	¹²⁷ I	−1929	−1766
CF ₃ I	¹²⁷ I	−2143.8	−2069

10. Determine the ³⁵Cl-quadrupole coupling constant for Cl[−] counter ion bound to N⁺H₃ group in the amphiphilic octacylammonium chloride. (C₈N⁺H₃Cl)–H₂O system from the following data, γ_∞ (for chlorine) = 59, $D \gg 1$, r (the distance between Cl[−] bound to amphiphilic sur-

faces and amphiphilic positive charge, i.e. N⁺H₃ end group) = 6.0×10^{-10} m, Q (for ³⁵chlorine) = -0.0802×10^{-28} m². The Cl[−] counterions are assumed to be hydrated [Ans: 0.6 MHz]

11. Calculate the ⁸¹Br-quadrupole coupling constant for Br[−] counter ion bound to N⁺(CH₃)₃ in the amphiphilic (C₁₆N⁺(CH₃)₃Br)–H₂O system from the following data: ($1 + \gamma_\infty$) for bromine = 110, $D \gg 1$, $r[\text{Br}^- - \text{N}^+(\text{CH}_3)_3] = 7.5 \times 10^{-10}$ m, Q (for ⁸¹bromine) = 0.282×10^{-24} cm². The Br[−] counter ions are assumed to be hydrated. [Ans: 2.0 MHz]

12. Draw the energy-level diagram depicting the amount of shift in the Zeeman levels due to first-order quadrupole interaction for a nucleus with $I = 5/2$.

13. Calculate the quadrupole relaxation rates of ⁸¹Br[−] and ¹²⁷I[−] ions in infinite dilute solutions of H₂O from the data given below:

Nucleus	$Q \times 10^{24}(\text{cm}^2)$	$1 + g_\infty$	r_0 (Å)	$\tau_{\text{H}_2\text{O}} \times 10^{12}(\text{s})$
⁸¹ Br [−]	0.28	100	3.36	2.5
¹²⁷ I [−]	−0.75	180	3.56	2.5

[Ans: 1348 s^{−1}, 5635 s^{−1}]

14. ¹⁴N(¹⁴HC=N-NH) quadrupole spectrum of 1, 2, 4-triazole at 77 K shows three lines at 3.8759, 2.4692 and 1.4070 MHz. Find the values of quadrupole coupling constant and asymmetry parameter.

[Ans: $\nu_Q = 4.2301$ MHz, $\eta = 0.6651$]

15. Predict (a) the positions of chloroatoms with respect to the chlorine atom whose frequency is being measured experimentally for the following trichlorobenzenes.

- (b) Assign also names to the chlorobenzenes.

[Ans: 1, 2, 3-trichloro – and 1, 2, 4, trichlorobenzenes]

Chlorobenzene	³⁵ Cl-NQR frequencies (MHz)
Trichlorobenzene (a)	35.189, 35.617, 36.173, 36.380, 36.400, 36.623
Trichlorobenzene (b)	35.545, 35.894, 36.115

16. Calculate the ³⁵Cl-NQR frequencies of pentachloro- and hexachloro benzenes

[Ans: 37.072 MHz (Obs (average) 37.760 MHz); 38.372 MHz (Obs (average):38.422 MHz)]

17. Calculate the partial double-bond character of C—Cl bond and sigma electron population for chlorine atom bonded to an sp² hybridised carbon atom in (a) H₂C = CFCl (b) o — ClC₆H₄OH (c) chloranil, from the following data.

[Ans: (a) 3.75, 1.323 (b) 4.23, 1.342 (c) 9.38, 1.282; 9.40, 1.281]

Compound	ν (MHz)	η
(a)	36.35	0.085
(b)	34.84	0.10
(c)	36.79, 36.86	0.21, 0.21

18. The ³⁵Cl-NQR spectrum of $\text{X} - \text{C}_6\text{H}_4 - \text{Cl}$ gives $\nu_Q = 69.116$ MHz. Determine the Hammett $-\sigma$ constant for the substituent X. [Ans: $\sigma = 0.268$]

19. Calculate (a) ³⁵Cl-NQR frequency for *p*-aminochlorobenzene, (b) ⁸¹Br-NQR frequency for *p*-aminobromo (81) benzene (c) ¹²⁷I-NQR frequency for *p*-aminoiodobenzene. $\sigma_{\text{para}}(\text{NH}_2) = -0.66$

[Ans: (a) 34.166 MHz (obs: 34.146 MHz) (b) 221.899 MHz (obs: 221.862 MHz)

(c) 266.060 MHz (Obs: 261.14 and 521.125 MHz)]

20. At 20 K two quadrupole resonances are observed for *t*-butylchloride, (CH₃)₃CCl, the stronger at 31.195 MHz and the weaker at 24.586 MHz. Interpret these observations.

[Ans: ³⁵Cl and ³⁷Cl resonances, $|\nu_Q|$: 62.39 and 49.17 MHz respectively, $\rho_p = 5.431$]

21. (a) ¹²⁷I-nuclear quadrupole coupling constants (MHz) of NH₄I₃ are 466.8 ($\eta = 0.130$), 1725.0 ($\eta = 0.151$), and 2458.7 ($\eta = 0.018$). Determine the ρ_σ population in the linear I₃[−] ion.

- (b) ³⁵Cl and ¹²⁷I quadrupole coupling constants (MHz) in KICl₂ are 36.81, 37.53, 38.00, 39.25 and 3081, 3129 respectively. Calculate the ρ_σ population in the linear ICl₂[−] ion.

Hint: Take the average of coupling constants in Part (b).

[Ans: (a) 1.78, 1.20, 0.92 (b) 1.65, 0.65, 0.635]

CHAPTER 9

ELECTRON SPIN
RESONANCE SPECTROSCOPY

No hypothesis can lay claim to any value unless it assembles many phenomena under one concept.

—Goethe

Immerse yourself in facts, especially the baffling facts, in the hope that illumination would come.

—Charcot

9.1 INTRODUCTION

Electron Spin Resonance (ESR), also called Electron Paramagnetic Resonance (EPR), was discovered in Kazan (USSR) in 1944 and the first experiments dealt with absorption resonance in salts of iron group ions. It deals with the study of absorption of electromagnetic radiation in the microwave region (0.1–100 cm) by free radical(s) under the influence of an external magnetic field. *A free radical is defined as an atom, a group of atoms, or a molecule in a certain state containing one unpaired electron which occupies an outer orbital*, e.g. atomic hydrogen ($\text{H}^\bullet$), hydroxyl ($\text{HO}^\bullet$) or methyl ($\text{H}_3\text{C}^\bullet$) radicals. By definition, naturally occurring stable and long-lived molecules with odd number of electrons in their normal state, e.g. nitrous oxide (NO), nitrogen dioxide (NO_2), nitrogen difluoride (NF_2), di-*t*-butylnitroxide [$(\text{CH}_3)_3\text{CN}^\bullet\text{OC}(\text{CH}_3)_3$], chlorine dioxide (ClO_2) are free radicals. A biradical contains two unpaired electrons in outer orbitals, e.g. methylene radical $\text{H}_2\text{C}^\bullet$ or oxygen (O_2) in the ground state. A radical ion is a free radical with positive or negative charge, e.g. protonated amine radical ($\text{H}_3\text{N}^{+\bullet}$) or naphthalene anion radical ($\text{C}_{10}\text{H}_8^\bullet$). Some of the transition metal ions and their complexes, e.g. Mn^{2+} , Cr^{3+} , Co^{2+} , Fe^{3+} , $[\text{Fe}(\text{CN})_6]^{3-}$, Cu^{2+} copper (II) acetate monohydrate, etc., have also unpaired *d* electrons and have, therefore, some properties common with free radicals. Although all transition metal ions have unpaired electrons, but according to a theorem by Kramer, the most suitable ions for ESR study are those containing an odd number of unpaired electrons. Naturally occurring free radicals, being stable and long-lived, can easily be studied by ESR whereas free radicals formed as intermediates in a chemical reaction or produced artificially by irradiation of a normal molecule with electric discharge or UV or *x*-ray or with a beam of nuclear particles are unstable, and can be detected by ESR provided their lifespan is $>10^{-6}$ s. The lifetimes of many organic free radicals and ionic radical intermediates are too short for observation by ESR spectroscopy. Such free radicals and radical ions may be stabilised by the following methods: (i) stabilisation of free radicals by cooling to low temperatures, e.g. liquid nitrogen ($-196^\circ\text{C} = 77\text{ K}$). (ii) stabilisation of free radicals on synthetic zeolites. They are good stabilising matrices for free radicals at relatively high temperatures. (iii) Stabilisation of free radicals and ionic radicals in organic glass matrices. Free electrons are trapped only in amorphous frozen (glassy) states but never in crystalline states, e.g. ESR spectra of γ -irradiated 3-methyl pentane glass at 77 K. (iv) Stabilisation of free radicals in organic crystalline matrices, e.g. alcohols. Methanol and alcohol glasses are frequently used as trapping matrices in radiation and photochemical studies. Generally, electrons and hydrogen abstraction radicals $\text{RC}^\bullet\text{HOH}$ of the alcohols are formed by ionising radiation; so alcohol glasses as trapping matrices should be used very cautiously.

9.2 SIMILARITIES BETWEEN ESR AND NMR

ESR is very similar to NMR in theory. The discussion and equations on NMR are equally valid for ESR except that the system under consideration is an electron rather than proton.

The electron is characterised by its rest mass, $m = 9.109558 \times 10^{-28}$ g; charge $e = 4.803 \times 10^{-10}$ esu, intrinsic angular momentum or spin $\left(S = \frac{1}{2}\right)$ and its magnetic moment (μ_e).

The magnetic moment for the unbounded electron is related to its magnetic spin quantum number (M_s) by the following equation:

$$\mu_e = -g_e \beta_s M_s \text{ erg } G^{-1} \quad (9.1)$$

where, g_e is dimensionless constant called the Lande g -factor of the electron or electron free spin g -factor or spectroscopic splitting factor of the electron, $g_e = 2.0023192778$, β_e is the Bohr magneton of the electron, $\beta_e = \frac{eh}{4\pi m_e c} = 9.274096 \times 10^{-21} \text{ erg G}^{-1}$, where c is the velocity of light $= 2.997925 \times 10^{10} \text{ cm s}^{-1}$. For $\left(S = \frac{1}{2}\right)$,

$$M_s = (2S + 1) = \left(2 \times \frac{1}{2} + 1\right) = 2. \text{ Thus, the two values of } M_s \text{ are } \pm \frac{1}{2}.$$

The minus sign in Eq. (9.1) indicates that the magnetic moment vector of an electron is in opposite direction to the angular momentum vector. The energy of the electron spin state is given by

$$E = g_e \beta_e H M_s \quad (9.2)$$

H is the strength of the applied magnetic field.

In the absence of a magnetic field, the electron may exist in one of the two degenerate states corresponding to $M_s = \pm \frac{1}{2}$. However, when the electron is placed in an external magnetic field (H), it precesses about the applied field axis (Z -axis) with a component of its spin angular momentum either parallel ($M_s = -\frac{1}{2}$; low energy state of $-\frac{1}{2} g_e \beta_e H$) or antiparallel ($M_s = +\frac{1}{2}$, high energy state of $+\frac{1}{2} g_e \beta_e H$) to applied field axis. The oscillating magnetic field of electromagnetic radiation having frequency, ν , when applied at right angles to the applied field axis (Z -axis) induces transitions between the two spin states provided the frequency of the field is at or near the Larmor frequency of the precessing electron, i.e. $\Delta E = h\nu = g_e \beta_e H$. Since the ratio of Larmor frequency of electron to proton is

$$\frac{\omega(\text{electron})}{\omega(\text{proton})} = \frac{\gamma(\text{electron})}{\gamma(\text{proton})} = 10^3 \quad (9.3)$$

the NMR experiments are carried out in the MHz range (radio frequency region), ESR experiments require frequencies in the GHz range ($1 \text{ GHz} = 10^9 \text{ Hz} = 10^3 \text{ MHz}$), i.e. microwave frequency region. In spite of the difference in the frequency regions of NMR and ESR, the s - s and s - l relaxation times play a key role in determining the nature of ESR signal. Although, as in NMR, the ESR spectrum can be obtained by varying the frequency or the field strength, in practice it is simpler to vary the latter.

More in common with the methods of pure quadrupole resonance and nuclear magnetic resonance, e^2qQ , η and the directions of the field gradient axes can all be determined by electron spin resonance measurements conducted on single crystals. In favourable cases, the absolute sign of coupling constant can be determined. The most general application of this method is the determination of quadrupole coupling constants of paramagnetic complexes of transition metals and the lanthanons.

Let us now see how an unpaired electron in different chemical environments behaves under the influence of an external magnetic field. But prior to that, certain features of ESR of bare electron and the various parameters associated with it deserve consideration.

9.3 BEHAVIOUR OF A FREE ELECTRON IN AN EXTERNAL MAGNETIC FIELD

The electron energy (E) of an electron under the influence of magnetic field (H) is

$$E = g_e \beta_e H M_s \quad (\text{Eq. 9.2})$$

In the absence of a magnetic field, the two spin states of the electron corresponding to $M_s = \pm \frac{1}{2}$ will have equal energy and are said to be degenerate. However, on the application of a magnetic field, the two M_s states split. The down spin of an electron is more stable than the up spin because of electron negative charge. The high-energy state will thus correspond to $M_s = +\frac{1}{2}$ whereas the low-energy state will correspond to $M_s = -\frac{1}{2}$. The selection rule for the transition between spin states is $\Delta M_s = \pm 1$. If $E_{+1/2}$ and $E_{-1/2}$ are energies of higher and lower states of the electron respectively, then from Eq. (9.2) we write

$$E_{+1/2} = \frac{1}{2} g_e \beta_e H \quad (9.4)$$

$$E_{-1/2} = -\frac{1}{2} g_e \beta_e H \quad (9.5)$$

From Eqs (9.4) and (9.5), we obtain

$$\Delta E = E_{+1/2} - E_{-1/2} = g_e \beta_e H \quad (9.6)$$

Now, when the electron in magnetic field (H) is irradiated with microwave radiation of frequency ν the energy $h\nu$ will be absorbed by the electron in state $M_s = -\frac{1}{2}$ and the transition between the two spin states will occur provided

$$\Delta E = h\nu = g_e \beta_e H \quad (9.7a)$$

This is the condition for resonance in ESR. The transition between the spin states and the ESR signal corresponding to it is shown in Fig. 9.1.

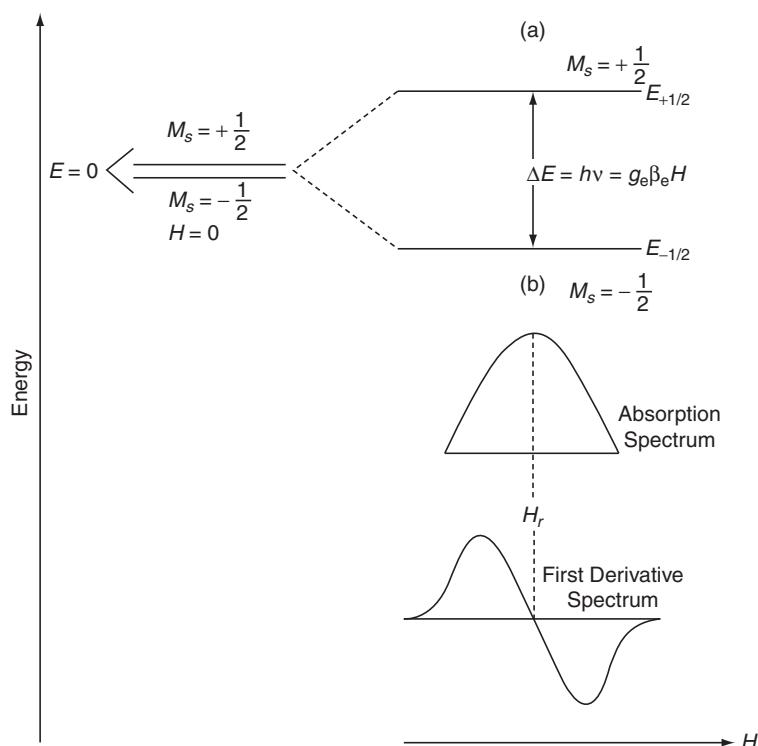


Fig. 9.1 (a) Splitting of electron (system $S = 1/2$, $I = 0$) energy levels by variable applied magnetic field and constant frequency $h\nu = \text{constant}$ (b) Absorption and first derivative ESR spectra of a free electron.

Problem 9.1: (a) Calculate the relation between field strength and frequency for $g_e = 2.0023$. (b) Compute the frequencies for ESR and PMR transitions if the strength of the applied magnetic field is 10 kG. (c) The magnetic moment of an electron is about -9270×10^{24} compared to $+14.1 \times 10^{24}$ erg G⁻¹ for proton. Determine the ratio of Lande splitting factor of proton to electron.

Solution (a) From Eq. (9.7a),

$$\frac{\nu}{H} = \frac{g_e \beta_e}{h} = \frac{2.0023 \times 9.274 \times 10^{-21} (\text{erg G}^{-1})}{6.625 \times 10^{-27} (\text{erg s})} = 2.80 \times 10^6 \text{ Hz(G}^{-1}) = 2.80 \text{ MHz (G}^{-1})$$

Thus, 1 G = 2.80 MHz

(b) The resonance frequency (ν_e) for an electron is given by

$$\nu_e = \frac{g_e \beta_e H}{h} \quad (9.7b)$$

Substituting the values of respective parameters into Eq. (9.7b),

$$\nu_e = \frac{2.0023 \times 9.274 \times 10^{-21} (\text{erg G}^{-1}) \times 10^4 (\text{G})}{6.625 \times 10^{-27} (\text{erg s})} = 2.80 \times 10^{10} \text{ Hz} = 28000 \text{ MHz}$$

Recall Eq. (7.16) from Chapter 7, i.e.

$$\begin{aligned} \nu_p &= \frac{g_p \beta_p H}{h} \\ &= \frac{5.585 \times 5.05 \times 10^{-24} (\text{erg G}^{-1}) \times 10^4 (\text{G})}{6.625 \times 10^{-27} (\text{erg s})} = 4.6 \times 10^7 \text{ Hz} = 46 \text{ MHz} \end{aligned}$$

(c) We know that

$$\mu_p = g_p \beta_p M_I (\text{erg G}^{-1}) \quad (\text{Eq. 7.8})$$

$$\mu_e = -g_e \beta_e M_S (\text{erg G}^{-1}) \quad (\text{Eq. 9.1})$$

For electron and proton, $M_S = M_I = \pm \frac{1}{2}$. Since we are to compare the magnitudes of g , for proton and electron, so the minus sign in Eq. (9.1) may be ignored.

Comparing Eqs (7.8) and (9.1), we obtain

$$\frac{g_p}{g_e} = \frac{\mu_p}{\mu_e} \times \frac{\beta_e}{\beta_p} = \frac{14.1 \times 10^{24} (\text{erg G}^{-1}) \times 9.274 \times 10^{-21} (\text{erg G}^{-1})}{9.270 \times 10^{24} (\text{erg G}^{-1}) \times 5.05 \times 10^{-24} (\text{erg G}^{-1})} = 2.79 \times 10^3$$

9.4 INTENSITY OF ESR LINES AND FACTORS AFFECTING IT

The properties of ESR absorption lines for Lorentzian and Gaussian line shapes (Figs 9.2 and 9.3) are listed in Table 9.1. Like NMR, the intensity of the ESR absorption line for these two types of line shapes is given by

$$I = \frac{I_0}{T_2^2 (H - H_r)^2 + 1} \quad \text{Lorentzian shape} \quad (9.8)$$

$$I = I_0 \exp [-b(H - H_r)^2 T_2^2] \quad \text{Gaussian shape} \quad (9.9)$$

where terms and symbols have their usual meanings, i.e. I_0 is the intensity of the absorption line at its centre, H_r is the field of resonance at line centre, T_2 is the spin-spin relaxation time, b is a constant.

The intensity of ESR line depends on the population of the unpaired electrons in the ground ($N_{-1/2}$) and excited ($N_{+1/2}$) spin states. The ratio of two populations in thermal equilibrium is governed by the Boltzmann law.

$$\frac{N_{-1/2}}{N_{+1/2}} = \exp \left[\left(E_{+1/2} - E_{-1/2} \right) / \kappa T \right] = \exp \left(\frac{\Delta E}{\kappa T} \right) = \exp \left(\frac{g_e \beta_e H}{\kappa T} \right) \quad (9.10a)$$

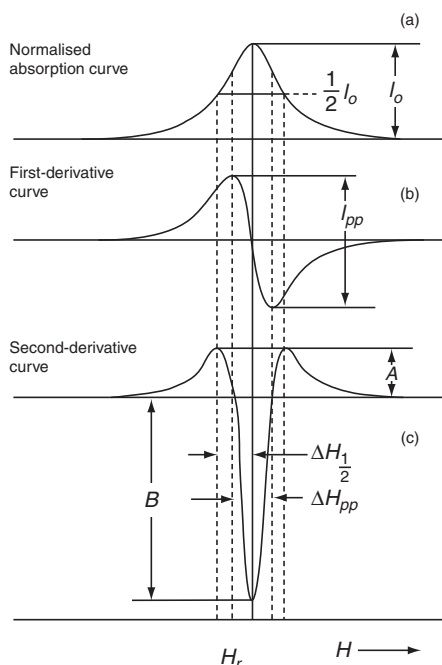


Fig. 9.2 Lorentzian line shape: (a) absorption spectrum (b) first-derivative spectrum (c) second-derivative spectrum.

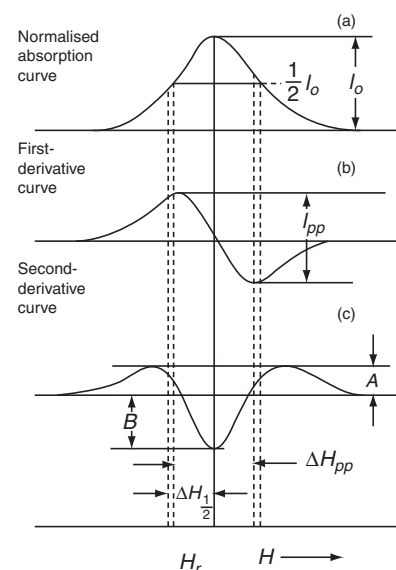


Fig. 9.3 Gaussian line shape: (a) absorption spectrum, (b) first-derivative spectrum, and (c) second-derivative spectrum.

Table 9.1 Properties of Lorentzian and Gaussian lines.

Property	Lorentzian Shape	Gaussian Shape
Half-width at half-height	$\Delta H_{1/2}$	$\Delta H_{1/2}$
Peak-to-peak width	$\Delta H_{pp} = \frac{2}{\sqrt{3}} \Delta H_{1/2}$	$\Delta H_{pp} = \left(\frac{2}{\ln 2} \right)^{\frac{1}{2}} \Delta H_{1/2}$
Peak amplitude	$I_0 = \frac{1}{\pi \Delta H_{1/2}}$	$I_0 = \left(\frac{\ln 2}{\pi} \right)^{\frac{1}{2}} \frac{1}{\Delta H_{1/2}}$
Equation for absorption line	$I = \frac{I_0 (\Delta H_{1/2})^2}{(\Delta H_{1/2})^2 + (H - H_r)^2}$	$I = I_0 \exp \left[\frac{(-\ln 2)(H - H_r)^2}{(\Delta H_{1/2})^2} \right]$
Peak-to-peak amplitude	$I_{pp} = \frac{3\sqrt{3}}{4\pi} \frac{1}{(\Delta H_{1/2})^2}$	$I_{pp} = \left(\frac{2}{\ln 2} \right)^{\frac{1}{2}} \Delta H_{1/2}$
Equation for first derivative absorption line	$I' = \frac{(-I_0) 2 (\Delta H_{1/2})^2 (H - H_r)}{[(\Delta H_{1/2})^2 + (H - H_r)^2]^2}$	$I' = \frac{(-I_0) 2 (\ln 2) (H - H_r)}{(\Delta H_{1/2})^2} \times \exp \left[\frac{(-\ln 2)(H - H_r)^2}{(\Delta H_{1/2})^2} \right]$
Peak amplitude of positive lobe	$A = I_0 \left[\frac{1}{2(\Delta H_{1/2})^2} \right]$	$A = I_0 \left[\frac{4e^{-3/2} \ln 2}{(\Delta H_{1/2})^2} \right]$
Peak amplitude of negative lobe	$B = -I_0 \left[\frac{2}{(\Delta H_{1/2})^2} \right]$	$B = -I_0 \left[\frac{2 \ln 2}{(\Delta H_{1/2})^2} \right]$

H_r is the field resonance at the centre.

Accordingly, the intensity of ESR signal increases as the ratio between the two populations, i.e. $N_{-1/2}/N_{+1/2}$ decreases. The intensity also increases when the temperature decreases,

The population difference (Δn) between the spin states is given by

$$\Delta n = N_{-\frac{1}{2}} - N_{+\frac{1}{2}} = \frac{Ng_e \beta_e H}{2kT} \quad (9.10b)$$

where, $N_{-1/2} + N_{+1/2}$ is the total number of unpaired electrons in both the spin states.

The signal intensity is directly proportional to Δn which is inversely proportional to temperature. Thus as the temperature decreases, the signal intensity increases. For this reason, the ESR experiments are performed at low temperatures. The intensity of ESR signal at liquid nitrogen temperature (77 K) is about four times higher than at room temperature.

The probability of the transition between two spin states is proportional to the incident microwave energy. As the microwave energy increases, the signal intensity also increases and becomes maximum. A further increase of microwave energy broadens and decreases the ESR signal till it completely disappears. This is the result of saturation process, where the population of both the spin states becomes equal. The return of the system to equilibrium is called *relaxation process*. The two types of relaxation processes, i.e. *s-l* and *s-s* are exponential in nature and are characterised by their relaxation times, T_1 and T_2 respectively.

9.5 ESR LINE WIDTH AND FACTORS AFFECTING IT

The line width of ESR lines is expressed in two ways: (i) Half line width ($\Delta H_{1/2}$), i.e. the width at half the height of the absorption line (Figs 9.2 and 9.3 and Table 9.1). (ii) Peak-to-peak width (ΔH_{pp}), i.e. the full width between the two extremes of the first derivative curve (Figs 9.2 and 9.3 and Table 9.1).

According to Heisenberg's uncertainty principle, the line width of ESR line is given by

$$g_e \beta_e \Delta H_{1/2} \Delta t \geq \frac{h}{2\pi} \text{ or } \Delta E \Delta t \geq \frac{h}{2\pi} \quad (9.11)$$

where $\Delta H_{1/2}$ is the line width (G), Δt is the lifetime of the excited spin state (s), ΔE is the energy difference between the two spin (electron) states. According to Eq. (9.11), $\Delta H_{1/2}$ depends on the lifetime of the excited spin state, i.e. if Δt is small, $\Delta H_{1/2}$ will be large. Thus the parameters which decrease the lifetime of the excited spin state cause broadening of the ESR resonance.

As already discussed in NMR (Chapter 7), the line width depends on either or both the spin-lattice (T_1) and spin-spin, i.e. dipolar (T_2) relaxation processes via which the spin in the excited state dissipates its energy to return to the ground state without emission of any energy and the exchange process.

Line broadening due to s - l process takes place due to the interaction of the paramagnetic ion with the thermal vibrations of the crystal lattice or with the rotation and vibration motions of solvent molecules in liquids. The s - l relaxation time depends on the intensity of s - l interactions. Thus the factors which decrease the s - l interactions, i.e. T_1 will increase the line width and vice versa. The s - l process is temperature dependent and is efficient at room temperature. Its efficiency decreases as the temperature is lowered and becomes several minutes at liquid nitrogen temperature. Thus at low temperatures, s - l process ($T_1 = \infty$) does not contribute to line broadening. So in order to obtain a good ESR spectrum, the sample should be cooled to liquid N_2 , or H_2 or He temperature. T_1 is also sensitive to the presence of neighbouring electronic excited states. The relaxation time is small when the electronic excited state is close ($\sim 100 \text{ cm}^{-1}$) to the magnetic nuclei. T_1 is also dependent on the symmetry of radicals. The reduction in symmetry of the radical leads to weakening of the spin-orbit coupling and to an increase in the s - l time and consequently narrowing of lines. T_1 for liquids (10^{-4} – 10 s) is less than that for solids (10^{-2} – 10^4 s) due to random motion of molecules in liquids. As a consequence, liquids exhibit broad line spectra whereas solids exhibit narrow line spectra. On the other hand, the s - s process (T_2) is very efficient and has relaxation times $T_2 \sim 10^{-4}$ s for solids and $T_2 \sim T_1$ for liquids. In the s - s interaction, the excited state unpaired electron shares its energy with the neighbouring electron spins rather than with the lattice as in the s - l process. Thus the larger the sharing rate, the smaller will be the relaxation time and broader will be the ESR line. Note that the local magnetic field (δH) produced by a paramagnetic centre, i.e. say paramagnetic ion, is given by

$$\delta H = \frac{3\beta_e}{r^3} \quad (9.12)$$

where r is the distance between the paramagnetic centres. The local field of the magnetic dipole influences the neighbouring electron spins and alters the field there. This magnetic dipolar interaction reduces the lifetime of the excited state electron spin and broad ESR line results. This is also called *concentration broadening* since $\delta H \propto \frac{1}{r^3}$. The effect of s - s interaction or concentration broadening can be reduced by increasing the distance between the paramagnetic ions by magnetically diluting the sample. In solids, this is achieved by diluting the paramagnetic ion in a diamagnetic isomorphous material, e.g. small amounts of $CuSO_4$ in a $ZnSO_4$ crystalline lattice. The dilution factor should be in excess of 100. The interaction of the magnetic nuclear spins in a crystalline compound can also broaden the ESR line and this effect is about 10^3 times smaller than the electron s - s interaction effect and is negligible in magnetically dilute samples.

In conclusion, the ESR linewidth is related to T_1 and T_2 as

$$\Delta H_{1/2} = \frac{1}{\tau} = \frac{1}{T_1} + \frac{1}{T_2} \quad (9.13)$$

At low temperature, the s - l relaxation time $T_1 = \infty$. Therefore, by Eq. (9.13) we obtain

$$\Delta H_{1/2} = \frac{1}{T_2} \quad (9.14)$$

i.e. at low temperature the ESR line width is governed only by s - s interaction.

The ESR lines are wider than the NMR lines, i.e. bandwidth of ESR lines > bandwidth of NMR lines, e.g. the width of ESR absorption line for a typical relaxation time say 10^{-7} s is $(2\pi\Delta t)^{-1} \approx 1 \text{ MHz}$ whereas the width of NMR line for a relaxation time of 10^{-1} s is 1 Hz (normal line width for a liquid sample). The advantage of wider ESR line is that the magnetic field homogeneity of 1 in 10^5 would suffice whereas this figure in NMR is 1 in 10^8 over the sample. On the disadvantage side, however, it is much more difficult to detect a wide line than a narrow line of the same intensity. Due to this reason, ESR spectrum is recorded in the derivative mode. We have already stated that ESR line width is also affected by exchange process between neighbouring unpaired electrons. In undiluted crystals, the paramagnetic ions

are so close to one another that overlapping of orbitals containing the unpaired electrons takes place. When exchange occurs between equivalent ions, the exchange energy will be large as compared to the value of hyperfine splitting, the hyperfine lines broaden at the base and become narrow at the centre. This is known as *exchange broadening*. On the other hand, when exchange takes place between non-equivalent ions, the exchange energy is almost equal to the value of hyperfine splitting, the resonances of separate hyperfine lines merge to produce a single broad line. This is called *exchange narrowing* phenomenon. Such an effect has been observed in the electron transfer reaction between tetracyanoethylene (TCNE or N) anion radical and its neutral molecule ($N^{\cdot-} + N \rightleftharpoons N + N^{\cdot-}$). As TCNE is added to the solution containing TCNE anion radical, the sharp nine lines in the spectrum (due to four equivalent nitrogen atoms) will begin to broaden and coalesce into a broad spectrum and finally at very high concentration of TCNE, only one sharp line is obtained (Fig. 9.4). $CuSO_4 \cdot 5H_2O$ also exhibits such an effect since it has two distinct sites per unit cell. Since the exchange interaction depends on the distance between the paramagnetic centres, it can be minimised by magnetic dilution. Note that in dilute solutions, the paramagnetic centres may come into contact with one another due to random molecular motion in a liquid. If the temperature is raised, the increased rate of molecular collisions results into greater exchange interaction and broadening of hyperfine lines.

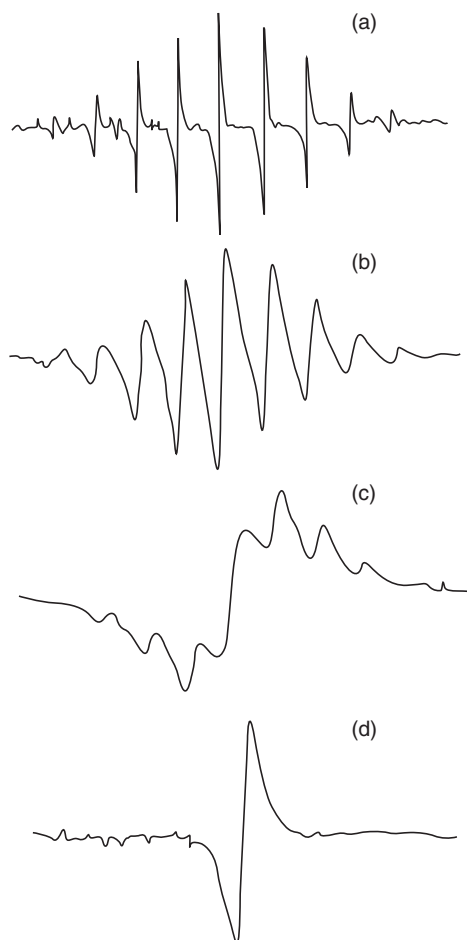


Fig. 9.4 ESR spectra of tetracyanoethylene anion radical ($TCNE^{\cdot-}$ or $N^{\cdot-}$) as a function of the transfer rate: no neutral TCNE is present (a) and the concentration of TCNE grows from (b) to (d).

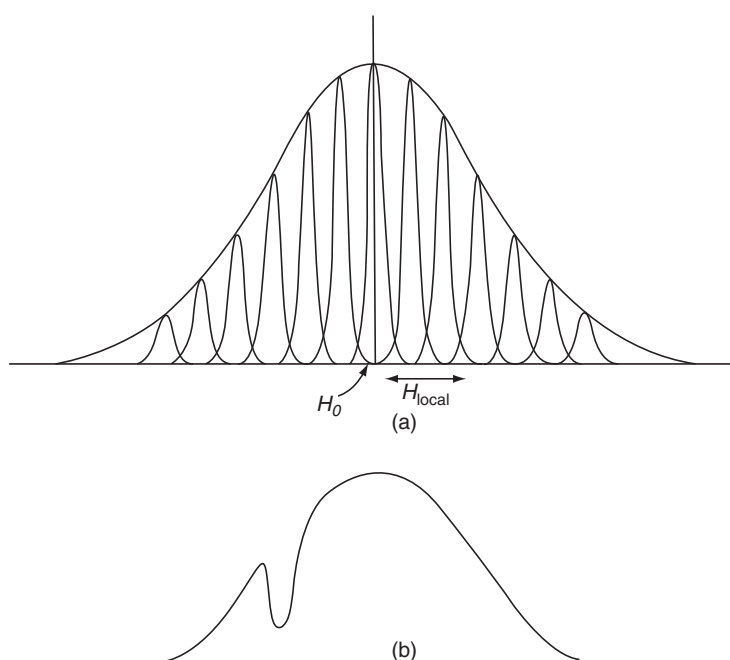


Fig. 9.5 Hole burning in inhomogeneously broadened line: (a) initial line, and (b) localised saturation develops and appears as hole.

The residual anisotropy in a viscous medium produces line broadening. This is termed as motional narrowing since free motion of the paramagnetic molecules if they are large is restricted. This effect can be reduced by raising the temperature.

Incident microwave energy also influences the line width. When the microwave power is increased, the lifetime of spin state increases and broadening of ESR line occurs up to the moment when the line completely disappears. This process is known as *microwave power broadening* or *saturation broadening* of a homogeneous line. The width of homogeneous broadened line is determined by Eq. (9.11).

Note that broadening of ESR lines may occur homogeneously or inhomogeneously. Homogeneous broadening results when all the spins have identical environment whereas inhomogeneous broadening arises when spins are in different environment [Fig. 9.5 (a) and (b)]. The inhomogeneous broadening arises due to the selective saturation of some particular population of spins. The intensity of line corresponding to such spins becomes zero and has indeed been observed. The resonance line shows typical holes and the process is called '*burning a hole*'. Most of the ESR spectra are inhomogeneously broadened, which may be due to irregularities in the external magnetic field and also due to heterogeneities in the samples. Anisotropies in the dipolar interaction in most of the powdered samples alter the inhomogeneous broadening. Inhomogeneous line broadening is also shown by viscous liquids.

9.6 g-VALUE AND FACTORS AFFECTING ESR LINES

Various ESR spectrometers use different frequencies and various types of samples require different frequencies for the experiment. For that reason the position of ESR lines cannot be indicated by the frequencies. The line positions are instead denoted in terms of '*g-value*' which is expressed as a function of microwave frequency (ν) and external magnetic field (H) at resonance. From Eq. (9.7), we obtain

$$g_e = \frac{h\nu}{\beta_e H} \quad (9.15)$$

As mentioned earlier, the g_e value of a free electron is 2.0023 due to a relativistic correction, whereas the g -values for free radicals in atoms, molecules and crystals depend on their electronic structure. This quantity specifies the strength of the interaction of a given electron with the applied magnetic field and is the spectroscopic gauge of the magnitude of the magnetic moment of the electron under study.

$$\mu_e = -g \beta_e \sqrt{S(S+1)} \quad (9.16)$$

The quantum mechanical expression for the Lande splitting factor is

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (9.17)$$

According to Russell–Saunders coupling, the total angular momentum of atom (characterised by quantum number J) is the sum of orbital angular momentum (characterised by quantum number L) and spin angular momentum (characterised by quantum number S), i.e.

$$J = L + S$$

$$J = L + S, L + S - 1, L + S - 2, L + S - 3, \dots, |L - S|$$

For

$$L \geq S \quad J = 2S + 1$$

$$L \leq S \quad J = 2L + 1$$

Accordingly, a set of terms of an atom with one and two electrons is given in Tables 9.2 to 9.4.

Table 9.2 Singlet terms of an atom with two electrons ($S = 0, J = L$).

Term	L		J		
^1S	0	0			
^1P	1		1		
^1D	2			2	
^1F	3				3

Table 9.3 Triplet terms of an atom with two electrons ($S = 1, J = L + 1, L, L - 1$).

Term	L		J			
^3S	0		1			
^3P	1	0	1	2		
^3D	2		1	2	3	
^3F	3			2	3	4

Table 9.4 Doublet terms of an atom with one outer electron ($S = 1/2, J = L + S$) and the Lande splitting factor.

Term	L	J			
		$\frac{1}{2}$	$\frac{1}{2}, \frac{3}{2}$	$\frac{3}{2}, \frac{5}{2}$	$\frac{5}{2}, \frac{7}{2}$
^2S	0	2			
^2P	1	g	$\frac{2}{3}, \frac{4}{3}$		
^2D	2			$\frac{4}{5}, \frac{6}{5}$	
^2F	3				$\frac{6}{7}, \frac{8}{7}$

For a free electron $L = 0, J = S = \frac{1}{2}$. Therefore, $g = 2.0$ (by Eq. 9.17).

All free radicals and some ionic crystals have $g = 2.0 \pm 0.003$. In free radicals, the electron is not localised in a particular orbital but it can move about freely over the orbitals encompassing the whole molecule so the spin orbit coupling constant of the parent atoms is small and the orbital degeneracy, i.e. electronic excited states, is removed or quenched. Consequently, the other contributions to magnetic moment other than those from electron spin are very small ($< 1 : 10^4$); the electron behaves as an electron in free space having $L = 0$, i.e. $g = 2.0$ [by Eq. (9.17)].

In transition metal systems, the electron is localised in a particular orbital about the atom, so the parent nucleus has large spin-orbital coupling constant and accessible orbital degeneracy. Consequently, the magnetic moment contains additional contribution and observed g -value differs significantly from 2.0. It is found to vary in the range 0.2–8 in some ionic crystals. In such cases, L couples with S to give g -values according to Eq. (9.17). The g -value of 2.0 in some ionic crystals may come in two ways: (i) When the electron in an ion is in S state, ($L = 0$); $g = 2$, e.g. ground state of Mn (II) with five d unpaired electrons (i.e. $S = 5/2, 2S + 1 = 6$) has zero orbital momentum. Thus $L = 0, J = S$ and the term symbol is $^6S_{5/2}$. By Eq. (9.17), $g = 2$. (ii) The internal crystal field (electric field due to ions in a crystal) may break down the L - S coupling and on application of external magnetic field, the electron spin precesses independently about the applied field direction. In such a case the value of L is immaterial and g becomes ~ 2 . On the other hand, if internal crystal field is weak or if the paramagnetic electron is well shielded from the field (rare earth metals), then L couples with S to give resultant J which itself precesses about the direction of the applied field and g is given by Eq. (9.17). Further when L and S are only partly uncoupled, the residual orbital contribution to the energy results in a g -value not easily predictable theoretically.

In transition metal systems, the additional contribution to g -value (2.0023) by orbital degeneracy and spin-orbital coupling is termed as orbital paramagnetism. This shifting of g -value is because of mixing via spin orbital coupling of metal orbitals involved in molecular orbitals containing the unpaired electron (s) with the empty or filled ligand orbitals. When mixing takes place with empty ligand orbitals, the result is negative shift ($g - \Delta g$) whereas positive shift ($g + \Delta g$) results when mixing is with filled ligand orbitals. The shift depends upon the amount of unpaired electron density at the donor sites of the ligands, i.e. on the degree of covalency of the complex. The degree of covalency increases as the value of Δg decreases.

Furthermore, the orbital paramagnetism reflects the ability of an unpaired electron to migrate from its parent orbital into other orbitals related to the original orbital by rotations about one or another coordinate axis. The rotational relationships of the d -orbitals are listed in Table 9.5, which shows that the rotational tendencies may be different about the X, Y, Z axes, e.g. rotation about Z -axis has no effect on d_{z^2} while rotation about X or Y axis takes d_{z^2} into d_{yz} or d_{xz} with a strength of $\sqrt{3}$.

Table 9.5 First-order perturbation solutions matrix elements for the g -tensor ($S = 1/2$) rotational properties of the real d -orbitals.

Term		L_x	L_y	L_z
e_g	d_{z^2}	$-i\sqrt{3}d_{yz}$	$i\sqrt{3}d_{xz}$	0
	$d_{x^2-y^2}$	$-id_{yz}$	$-id_{xz}$	$2id_{xy}$
t_{2g}	d_{xy}	id_{xz}	$-id_{yz}$	$-2id_{x^2-y^2}$
	d_{xz}	$-id_{x^2-y^2}$	$-i\sqrt{3}d_{z^2} + id_{x^2-y^2}$	id_{yz}
	d_{yz}	$id_{x^2-y^2} + i\sqrt{3}d_{z^2}$	id_{xy}	$-id_{xz}$

$g_i = g_e + \frac{n_i \lambda}{\Delta_i}$; $i = x, y, z$; $n_i = 2$. < matrix element >, n_i is an integer and may have positive or negative value. + refers to the mixing of the electron with an empty orbital and – refers to the mixing of the electron with a filled orbital. The value of n_i may also be obtained from the magic pentagon (Fig. 9.6). For electronic transition between $d_{x^2-y^2}$ and d_{xy} ; $n = 8$. For electronic transition between $d_{x^2-y^2}$ and d_{yz} ; $n = 2$; $10 Dq = \Delta = E_{e_g} - E_{t_{2g}}$, λ -spin-orbital coupling constant of free ion, e.g. for an electron in $d_{x^2-y^2}$ the matrix element for rotation into d_{xy} is: $\langle xy | L_z | x^2 - y^2 \rangle = 2i$; $n = 2$. $(2i)^2 = -8$; $g_z = 2 - \frac{8\lambda}{\Delta_{(xy \rightarrow x^2-y^2)}}$. For square planar Cu(II), $\lambda = -830 \text{ cm}^{-1}$, $\Delta_{(xy \rightarrow x^2-y^2)} = 16000 \text{ cm}^{-1}$; $g_z = 2 + 0.42 = 2.42$. $1 \text{ cm}^{-1} = 10 \text{ kG}$.

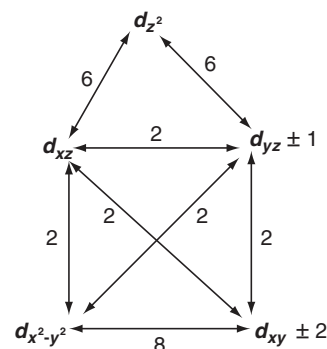
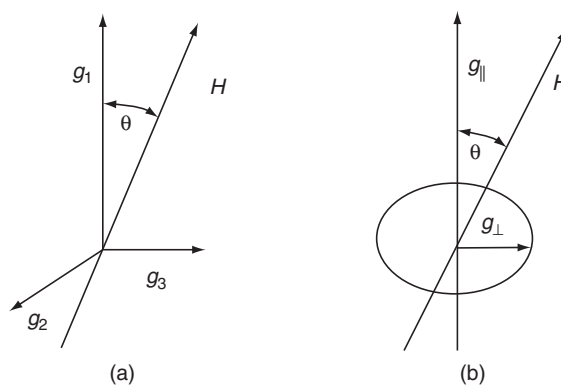
The total magnetic moment has contribution from both the spin and orbital magnetic moments and will also thus vary with the direction of the molecule in the applied magnetic field. Consequently, g -factor being the spectroscopic manifestation of magnetic moment will also be orientation dependent, i.e. it is anisotropic.

In single crystals, the g -value depends on the direction of the applied field in relation to the crystallographic or molecular axes X , Y and Z . Z -direction is defined coincident with the highest fold rotation axis which can be determined by x -ray technique. In polycrystalline samples (powdered samples) a set of g_1 , g_2 and g_3 [Fig. 9.7(a)] are used to define the anisotropy of the g -value, i.e.

$$g^2 = g_1^2 l_x^2 + g_2^2 l_y^2 + g_3^2 l_z^2 \quad (9.18)$$

where $l_x^2 = \sin^2 \theta \cos^2 \varphi$; $l_y^2 = \sin^2 \theta \sin^2 \varphi$ and $l_z^2 = \cos^2 \varphi$ are the normalised direction cosines of the g -tensor. The anisotropy of g -value causes an asymmetry of ESR absorption line one for each of the three mutually perpendicular orientations of the paramagnetic centre with respect to the magnetic field. For cubic crystals, $g_1 = g_2 = g_3$ or $g_{\min} = g_{\text{mid}} = g_{\max}$ or $g_x = g_y = g_z$, where the subscripts min., mid., max. refer to the smallest, intermediate and largest values of g . The ESR spectrum is being described as cubic or isotropic [Figs 9.2/9.3(a) and (b)]. For crystals having axial symmetry, i.e. tetragonal crystals, $g_1 = g_2 < g_3$, or $g_1 = g_2 > g_3$; the spectrum is described as tetragonal. The identical pair, i.e. $g_1 = g_2$ is referred as $g_{\perp}$ whereas the unique g -value is called $g_{\parallel}$ [Figs 9.7(b), 9.8, 9.9(a) and (b)]. For rhombic crystals, $g_1 \neq g_2 \neq g_3$, the spectrum is described as rhombic [Figs 9.9(c) and (d)].

Experimentally observed, ESR spectrum of some molecule or ion in solution phase is also shown in Figs 9.9(e) and (f).

**Fig. 9.6** Magic pentagon: M_i stands for values of different orbitals.**Fig. 9.7** (a) Relations between the directions associated with g_1, g_2, g_3 and H , and (b) relations between the directions associated with $g_{\parallel}, g_{\perp}$ and H .

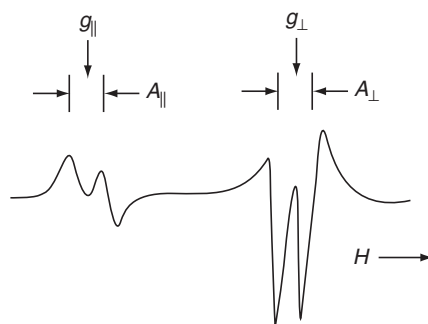


Fig. 9.8 ESR spectrum of Ag(II) in nitric acid at 77K.

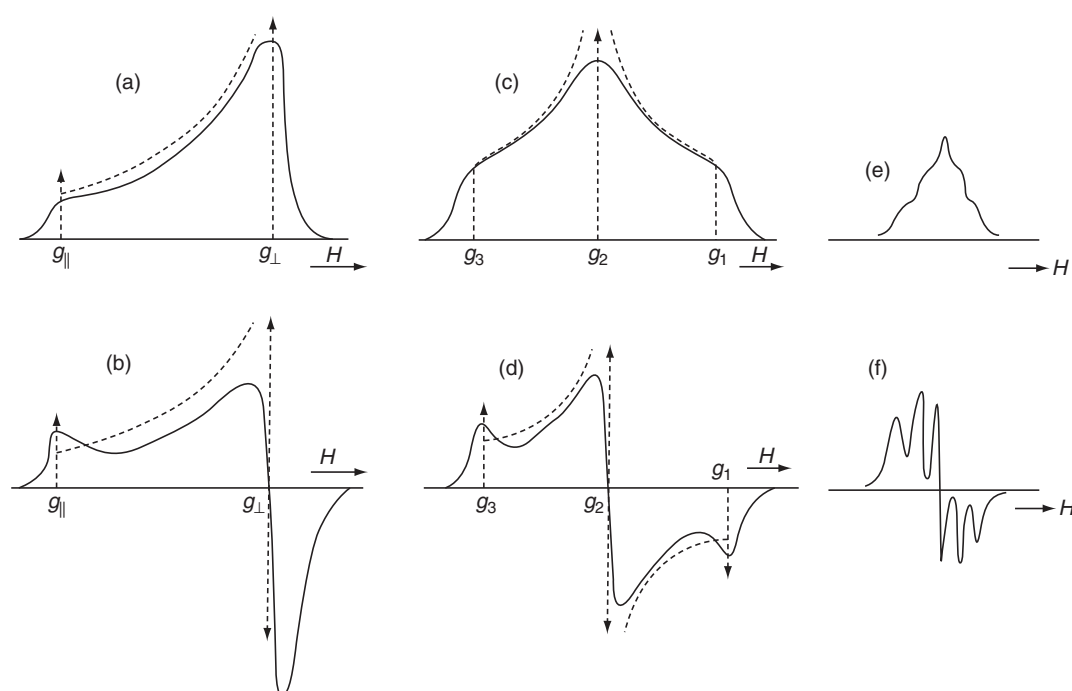


Fig. 9.9 (a) and (b) Axial symmetry $g_{\parallel} \neq g_{\perp}$ ($g_{\parallel} > g_{\perp}$): (a) absorption spectra; (b) first derivative spectrum. For $g_{\parallel} < g_{\perp}$: ESR spectra are obtained by inverting curves (a) and (b). (c) and (d): An asymmetry g -tensor $g_1 < g_2 < g_3$, (c) absorption spectrum, (d) first derivative spectrum, (e) experimentally observed absorption spectrum and (f) first derivative spectrum of some free radical in the solution phase.

In bulk susceptibility measurements, a powdered sample or frozen solution is used and hence g works out as an average (g_{av}). The g_{av} value for a tetragonal complex is given by

$$\begin{aligned} g_{av}^2 &= \frac{1}{3}(g_x^2 + g_y^2 + g_z^2) \\ &= \frac{1}{3}(g_{\parallel}^2 + 2g_{\perp}^2) \end{aligned} \quad (9.19)$$

or approximately as,

$$g_{av} \approx \frac{1}{3}(g_{\parallel} + 2g_{\perp}) \quad (9.20)$$

For $S = \frac{1}{2}$ systems, anisotropy in g can be considered in terms of two limiting cases:

(i) $\Delta \gg \lambda$; e.g. Cu^{2+} , Mo^{5+} and low spin Co^{2+} .

Then,

$$g_i = g_e + \frac{n_i \lambda}{\Delta_i} \quad i = x, y, z \quad (\text{From Table 9.5}) \quad (9.21)$$

λ has a positive value for d^1-d^4 . The use of this equation has been elaborated in Table 9.5. This relation holds good provided $\lambda/\Delta \leq 0.1$. Covalency effects reduce the magnitude of λ and this is accommodated in Eq. (9.21) by multiplying the last term by α^2 , the fraction of unpaired electron confined to the metal. Thus Eq. (9.21) becomes

$$g_i = g_e + \frac{n_i \lambda \alpha^2}{\Delta_i} \quad i = x, y, z \quad (9.22)$$

- (ii) $\Delta \approx \lambda$, e.g. low-spin Fe(III) as found in haeme proteins. In low-spin Fe(III), the single unpaired electron is found in the configuration $(t_{2g})^5$, specifically $(d_{xy})^2, (d_{xz})^2, (d_{yz})^1$. These orbitals are nondegenerate and the differences in energy between them is described in terms of two parameters V and Δ . Δ is a measure of the strength of the Z -directed axial ligand field perturbation which stabilises d_{xy} with respect to the centre of gravity of d_{xy} and d_{yz} , whereas V is a measure of the strength of the rhombic (X, Y) perturbation and is the energy separation between d_{xy} and d_{yz} . V and Δ can be obtained directly from g -values.

$$\frac{V}{\lambda} = \frac{g_x}{g_z + g_y} + \frac{g_y}{g_z - g_x} \quad (9.23)$$

$$\frac{\Delta}{\lambda} = \frac{g_x}{2(g_z + g_y)} - \frac{g_y}{2(g_z - g_x)} \quad (9.24)$$

Δ is an index of the crystal field intensity at the iron centre and ratio V/Δ is a measure of the magnitude of the distortion imposed upon the iron atom by the six pseudo-octahedrally disposed ligands.

9.7 HYPERFINE INTERACTION

When the unpaired electron in the molecule is delocalised over the whole or at least a large part of it, it may interact with the many nuclei possessing magnetic moment in the molecule to cause a further splitting of the electron resonance line. This type of magnetic interaction between the electron and the nuclear spins in the same molecule is known as *hyperfine coupling* and produces ESR spectra with hyperfine splitting, i.e. spectra with a number of lines. From the number of lines, their relative intensities and their separation, one can determine the type and number of nuclear spins which interact with the electron, i.e. the structure of free radical. The line separation depends on the interaction between the electron spin and each nuclear spin, and on the magnetic moment of the involved nuclei.

The nuclei spin (I) in an external magnetic field have the restricted orientations: $I, I-1, I-2, I-3, \dots, 0, \dots, -(I-1), -I$. In this way, the number of nuclear spin quantum numbers $M_I = 2I + 1$, i.e. they split an electron magnetic level into $2I + 1$ sublevels.

The energies of a coupled level are given by

$$E = g_e \beta_e H M_S + E_{\text{loc}} \quad (9.25)$$

The second term on the right-hand side of Eq. (9.25), i.e. E_{loc} , appears due to local magnetic fields at the electron produced by the nuclei.

Single nucleus of $I = \frac{1}{2}$, e.g. ^1H , ^{19}F , ^{13}C and ^{31}P and single deuterium or nitrogen nucleus (^2H or ^{14}N ; $I = 1$) exhibit hyperfine splitting. Hyperfine splitting in poly-atomic radicals by ^6Li , ^7Li , ^{10}B , ^{11}B , ^{23}Na and ^{39}K have also been reported as have been splittings by nuclei of transition elements, rare earths, and trans uranic elements in compounds.

9.8 TYPES OF HYPERFINE INTERACTIONS

There are two types of hyperfine interactions that give rise to hyperfine splittings: (i) Contact or Fermi hyperfine interaction, and (ii) anisotropic hyperfine interaction.

9.8.1 Contact or Fermi Hyperfine Interaction

This is a quantum mechanical interaction that depends on the electron spin density in the immediate vicinity of the nucleus. This interaction is isotropic (orientation independent) and, therefore, also known as isotropic hyperfine interaction. We know that the electron spin density is nonzero for electrons in s -orbitals, and consequently

the Fermi interaction can take place. On the other hand, the wave function for electrons in p , d , f and higher orbitals have a node at the nucleus so that the electron density vanishes at that point and no contact interaction takes place.

(a) ESR Spectrum due to Single Proton The contact interaction energy (E_{loc}) for hydrogen atom is given by

$$E_{\text{loc}} = h A M_S M_I \quad (9.26)$$

where A (in MHz) is a frequency factor (also called the isotropic hyperfine coupling constant and is written as $A_{\parallel}$, when the interaction is parallel to the direction of the applied field) that can be computed from the square of the wave function evaluated at the nucleus. Thus, Eq. (9.25) can be written as

$$E = g_e \beta_e H M_S + h A M_S M_I \quad (9.27)$$

In a strong applied magnetic field, the first-order energies, i.e. $g_e \beta_e H M_S$, are 10^3 fold or more than the contact interaction energies.

For a system of one paramagnetic electron and a nucleus with $S = \frac{1}{2}$ and $I = \frac{1}{2}$, there are two possible orientations $\left(\pm \frac{1}{2}\right)$ for the magnetic moment of nucleus in an external magnetic field, i.e. $M_I = \pm \frac{1}{2}$. The energy of these nuclear spin states affects the energy levels of an electron ($E_{+1/2}$ and $E_{-1/2}$) and split them into four sublevels (E_1 , E_2 , E_3 and E_4). This process of splitting electron energy levels into sublevels by nuclear magnetic levels is known as the Zeeman hyperfine splitting for nucleus, i.e. proton in the present case [Fig. 9.10(a)].

The energies of the four sublevels can be written in order of decreasing energy as

$$\begin{aligned} E_1 &= \frac{1}{2} g_e \beta_e H + \frac{hA}{4} \text{ for } M_S = +\frac{1}{2} \text{ and } M_I = +\frac{1}{2} \\ E_2 &= \frac{1}{2} g_e \beta_e H - \frac{hA}{4} \text{ for } M_S = +\frac{1}{2} \text{ and } M_I = -\frac{1}{2} \\ E_3 &= -\frac{1}{2} g_e \beta_e H + \frac{hA}{4} \text{ for } M_S = -\frac{1}{2} \text{ and } M_I = -\frac{1}{2} \\ E_4 &= -\frac{1}{2} g_e \beta_e H - \frac{hA}{4} \text{ for } M_S = -\frac{1}{2} \text{ and } M_I = +\frac{1}{2} \end{aligned} \quad (9.28)$$

Transition between energy levels E_1 and E_3 and levels E_2 and E_4 are not permissible since they require a simultaneous absorption and emission of energy by both the electron and the nucleus. As stated earlier, when the electron absorbs microwave energy and flips from one spin state to the other, it does so with no change in M_I . However, M_I will change if irradiation is done with oscillating radio frequency field of energy ($h\nu$). Thus, the selection rules are

- (i) $\Delta M_S = \pm 1$ and $\Delta M_I = 0$ for allowed transitions
 (ii) $\Delta M_S = \pm 1$ and $\Delta M_I = \pm 1$ for forbidden transitions

Applying the selection rules from Eq. (9.29) to the Eq. (9.28), we obtain the energy change for the two transitions as,

$$\Delta E_{1-4} = E_1 - E_4 = g_e \beta_e H + \frac{hA}{2} \text{ for } M_I = +\frac{1}{2} \quad (9.30)$$

$$\Delta E_{2-3} = E_2 - E_3 = g_e \beta_e H - \frac{hA}{2} \text{ for } M_I = -\frac{1}{2} \quad (9.31)$$

At constant external magnetic field, the transition from level E_4 to level E_1 occurs at higher frequency (ν_2) than the transition from level E_3 to level E_2 which occurs at (ν_1). The difference between the two frequencies is called the *hyperfine frequency* ($\Delta\nu$) and is equal to A (MHz). In other words, we can say that in a constant magnetic field, the transition in energy differs by the isotropic hyperfine coupling constant (A).

In an ESR experiment, the frequency ν usually is fixed and the applied field is varied until resonance is achieved where $\Delta E = h\nu$ and $H = H_r$. Substituting these relationships in Eqs (9.30) and (9.31), we obtain

$$\Delta E_{1-4} = h\nu = g_e \beta_e H_{1-4} + \frac{hA}{2} \quad (9.32)$$

$$\Delta E_{2-3} = h\nu = g_e \beta_e H_{2-3} - \frac{hA}{2} \quad (9.33)$$

Rearranging Eqs (9.32) and (9.33), we get the resonant fields at which the electron resonance transitions occur:

$$H_{1-4} = \frac{h\nu}{g_e \beta_e} - \frac{a}{2} \quad \text{for } M_I = +\frac{1}{2} \quad (9.34)$$

$$H_{2-3} = \frac{h\nu}{g_e \beta_e} + \frac{a}{2} \quad \text{for } M_I = -\frac{1}{2} \quad (9.35)$$

At constant frequency [Fig. 9.10(a)], the transition from level E_1 to E_4 occurs at a lower magnetic field than the transition from level E_2 to E_3 . The two normal absorption and their corresponding first derivative signals for the two transitions are shown in Fig. [9.10(b)]. The separation between the two signals is

$$\Delta H = H_{2-3} - H_{1-4} = \frac{hA}{g_e \beta_e} = a \quad (9.36)$$

The value of $\Delta H = a = \frac{hA}{g_e \beta_e}$ is called the *hyperfine splitting constant (HSC)* and expresses in gauss (G) the separation between two hyperfine lines in the spectrum.

(b) Quantum Mechanical Considerations of ESR Spectra of Hydrogen Atom The general Hamiltonian used in the analysis of ESR spectra due to radicals is given by

$$H = H_{\text{Zeeman}} + H_{d-d} + H_c \quad (9.37)$$

where, H_{Zeeman} refers to the interaction of electron and the nucleus with the applied magnetic field, H .

$$H_{\text{Zeeman}} = g_e \beta_e S H - g_N \beta_N I H \quad (9.38)$$

where the symbols have their conventional meanings; S and I are respectively, the electronic and nuclear spin vectors, g_e and g_N are the Lande factors for the electron and nucleus, β_e and β_N are the electron Bohr magneton and nuclear magneton.

H_{d-d} refers to the classical $d-d$ interaction between electron and nuclear magnetic moments.

$$H_{d-d} = g_e \beta_e g_N \beta_N \left[\frac{S \cdot I}{(r_e - r_n)^3} - \frac{3(S \cdot r)(I \cdot r)}{(r_e - r_n)^5} \right] \quad (9.39)$$

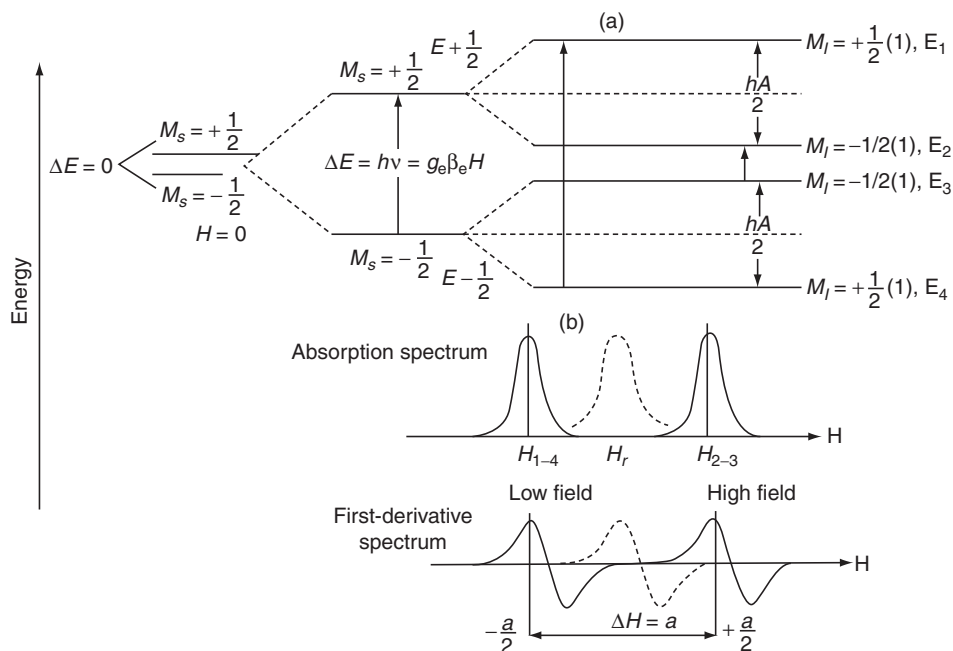


Fig. 9.10 (a) Energy levels of the hydrogen atom (system: $S = 1/2$, $I = 1/2$) in a variable applied magnetic field and constant frequency ($\nu = \text{constant}$), and (b) absorption and first derivative spectra of hydrogen atom.

where, r_e and r_n , refer to the vector position of electron and nucleus respectively. For dilute solutions of free radicals, the electron-electron interaction, i.e. interaction between unpaired electrons on different molecules can be neglected.

H_c refers to the Fermi contact interaction and does not vanish in solution.

$$H_c = g_e \beta_e g_N \beta_N \cdot \frac{8\pi}{3} \cdot S \cdot I \cdot \delta(r_e - r_n) \quad (9.40)$$

Here, $\delta(r_e - r_n)$ is known as the Dirac delta function. $\delta(r_e - r_n) \neq 0$, provided the wave function of the unpaired electron in the radical has a non-vanishing value at the nucleus.

The total energy due to various magnetic interactions is given by

$$E = \int \psi H \psi d\tau \quad (9.41)$$

where ψ contains both the space and the spin part of the wave function of the electron.

If the spin part of the wave function is denoted by ψ_α or ψ_β then

$$\int \psi_\alpha (g_e \beta_e S \cdot H) \psi_\alpha d\tau = \frac{1}{2} g_e \beta_e H \quad (9.42)$$

$$\int \psi_\beta (g_e \beta_e S \cdot H) \psi_\beta d\tau = -\frac{1}{2} g_e \beta_e H$$

In general, we write

$$\int M_S (g_e \beta_e S \cdot H) M_S d\tau = g_e \beta_e H M_S \quad (9.43)$$

In solution, $H_{d-d} = 0$. The nuclear Zeeman interaction, being very small as compared to its electron counterpart is also neglected. In a strong applied field, there is no interaction between the orbital and spin angular momenta but both the momenta interact independently with the applied field. This is known as Paschen–Back effect. This effect manifests itself in the ESR and NMR spectra. In the Paschen–Back region the strength of applied field is greater than the multiplet splittings and only the normal Zeeman effect is observed even when doublets studies doubts or higher spin states are present. In principle, the ESR alike NMR studies can be performed at any magnetic field but the usual studies are always preferred in the Paschen–Back region. Equation (9.41) in the Paschen–Back region becomes

$$\begin{aligned} E &= \int \psi [g_e \beta_e S \cdot H + g_e \beta_e g_N \beta_N \frac{8\pi}{3} S \cdot I \delta(r_e - r_n)] \psi d\tau \\ &= g_e \beta_e H M_S + a M_I M_S \end{aligned} \quad (9.44)$$

Here, a is the hyperfine splitting constant and is given by

$$a = \frac{8\pi}{3} g_e \beta_e g_N \beta_N |\psi(0)|^2 \quad (9.45)$$

$|\psi(0)|^2$ is the probability of finding the unpaired electron in contact with the nucleus giving rise to isotropic coupling. This term vanishes except when the atomic orbital containing the unpaired electron has some s -character. Hartree Fock calculations have made available the theoretical values of $|\psi(0)|^2$ for elements of the Periodic Table. Applying Eq. (9.44) to hydrogen atom, we get

$$\begin{aligned} E_1 &= \frac{1}{2} g_e \beta_e H + \frac{a}{4} \quad \text{for } M_S = +\frac{1}{2} \text{ and } M_I = +\frac{1}{2} \\ E_2 &= \frac{1}{2} g_e \beta_e H - \frac{a}{4} \quad \text{for } M_S = +\frac{1}{2} \text{ and } M_I = -\frac{1}{2} \\ E_3 &= -\frac{1}{2} g_e \beta_e H + \frac{a}{4} \quad \text{for } M_S = -\frac{1}{2} \text{ and } M_I = -\frac{1}{2} \\ E_4 &= -\frac{1}{2} g_e \beta_e H - \frac{a}{4} \quad \text{for } M_S = -\frac{1}{2} \text{ and } M_I = +\frac{1}{2} \end{aligned} \quad (9.46)$$

By selection rules $\Delta M_S = \pm 1$ and $\Delta M_I = 0$, the two permissible transitions are

$$\Delta E_{1-4} = E_1 - E_4 = g_e \beta_e H + \frac{a}{2} \quad (9.47)$$

$$\Delta E_{2-3} = E_2 - E_3 = g_e \beta_e H - \frac{a}{2} \quad (9.48)$$

The two resonance lines are presented in Fig. 9.11.

For a system in which more than one type of proton interacts with the unpaired electron, Eq. (9.44) may be written as

$$E = g_e \beta_e H M_S + a_1 M_S \sum_{i=1}^n M_{I(i)} + a_2 M_S \sum_{i=1}^n M_{I(i)} + \dots \quad (9.49)$$

where n is the number of protons of a particular type, $a_1, a_2, \dots$ are the hyperfine constants for protons of type 1, 2, ... a is expressed either in MHz or in gauss. The conversion from one unit to the other is given by:

$$a(G) = 0.35683 \left(\frac{g_{\text{free electron}}}{g_{\text{radical}}} \right) a(\text{MHz}) \quad (9.50)$$

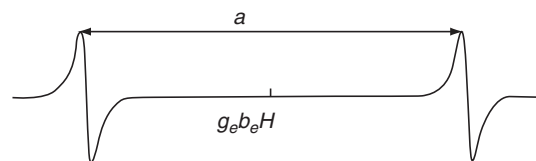


Fig. 9.11 First derivative ESR spectrum of hydrogen atom.

The hydrogen atom produced by electric discharge or trapped in solids exhibits two-line ESR spectrum. The separation between the two lines has been found to be 506 G (calc. 539.866). This is incidently the largest splitting for a proton since the unpaired electron is in the 1s orbital and so has 100 per cent s character. When two unpaired electrons are present in a molecule, i.e. triplet molecule, then we write

$$H_{\text{Zeeman}} = +g_e \beta_e (S_1 + S_2) H - g_N \beta_N I H \quad (9.51)$$

$$H_c = \frac{8\pi}{3} g_e \beta_e g_N \beta_N (S_1 + S_2) \cdot I \cdot \delta(r_e - r_n) \quad (9.52)$$

and

$$H_{d-d} = g_e^2 \beta_e^2 \left[\frac{S_1 \cdot S_2}{r^3} - \frac{3(S_1 \cdot r)(S_2 \cdot r)}{r^5} \right] \quad (9.53)$$

Here, S_1 and S_2 (the spin angular momentum vectors) refer to electrons 1 and 2 and r is the vector joining them.

Problem 9.2: Express the hyperfine coupling frequency ($\Delta\nu$) in terms of hyperfine splitting constant (a) for $g = 2.0023$.

Solution We know that $\Delta\nu = A$ and $a = \frac{hA}{g_e \beta_e}$.

Thus,

$$\Delta\nu = \frac{g_e \beta_e a}{h}$$

For

$$g = 2.0023$$

$$\Delta\nu = \frac{2.0023 \times 9.274 \times 10^{-21} (\text{erg G}^{-1}) a(G)}{6.625 \times 10^{-27} (\text{erg s})}$$

$$= 2.80 \times 10^6 a \text{ s}^{-1} = 2.80 a \text{ Mc s}^{-1}$$

$$= 2.80 a \text{ MHz}$$

(c) ESR Spectrum of $\dot{C}H$ (System with $S = 1/2, I = 1/2$) When the magnetic moment of a paramagnetic electron is perturbed by the magnetic field of a nucleus with $I = \frac{1}{2}$ (say proton), the transitions occur at two resonance fields [Fig. 9.10(a)]:

$$H_{1-4} = \frac{h\nu}{g_e \beta_e} - \frac{a}{2} \quad \text{for} \quad M_I = +\frac{1}{2} \quad (9.54)$$

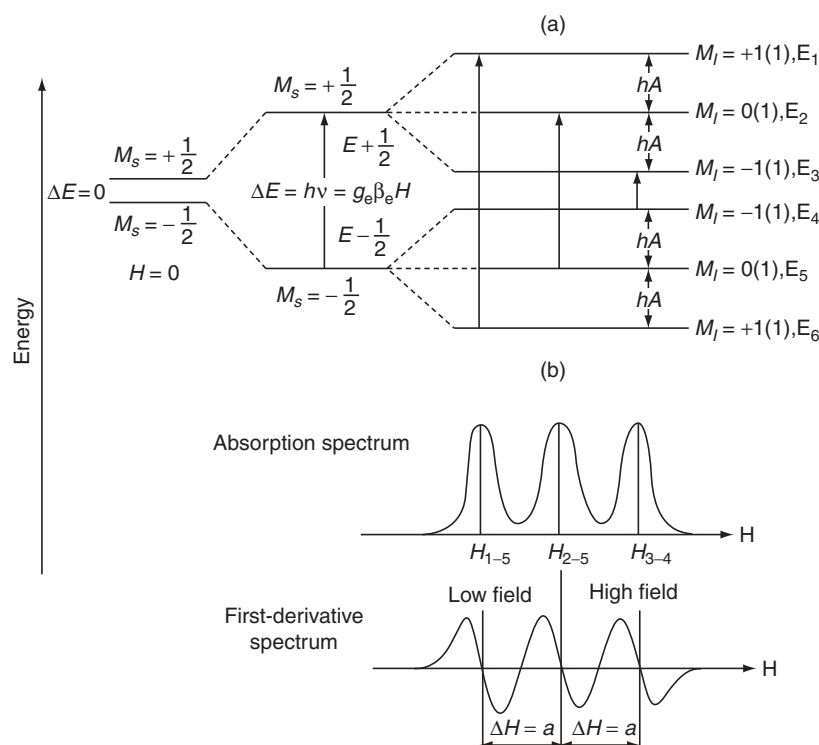


Fig. 9.12 (a) Energy levels of the deuterium atom (system $S = 1/2$, $I = 1$) in variable applied magnetic field and constant frequency ($\nu = \text{constant}$), and (b) absorption and first-derivative spectra of deuterium atom.

$$H_{2-3} = \frac{h\nu}{g_e \beta_e} + \frac{a}{2} \quad \text{for } M_I = -\frac{1}{2} \quad (9.55)$$

The absorption signals corresponding to these transitions are shown in Fig. 9.10(b). ESR spectrum for a system with $S = \frac{1}{2}$ and $I = 1$ [the ^2H -deuterium, nitrogen (^{14}N)]. The number of sublevels in this case is $(2I + 1) = (2 \times 1 + 1) = 3$ and $M_s = +1, 0, -1$. The transition occurs at three resonance fields [Fig. 9.12(a)].

$$H_{1-6} = \frac{h\nu}{g_e \beta_e} - a \quad \text{for } M_I = +1 \quad (9.56)$$

$$H_{2-5} = \frac{h\nu}{g_e \beta_e} \quad \text{for } M_I = 0 \quad (9.57)$$

$$H_{3-4} = \frac{h\nu}{g_e \beta_e} + a \quad \text{for } M_I = -1 \quad (9.58)$$

Thus, the ESR spectrum for such a system consists of three lines of equal intensity as shown in Fig. 9.12(b).

Generally speaking, for a system where a single nucleus interacts with one unpaired electron, $2I + 1$ lines of equal intensity are obtained. They are separated by the hyperfine splitting constant (a).

(d) ESR Spectrum of $\dot{\text{C}}\text{H}_2$ (System with $S = 1/2$, $I = 1/2$, $I = 1/2$) In this system, the total nuclear spin of two equivalent protons $= 2 \times 1/2 = 1$ so M_I can take on $(2 \times 1 + 1) = 3$ possible values, viz., $+1, 0, -1$. Thus the magnetic field of two equivalent protons will split the two paramagnetic electron spin states $\left(M_s = \pm \frac{1}{2}\right)$ into six sublevels characterised by the nuclear spin quantum numbers $M_I = +1, 0, -1, -1, 0, +1$. The splitting is displayed in Fig. 9.13(a). Just like $S = \frac{1}{2}$, $I = \frac{1}{2}$ system, i.e. $\dot{\text{C}}\text{H}$, the transitions for $\dot{\text{C}}\text{H}_2$ system also occurs at three resonant magnetic fields H_{1-6} , H_{2-5} and H_{3-4} except that the degeneracy of the middle transition is two.

$$H_{1-6} = \frac{h\nu}{g_e \beta_e} - a \quad \text{for } M_I = +1 \quad (\text{degeneracy} = \alpha\alpha = 1) \quad (9.59)$$

$$H_{2-5} = \frac{h\nu}{g_e \beta_e} \quad \text{for } M_I = 0 \quad (\text{degeneracy} = \alpha\beta, \beta\alpha = 2) \quad (9.60)$$

$$H_{3-4} = \frac{h\nu}{g_e \beta_e} + a \quad \text{for } M_I = -1 \quad (\text{degeneracy} = \beta\beta = 1) \quad (9.61)$$

Thus, the absorption spectrum of $C \cdot H_2$ consists of three peaks with intensity ratio 1 : 2 : 1 [Fig. 9.13(b)].

The above treatment may be extended to the interaction of a paramagnetic electron with varying number of equivalent protons. The splitting of unpaired electron levels $\left(M_S = \pm \frac{1}{2}\right)$ into sublevels by magnetic field of varying numbers of equivalent protons is shown in Fig. 9.14.

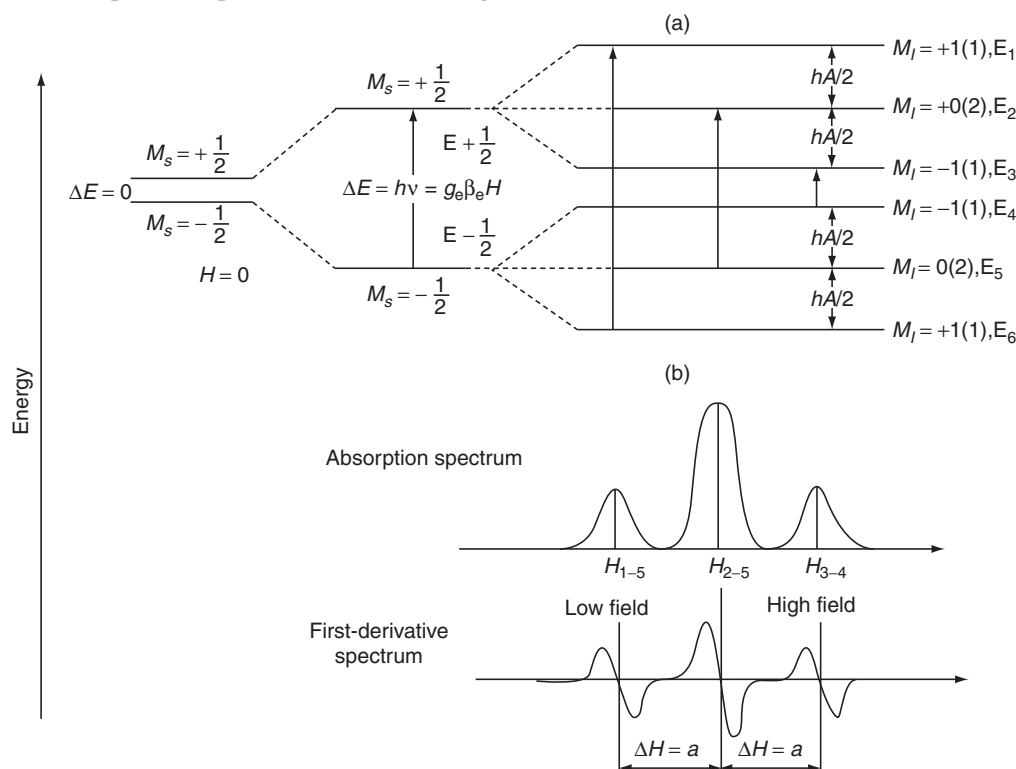


Fig. 9.13 (a) Energy levels of the free radical with two equivalent protons (system: $S = 1/2$, $I = 1/2$) in a variable applied magnetic field and constant frequency ($\nu = \text{constant}$), and (b) absorption and first derivative ESR spectra of $C \cdot H_2$.

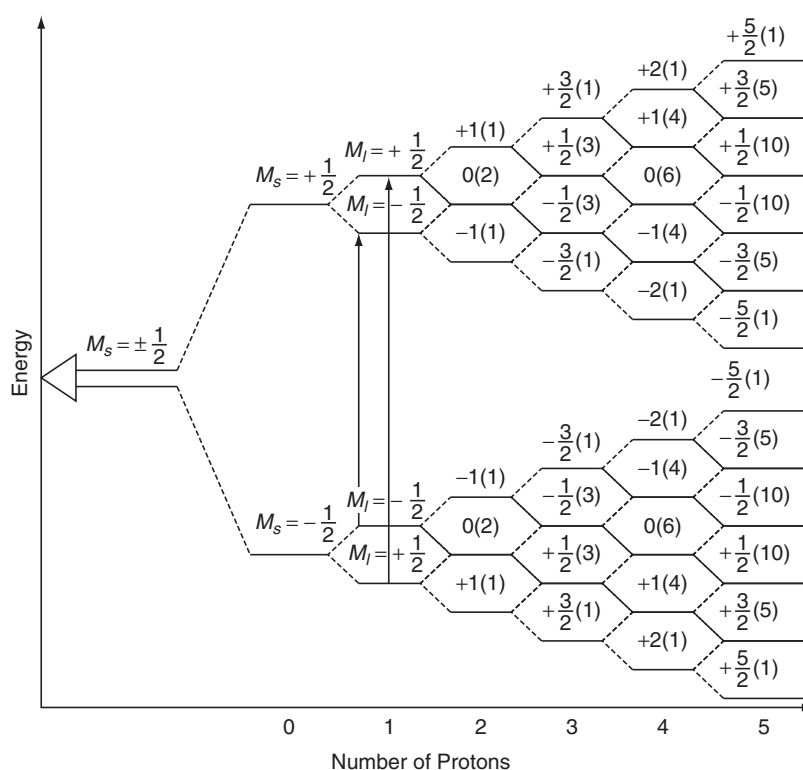


Fig. 9.14 Hyperfine energy levels, arising from the interaction of an unpaired electron with varying numbers of equivalent protons. The quantities with brackets represent the intensity of the lines in a multiplet.

In conclusion, for a system where n equivalent nuclei (protons) interact with one paramagnetic electron, $2nI + 1$ lines are obtained. The intensity of the lines corresponds to the coefficients of the binomial expansion $(1 + x)^n$.

(e) Second-order Splitting When hyperfine coupling energy (hA) is very large as compared to that of the electron energy ($g_e \beta_e H$) or when a small magnetic field is used, additional splitting of some line may occur, which is known as 'second-order splitting' (Fig. 9.15). This is a quantum mechanical effect.

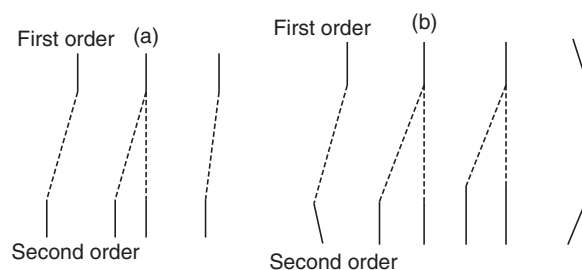


Fig. 9.15 Second order splitting (a) 1:2:1 triplet arising from two equivalent nuclei and $I = 1/2$, (b) for 1:3:3:1 quartet arising from three equivalent nuclei, $I = 1/2$.

9.8.2 Anisotropic Hyperfine Interaction

This is a nonquantum mechanical interaction and is not restricted only to s -electrons. The contribution to splitting by anisotropic splitting as worked out from classical physics is given by $h(\mu_{N(Z)}/r^3)(3\cos^2\theta - 1)$ where $\mu_{N(Z)}$ is the Z -component of nuclear magnetic moment, μ_N at a distance r from a paramagnetic electron with magnetic moment μ_e . r subtends an angle θ with the direction of the applied field. Both μ_N and μ_e are parallel to the applied field direction (Fig. 9.16). $\mu_{N(Z)}$ can take on $2I + 1$ values. The anisotropy in coupling constant has the same angular dependence as the g -value. Thus Eq. (9.27) may be written to take account of anisotropy in both g and A for an axial system as

$$E = \left(\frac{1}{3}g_{\parallel} + \frac{2}{3}g_{\perp} \right) \beta_e H M_S + hA M_I M_S + \left[\frac{1}{3}(g_{\parallel} - g_{\perp}) \beta_e H M_S + hB M_I M_S \right] (3\cos^2\theta - 1) \quad (9.62)$$

Here, B is the anisotropic frequency factor (MHz). It is denoted by $B_{\perp}$, when this interaction is perpendicular to the direction of the applied field. For $M_S = \pm \frac{1}{2}$

$$\Delta E = h\nu = \left(\frac{1}{3}g_{\parallel} + \frac{2}{3}g_{\perp} \right) \beta_e H + AhM_I + \left[\frac{1}{3}(g_{\parallel} - g_{\perp}) \beta_e H + BhM_I \right] (3\cos^2\theta - 1) \quad (9.63)$$

If there is a fast tumbling of molecules in a system (samples in solution), the anisotropic contribution averages to zero and only the isotropic (contact) interaction is left, i.e. Eq. (9.62) reduces to Eq. (9.27). On the other hand, in a powdered sample, the crystals are randomly oriented, and a wide range of angles are present. Consequently, a poorly resolved asymmetric broad line spectrum results as compared to the spectrum in the solution phase, e.g. the spectra of di-*t*-butyl nitroxide in liquid ethanol at 292 K [Fig. 9.17(a)] and in solid gas at 77 K

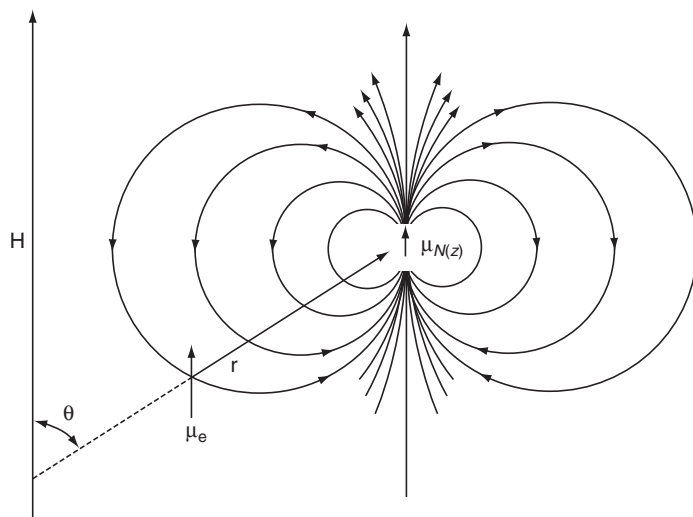


Fig. 9.16 Interaction of nuclear magnetic dipole μ_N and electron magnetic moment μ_e . Magnetic flux lines associated with μ_N are indicated.

[Fig. 9.17(b)] show that the lines are broadened and poorly resolved due to anisotropic effects in the latter as compared to the former. The lines are also shifted in position in the solid glass spectrum as compared to the spectrum in the solution phase. It is to be noted that an asymmetry of the absorption lines in the solid spectra is caused by the anisotropy of the g -values. The anisotropic hyperfine interaction parameters determined from measurements on oriented single crystals of di-*t*-butyl nitroxide radical, with the magnetic field successively applied along each of the three principal axes of the molecule are listed in Table 9.6. The parameters a_x , a_y , and a_z , determined on oriented crystals contain both isotropic and anisotropic contributions to the hyperfine splitting. The value of a_z reveals that the unpaired electron spends most of its time in the $2p\pi$ orbital that lies along the Z -axis.

The experimental values of g and a measured in solution are in good agreement with that calculated from g_x , g_y , g_z and a_x , a_y , a_z respectively measured on the radical in oriented crystals. In general, ESR spectra of systems in a gas phase are complicated since rotational transitions also occur in the microwave region of electromagnetic radiation. However, the spectra of halogen atoms, i.e. F, Cl and Br are simple. These atoms exist in a $^2P_{3/2}$ ($L = 1$, $S = 1/2$, $J = 3/2$) state and give $g = 4/3$. The degeneracy of this state is $(2J + 1)$ and the possible number of transitions corresponding to $(2J + 1)$ will be $2J$. Thus the number of lines expected in the spectra of halogen atoms is $2J(2I + 1)$, i.e. six for fluorine atom and twelve each for chlorine and bromine atoms. This has been experimentally verified in the respective halogen atoms. These effects are not observed in the ESR spectra of solutions and solids since rotational levels are nonquantised and orbital contributions are largely quenched.

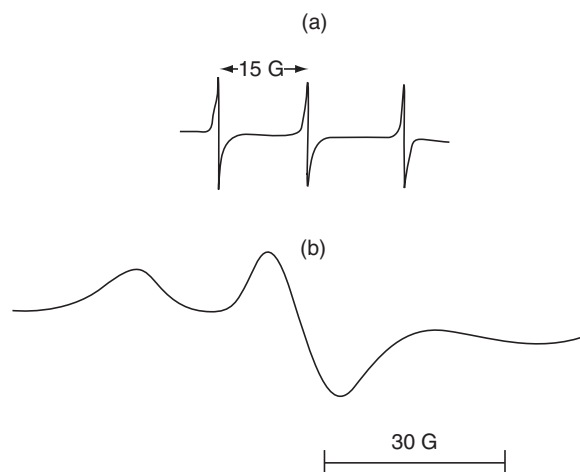


Fig. 9.17 ESR spectrum of di-*t*-butyl nitroxide radical (a) in liquid ethanol (at 292 K), and (b) in solid glass (at 77 K).

Table 9.6 ESR parameters for the di-*t*-butyl nitroxide.

g_x	2.0089
g_y	2.0061
g_z	2.0027
$\frac{1}{3}(g_x + g_y + g_z)$	2.0059
g_e (solution)	2.0060 ± 0.0002
a_x	7.1 ± 0.5
a_y	5.6 ± 0.5
a_z	32.0 ± 1.5
$\frac{1}{3}(a_x + a_y + a_z)$	14.9 ± 0.8
a (solution)	15.1 ± 0.5

* a values are in gauss.

9.9 ZERO-FIELD SPLITTING (FINE STRUCTURE TERMS) AND KRAMER'S DEGENERACY

There are certain systems which contain more than one paramagnetic electron (even or odd 1) rather than a single unpaired electron. When the number of electrons is even, the two electrons may be present on the same atom or one electron each on the two atoms of a dimer. The degeneracy of spin states of electrons in such atoms is resolved by the internal magnetic field (δH) of the electrons even in the absence of an external magnetic field. This phenomenon of removal of degeneracy of spin states by the internal magnetic field of paramagnetic electrons is termed as *zero-field splitting* and is also called *fine splitting* rather than hyperfine splitting and occurs mainly in crystals [Fig. 9.18(b)]. Such a resolution of spin states is encountered in systems having noncubical crystal fields, e.g. trigonal, tetragonal and rhombic, spin-orbit and spin-spin interactions. When the system contains an odd number of electrons, the spin degeneracy of energy level (and no $M_s = 0$ state) remains doubly degenerate;

this is known as *Kramer's degeneracy* which can be removed only by the application of an external magnetic field. For even number of paramagnetic electrons, the spin degeneracy may be resolved by the crystal field.

For a system with two unpaired electrons on the same atom ($S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$, $S = 1$ and $M_S = +1, 0, -1$), the state S is made up of two unpaired electrons, i.e. S_1 and S_2 . Each of the electrons generates a small internal magnetic field (δH) which contributes to the external field. When the spins of the electrons are parallel to the applied field (H), the field experienced by the system will be $H + \delta H$ while $H - \delta H$ when the spins are anti-parallel to the applied field direction, i.e. spin state $M_S = +1$ will sense a magnetic field $H + \delta H$, and spin state $M_S = -1$ will sense a magnetic field $H - \delta H$, both the states shift upward by a factor D [Fig. 9.18(b)] called the dipolar shift or zero-field shift which is independent of the applied field. Since at a fixed frequency, the resonance condition is $h\nu = g_e \beta_e H$, the energy for the transition $M_S = 0 \rightarrow 1$ will be large as compared to the transition $M_S = -1 \rightarrow 0$ [Fig. 9.18(b)]. Thus in the absence of internal magnetic field, the transitions (by selection rule, $\Delta M_S = \pm 1$) among the degenerate levels corresponding to $M_S = \pm 1, 0$ will exhibit a single line spectrum [Fig. 9.18(a)] whereas a two-line spectrum is expected in the presence of internal magnetic field [Fig. 9.18(b)]; e.g. ground state of $d^8\text{Ni(II)}$, i.e. $^3A_{2g}$ in octahedral field when spin-orbital coupling is large exhibits zero-field splitting. It is to be noted that when δH is small, it is likely that both the $M_S = \pm 1$ states will be above the $M_S = 0$ state. Conventionally, the $M_S = \pm 1$ states are shown as degenerate states above the $M_S = 0$ state.

Further, if one paramagnetic electron is located on each of the two atoms of a dimer (electron of each atom influences the electron of the other atom), then in addition to the $\Delta M_S = \pm 1$ transitions, one can also observe resonance lines corresponding to $\Delta M_S = +2$ transition. Consequently, a three-line spectrum results (Fig. 9.19). Since $\Delta M_S = +2$ transition is forbidden according to the ESR rules, it appears as a weak signal. So such a transition is best observed at low temperature on a highly sensitive instrument. These transitions ($\Delta M_S = +2$) occur at about half the resonant magnetic field to the $\Delta M_S = \pm 1$ transitions and, therefore, are also called half-resonance or transitions. Thus, the ESR spectrum of such a system should give a value of $g_e \sim 2$ for $\Delta M_S = \pm 1$ transitions and a value of $g_e \sim 4$ for the $\Delta M_S = +2$ transitions since the resonance condition is $\Delta E = h\nu = g_e \beta_e H$, e.g. dimeric $3d^9\text{Cu(II)}$ or dimeric $3d^1$ oxovanadium (IV) complexes. The influence of zero-field splitting parameters D and E on the ESR spectrum is shown in Fig. 9.19. ESR spectra, of $(\text{C}_6\text{H}_5)_2\text{C}:$ and $(\text{C}_6\text{H}_5)_2\text{N}:$ prepared by the photo excitation of $(\text{C}_6\text{H}_5)_2\text{CN}_2$ and $(\text{C}_6\text{H}_5)_2\text{N}_3$ respectively reveal that the two paramagnetic electrons mainly reside on the carbon and nitrogen atoms in the respective systems. Further, we know that H varies with θ (the angle between Z -axis and applied field direction) and for a rigid solution containing randomly oriented triplet molecules, θ can take

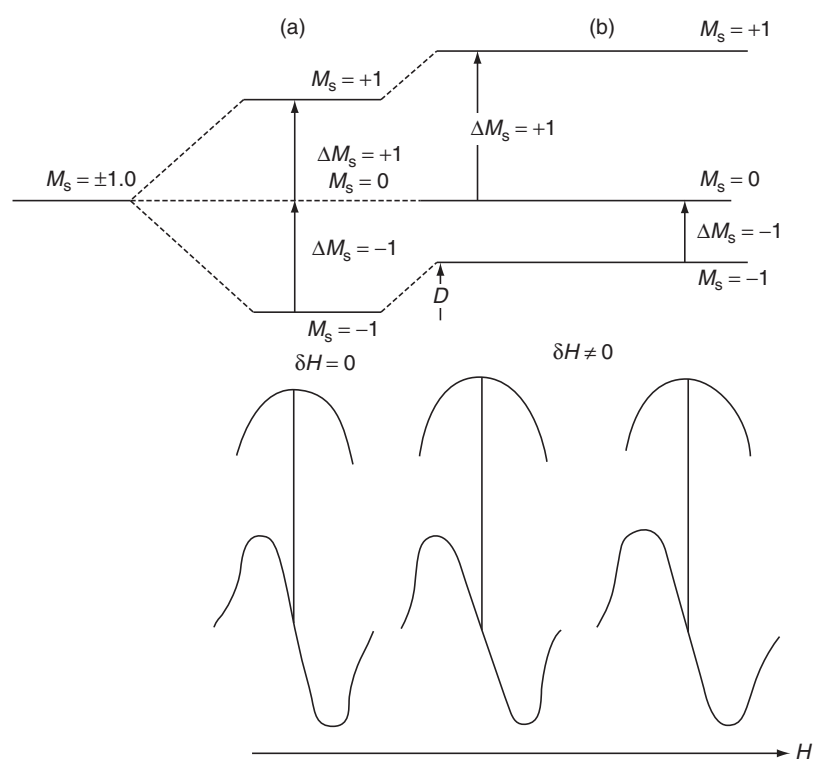


Fig. 9.18 The energy-level diagram and spectra of a molecule or ion with $S = 1$ (a) zero internal field ($\delta H = 0$), and (b) with non-zero internal field ($\delta H \neq 0$).

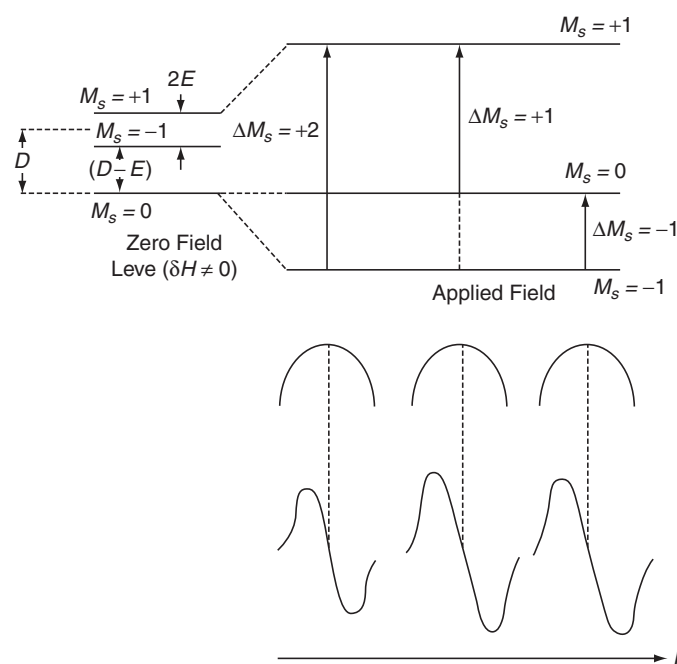


Fig. 9.19 The energy-level diagram and spectra for a dimeric molecule or ion in the presence of zero-field splitting.

on any value and the absorption spectrum will then be a series of overlapping lines (arising from the $\Delta M_s = \pm 1$ transitions) of varying separations, the overall signal will be too broad to be detected. This problem can be tackled by preparing a diluted single crystal of triplet state—a molecule in some other molecule with geometry identical to the triplet molecule. In such a situation, all the triplet molecules will be aligned in the same manner and there is only one value of θ , e.g. ESR spectrum of a dilute single crystal of triplet naphthalene in durene (at 77 K) gives a g -value of 2.003. The value of g reveals that Kramer's degeneracy is not due to crystal field effect on spin-orbital coupling but because of s - s coupling between the two π electrons in the triplet state. For triplets ($S = 1$) the s - s interaction is often solely responsible for zero-field splitting. On the other hand, the most important feature of the half-resonance lines is that the anisotropic line broadening is reduced and it is often possible to study these transitions in randomly oriented molecules, e.g. ESR spectrum of triplet state naphthalene produced by irradiating it with UV light and stabilised at low temperature. In general, ESR studies of triplet molecules are difficult and hence limited since their lifetimes are too short at high temperature and anisotropic line broadening effect is too great. Further, in a triplet molecule, the energy due to electron–nucleus contact interaction, which is of primary importance in the doublet state in solution is smaller than the dipolar interaction. Therefore, ESR spectra of triplet molecules rarely show any resolved hyperfine structure due to this contact interaction.

Let us now extend the foregoing treatment to systems with odd number of electrons other than one: Such systems exhibit Kramer's degeneracy, e.g. $d^3\text{Cr}$ (III), high spin $d^5\text{Mn}$ (II). The energy level diagram for the S^6 state of Mn (II) (d^5) is displayed in Fig. 9.20. Zero-field splitting generates pairs of degenerate spin states, $M_s = \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2}$ (Kramer's degeneracy). These pairs have slightly different energies from each other because of zero field already present. Under the influence of the applied field, each of these doublets split into singlets resulting into six levels. The allowed ESR transitions (by $\Delta M_s = \pm 1$) between these levels result in fine line ESR spectrum. Further, each of these spectral lines interacts with spin of magnitudes, $I = \frac{5}{2}$ to give $\left(2 \times \frac{5}{2} + 1\right) = 6$ hyperfine components. Components of hyperfine splitting have varying intensity: the intensity is greatest for the central lines and smallest for the outermost lines. In simple cases the separation between lines varies as $(3 \cos^2 \theta - 1)$ where θ is the angle between applied field and Z -axis.

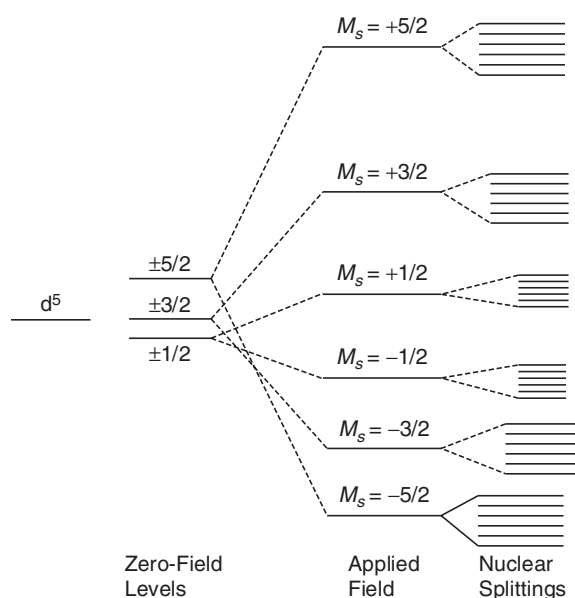


Fig. 9.20 The energy-level diagram for Mn(II) (d^5).

In certain cases where the magnitude of zero-field splitting exceeds the energies of ESR resonances, it is possible to observe weak ESR transitions corresponding to $\Delta M_s = \pm 2$ but not corresponding to $\Delta M_s = \pm 1$, e.g. in $V^{3+} \left(I = \frac{7}{2} \text{ for } ^{51}V \right)$, the line corresponding to $\Delta M_s = \pm 2$, further splits into $\left(2 \times \frac{7}{2} + 1 \right) = 8$ components.

9.10 NUCLEAR QUADRUPOLE EFFECTS IN ESR SPECTRA OF SOLIDS

We know that ESR theory is the simplest for liquid solution and it is in these systems most of its chemical applications are found. Let us see how quadrupole effects operate in the ESR spectra of solids. To start with, the Hamiltonian operator for the paramagnetic system possessing both the magnetic and quadrupole nucleus can be expressed as

$$\hat{H}_{FS} = \hat{H}_M + \hat{H}_Q$$

$$\hat{H} = a(SI) - \frac{\mu_N}{I}(HI) + A(3I_z - I^2) \quad (9.64)$$

where the terms and symbols have their usual meanings and the terms within the braces are vectorial in character. The first term stands for the interaction between nuclear and electron spins, the second term stands for the direct interaction between nuclear spin and external magnetic field and the third term stands for the quadrupole interaction.

The first term may arise due to the following two mechanisms. (i) In the first mechanism, the magnetic field at the nucleus is sum total of external magnetic field (H) and the average magnetic field produced by the unpaired electron. Since the electrons move faster than the nuclei, so the field produced by the electron can be replaced by one or more magnetic dipoles residing at a particular points on the molecular frame work. Since the nuclear dipole and the equivalent electron dipole are always parallel to the external field, the field produced by the electron at the nucleus depends on the angle(s) between the vectors joining the nucleus to the equivalent dipole(s). The average of this interaction over all directions in space is zero. Hence this term does not contribute to electron resonance spectra of substances in the gas or liquid phases. (ii) The second mechanism of electron-nuclear magnetic interaction arises if there is a spin imbalance at the nucleus in question, i.e. if the wave function describing the motion of unpaired electron has a finite value at the nucleus. This term is independent of orientation and is responsible for the hyperfine structure of spectra of gaseous or liquid substances. We know that the factor representing the sum of these two effects is a tensor quantity ' a ' and is uniquely given by its two components $a_{\parallel}$ and $a_{\perp}$, parallel and perpendicular to the symmetry axis respectively. In the absence of quadrupole coupling the eigen values of the fine structure Hamiltonian H_{FS} , are given, to first order by

$$E_{FS} = aM_s M_I - \frac{\mu_N H M_I}{I} \left[\frac{a_{\parallel} g_{\parallel}}{a g} \cos^2 \theta + \frac{a_{\perp} g_{\perp}}{a g} \sin^2 \theta \right] \quad (9.65)$$

$$\text{where } a = \sqrt{\frac{a_{\parallel}^2 g_{\parallel}^2}{g^2} \cos^2 \theta + \frac{a_{\perp}^2 g_{\perp}^2}{g^2} \sin^2 \theta}$$

The quadrupole effects will manifest themselves in the ESR spectra provided the nuclear-electronic magnetic moments are coupled, i.e. the tensor $a \neq 0$. There is no direct interaction between a nuclear quadrupole and an electronic magnetic dipole so that if a quadrupole nucleus in a molecule is at a very large distant apart from the paramagnetic site, the electron-spin resonance spectrum will reveal nothing about the quadrupole coupling constant.

Further, if we assume that a quadrupole interaction energy is much smaller than magnetic interaction of the nucleus with the electron spin and external magnetic field, i.e. the axis of precession of nuclear spin remains unchanged, then the quadrupole interaction introduces a further term into the expression for the eigen values of H_{FS} given by

$$E_Q = \frac{eq^2 Q}{4I(I-1)} \left[\frac{3M_I^2 - I(I+1)}{2} \right] \left[\frac{3a_{\parallel}^2 g_{\parallel}^2 \cos^2 \theta}{a^2 g^2} - 1 \right]$$

$$= \frac{e^2 q Q}{4I(I-1)} - [3M_I^2 - I(I+1)] f'(\theta) \quad (9.66)$$

Selection Rules

- $\Delta M_I = 0$, the limit of first-order theory, the quadrupole coupling does not produce any effect on the ESR spectrum.
- $\Delta M_I = \pm 2$, the quadrupole transitions become allowed for directions of the magnetic field at angle to the symmetry axis.
- $\Delta M_I = \pm 1$, becomes also allowed when the magnetic coupling tensor "a" is highly anisotropic and the magnetic field is in directions neither parallel nor perpendicular to the symmetry axis.

Let us now describe the effect of quadrupole coupling for a nucleus with $I = 3/2$. The hyperfine energy levels are given by

$$\begin{aligned}
 E_{+\frac{3}{2}} &= \pm \frac{3a}{4} - \frac{3}{2} \frac{\mu_N H}{I} f(\theta) + \frac{3}{2} A f'(\theta) \\
 E_{+\frac{1}{2}} &= \pm \frac{1a}{4} - \frac{1}{2} \frac{\mu_N H}{I} f(\theta) - \frac{3}{2} A f'(\theta) \\
 E_{-\frac{1}{2}} &= \mp \frac{1a}{4} + \frac{1}{2} \frac{\mu_N H}{I} f(\theta) - \frac{3}{2} A f'(\theta) \\
 E_{-\frac{3}{2}} &= \mp \frac{3a}{4} + \frac{3}{2} \frac{\mu_N H}{I} f(\theta) + \frac{3}{2} A f'(\theta)
 \end{aligned} \tag{9.67}$$

Here, $f(\theta) = [1 + (I + \frac{1}{2})^2 \tan^2 \theta]^{\frac{1}{2}}$

where the angle θ has its usual meanings and $A = \frac{e^2 q Q}{4I(I-1)}$. The upper signs in the formula give the position of the energy levels relative to $\frac{1}{2} g \beta H$ for $M_S = +\frac{1}{2}$ while the lower signs give the corresponding position of the energy levels relative to $-\frac{1}{2} g \beta H$ for $M_S = -\frac{1}{2}$. The energy-level diagram is given in Fig. 9.21 (a) and the corresponding spectrum for the various transition in Fig. 9.21(b) given below.

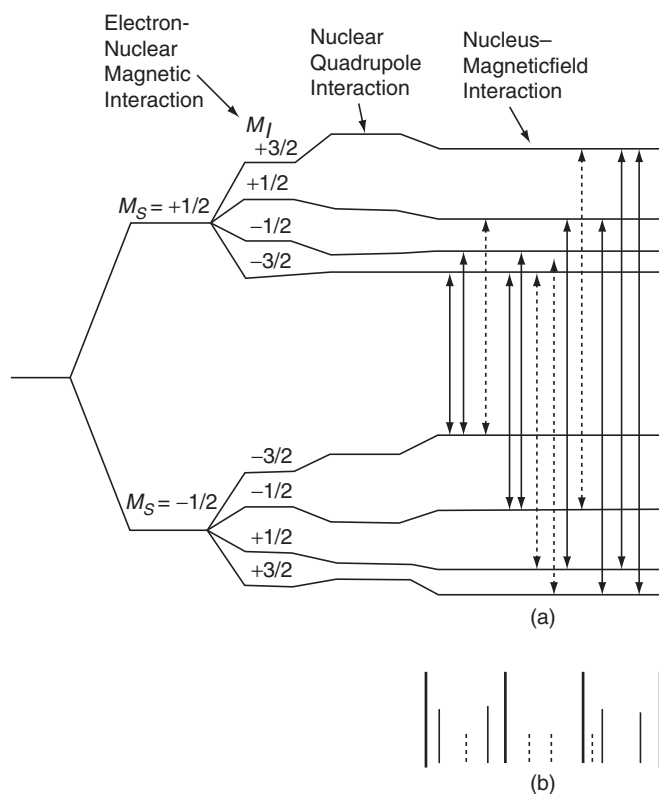


Fig. 9.21 (a) Energy levels, and (b) spectrum of a paramagnetic molecule, $S = 1/2$, $I = 3/2$. Heavily shaded full lines are transitions for $\Delta M = 0$; light shaded full lines are for transitions $\Delta M = \pm 1$; dotted lines are $\Delta M = \pm 2$.

Figure 9.21 and the equations reveal the immediately that the relative sign of ' a ' and e^2qQ can be obtained from ESR measurements. It is often probable to obtain probable absolute sign of ' a ' on the theoretical grounds so that the absolute sign of e^2qQ is then revealed.

When the asymmetry parameter is also taken into account so that as a consequence thereof all three components of ' a ' are different. The directions of axes and value of η are given directly by the spectrum. The general case in which none of the directions of the principal axes of g , ' a ' and A coincide has not been treated theoretically but in any case an analytical solution to this problem would not be possible.

In summary and also recall from Chapter 7 on NMR and Chapter 8 on NQR respectively that nuclei with spin $I \geq 1$ such as deuterium ^{14}N , ^{35}Cl , ^{37}Cl , ^{63}Cu , ^{65}Cu [$\mu_1(\text{Cu}^{65}) > \mu_1(\text{Cu}^{63})$], ^{67}Zn , ^{127}I , etc., besides nuclear magnetic moment (which makes them NMR active) possess electric quadrupole moment ' eQ ' also. The electric quadrupole moment interacts with the local electric field gradient (EFG), which is because of the electrons at the site of the probe nucleus. This type of interaction is called the *nuclear electric quadrupole interaction* and causes a splitting of the Zeeman energy levels. In most of the complexes with paramagnetic electron, the quadrupole interaction is small or not observed.

However, such an effect has been observed in some Cu^{2+} complexes. Thus, in paramagnetic systems, the unpaired electron experiences both the magnetic dipole moment and the nuclear quadrupole interaction. Consequently, additional signals which are not permissible by the selection rule $\Delta M_I = 0$ appear in the ESR spectrum. Sometimes the signals permissible by both the selection rules $\Delta M_I = \pm 1$ and $\Delta M_I = \pm 2$ are also observed, e.g. the ESR spectrum of $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ shown in Fig. 9.22 exhibits four major peaks due to the interactions of Cu^{63} ($I = 3/2$) with the unpaired electrons. Cu^{65} with higher gyromagnetic ratio should also exhibit four peaks, of which only two peaks, at the extremes of the spectrum, are resolved [Fig. 9.22(a)]. The four minor peaks, which are also split into two components because of the different gyromagnetic ratios of Cu^{63} and Cu^{65} nuclei are permissible by the selection rule $\Delta M_I = \pm 1$. An expanded view of two of these peaks has been shown in Fig. 9.22(b).

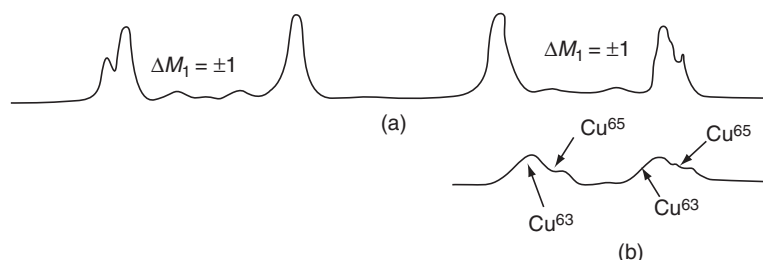


Fig. 9.22 ESR spectrum of $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$: (a) normal view of the spectrum, and (b) expanded view of the spectrum.

9.11 RULES FOR THE PREDICTION OF NUMBER OF HYPERFINE LINES AND THEIR RELATIVE INTENSITIES

In general, the number of hyperfine lines in the ESR spectrum of the free radical system having a set of n equivalent nuclei with nuclear spin, I is given by the quantity $(2nI + 1)$. However, if the electron is delocalised over a set of n equivalent nuclei with nuclear spin I_1 and another set of m equivalent nuclei with nuclear spin I_2 , then the maximum number of possible hyperfine lines is given by the quantity $(2nI_1 + 1)(2mI_2 + 1)$, i.e. $\prod_i (2n_i I_i + 1)$ where $i = 1, 2$. Let us now apply these rules to free radicals with different structures.

The interaction of the unpaired electron with n equivalent protons ($I = \frac{1}{2}$) results in $\left(2 \times \frac{1}{2} \times n + 1\right) = n + 1$ lines whose relative intensities are proportional to the coefficients of the binomial expansion of $(1 + x)^n$ (Fig. 9.23). Thus, the maximum number of lines expected in the ESR spectra of $\dot{\text{C}}\text{H}_3$ and $\text{C}_6\bar{\text{H}}_6$ (benzene anion radical) would be four and seven respectively and same has indeed been observed experimentally [Figs 9.24(a) and (b)]. The intensity ratios of the quartet and septet also conform to the expected ratios of 1:3:3:1 and 1:6:15:20:15:6:1 respectively. It is important to note that the overall shape of the ESR spectra is influenced by the ratio of splitting to line width (Fig. 9.25). In naphthalene anion radical ($\text{C}_{10}\bar{\text{H}}_8$)/($\bar{\text{N}}$), prepared by the reduction of naphthalene with alkali metals in ether, there are two different sets of four equivalent protons, so the expected number of lines in the spectrum is $\left(2 \times 4 \times \frac{1}{2} + 1\right) \left(2 \times 4 \times \frac{1}{2} + 1\right) = 25$. However, the number of lines in the observed experimental spectrum [Fig. 9.24(c)] is 21. The difference may be due to overlapping of lines in the observed spectrum.

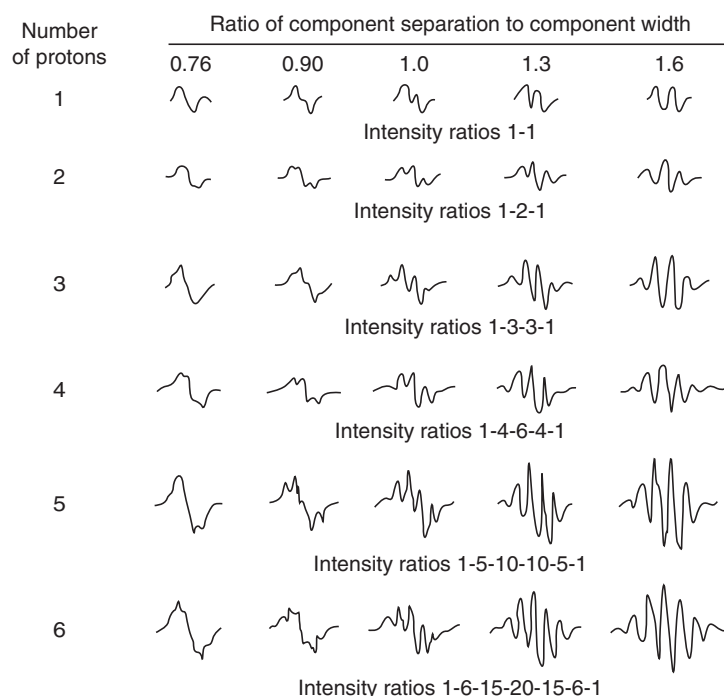


Fig. 9.25 Theoretical hyperfine structure curves for Gaussian derivative curves.

Table 9.7 Relative intensities of ESR lines for n equivalent nuclei with nuclear spin I .

$I = \frac{1}{2}$													
$n = 1$	1	1											
$n = 2$	1	2	1										
$n = 3$	1	3	3	1									
$I = 1$													
$n = 1$	1	1	1										
$n = 2$	1	2	3	2	1								
$n = 3$	1	3	6	7	6	3	1						
$I = \frac{3}{2}$													
$n = 1$	1	1	1	1									
$n = 2$	1	2	3	4	3	2	1						
$n = 3$	1	3	6	10	12	12	10	6	3	1			
$I = 2$													
$n = 1$	1	1	1	1	1								
$n = 2$	1	2	3	4	5	4	3	2	1				
$n = 3$	1	3	6	10	15	18	19	18	15	10	6	3	1

The first quartet involves lines 1, 3, 6 and 9; the second quartet consists of lines 2, 5, 8 and 11; and the lines 4, 7, 10 and 12 constitute the third quartet. The individual members of the three-line pattern have been located from the centre of each quartet. The observed values of hyperfine splitting constants for the triplet (1:1:1) and each of the three quartets are 18.1 and 25 G respectively. In case of transition metal ions, the hyperfine splitting arises due to the coupling of metal nucleus having spin $I > \frac{1}{2}$ with the unpaired electron of its ion. Thus, the ESR spectrum of Mn^{2+} ions in water exhibits six lines of equal intensity [Fig. 9.24(e)] as expected, i.e. $\left(2 \times \frac{5}{2} + 1\right) = 6$ whereas the expected number of lines in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is $\left(2 \times \frac{3}{2} + 1\right) = 4$ with intensity ratios 1:1:1:1. The dimer of Cu(II) acetate monohydrate exhibits seven lines with intensity ratios 1 : 2 : 3 : 4 : 3 : 2 : 1 in ESR spectrum as expected, i.e. $\left(2 \times 2 \times \frac{3}{2} + 1\right) = 7$. Spectrum reveals the formation of metal-metal bond in the dimer and the same has been confirmed by x -ray studies.

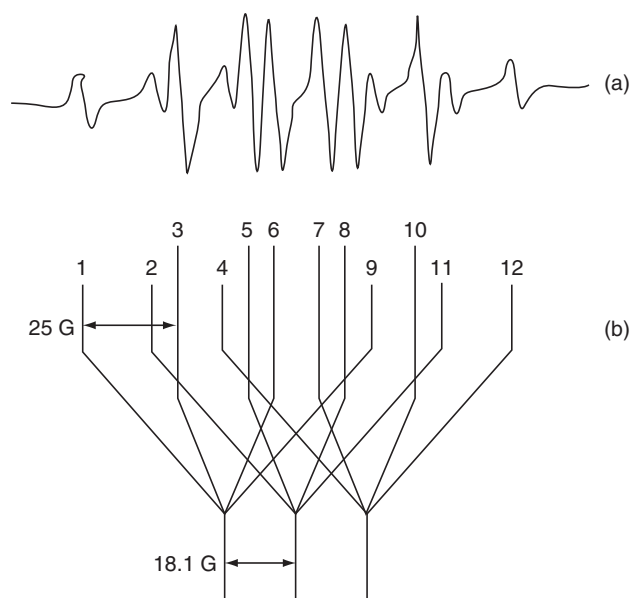
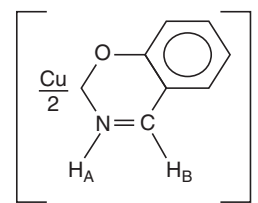


Fig. 9.26 ESR spectrum of $\dot{\text{N}}\text{H}_3$ formed by x-ray irradiation of ammonium perchlorate crystals.

The ESR spectrum of bis-salicylaldimine Cu(II) as illustrated here consists of four major signals and each of the four major signals consists of eleven lines of intensity ratio 1 : 2 : 3 : 4 : 5 : 6 : 5 : 4 : 3 : 2 : 1. The four major signals in the spectrum are due to the interaction of unpaired electron of Cu^{2+} with the nuclear spin $I = 3/2$ of ^{63}Cu nucleus, i.e. $\left(2 \times \frac{3}{2} + 1\right) = 4$.

Now each of these four main signals undergoes splitting by two equivalent nitrogen atoms ($I = 1$) and two hydrogen (H_A) atoms to yield $(2 \times 2 \times 1 + 1) \left(2 \times 2 \times \frac{1}{2} + 1\right) = 15$ lines.



H_B hydrogen being away does not contribute to splitting. The overlapping between the expected lines results into eleven lines in the observed experimental spectrum. It is to be noted that the splitting of main ESR signal into a number of lines by the donor atoms of the ligand in the coordination complexes is termed *super-hyperfine splitting*. Let us now examine the ESR spectrum of distorted tetrahedral dichloro (orthophenanthroline) Cu(II) in isomorphous diamagnetic dichloro (orthophenanthroline) Zn (II) which consists of four main groups and each of the main groups contains five lines of intensity ratio 1 : 2 : 3 : 2 : 1. The expected number of super-hyperfine lines in each of the four major groups which arises by the interaction of two nitrogen atoms ($I = 1$) of donor orthophenanthroline is also $(2 \times 2 \times 1 + 1) = 5$. Although ^{35}Cl has nuclear spin $I = \frac{3}{2}$, the chloride hyperfine interaction has not been observed as the chloride splitting constant is small in a Cu(II) complex. Further, the presence of super-hyperfine lines in the ESR spectrum of a coordinate ion complex is an evidence to the delocalisation of the unpaired electron of the metal ion to the ligand atom orbitals which is contrary to the basic assumption of crystal field theory, i.e. 'the metal and the ligand orbitals do not overlap in coordination complexes.'

Problem 9.3: Predict the number of ESR lines for the triphenyl methyl radical, i.e. $(\text{C}_6\text{H}_5)_3\dot{\text{C}}$.

Solution In this radical, three-proton spin systems correspond to the ortho-, para- and meta-protons. Each ortho- and meta-system contains six protons, the para-system contains three protons. Thus, the total number of ESR hyperfine spectral lines is $\left(2 \times 6 \times \frac{1}{2} + 1\right)^2 \left(2 \times 3 \times \frac{1}{2} + 1\right) = 196$. However, in the observed spectrum about 100 lines are resolved.

Problem 9.4: Predict the number of lines in the ESR spectrum of ethyl free radical, i.e. $\dot{\text{C}}\text{H}_3\text{CH}_2$.

Solution CH_3 and CH_2 are three- and two-proton systems in this radical, Consequently, the total number of hyperfine ESR lines will be

$$\left(2 \times 3 \times \frac{1}{2} + 1\right) \left(2 \times 2 \times \frac{1}{2} + 1\right) = 12$$

(Number of observed lines is also twelve.)

Problem 9.5: Analyse the hypothetical spectrum shown in Fig. 9.27 (a) for the radical $\text{H}\cdot\text{X}^+$. $\text{H} - \dot{\text{X}}^+ \leftrightarrow \dot{\text{H}} - \text{X}^+$ ($I = 1$ for X).

Solution The hypothetical radical $\text{H}\cdot\text{X}^+$ exhibits $\left(2 \times \frac{1}{2} \times 1 + 1\right) = 2$ major signals of equal intensities [Fig. 9.27(b)] due to coupling of unpaired electron with hydrogen atom $\left(I = \frac{1}{2}\right)$. Each of these two signals splits into $(2 \times 1 + 1) = 3$ lines due to the interaction of X atom ($I = 1$). Thus, the expected number of lines for the hypothetical radical $\text{H}\cdot\text{X}^+$ is $3 \times 2 = 6$. However, there are only five peaks in the hypothetical spectrum of the radical [Fig. 9.27(a)]. Most probably, the two innermost lines are not well resolved [Fig. 9.27(c)], and consequently a five line spectrum results.

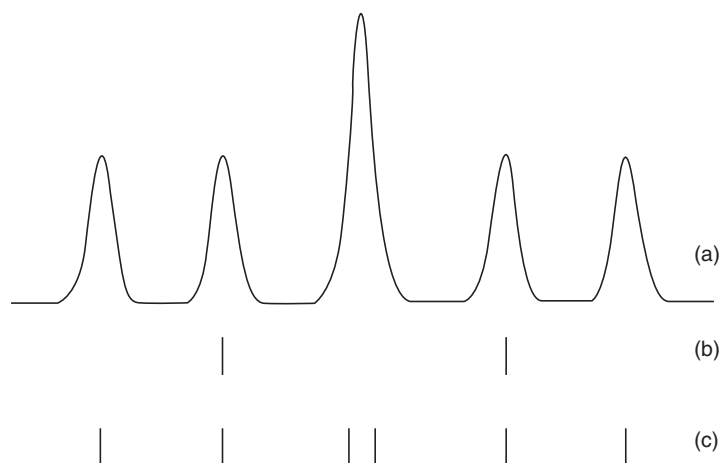


Fig. 9.27 Hypothetical ESR spectrum of $\text{H}\cdot\text{X}^+$ ($I = 1$ for X) radical.

Problem 9.6: Analyse the ESR spectrum shown in Fig. 9.28 for Mo(V) complex ($4d^1$), i.e. $\text{K}_3[\text{Mo}(\text{CN})_8]$ in water at room temperature. The natural abundance of different isotopes of molybdenum is ^{94}Mo and ^{96}Mo ($I = 0$) = 75 percent, ^{95}Mo $\left(I = \frac{5}{2}\right)$ = 15.78 per cent, ^{97}Mo $\left(I = \frac{5}{2}\right)$ = 9.60 per cent. At a high gain of ESR spectrometer, each of the six weak lines (marked with arrows) exhibits two small peaks similar to the ones on either side of the central line.

Solution The nonmagnetic isotopes (^{94}Mo , ^{96}Mo) with $I = 0$ will give $(2 \times 0 + 1)$ 1 ESR line. On the other hand, each of the magnetic isotopes ^{95}Mo and ^{97}Mo (with $I = \frac{5}{2}$) will give $\left(2 \times \frac{5}{2} + 1\right) = 6$ ESR lines. However, the lines due to ^{95}Mo and ^{97}Mo overlap to give rise to only six broad lines in the spectrum. These lines are symmetrically distributed on either side of the central line due to nonmagnetic isotopes, i.e. ^{94}Mo and ^{96}Mo . The intensity of ESR line for an isotope is directly proportional to the natural abundance and inversely to the number of lines, i.e. $(2I + 1)$ it exhibits. Thus, the intensity of the line corresponding to nonmagnetic isotopes (^{94}Mo , ^{96}Mo) is $= \frac{75}{25} \times \frac{6}{1} = 18$ times more than those of the magnetic isotopes. The two small peaks on either side of the central line are due to the hyperfine interaction of ^{13}C $\left(2 \times \frac{1}{2} + 1 = 2\right)$ of CN^- . The splitting of each of the six broad lines into two peaks is also due to the hyperfine interaction of ^{13}C of CN^- . This splitting pattern shows the presence of Mo—CN rather than Mo—NC bond in the molecule.

9.12 BASIC PRINCIPLE OF AN ESR SPECTROMETER

The block diagram of a spectrometer is shown in Fig. 9.29. The main seven components of the spectrometer are klystron power supplies, klystron, magnet, cavity system, modulator, phase sensitive detector, and recorder. As shown in Fig. 9.29, klystron is a source of monochromatic microwave radiation. The frequency of radiation is

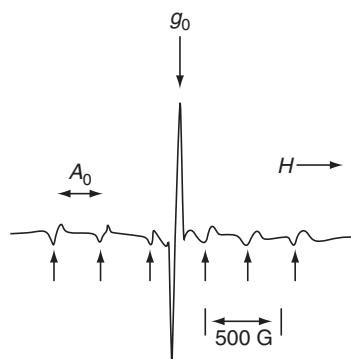


Fig. 9.28 ESR spectrum of $K_3[Mo(CN)_6]$ in water at room temperature.

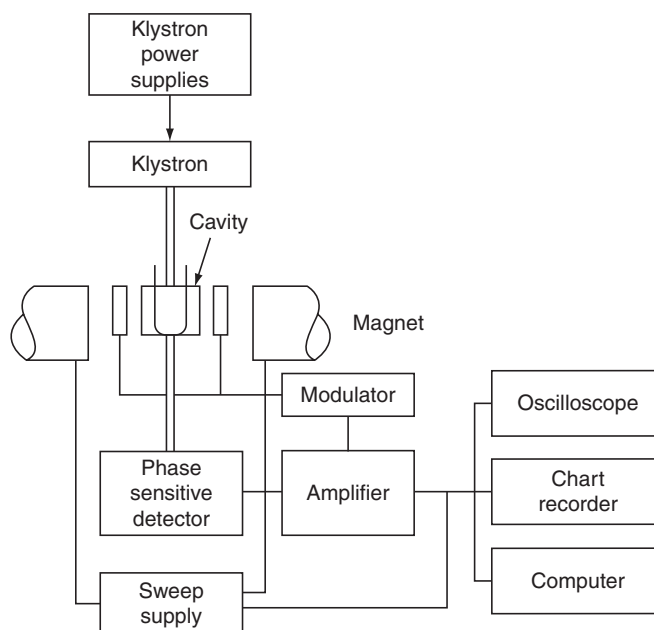


Fig. 9.29 Block diagram of an ESR spectrometer.

determined by the voltage applied to the klystron from the klystron power supplies. Power in klystron used is usually a few hundred milliwatts. The frequency of microwave radiation is stabilised by an automatic frequency control (AFC) system (not shown in Fig. 9.29) which works on the voltage. Heat produced by the klystron is removed by circulating water. The lifetime of modern klystrons is about 7000 hours. The frequency range of klystrons is as under.

Band	S	X	K	Q	E
Approximate frequency (in GHz)	3	9	24	35	70
Approximate field (in kG)	1.1	3.3	8.5	12.5	25

There are differences between the European and American names for the bands, so the frequencies should be reported also. Commonly used frequencies are around 9.5 GHz (X-band) and 35 GHz (Q-band). The radiation is transmitted with the help of a wave guide through the sample contained in the sample tube placed in a cavity located between the poles of a magnet. A wave guide consists of copper or brass tube (2.2 cm by 10 cm) with silver or gold plating inside to produce a highly conducting flat surface and has the dimensions close to the wavelength of radiation. When a sample and sample holder are introduced into the cavity, the quality factor, Q of the cavity, which is a measure of its power to store energy, should not change too much. Q is given by

$$Q = \frac{2(\text{maximum microwave energy in the cavity})}{\text{energy lost per cycle}} \quad (9.68)$$

Rectangular cavity is used for large samples, especially for liquid samples. A cylindrical cavity is used for gaseous systems and liquid samples in capillaries. A tubing of 3–5 mm internal diameter with a sample volume 0.15–0.5 ml can be used with samples which do not possess a high dielectric constant. For samples with a high dielectric constant, flat cells with a thickness of about 0.25 mm and sample volume of 0.05 mL, are often used. Rotatable cavities are used for studying anisotropic effects in single crystals and in solid samples. The microwave radiation enters and leaves the sample cavity by the same hole, called the *iris*. An electromagnet is a source of static magnetic field and it should have a large field region (500–5000 G is required to handle samples whose g -factor ranges from 1.5–6), a wide air gap and good field homogeneity, it should be about 1 part in 10^6 for solution studies. The line widths for paramagnetic ions and for free radicals in solid matrices are rarely less than a few gauss, so that homogeneity and stability might be as low as 1 part in 10^3 before serious line broadening takes place. The stability of a magnet is obtained by regulation with a Hall crystal (Indium arsenide; In As) in the magnet gap. The crystal gives voltage proportional to the field and any change can be corrected with a feedback circuit to the current. The modulation system consists of small Helmholtz coils, one on each side of the cavity,

along the axis of the magnetic field. The strength of the magnetic field may be determined from the current flowing through the Helmholtz coils.

$$H = \frac{32\pi n}{10\sqrt{125} r_c} \cdot I \quad (9.69)$$

where, n is the number of turns in each coil, r_c is the radius of coils, I the current (in amp) flowing through the coils.

The microwave radiation absorbed by the sample is detected by a phase-sensitive detector which is usually the semiconducting silica crystal. A superheterodyne electronic system is also used, especially for lines which are quite narrow. The absorption signal is amplified and the absorption spectrum is displayed on an oscilloscope or recorded on paper chart. The phase detected signal is usually represented as the first derivative. The absorption curve and the first and the second derivatives are shown in Figs 9.2 and 9.3. Modern ESR spectrometers are coupled with computers for storing and analysing data. A computer is especially convenient for storing time-dependent signals which change too fast to be monitored accurately by mechanical recorders.

A good spectrometer should have maximal sensitivity. The sensitivity at room temperature of X-band (9.5 GHz) ESR spectrometers is given by

$$N_{\min} = 1 \times 10^{11} \frac{\Delta H_{PP}}{\sqrt{\tau}} \quad (9.70)$$

where, $N_{\min}$ is the minimum number of detectable spins per gauss, ΔH the width between the deflection points on the derivative absorption curve and τ is the time constant of the detecting system which is inversely proportional to the bandwidth of the detection circuit. The sensitivity of ESR spectrometers in the X-band is 5×10^{10} spin G^{-1} for 100 kHz modulation and in the Q-band 6×10^9 spin G^{-1} for 100 kHz modulation. It is to be noted that for a sample of very small dielectric loss, the minimum sensitivity is about 6×10^{14} spin G^{-1} to barely see the line.

Further, in order to measure line widths and hyperfine splittings, the accurate calibration of the field is carried out with standard sample, in which the line positions can be carefully determined. The standard sample can be introduced in the dual cavity and the spectra recorded simultaneously. The standards used are Mn^{2+} in SrO powder characterised by 6 lines, 1.6 G wide, totally over 420 G, splittings 84 ± 0.2 G, peroxyaminedisulphate ion in solution characterised by 3 lines, 250 mG wide, outer splitting 26.18 G, splittings 13.1 ± 0.004 G; tetracyanoethylene anion radical (TCNE) $^{\bullet-}$ in solution characterised 9 lines, 100 mG wide, outer splitting 1.6 G, splitting 1.57 G, Wurster's blue perchlorate characterised by 39 lines listed for half spectrum, total spectrum 86 G, accuracy ± 0.01 G.

9.13 DETERMINATION OF g -VALUE

The position of resonance of ESR line of an unknown sample can be determined if operating microwave frequency (ν) of the instrument and resonance magnetic field (H_r) of the sample is known.

$$g_{un} = \left(\frac{h\nu}{\beta_e H_r} \right) = 714.44 \frac{\nu(\text{GHz})}{H_r(\text{G})} \quad (9.71)$$

If the microwave frequency (ν) is not accurately known, then

$$g_{un} = g_{std} \left(1 - \frac{\Delta H}{H_r} \right) \quad (9.72)$$

where g_{std} is the g -value of the standard free radical which is used to calibrate the ESR spectrum. Most commonly used standard, α, α' -diphenyl- β -picrylhydrazyl (DPPH) contains 1.53×10^{21} unpaired spins per gram. Line width and g_e values for DPPH are listed in Tables 9.8 and 9.9 respectively. ESR spectra of DPPH in different media are displayed in Fig. 9.30. $\Delta H = H_{r(un)} - H_{r(std)}$ is negative if $H_{r(un)} < H_{r(std)}$ and positive if $H_{r(un)} > H_{r(std)}$. From Eq. (9.68) we note that for negative ΔH , $g > 2$ whereas $g < 2$ for positive ΔH . Substandards can be prepared by dilution with carbon black.

In addition to DPPH, the other primary standards are (i) fresh, deep blue $CuSO_4 \cdot 5H_2O$ crystal; (ii) fresh $MnSO_4 \cdot H_2O$; (iii) $K_2NO(SO_3)_2$ in aqueous solution; (iv) O_2 gas; and (v) solutions of peroxyaminedisulphonate.

Some secondary standards which are more stable than primary standards may also be used to calibrate the ESR spectrum, but before use they should be calibrated against primary standards with spin concentration that are determined by independent methods. Various secondary standards in use are (i) synthetic ruby crystal; which can be placed in the cavity permitting simultaneous observation of standards and unknown sample. It shows a

strong resonance ($g = 1.4$); (ii) charred dextrose, which does not change properties between 4 K and 500 K; and (iii) powdered coal (pitch) diluted with KCl. Varian supplies two such standards (peak-to-peak line width 1.7 G, $g_e = 2.0028$) of different concentrations (1×10^{13} and 3×10^5 spin cm^{-1}) with each spectrometer; (iv) Mn (II) in MgO, CaO and CaCO_3 .

Table 9.8 Line width in DPPH samples crystallised from various solvents.

Solvent	$\Delta H_{1/2}$ (G)		
	$\nu = 300 \text{ MHz}$		$\nu = 9400 \text{ MHz}$
	295 K	90 K	295 K
Benzene	6.8	4.6	4.7
Toluene	2.9	2.6	2.6
Xylene (mixture)	2.5	2.2	2.3
Pyridine	5.3	5.0	5.0
Bromoform	2.2	2.5	2.5
Carbon tetrachloride	1.9	2.7	2.3
Chloroform	1.7	2.1	2.0
Carbon disulphide	1.3	1.3	1.5

Table 9.9 Variation in g_e -values of DPPH at room temperature and 77K.

Sample	g_e -value
Single Crystal*	2.0027–2.0039
Single Crystal	2.0035–2.0041
	2.0028–2.0038
	2.0030–2.0040
Powder*	2.0037
Polycrystalline	2.0036 ($g_{\parallel} = 2.0028$ and $g_{\perp} = 2.0039$)

*Difference in the g_e -value for single crystals may occur, because the number of spins in crystal samples depends on the solvent used for the growing of the crystal. The ESR lines of DPPH in the whole temperature range from 293 K–1.7 K have Lorentzian shape.

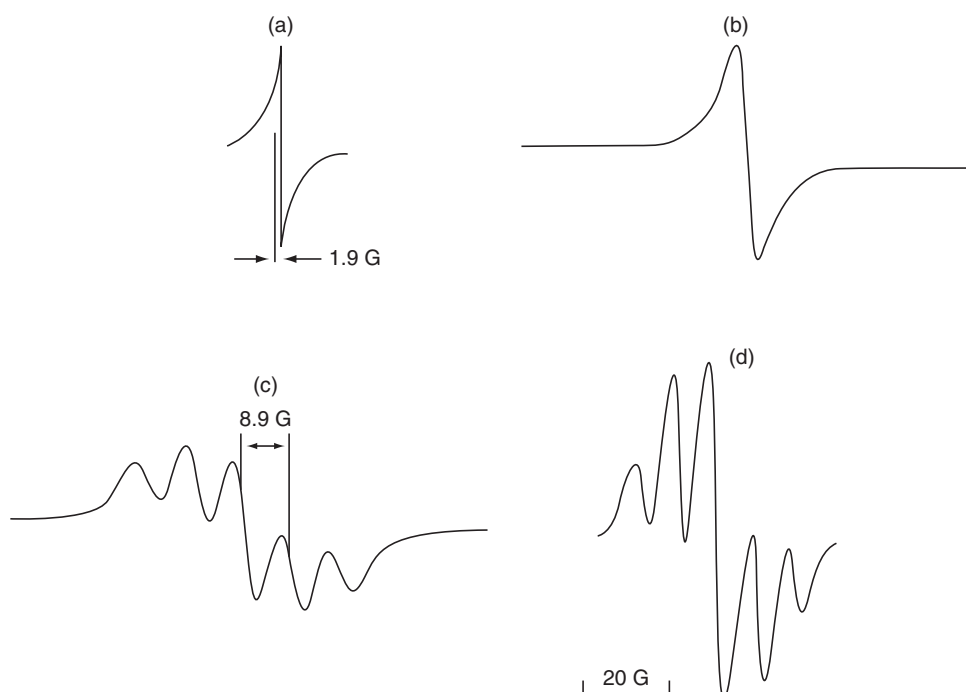


Fig. 9.30 ESR spectra of α, α' -diphenyl- β -picrylhydrazyl (DPPH) in different media: (a) solid powdered sample, (b) saturated solution of DPPH in tetrahydrofuran, (c) saturated solution diluted by a factor of 10^3 , and (d) in benzene solution (5×10^3 mole lit^{-1}).

9.14 FOURIER TRANSFORM ESR SPECTROSCOPY (FTESRS)

The principle of FTESR is similar to FTNMR except that in FTESR, a microwave pulse is used instead of a radio frequency pulse. FTESR technique is faster than FTNMR because the relaxation times are much faster in ESR. ESR requires 10–20 ns pulses. The main problem encountered in FTESR is the dead time of the pulsed ESR instrument that prevents observation of FID during the first 50–100 ns after the pulse. It is, therefore, difficult to measure broad resonance lines employing FTESR. However, with FTESR method, the ESR spectrum can be recorded within a few microseconds. This enables the detection of transient paramagnetic species.

9.15 ELECTRON NUCLEAR DOUBLE RESONANCE (ENDOR)

ENDOR is a method to detect changes in the amplitude of a particular monitored ESR signal due to the induction of a nuclear transition of nuclei coupled to the paramagnetic centre. This method is used to improve the resolution of ESR spectrum. The resolution and specificity increase are because of smaller number of ENDOR transitions and selectivity of ESR line. This method is used when hyperfine lines are not well resolved in the ESR spectrum and when the identity of the interacting nucleus is to be established by measuring the nuclear g -factor, i.e. g_N . A spin $S = \frac{1}{2}$ system coupled to n inequivalent nuclei of nuclear spin $I = \frac{1}{2}$ yields only $2n$ lines while an ESR spectrum would give 2^n lines. A schematic diagram of ENDOR transitions for an electron $\left(S = \frac{1}{2}\right)$ coupled to a nucleus $\left(I = \frac{1}{2}\right)$ is shown in Fig. 9.31. Remember that the down-spin (β) of an electron is more stable than

the up-spin (α) because the electron is negatively charged whereas the reverse is true for nucleus because of its positive charge. Because of the mutual interaction of energy states, the states with paired spins ($\alpha\beta$, $\beta\alpha$) tend to be stabilised or lowered in energy while parallel spins ($\alpha\alpha$, $\beta\beta$) are raised in energy. Thus, two ENDOR lines would appear at the two nuclear transitions, say ν_{n1} and ν_{n2} , as shown in Fig. 9.32. Further, when the unpaired electron interacts with more than one proton or with more nuclear spin systems, the ENDOR lines appear at frequencies corresponding to the hyperfine coupling constants, no matter how many equivalent spins are present in each spin system.

In ENDOR method, the radio frequency (r_f) generator having power (200 W) and NMR radio frequency (2–30 MHz), and large power output is connected to ferrite-core transformers to the side of the coils of the special designed cavity. The sample is subjected simultaneously to a microwave frequency (MW) suitable for electron resonance and a radio frequency suitable for nuclear resonance. The radio frequency is slowly altered while observing the one point of ESR spectrum under conditions of microwave saturation or partial saturation. A change occurs in the spin population of the electronic levels at the values corresponding to the resonance of a given type of nuclei. This change in population alters the amplitude of the original ESR signal. The magnitude of the difference in amplitudes is measured as a function of radio frequency. This process is known as ENDOR. The ENDOR displays an ESR signal amplitude as a function of the swept nuclear radio frequency. At two frequencies of the r_f generator (ν_1 and ν_2), two separate peaks will be observed (Fig. 9.32). The difference $\nu_2 - \nu_1$ is numerically equal to the hyperfine coupling constants (A). For systems with short nuclear relaxation times, such as free radicals in solution, or with small nuclear magnetic moments, large r_f fields are required. However, for systems with long relaxation times, low power (5W) r_f generator would suffice. The pulsed ENDOR sequences due to Davies and Mims have been displayed here.

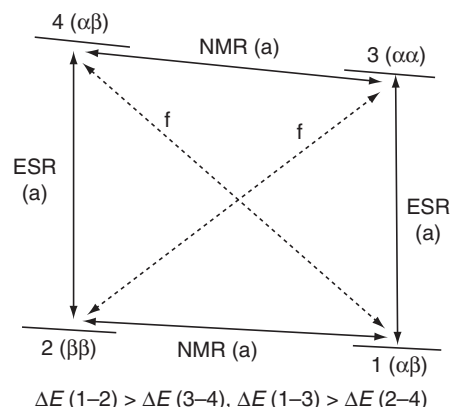


Fig. 9.31 Schematic representation of ENDOR transitions for an electron ($S = 1/2$) coupled to a nucleus ($I = 1/2$): (a) Allowed transitions (f) Forbidden transitions.

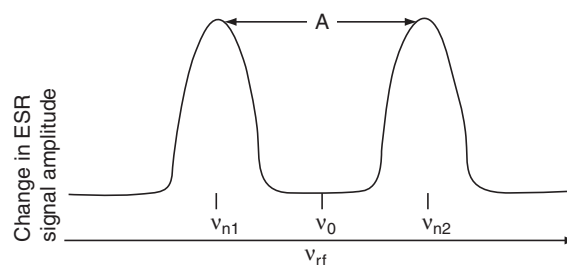


Fig. 9.32 ENDOR lines for a system with $S = 1/2$ and $I = 1/2$.

9.16 ELECTRON DOUBLE RESONANCE (ELDOR)

ELDOR is a method to study the changes in the amplitude of an ESR signal of the sample at some point of the spectrum induced by the second microwave resonance frequency. It leads to higher resolution of hyperfine structure. This method is used to study relaxation processes including chemical and spin exchange and to separate overlapping multiradical spectra. In this method, the sample is subjected simultaneously to two microwave frequencies. One of these is used to observe an ESR signal at some point of the spectrum, while the other is swept through other parts of the spectrum to display the amplitude of ESR signal as a function of the difference of the two microwave frequencies.

9.17 APPLICATIONS OF ESR SPECTROSCOPY

Like all other spectroscopic tools, viz., NMR, IR, UV/V, MW, etc the applications of ESR spectroscopy are based on the four properties of ESR lines, i.e. their intensity, width, position (g -factor) and multiplet structure and may be broadly divided into two categories. The first of these exploits the specific features of ESR spectrum to obtain structural and physical information characteristic of the paramagnetic sample under investigation. The second approach exploits the ability of ESR to provide quantitative information on the concentration of a paramagnetic centre available in the sample.

9.17.1 Determination of Concentration of Free Radicals

The concentration of free radicals or number of spins in the sample (per g, per mL or per mm of the sample) is proportional to the total area under the absorption curve. The area is obtained by integrating the derivative signal. The integration is made graphically, electronically or digitally with a computer. The accuracy of all the methods decreases when the signals have long wings or signal-to-noise ratio is more and the baseline is affected by a background signal. These problems are overcome by using a digital computer.

In the graphical method, the spectrum is divided into constant intervals and the amplitude is measured in each interval. These intervals are cumulatively added and each partial sum is obtained. The last value of the partial sum should be zero. If it is nonzero, it is divided by the number of intervals, and the parameter so obtained is cumulatively subtracted from the partial sums. The second integral is then obtained by adding all the partial sums. The accuracy of the graphical method depends on the number of intervals. Let us demonstrate this method by dividing the first derivative absorption curve into eight equal intervals as shown in Fig. 9.33. If suffixed, (x) and A denote the interval and the amplitude respectively. We may write

$$\begin{aligned}x_0 &= A_0 (= 0) \\x_1 &= A_0 + A_1 \\x_2 &= A_0 + A_1 + A_2 \\x_3 &= A_0 + A_1 + A_2 + A_3\end{aligned}\tag{9.73}$$

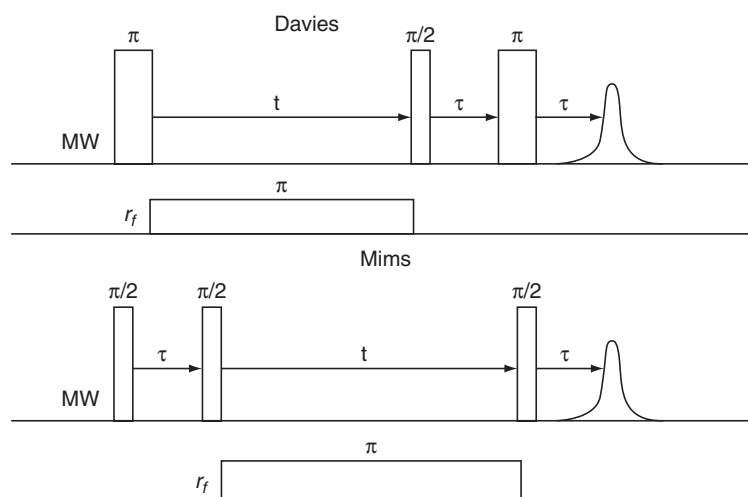


Fig. 9.33 Pulsed EN DOR sequences due to Davies and Mims.

$$\begin{aligned}x_4 &= A_0 + A_1 + A_2 + A_3 + A_4 \\&\vdots \\x_8 &= A_0 + A_1 + A_2 + A_3 + A_4 + A_5 + A_6 + A_7 + A_8\end{aligned}$$

If the value of the last interval is zero, i.e. $x_8 = A_0 + A_1 + A_2 + A_3 + \dots + A_8 = 0$, then the value of integral, i.e. the area under the absorption curve

$$= \sum_{i=0}^{i=8} x_i \quad \text{where } i = 0, 1, 2, \dots, 8. \quad (9.74)$$

If $x_8 \neq 0 = \lambda$ (say),

$$\text{then,} \quad \text{Error} = \frac{\lambda}{8 \text{ (no. of intervals)}} = \varphi \quad (9.75)$$

Applying the correction, we write

$$\begin{aligned}x'_0 &= A_0 (= 0) - \varphi \\x'_1 &= A_0 + A_1 - \varphi \\x'_2 &= A_0 + A_1 + A_2 - \varphi \\x'_3 &= A_0 + A_1 + A_3 - \varphi \\x'_8 &= A_0 + A_1 + A_2 + A_3 + A_4 + A_5 + A_6 + A_7 + A_8 - \varphi\end{aligned} \quad (9.76)$$

Thus $x'_8 = 0$ and the area under the curve

$$= \sum_{i=0}^{i=8} x'_i \quad \text{where } i = 0, 1, 2, 3, \dots, 8. \quad (9.77)$$

Since many experimental factors such as (i) the overall spectrometer gain, (ii) the microwave frequency, (iii) the g -factor of the sample, (iv) the sample temperature, (v) the transition probability, (vi) the concentration of free radicals in the sample, (vii) the filling factor of the sample, and (viii) the modulation, amplitude at the sample, affect the intensity of the ESR signal, a number of corrections need be applied for accurate measurements of the concentration of free radicals in the sample.

The most common method used for the determination of concentration of free radicals in an unknown sample is to compare its ESR signal with that of some standard sample containing a known amount of free radicals. The standard sample should have the following properties: (i) line width and line shape of its ESR spectrum should be identical to that of the unknown sample, (ii) number of spins, the line width, and the g -value should be constant, i.e. independent of temperature and time, (iii) concentration should be similar to that of the unknown sample, (iv) the s - l relaxation time should be short otherwise saturation of the signal will take place easily, and (v) physical shape and dielectric loss of the standard sample should be similar to that of the unknown sample.

Vanadium over the range 0.1 to 50 $\mu\text{g/mL}$ can be determined in petroleum products. Mn (II) ion in aqueous solutions can be determined. The sensitivity of determination lies in the range 10^{-6} M–0.1 M. Cu (II), Cr (III), Fe (III), Ti (III) and Gd (III) ions can also be determined quantitatively by ESR method. Polynuclear hydrocarbons such as anthracene, perylene and naphthalene have been determined after conversion to radical cations and adsorption on to the surface of an activated silica–alumina catalyst.

9.17.2 Study of Electron Transfer Reactions

The ESR technique is best suited for the study of free radical reactions. The appearance of an ESR signal during the course of a reaction indicates that the reaction proceeds via some free radical mechanism. However, the low concentration of free radicals formed at one or another stage of a reaction due to their short lifetimes pose a problem for their detection by ESR measurements. This problem has been overcome with the help of some specially designed cells. One such cell is due to Dixon and Norman (Fig. 9.35). It consists of two tubes with a flat cell on the top. The inner tube contains a spray head, from which one solution (e.g. the reductant) is injected into the second solution (e.g. the oxidant). The mixed solution then rapidly flows through the cavity under hydraulic pressure. The rate of flow is kept faster than the rate of production of radicals. A steady concentration of the radicals can be attained with proper adjustment of pressure. Free radicals with lifetimes of the order of 10^{-2} s can be

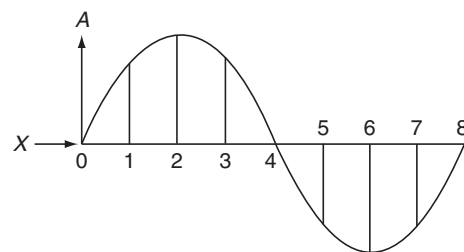


Fig. 9.34 Representation of graphical method to determine the area under the curve; X stands for the interval and A stands for the amplitude.

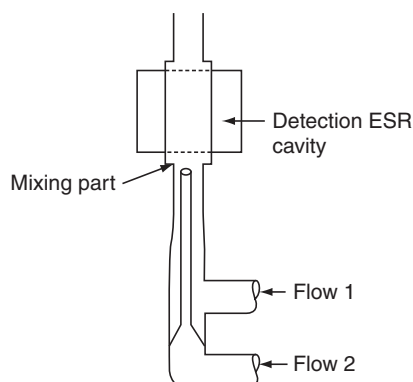


Fig. 9.35 Rapid flow apparatus/Dixon-Norman type mixing cell for ESR studies of free radicals.

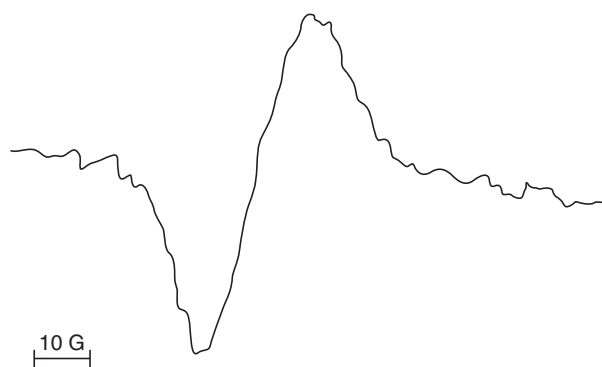
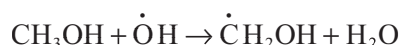
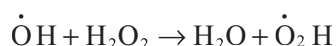
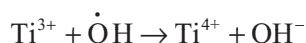


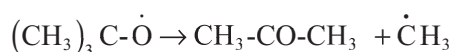
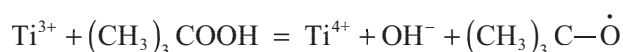
Fig. 9.36 ESR spectrum of isobutylvinyl ether-iodine system measured at 77 K.

detected by this technique. Figure 9.36 shows the ESR spectrum of radical cation generated by mixing iodine solution with isobutylvinyl ether at 77 K. The radical cation is formed according to the following scheme. The radical cation (a) is stabilised by the isobutoxy group. The observed g_e value of 2.0057 is larger than that for a free electron value of 2.0023. This may be attributed to considerable spin density on oxygen due to conjugation, which makes the radical cation reluctant to recombine. Unstable aliphatic and aromatic free radicals formed in liquid phase reactions are detected by this method. The ESR spectrum of TiCl_3 (acidified solution)— $\text{CH}_3\text{OH} + \text{H}_2\text{O}_2$ (acidified solution) system when recorded by the rapid flow method exhibits a three-line multiplet with intensity ratio 1:2:1,

The triplet is due to $\dot{\text{C}}\text{H}_2\text{OH}$ radical formed according to the following scheme:



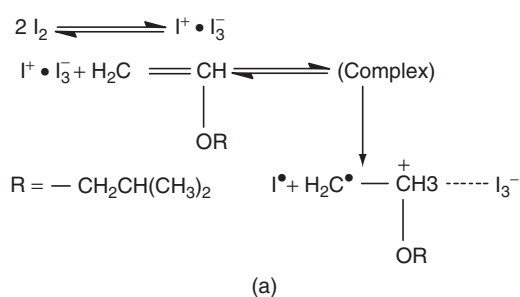
When aqueous solution of TiCl_3 and $(\text{CH}_3)_3\text{COOH}$ at $\text{pH} < 2$ are mixed in the resonance cavity of the ESR spectrometer, a quartet spectrum of narrow lines with a separation of about 23G has been observed and is attributed to $\dot{\text{C}}\text{H}_3$ radical produced in a two-step reaction.



9.17.3 Determination of Rotational Correlation Time

The stable nitroxide radicals has tertiary carbon bonded to the nitrogen, e.g. di-tert-butyl nitroxide (a), 2,2-dimethyl-oxazoline derivatives, (b) pyrroline, (c) piperidine, and (d) nitroxides. They are used as both paramagnetic markers and reactants.

The ESR spectra of these radicals consists of $(2 \times 1 + 1) = 3$ lines of equal intensities. These radicals in solution (organic solvents, e.g. C_6H_6) of low viscosity are in rapid Brownian motion. In viscous medium, the rotational motion is hindered and tumbling rate of molecules decreases. Consequently, the broadening of spectra occurs and hyperfine coupling constants increase (Fig. 9.37). The rotational motion of these radicals in solution is characterised by a parameter called the 'rotational correlation time (τ)'. It is defined as the time required for complete rotation of a nitroxide radical about its axis and is $10^{-11} < \tau < 10^{-6}$ s. It may be defined as the time required



for the nitroxide radical to rotate through an angle of one radian. It can be calculated from one of the following equations:

$$\tau = \Delta H_{pp} \left[\left(\frac{I_{pp^0}}{I_{pp^{+1}}} \right)^{\frac{1}{2}} - \left(\frac{I_{pp^0}}{I_{pp^{-1}}} \right)^{\frac{1}{2}} \right] C \quad (9.78)$$

$$\tau = \Delta H_{pp} \left[\left(\frac{I_{pp^0}}{I_{pp^{+1}}} \right)^{\frac{1}{2}} + \left(\frac{I_{pp^0}}{I_{pp^{-1}}} \right)^{\frac{1}{2}} \right] - 2C' \quad (9.79)$$

where ΔH_{pp} is peak-to-peak width, $I_{pp^{-1}}$, I_{pp^0} , $I_{pp^{+1}}$ are the measured peak-to-peak amplitudes of three lines of ESR spectrum of nitroxide radical (Fig. 9.38). C and C' are the characteristic parameters for the nitroxide and the particular experimental conditions employed. Because of the rotational behaviour of organic nitroxide radicals in solution of low viscosity, they have been used as spin probes to study their interactions with host polymers in which they are dissolved.

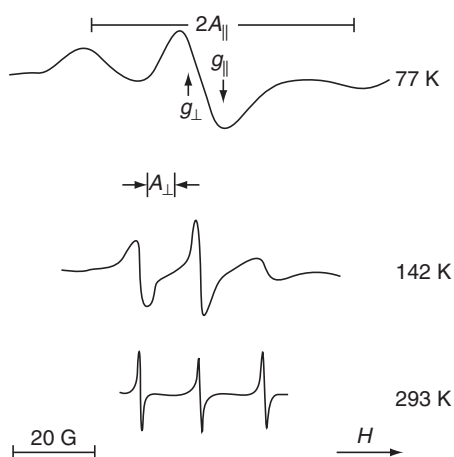
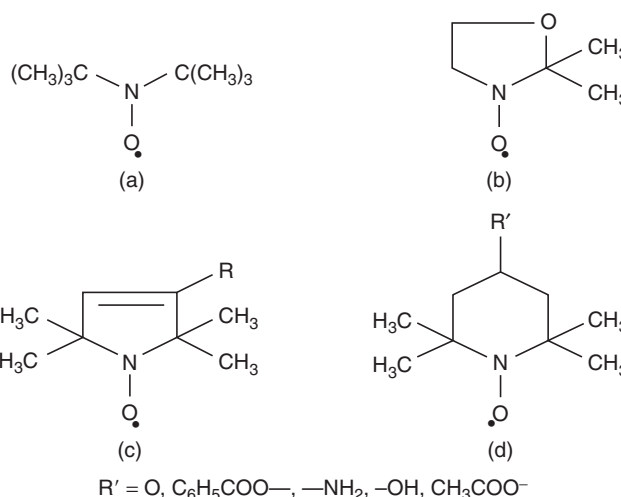


Fig. 9.37 ESR spectrum of di-tert-butyl nitroxide radical at 293, 142 and 77 K.

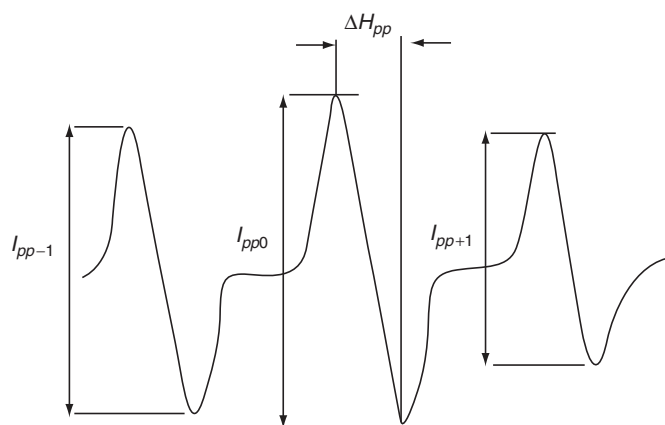


Fig. 9.38 Notation of the symbols used for the determination of the rotational correlation time (τ) from ESR spectrum.

Some of the radicals easily diffuse into various polymers and they have been found to reside in the amorphous phase of the solid. Since the glass transition temperature (T_g) corresponds to the onset of liquidlike translational motions of the long segments of molecules in amorphous phase, and the rotations of nitroxyl radicals are sensitive to changes of geometry of their surroundings, the rotational correlation times of spin probe radicals in polymers at temperatures near T_g can be measured, e.g. the well-resolved triplet line ESR spectra of polyethylene (at different temperatures, 90–333 K) and poly (vinylchloride) (93–423 K) above the glass transition temperature (T_g) containing 2,2,6,6-tetramethyl-4-hydroxy-piperidine-1-oxyl benzoate shows rotational motion of radicals in the amorphous part of the polymers. The broad line shape of the spectra in the low-temperature range indicates that the polymer matrix is in the rigid state. When the temperature is raised, a small splitting takes place because a part of the chain in the probe begins to rotate to cause change in the hyperfine pattern. ESR spectra of 2,2,6,6-tetramethyl-4-hydroxy-piperidine 1-oxyl obtained as grown polyethylene crystals at 348.5 K in the temperature range, 143–333 K also show similar behaviour (Fig. 9.39). From these spectra, the rotational correlation time of free radical can be computed. The rotational correlation time (τ) obeys the Arrhenius equation,

$$\tau = \tau_0 e^{E_a/RT} \quad \text{valid for } T > T_g \quad (9.80)$$

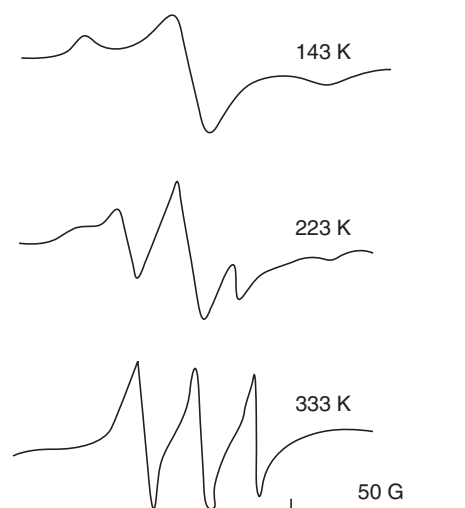


Fig. 9.39 ESR spectra of 2,2,6,6-tetramethyl-4-hydroxy-piperidine-1-oxyl obtained as grown polyethylene crystals at 348.5 K in the temperature range 143–333 K.

Table 9.10 Rotational activation energy of some spin-probe nitroxide radicals in linear polymers.

Polymer	Piperidine Nitroxide with R	E_a kcal mole ⁻¹
Polyethylene (0.918 g/cm ³)	H	10.7
Polyethylene (0.918 g/cm ³)	C ₆ H ₅ COO	11.0
Polyethylene (0.950 g/cm ³)	H	10.4
Polyethylene (0.950 g/cm ³)	C ₆ H ₅ COO	10.0
Polystyrene	H	18.2
Polystyrene	C ₆ H ₅ COO	18.3

E_a is the rotational activation energy of the free radical. T is the absolute temperature (K) and R is gas constant. E_a can be calculated from the slope (E_a/R) of the straight-line plot of $\log \tau$ against $\frac{1}{T}$. The rotational activation energies of some spin probe radicals in linear polymers are listed in Table 9.10.

The rotational activation energy of free radicals is independent of the size of the radical but dependent only on the properties of the polymer matrix. Thus, the radical rotational frequency is determined by the mobility of the polymer segments.

The rotational correlational time (τ) depends on molecular volume (V_m) and obeys the relation

$$\tau = A e^{-kV_g}$$

$$\tau = B E^{-kV_1} \quad (9.81)$$

where V_g and V_1 , are the molar volumes (cm³ mole⁻¹) when $T < T_g$ and $T > T_g$ respectively, $k \approx 1$, A and B are constants.

The interaction of polymers with plasticisers can be measured by using nitroxide radicals as spin probes. The rotational correlation time (τ) of probe radicals in plasticised polyvinylchloride at 298 K, decreases strongly when the amount of plasticiser is increased.

9.17.4 Study of Ion Pairs

ESR spectrum of alkali salts of naphthalenide ion in tetrahydropyran shows that the hyperfine lines of naphthalenide are split into quadruplets by the presence of Na²³. This indicates the presence of sodium naphthalenide ion pair, i.e. $\bar{N}Na^+$ in tetrahydropyran. The character of the ion pair depends on the solvent and temperature of the solution. The magnitude of splitting (a_{Na}) varies from about 1.4 G at 320 K to 1.0 G at 236 K, when a small amount of tetra-adenate ether (tetraglyme) (~ 0.24 mole lit⁻¹) is added, the splitting constant a_{Na} decreases. The splitting is about 0.4 G at 300 K. On lowering the temperature, a_{Na} decreases further and at 236 K, the four lines merge into one. Thus, the reduction in a_{Na} on addition of tetraglyme to solution of alkali salt of naphthalenide ion in tetrahydrofuran is attributed to the formation of glymated pair, $\bar{N}(G)Na^+$. On the other hand, a comparison of ESR spectra of alkali salt of naphthalenide ion in tetrahydrofuran at 300 K in the absence of tetraglyme [Fig. 9.40(a)] and in the presence of intermediate concentrations of glyme [Fig. 9.40(b)] shows that the two sets of lines in the latter spectrum are characteristic of the tight ion pair $\bar{N}Na^+$ and glymated pair $\bar{N}(G)Na^+$, respectively. The lines for the glymated pair are marked in Fig. 9.40(b) by arrows. The equilibrium in this system is presented as

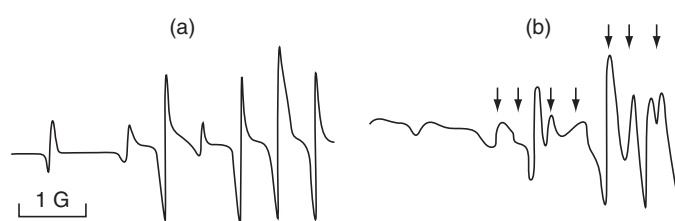
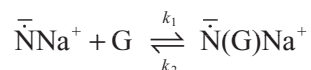


Fig. 9.40 Low field wing of ESR spectrum of $\bar{N}Na^+$ in tetrahydrofuran at 300 K: (a) In the absence of tetraglyme, and (b) in the presence of 0.006 mole lit⁻¹ tetraglyme.



From the width of the lines in Fig. 9.40(b), the values of k_1 and k_2 have been found to be $\sim 10^8(\text{mole/lit})^{-1}\text{s}^{-1}$ and $10^6(\text{mole/lit})^{-1}\text{s}^{-1}$, respectively.

9.17.5 Kinetics of Electron-Exchange Reactions

The electron-exchange reactions between radical ion $\bar{N}$ and the corresponding neutral molecule (N) in the solution phase are studied by the rapid-flow technique, e.g. when naphthalene is added to the solution of naphthalenide radical ion an electron-exchange reaction occurs $\bar{N} + N \rightleftharpoons N + \bar{N}$ which causes a broadening of the hyperfine components of the ESR line. The additional width of resonance line $\Delta H_{1/2}(G)$, i.e. the difference between the line widths of a particular line in the absence and presence of electron transfer, is given by the equation

$$\Delta H_{1/2}\tau = \frac{1}{2\pi} \quad (9.82)$$

where τ is the mean jump time for an electron. If M is the molarity of naphthalene, the pseudo first-order rate constant (k) may be expressed as

$$k[M] = \frac{1}{\tau} = 2\pi \Delta H_{1/2} \quad (9.83)$$

It is not required to know the concentration of the radical as long as its concentration is kept low. The rate constant of electron transfer can be determined at slow and at fast exchange limits from the plots between $\Delta H_{1/2}(G)$ and

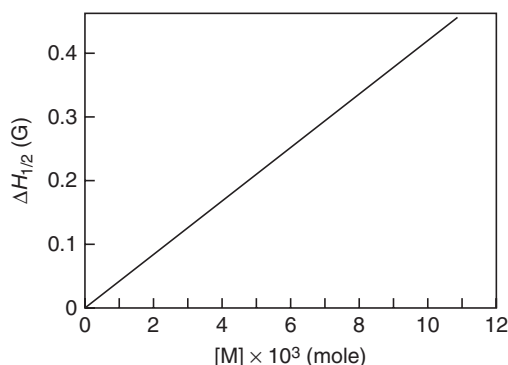


Fig. 9.41 Dependence of ESR line width $\Delta H_{1/2}$ on naphthalene concentration $[M]$ in the slow exchange $\bar{N} + N \rightleftharpoons N + \bar{N}$ in hexamethylphosphoramide.

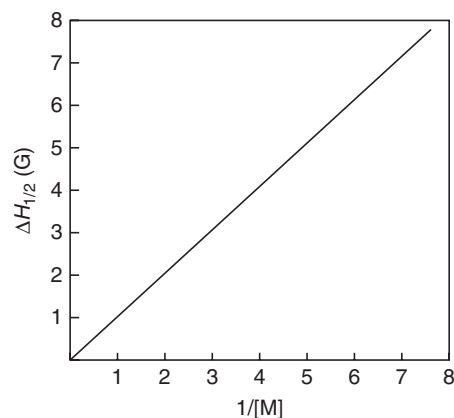


Fig. 9.42 Dependence of ESR line width $\Delta H_{1/2}$ on $\frac{1}{[M]}$ in the fast exchange $\bar{N} + N \rightleftharpoons N + \bar{N}$ in hexamethylphosphoramide.

high concentration (Fig. 9.41) and low concentration (Fig. 9.42) of naphthalene in hexamethylphosphoramide solvent, respectively.

Similarly, the rate of electron transfer reaction between a tetracyanoethylene anion radical (TCNE^-) and its neutral molecule (TCNE) can be studied. TCNE^- is formed by the reduction of TCNE with alkali metal in ether. TCNE^- exhibits $(2 \times 4 + 1) = 9$ lines ESR spectrum. As already discussed, the broadening of lines occurs. When the concentration of TCNE is increased and at very high concentration of TCNE the electron jumps from one molecule to another so fast that the hyperfine structure is lost and only one sharp line in the spectrum is observed. From the addition line width, the rate constant for the electron transfer reaction, $\text{TCNE}^- + \text{TCNE} \rightleftharpoons \text{TCNE} + \text{TCNE}^-$ is determined from the equation

$$k = \frac{1.5 \times 10^7 \cdot \Delta H_{1/2}}{[M]} \quad (9.84)$$

Here, $[M]$ is the concentration of neutral species added, i.e. naphthalene.

When the solution of hydroquinone is mixed with oxygen in the observation area of the ESR spectrometer by the rapid-flow method, an ESR spectrum consisting of five lines multiplet with intensity ratio of 1:4:6:4:1 results. The multiplet is attributed to the formation of semibenzoquinone since the five-line pattern corresponds to the

magnetic interaction between odd electron and four protons of the ring. Results of kinetic study of the formation and decay of semiquinone according to the scheme indicate that the half life of the formation reaction is about 0.15 second.



Semibenzoquinone

$$\nu = 9500 \text{ MHz}$$

$$H = 3400 \text{ G}$$

9.17.6 Determination of Exchange Integral

In systems with two unpaired electrons, one electron located on each of the two atoms, the interaction between the two electrons gives rise to a spin singlet state ($S = 0$) and spin triplet state ($S = 1$) separated by the exchange integral J (Fig. 9.43), e.g. dimeric copper (II) acetatemonohydrate, dimeric oxavanadium (IV) tartrates. The population in the two spin states depends on the magnitude of J and temperature. In a ferromagnetic complex ($J > 0$), the paramagnetic triplet state ($S = 1$) is the ground state whereas the diamagnetic singlet state ($S = 0$) is the excited state. With decreasing temperature, the population in the triplet state grows at the cost of the singlet state; consequently, the intensity of the ESR line grows. On the other hand, in an anti-ferromagnetic complex ($J < 0$), with the decreasing temperature, the population in the ground diamagnetic singlet state grows at the cost of the excited paramagnetic triplet state. As a result, the intensity of the ESR line will decrease. Thus, the magnitude of J can be determined by measuring the intensity of ESR lines at different temperatures. The relative intensity (I_R) of ESR signal is related to J by the expression

$$I_R = \frac{1}{T} \frac{\exp\left[\frac{-J}{\kappa T}\right]}{1 + 3 \exp\left[\frac{-J}{\kappa T}\right]} \quad (9.85)$$

The intensity is measured relative to the signal from a small amount of DPPH mixed with the sample. The appearance of an ESR line in the spectrum of a sample corresponding to $\Delta M_S = +2$ transition, indicates the presence of the triplet state in the complex involved in the magnetic exchange interaction. It is to be noted that a weak magnetic exchange interaction (J or $-J \leq 30 \text{ cm}^{-1}$) which cannot be detected by magnetic susceptibility measurements at room temperature or even single crystal, x-ray studies, can be detected through ESR measurements. It is possible to detect the presence of magnetic exchange in the magnetically concentrated coordination compounds in which the single crystal x-ray studies have shown the M–M distance to be greater than $4 \text{ \AA}$.

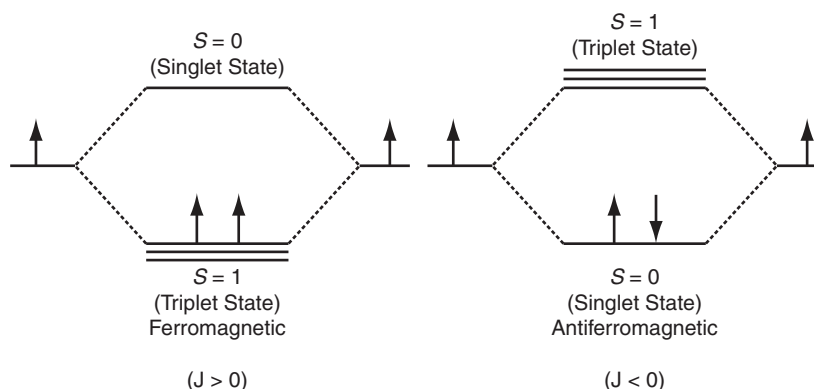


Fig. 9.43 Coupling of two $S = 1/2$ spins of two interacting metal ions.

9.17.7 Determination of Unpaired Electron Spin Density and the Molecular Shape of Free Radical

The ESR technique, like NMR, does not give information about the arrangement of functional groups in the molecule. However, it allows the determination of the distribution of unpaired electron spin density over the atoms in the molecule and in some cases the shape of the free radicals.

The main parameter which influences the magnitude of electron-nucleus interaction is the amount of time which the electron spends in the neighbourhood of the coupled nucleus or in other words the electron spin density at the nucleus.

Quantum mechanical considerations on the electron nucleus interaction show that

$$a = \frac{8\pi}{3} g_e \beta_e g_N \beta_N |\psi(0)|^2 \quad (9.86)$$

and

$$\tau = g_e \beta_e g_N \beta_N \left\langle \frac{3 \cos^2 \theta - 1}{r^3} \right\rangle \quad (9.87)$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{n^3 a_0^3 l \left(l + \frac{1}{2} \right) (l+1)} \quad \text{where the symbols have their conventional meanings, } Z \text{ is atomic number, } a_0, \text{ (Bohr}$$

radius for hydrogen atom) = 0.53 Å, n , the principle quantum number, and l , the orbital quantum number. The importance of these isotropic- a and anisotropic- τ , coupling constants results from the fact that these parameters are directly related to the electronic configuration of the radical.

As already discussed, Eq. (9.86) represents the Fermi interaction. $|\psi(0)|^2$ is the probability of finding the electron in contact with the nucleus giving rise to isotropic coupling. $|\psi(0)|^2 \neq 0$, when the electron has some s character C_s^2 . Equation (9.87) represents the dipolar interaction. The s orbital makes no contribution to this anisotropic interaction, because in this case the spherical symmetry results in an averaging of $(3 \cos^2 \theta - 1)$ to zero. If the unpaired electron is in a p_z orbital then

$$\tau_z = \frac{4}{5} g_e \beta_e g_N \beta_N \left\langle \frac{1}{r^3} \right\rangle = 2B_0 \text{ (in G)} \quad (9.88)$$

and

$$\tau_x = \tau_y = \frac{-2}{5} g_e \beta_e g_N \beta_N \left\langle \frac{1}{r^3} \right\rangle = -B_0 \text{ (in G)} \quad (9.89)$$

Hartree Fock calculations have made available the theoretical values of $|\psi(0)|^2$ and $\left\langle \frac{1}{r^3} \right\rangle$ for elements of the Periodic Table. Electron spin density and isotropic coupling constant of some representative elements are listed in Table 9.11.

Table 9.11 Isotropic hyperfine coupling constant (a^N) and the density of valence s orbital of atom N evaluated at the nucleus $|\psi_N(0)|^2$.

Nucleus	a_N (G)	$ \psi_N(0) ^2$ (au) ⁻³
¹ H	539.86	0.338
¹³ C	820.10	2.042
¹⁴ N	379.34	3.292
¹⁷ O	-888.68	41.082
¹⁹ F	44829.20	29.840

Thus, it is possible to calculate the isotropic coupling constant A_{iso} and anisotropic coupling constants, $2B_0$, $-B_0$, $-B_0$, associated respectively with the ns and np orbital of each atom. The principal aim in the analysis of ESR spectra of solid samples is to obtain the experimental parameters which make it possible, after comparison with the atomic constants, to estimate the s character, $C_s^2 = \frac{a}{A_{\text{iso}}}$, and the p character, $C_p^2 = \frac{\tau_z}{2B_0}$ of the atomic orbital containing the unpaired electron. When the values of C_s^2 and C_p^2 are determined, one can calculate the hybridization ratio $\lambda^2 = \left(\frac{C_p^2}{C_s^2} \right)$, and thus estimate certain structural parameters, e.g. if C_{3v} symmetry is assumed, it can be shown that for $R_3\dot{A}$ radical

$$\varphi = \cos^{-1} \left(\frac{1.5}{2\lambda^2 + 3} - \frac{1}{2} \right) \quad (9.90)$$

and

$$\cos^2 \theta = \frac{1}{3} (1 + 2 \cos \varphi) \quad (9.91)$$

where, φ is the interbond angle RAR and θ is the angle between the symmetry axis and an AR bond.

It is apparent that the isotropic coupling constant can be obtained from both liquid phase (direct measurement of a_{iso}) and solid state

$$a_{\text{iso}} = \frac{(a_x + \tau_x) + (a_y + \tau_y) + (a_z + \tau_z)}{3}$$

since for dipolar interaction $\tau_x + \tau_y + \tau_z = 0$] ESR studies, In contrast, the anisotropic components are available only from solid-phase measurements.

Let us now examine how these concepts could be applied to determine the distribution of unpaired electron density in the entire molecule. For a free atom, the dependence of a_N on ρ_N is expressed as

$$a_N = R_N \rho_N \quad (9.92)$$

where, a_N is the hyperfine constant in an atom N, ρ_N is the fraction of unpaired electrons in the valence state, R_N is the hyperfine coupling constant for a single electron in the valence state. For hydrogen atom $R_N = 506$ G (Calc: 539.86), $\rho_N = 1$, since the electron spends its time in 1s orbital only. Thus, for hydrogen atom $a_N = R_N$.

(a) $\dot{\text{C}}\text{H}_3$ Radical The ESR spectrum of trimethyl radical in solution exhibits a quartet with intensity ratio of 1:3:3:1 due to splitting by the protons ($I = \frac{1}{2}$, natural abundance 99.985 per cent). Splitting due to carbon is not readily observed, as principal isotope ^{12}C (natural abundance 98.9 per cent) is nonmagnetic and ^{13}C ($I = \frac{1}{2}$) has a natural abundance of only 1.1 per cent. The observed value of the $\dot{\text{C}}\text{H}_3$ hyperfine coupling constant is -23 G. Applying Eq. (9.92) to $\dot{\text{C}}\text{H}_3$ radical with $a_{\text{H}} = -23$ G, we get $\rho_{\text{H}} = \frac{-23}{506} = -0.045$. It follows that the electron density at the carbon atom is $(1 - 3 \times 0.045) = 0.865$. Thus, we know the electron density at each atom of the $\dot{\text{C}}\text{H}_3$ radical: each hydrogen, -0.045 ; carbon, 0.865 . This implies that the unpaired electron spends 4.5 per cent of its time in the 1s orbital of each hydrogen atom and 86.5 per cent in the vicinity of the carbon atom.

(b) π -spin Density In the planar p -type hydrocarbon radicals there is zero overlap of the s orbitals of the hydrogen and carbon atoms with the p -orbitals (p_z) perpendicular to the molecular plane. The s atomic orbitals (AOs) cannot contribute at all to the half-filled molecular orbital (MO), which is composed of p_z AOs only. Although no unpaired electron spin density can enter the AOs directly, the spin polarisation leads to a small spin density in both the carbon and the hydrogens AO's, the former being of the same sign as that of the unpaired electron (α or positive spin) and the latter being 'opposite in sign (β , or negative spin). Furthermore, the magnitude of spin density on the ring proton is roughly 5 per cent as large as the p_z spin density on the adjacent ring carbon. The splitting constant $a_{\text{H},\mu}$ of proton on ring carbon μ is related to the π -spin density ρ_μ on carbon μ by the McConnell relation

$$a_{\text{H},\mu} = Q\rho_\mu \quad (9.93)$$

Here, Q or (Q_{CH}) is the proportionality constant, also called the spin polarisation parameter and roughly constant for π -radicals and is usually taken to be about -27 G (or -25 G (or -25G)), approximately 5 per cent of the coupling constant of hydrogen atom (540 G) but of opposite sign. The constant Q is the proton hyperfine splitting constant per unit spin density on the sp^2 carbon containing CH bond. The value of Q has also been estimated from the spectrum of benzene negative ion which consists of seven peaks with 'a' value of 3.75 G. The probability of the unpaired electron being at any one carbon is 1/6, so from Eq. (9.93), we obtain

$$|Q| = 3.75 \times 6 = 22.5 \text{ G.}$$

The value of $Q = -22.5$ G being based on experimental data is preferred over the value of $Q = -27$ G from theoretical considerations.

(c) Shape of $\dot{\text{C}}\text{H}_3$ Radical The geometry of $\dot{\text{C}}\text{H}_3$ radical could either be planar (C atom is sp^2 hybridised) or tetrahedral (C atom is sp^3 hybridised). We know that for planar hydrocarbon π -radicals

$$a_{\text{H},\mu} = Q\rho_\mu \quad (\text{Eq. 9.89})$$

The proton hyperfine coupling constant for $\dot{\text{C}}\text{H}_3$ is -23 G. Using $a_{\text{H}} = -23$ G and $\rho_{\text{H}} = 1$, $Q = -23$ G which is close to the value of Q for most of the aromatic radicals, i.e. $Q_{\text{CH}} = -22.5$ G. This implies that $\dot{\text{C}}\text{H}_3$ radical has a planar structure. However, the observed splitting could not be fixed as the sole criterion for the planarity of $\dot{\text{C}}\text{H}_3$ radical since it is not possible to estimate the proton splitting coupling from theoretical calculations for non planar $\dot{\text{C}}\text{H}_3$. On the other hand, the ^{13}C coupling constant can be estimated in planar and tetrahedral $^{13}\dot{\text{C}}\text{H}_3$ radical. The

observed and calculated isotropic coupling constants for ^{13}C and $^{13}\dot{\text{C}}\text{H}_3$ have been found to be (+) 38.34 and 45 G, respectively. For methyl radical to be tetrahedral, the unpaired electron should reside in one of the four sp^3 hybrid orbitals each of which has 25 per cent s character. Thus, the interaction of unpaired electron with carbon nucleus should give rise to coupling constant of $(75 \times 4) = 300$ G. The very small value of observed ^{13}C splitting constant suggests that the unpaired electron has a very small amount of s character and it resides mostly in $p\pi$ -type orbital, which implies that $\dot{\text{C}}\text{H}_3$ has planar structure.

(d) π -electron Density and Molecular Conformation of Triphenylmethyl Radical; $(\text{C}_6\text{H}_5)_3\dot{\text{C}}$ The ESR spectrum of $(\text{C}_6\text{H}_5)_3\dot{\text{C}}$ radical in solution exhibits hyperfine splitting due to ring protons ($I = \frac{1}{2}$, natural abundance 99.985 per cent). Splitting due to carbon atom which is essential for the estimation of π -electron density and determination of conformation of $(\text{C}_6\text{H}_5)_3\dot{\text{C}}$ is not observed since ^{12}C is nonmagnetic ($I = 0$, natural abundance 98.9 per cent) and ^{13}C ($I = \frac{1}{2}$) has natural abundance of only 1.1 per cent. On the other hand, the radical tris-(3,5-di-*t*-butylphenyl)-methyl with isotopic enrichment at C-1 has a simpler spectrum than $(\text{C}_6\text{H}_5)_3\dot{\text{C}}$ and gives ^{13}C -splitting constants for all the five types of positions. Thus, it is used as a model radical to obtain π -electron spin density and molecular conformation of $(\text{C}_6\text{H}_5)_3\dot{\text{C}}$. The proton and ^{13}C splitting constant, a_{H} and $a_{^{13}\text{C}}$ for the model radical have been listed in Table 9.12. The signs of the a_{H} and $a_{^{13}\text{C}}$ values have not been determined experimentally, but are assumed on the basis of MO calculations.

Recalling McConnell equation

$$a_{\text{H},\mu} = Q\rho_{\mu} \quad (\text{Eq. 9.93})$$

and using $Q = -22.5$ G, we obtain $\rho_{\text{ortho}} = +0.114$ and $\rho_{\text{para}} = +0.124$ for radical $(\text{C}_6\text{H}_5)_3\dot{\text{C}}$. Spin densities at C-1, C-2, C-2' and C-2'', cannot be estimated by this method since these positions do not have attached proton. MO calculations reveal that there is induced negative π -electron spin density at the metacarbons, resulting in a positive a_{H} (meta) and a negative $a_{^{13}\text{C}}$ (meta). Because the phenyl rings are twisted, Eq. (9.93) is not applicable. However, ρ_{meta} can be calculated from the modified McConnell relation of the form

$$a_{\text{CH}_3,\mu} = Q_{\text{CH}_3}\rho_{\mu} \quad (9.94)$$

where, a_{CH_3} is the methyl proton splitting of *m*-tolylidiphenyl methyl radical, $a_{\text{CH}_3} = -0.84$ G and $Q_{\text{CH}_3} = +29$ G.

Thus,

$$\rho_{\text{meta}} = \frac{-0.84}{+29} = -0.029.$$

Further, the total spin density must be unity,

$$\rho_1 + 3\rho_2 + 6\rho_{\text{ortho}} + 6\rho_{\text{meta}} + 3\rho_{\text{para}} = 1$$

Substituting the values of ρ_{ortho} , ρ_{meta} and ρ_{para} we get,

$$\rho_1 + 3\rho_2 = 1 - 0.882 = 0.118 \quad (9.95)$$

The ^{13}C coupling constants $a_{^{13}\text{C},i}$ of a planar π -radical are related to the π -electron spin density ρ_i of carbon i and on the neighbouring carbons j by the Karplus–Fraenkel expression

$$a_{^{13}\text{C},i} = Q_{\text{C}}\rho_i + \sum_j Q_{\text{C}'\text{C}}\rho_j \quad (9.96)$$

Table 9.12 The proton and ^{13}C splitting constants —(the $a_{^{13}\text{C}}$ values are those measured for the model radical tris-(3, 5-di-*t*-butylphenyl)-methyl.

Position	$a_{\text{H}}(\text{G})$	$a_{^{13}\text{C}}(\text{G})$
1	—	+23.5
2	—	-11.3
ortho	-2.57	+6.5
meta	+1.13	-3.2
para	-2.81	+4.1

where, Q_c and $Q_{c'}$ are proportionality constants. $Q_c = 30.5$ and $Q_{c'} = -13.9$ G. For C-2 of triphenyl methyl radical, we use the observed value of $a_{13c} = -11.3$ G, $\rho_{ortho} = +0.114$.

Thus, Eq. (9.96) becomes

$$-11.3 = 30.5 \rho_2 - 13.9 (\rho_1 + 2 \times 0.114) \quad (9.97)$$

$$-11.3 = 30.5 \rho_2 - 13.9 (\rho_1 + 0.228)$$

Solving Eqs (9.95) and (9.97) for ρ_1 and ρ_2 we get, $\rho_1 = +0.387$ and $\rho_2 = -0.089$.

Thus, C-1, ortho-and para-positions have large positive n -spin densities whereas intervening C-2 and meta positions have smaller induced negative spin densities.

The deviation from planarity can have a pronounced affect on the a_{13c} of carbon centred radicals because the $2s$ AO directly contributes to the half filled MO. As the $2s$ spin density from orbital mixing and that from spin polarisation are both positive, nonpolarity results in an enhanced positive a_{13c} . The a_{13c} values for planar (or nearly planar) $\dot{C}H_3$ and the pyramidal $\dot{C}F_3$ are + 38.34 and + 271.6 G respectively.

In case of $(C_6H_5)_3\dot{C}$, the angle (θ') between the C-1 : C-2 bond and the plane defined by C-2, C-2' and C-2'' can be calculated from the relation

$$a_{13c}(\text{calc}) - a_{13c}(\text{obs}) = 2400 \tan^2 \theta' \quad (9.98)$$

The experimental value of a_{13c} for C-1 of $(C_6H_5)_3\dot{C}$ is + 23.6 G and the pure spin polarisation value, $a_{13c}(\text{calc})$ is 30.5 G [from Eq. 9.96]. These parameters give $\theta' = 3^\circ$ and a hybrid orbital containing less than 1 per cent s character. The higher spin density of +0.525 and -0.078 at C-1 and C-2 respectively, a θ' value of less than 1° , and less than 0.1 per cent s character in the hybrid AO has also been reported in the literature. Thus, it appears on the basis of ESR studies of $(C_6H_5)_3\dot{C}$ in solution that C-1 is sp^2 -hybridised and is virtually coplanar with its three nearest neighbours, i.e. C_2 , C_2' and C_2'' .

The angle of twist ϕ' , of the phenyl rings, i.e. the angle between the $2p$ orbitals of the ring and central carbon $2p$ orbital can be obtained from the observed and calculated values $a_{13c}(\text{ortho})$. Both these parameters are related to each other through Eq. (9.99).

$$a_{13c}(\text{ortho}) = \rho_{(\text{ortho})} Q \sin^2 \phi' \quad (9.99)$$

Use of $a_{13c}(\text{ortho}) = 6.5$ G, $Q = 355$ G and $\rho_{(\text{ortho})} = +0.095$ yields $\phi' = 26^\circ$.

The hybridisation of the central carbon atom C-1 as well as the spin density on it can also be determined directly from the anisotropic components of the hyperfine splitting constants measured from the ESR spectrum of the radical in the solid state. ESR spectrum of a single crystal of $(C_6H_5)_3\dot{C}$ gives $a_{13c} = 25$ G and $\tau_{||} = 35$ G for the central carbon atom. The calculated values of the isotropic coupling constant, A_{iso} and the anisotropic coupling constant $2B_0$ associated respectively with $2s$ and $2p$ orbitals of central carbon atom C-1 are $A_{iso} = 1100$ G and $2B_0 = 65$ G. These data yields $C_s^2 = 0.02$ and $C_p^2 = 0.53$. The high value of C_p^2 in combination with a near zero value for C_s^2 indicates that the radical centre C-1 is planar. The small C_s^2 value is due to spin polarisation mechanism.

In conclusion, complementary chemical information can be obtained from the solution spectra and from single-crystal ESR spectra.

9.17.8 Absolute Dating

ESR measures the electrons captured in bone or shell sample up to two million years. ESR testing on human tooth enamel dates some of the earliest anatomically modern humans to about 100,000 ($=10^5$) years.

9.18 BIOLOGICAL APPLICATIONS

ESR was first introduced into biology as a tool to probe the participation of free radicals in oxidation-reduction reactions and is a major tool in the characterisation of metallo proteins. Iron is the element which provides by far and wide the richest variety of ESR spectra with diagnostic characteristics established by high spin, low

Table 9.13 ESR parameters of metal ions in biochemical systems.

Metal Ion	Electronic Configuration	Spin State	Biological System	<i>g</i> -values	Nuclear Spin	Temperature (K)
Fe(III)	$3d^5$	1/2	Cytochrome	3.8–0.5	0	<100
Fe(III)	$3d^5$	5/2	Hemoproteins	8–1.8	0	<100
F(III)	$3d^5$	5/2	Non-heme iron	10–0.5	0	<100
Fe(III),	$3d^5, 3d^6$	1/2	Spinach	1.7–2.1	0	<50
F(II) pair			Ferredoxin			
3Fe(III),	$(3d^5)_3 3d^6$	1/2	HiPiP	2–2.2	0	< 50
Fe(II) tetrad						
Fe(III),	$3d^5(3d^6)_3$	1/2	Bacterial	1.7–2.1	0	<50
3Fc(II) tetrad			Ferredoxin			
Mn(II)	$3d^5$	5/2	Concanavalin A	2–6	5/2	<300
Co(II)	$3d^7$	1/2	Cobalamin (B_{12} r)	2.0–2.3	7/2	< 120
Co(II)	$3d^7$	3/2	Cobalt substituted proteins	1.8–6	7/2	<40
Cu(II)	$3d^9$	1/2	Plastocyanin	2–2.4	3/2	<100
Mo(V)	$4d^1$	1/2	Xanthine oxidase	1.95–2.0	5/2	<100

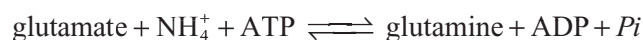
The ranges of *g*-values shown encompass both *g*-anisotropy in a given system and the variation among proteins.*

spin and polynuclear iron species. The unique contributions of ESR to the chemistry of iron sulphur proteins are an example of the power of the method. The technique is also of major value in the characterisation of heme proteins. The characteristic parameters of metal ions found in some biological systems have been listed in Table 9.13.

Biological molecules like hemins, chlorophyllins, polypeptides, amino acids are studied by substitution or introduction of different transition metal ions. By following the changes of the ESR spectrum of the metal ion in the free and bound state, one can deduce information about the environment close to the binding site or about the biomolecule as a whole.

ESR also provides a quantitative information on the concentration of a paramagnetic centre available in a given biological sample, e.g. it has been used to study the kinetics of reactivity of molybdenum in xanthine oxidase, the intensity of the ESR signal at $g \sim 1.95$ quantify the amount of Mo^{5+} , present at any time during the turnover of enzyme.

The enzyme glutamine synthetase is an oligomer which can bind $2Mn^{2+}$ per sub unit. It catalyses the reaction



and thus one can assume that there is a site for ATP on each sub-unit. On addition of Cr^{3+} -ATP, a paramagnetic analog of nucleotide to the enzyme-glutamate complex, the amplitude of low-field hyperfine line due to Mn^{2+} ($g_{||} = 2.0$) in the ESR spectrum of enzyme-glutamate complex recorded at 35 GHz decreases without any increase in linewidth and without any change in the shape of the ESR spectrum. The decrease in amplitude of ESR signal with concentration of CrATP is hyperbolic which implies that a single dissociation step is operating ($K_d = 280 \mu M$). From the total decrease in the ESR signal amplitude, distance between two paramagnetic metal ions, i.e. Mn—Cr has been found to be $5.2 \pm 0.5 \text{ \AA}$. The metal–metal distance in Mn—CrATP is $7.1 \text{ \AA}$. This increase in metal-metal, i.e. Mn—Cr distance in the absence of substrate provides an evidence for the conformational change on substrate binding to this enzyme. The metal–metal distance in the presence of a number of substrate and substrate analogs, have been listed in Table 9.14.

Table 9.14 Distance between Mn^{2+} – and Cr^{3+} – or Co^{2+} nucleotides for various complexes of glutamine synthetase.

Enzyme Complex	Distance ($\text{\AA}$)
Mn–Cr ATP	7.1
Mn–Cr ATP-glutamate	5.2
Mn–Cr ATP-glutamate- NH_4^+	5.9
Mn–Cr ATP-glutamine	5.9
Mn–Cr ATP-methionine-SR-sulfoximine	6.8
Mn–Cr ADP	5.9
Mn–Cr ADP- P_i	5.2
Mn–Cr ADP-glutamine	6.2
Mn–Cr ADP-glutamine- P_i	4.8
Mn–Cr ADP-methionine-SR-sulfoximine	5.8
Mn–Cr ADP-methionine-SR-sulfoximine- P_i	7.6
Mn–Co-methionine-SR-sulfoximine	7.3
Mn–Co-ADP-methionine-SR-sulfoximine	6.5
Mn–Co-ADP-methionine- SR-sulfoximine- P_i	4.9
Mn–Co-ATP-methionine-SR-sulfoximine	5.2

$g = 4$ for Co^{2+}

Erythrocyte is a copper-transporting protein. The ESR signals of oxidised bovine erythrocyte are similar to those obtained with human erythrocyte, i.e. $g_{||} = 2.263$, $g_{\perp} = 2.062$ and $A_{||} = 0.014 \text{ cm}^{-1}$. At 7.5 pH, four hyperfine components are centred at the $g_{||}$ position and the superhyperfine splitting is approximated 14 G [Fig 9.44(a)]. Exposure of the protein to 6M guanidine hydrochloride causes no measurable changes in the ESR spectrum. Thus, the detection of the number of transferable electrons is possible. Aqueous dithionite effectively reduced erythrocyte. The plot of height of the $g_{\perp}$ signal against dithionite concentration is straight line [Fig. 9.44(b)]. One mole of erythrocyte required one mole of dithionite indicating the transfer of two electrons per mole of erythrocyte.

ESR measurements of cyanide-, cyanate-, thiocyanate- and azide-treated erythrocyte revealed changes in the ESR parameters (Table 9.15). Data revealed that there are at least four anion-binding sites of different nature on the protein. These can be classified into two portions. One of these portions strongly binds two moles of azide causing a substantial change in the ESR spectrum. These two binding sites are thought to be the Zn^{2+} of the protein. The second portion of binding sites is attributed to the Cu^{2+} which binds the cyanide. The evidence of the proximity of Zn^{2+} and Cu^{2+} , i. e. Cu^{2+} and Zn^{2+} form a ligand bridged by metal ligand complex, is obtained by using erythrocyte with the Zn^{2+} partially replaced by Co^{2+} . This substitution caused a marked reduction of the Cu-ESR signal indicating magnetic interaction between the two paramagnetic ions.

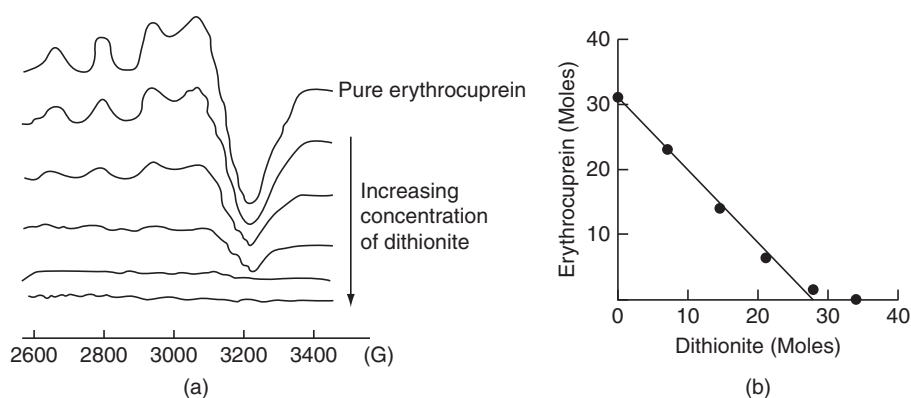


Fig. 9.44 (a) ESR spectra of bovine erythrocyte (0.305 mM) in absence and presence of aqueous (sodium or potassium) dithionite (7.04 mM) under argon for 2.5 min at 20°C before freezing to 77 K (pH = 7.5, microwave frequency 9.175 GHz) (b) Behaviour of erythrocyte reduction with concentration of dithionite.

Table 9.15 ESR parameters of anion-erythrocyte complexes.

Complex	$g_{ }$	$g_{\perp}$	$A_{ } (G)$
Native erythrocyte in water	2.27	2.09	137
Azide			
2 per mole	2.263	2.074	175
3 per mole	2.260	2.072	148
4 per mole	2.254	2.069	153
8 per mole	2.253	2.066	155
200 per mole	2.242	2.054	158
2 azide and 2 cyanide	2.22		180
Excess cyanide	2.21		188
Excess cyanate	2.268	2.068	160
Excess thiocyanate	2.27	2.076	148

Chemical, structural and kinetic properties of ESR inactive biological molecules such as the enzymes (lysozyme, ribonuclease, DNA polymerase, citrate synthase), lipids, peptides and amino acids can be obtained from ESR studies of synthetic organic free radicals which are chemically attached to these molecules. Such radicals are called spin label radicals (i.e., paramagnetic markers). They are generally nitroxide radicals of the type $R_2\dot{N}O$. They are very stable and inert and have characteristic, intense and simple ESR spectra that are sensitive to molecular environment. Specific sites in a molecule can be tagged by choosing suitable spin label and reaction conditions. Thus, by following the changes of the ESR spectrum, i.e. line splitting and g -factor parameters of the spin label radical in the free and bound state, one can deduce information regarding the environment close to the binding site or about the biomolecule as a whole. For example the spin label radical: N-(1-oxyl-2,2,5,5-tetramethylpyrrolidinyl)-maleimide (I) is attached to bovine serum albumin (BSA). This particular radical is chosen because N-ethyl maleimide (II) reacts specifically with the —SH groups of BSA. Thus, in order to study the environment close to the —SH site we need a radical which contains a functional group to react with the sulphur atom. This radical can also be attached to an amino site in the lysine group in BSA. The spin-labelled lysine is prepared by blocking the —SH group of BSA with N-ethylmaleimide and then reacting the product with nitroxide radical. The ESR spectra of the nitroxide radical when it is attached to the —SH group and when it is attached to the lysine group of BSA is shown in Fig. 9.45. The arrows in Fig. 9.45(a) shows that the spectra is a superposition of two spectra of the radicals because of two different environments. The similarity between the central spectrum of BSA with spin labelled —SH group [Fig. 9.45(a)] and central spectrum of BSA with spin labelled lysine group [Fig. 9.45(b)] suggests relative free motion of the spin-label radical. The broad line spectrum of BSA with spin labelled —SH group indicates that the spin label cannot rotate freely. The rotational time estimated from peak-to-peak width and the measured peak-to-peak amplitudes of three lines of ESR spectrum of spin label is about 10^{-8} s. At pH 2.1, the reversible denaturation of BSA occurs. In such a situation, the intensity of the ESR signal of protein with spin-labelled —SH group becomes zero, whereas becomes double in case of protein with spin-labelled lysine. It is to be noted that even in the mobile spin label case, the intensity of the three lines is not equal as expected thereby leading to suggest that the spin label does not have complete rotational freedom and asymmetry of lines is caused by anisotropic effects. A schematic diagram for the native and spin-labelled protein is shown in Fig. 9.46. In conclusion, the ESR studies reveal that (i) the

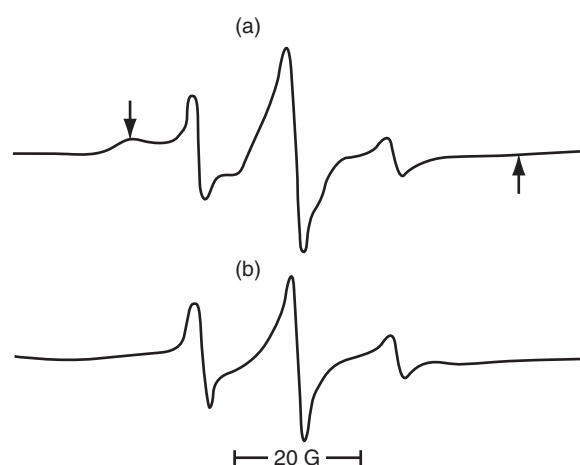
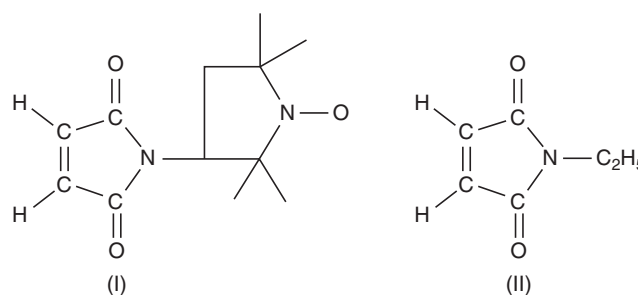


Fig. 9.45 ESR spectrum of bovine serum albumin (BSA) spin labelled with the nitroxide maleimide. (a) BSA with spin labelled —SH group, and (b) BSA spin labelled lysine group.

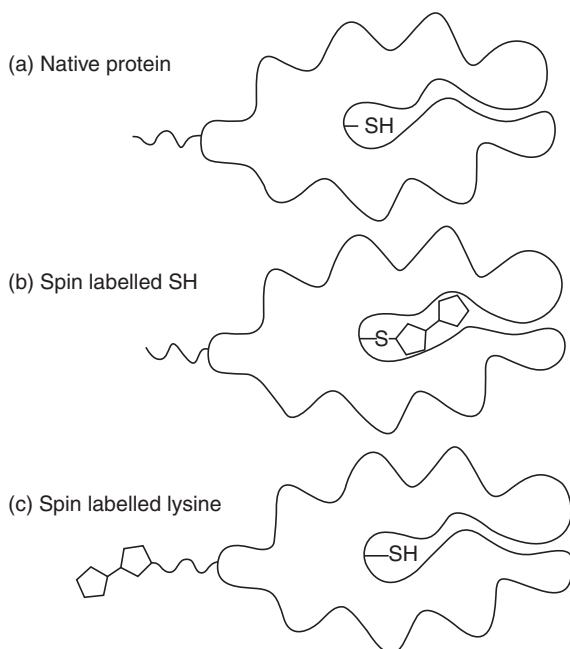


Fig. 9.46 Schematic diagram of (a) native protein, (b) protein with spin-labelled —SH group yielding an immobile spin, and (c) protein with spin-labelled lysine group yielding mobile spin.

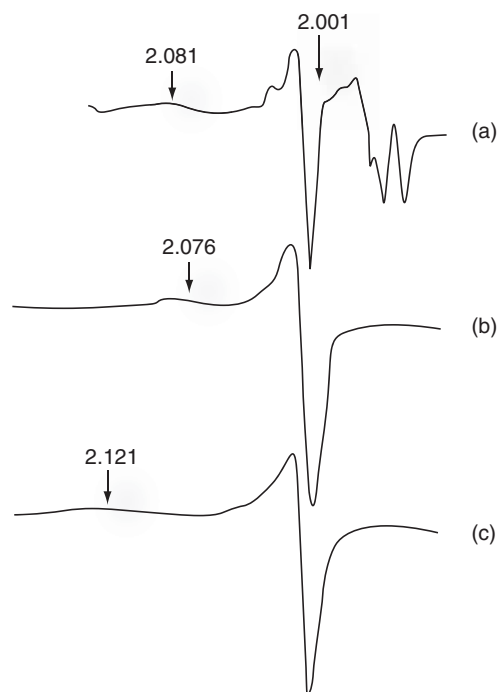


Fig. 9.47 ESR signals of $\bar{\text{O}}_2$ obtained both enzymically and non-enzymically obtained at -170°C (a) Xanthine-Xanthine oxidase reaction. The sloping baseline is attributed to an iron signal. Note the molybdenum signals (over modulated). (b) and (c): Non-enzymically induced $\bar{\text{O}}_2$ from H_2O_2 and NaIO_4 at pH 9.9 and 13.2 respectively.

protein structure is sufficiently open for the entry of spin label for reaction with —SH group, and (ii) the protein structure in the neighbourhood of —SH group is sufficiently close for the immobility of the spin label, i.e. the spin label cannot rotate freely. Thus the protein has an elastic character.

The conformational changes of biomolecules in the solution phase can be studied using biradicals, i.e. molecules containing two radicals in a single molecule connected by long chains. Spin exchange occurs between two radicals. The conformational changes of biomolecules cause dynamic changes in the exchange coupling between the radicals. This results in a time-dependent ESR spectrum.

Many biological reactions take place via free radical mechanism. The enzymatic catalysis occurs through free radical intermediates. The study of oxygen, superoxide and hydroxyl radicals are of importance in cancer research. The most established source of superoxide ($\bar{\text{O}}_2$) in enzymic systems proved to be flavoproteins. The actual presence of ($\bar{\text{O}}_2$) is determined by ESR studies using the enzymic reactions of flavoproteins. The ESR signals of $\bar{\text{O}}_2$ obtained both enzymically and non-enzymically recorded at -170°C , by rapid freezing technique is displayed in Fig. 9.47(a–c).

Nitric oxide is a relaxant of blood vessels. These radicals may be studied *in vivo* by CW and FTESR methods to determine their activity in different organs and tumours. A special technique called the spin-trap is employed for their identification and detection. A spin-trap is an ESR inactive molecule by itself but forms an adduct by extracting a free radical thereby becoming ESR active. Nitrogen and proton, etc., hyperfine splittings of the spin adducts are diagnostic parameters for the identification of the radical spin adduct formed.

Several narrow line spin probes capable of targeting the organs of living animals have been developed. ESR imaging on animals is done to study the action of brain, heart, liver and tumour growth. *In vivo* ESR imaging of drug distribution and oxygen and nitric oxide mapping have been reported. ESR images of nitric oxide have been measured at 700 MHz in the head of a rat. Anatomic FTESR images of mice have been measured at an operating frequency of 280 MHz.

PROBLEMS

1. At what temperature, will the intensity of ESR signal reduce to one-fourth of its value at 77 K?

[Ans: 308 K]

2. Prove that

$$a(G) = 0.35683 \left(\frac{g_{\text{free electron}}}{g_{\text{radical}}} \right) a(\text{MHz})$$

3. For an ESR instrument that operates at a frequency of 70 GHz, calculate the static magnetic field required and the value of ΔE . [Ans: $H = 25$ kG; $\Delta E = 4.63 \times 10^{-16}$ erg]

4. Predict the number of ESR lines in (a) *p*-semibenzoquinone, (b) monochloro-, (c) 2,3-dichloro-, (d) trichloro-, and (e) tetrachloro semibenzoquinone, (f) NH_2 , (g) AB_3 (I for $A = 0$ and $B = 3/2$), (h) atomic oxygen, (i) NF_2 , (j) carbon black. How does the splitting of each spectrum arise?

[Ans: (a) 5, (b) 4, (c) 3, (d) 2, (e) 1, (f) 9 (Three major lines with intensity ratio 1:1:1 are due to coupling of electron with nitrogen nucleus. Each of these lines then again split into triplet by weak coupling of two equivalent protons), (g) 4, (h) 6, (i) 9, (j) 1]

5. Predict the number of ESR lines in the spectrum of K_3CrO_8 . The natural abundance of nonmagnetic isotopes of chromium ($I = 0$), i.e. ^{50}Cr , ^{52}Cr , $^{54}\text{Cr} = 90.5$ per cent and of magnetic isotope ^{53}Cr ($I = \frac{3}{2}$) is 9.5 per cent

Also compute the relative intensity of ESR lines.

[Ans: 1 (nonmagnetic isotopes) + 4 (magnetic isotope) = 5.

$$\frac{I(\text{nonmagnetic isotopes})}{I(\text{magnetic isotope})} = 38]$$

6. The measured 'a' values for the two non-equivalent 1 and 2 sets of protons of naphthalenide ion are (–) 4.9 and (–)1.83 G respectively. What would be the electron density at each of the 1 and 2 carbon atoms?

[Ans: 0.21 and 0.08]

7. (a) How many lines are expected in the spectrum of free radical *p*-benzosemiquinone and what would be the relative intensities of these?

- (b) The magnitude of coupling between each ring hydrogen and the paramagnetic electron is about –2.4 G. Calculate the electron density at each atom of the molecule.

[Ans: (b) each H = – 0.005, each C = – 0.085, each O (by difference) = – 0.24]

- **Hint:** Electron density on carbon atom of $\dot{\text{C}}\text{H}_3$ radical is – 0.85 [$a(\dot{\text{C}}\text{H}_3) = -23.7$ G].

8. Predict the number of lines in the ESR spectrum of 2-methyl-1-4-benzo-semiquinone radical ion and what would be the relative intensity of these lines?

[Ans: 7, 1 : 6 : 15 : 20 : 15 : 6 : 1]

- **Hint:** If a double bond or a system of double bonds is followed by a single bond, e.g. methyl substituted aromatic radicals, the double-bond character may be partially transferred to the single bond. The spin density is the same at the methyl protons as at the ring protons, i.e. the methyl protons are equivalent to ring protons.

9. Predict the number of lines in the ESR spectrum of 2,5-methyl-1,4-benzosemiquinone and what would be the number of different types of coupling constant?

[Ans: 21, 2]

- **Hint:** Protons in two different environments are involved. The large septet with an intensity ratio of 1 : 6 : 15 : 20 : 15 : 6 : 1 arises from six equivalent protons. Each of these lines is then split into triplet by weak coupling of two protons ($2 \times 1/2 \times 2 + 1$) = 3 Distance between triplet centres corresponds to larger coupling constant while the distance between the hyperfine pattern of each triplet corresponds to the smaller coupling constant.

10. Predict the number of lines in the ESR spectrum of $(\text{SO}_3)_2\text{NO}^{2-}$. The natural abundance of N^{14} ($I = 1$) is 99.635 per cent and of N^{15} ($I = 1/2$) is 0.365 per cent, Also calculate the relative intensity of ESR lines.

[Ans: $3(^{14}\text{N}) + 2(^{15}\text{N}) = 5$; $I(^{14}\text{N})/I(^{15}\text{N}) = 182$]

11. Calculate the π -spin density ρ_μ on carbon atom μ in the following planar ring system.

System	μ	$a_{H, \mu}$ (G)
Anthracene $^{\cdot-}$	1	(–) 2.74
	2	(–) 1.51
	9	(–) 5.34
Phenanthrene $^{\cdot-}$	1	(–) 3.60
	2	(+) 0.72
	3	(–) 2.88
	4	(+) 0.32
	9	(–) 4.32

[Ans: Anthracene $^{\cdot-}$: $\rho_1 = +0.122$; Phenanthrene $^{\cdot-}$: $\rho_9 = +0.192$]

12. Show that the Zeeman interaction for electron is very large as compared to that of proton at 3.3 kG.

13. The hyperfine splitting constant for ^1H in $\dot{\text{C}}\text{H}_3$ radical is 25 G. Draw an energy-level diagram to show the expected number of lines and intensities and hence construct a theoretical stick diagram. Extend the problem to tetracyanoethylene anion radical, $a(^{14}\text{N})$ in $\text{TCNE}^{\cdot-} = 1.56$ G.

14. Calculate the population difference between the two states of the electron at $T = 300$ K and $H = 3.3$ kG provided the total number of unpaired electrons in both populations is 10^5 . What would be the effect on population if (i) applied field is doubled and temperature is reduced to one half, (ii) temperature is doubled and field is kept constant, and (iii) temperature is doubled and field is reduced to one half?

15. The ratio of the two unpaired electron populations in thermal equilibrium is governed by the Boltzmann distribution law. Determine the ratio between two populations at $T = 300$ K and $H = 3.3$ kG if the total number of unpaired electrons in both populations is 10^5 . What would be the effect on the population ratio if (i) applied field is doubled and temperature is reduced to one half,

(ii) temperature is doubled and field is kept constant, and (iii) temperature is doubled and field is reduced to one half? Draw a graph between population ratio and applied field at 300 K and also between population ratio and $\frac{1}{T}$ at $H = 3.3$ kG.

16. The ESR spectrum of some hypothetical free radical consists of five lines with intensity ratio of 1:3:5:3:1. Draw absorption curve from the data and convert it to the first derivative curve and vice versa.
17. From the experimental and theoretical ESR data given below in the tabular form, calculate the values of angles θ and ϕ .

Variation Number	Radical	Nucleus	Hyperfine Constants (G)			
			Observed		Calculated	
			a	$\tau_{\parallel}$	$A_{iso}(2s)$	$2B_o(2p)$
1	$(C_6H_5)_3\dot{S}i$	^{29}Si	80	40	1600	70
2	$(C_6H_5)_3\dot{G}e$	^{73}Ge	83	25	830	31
3	$(C_6H_5)_3\dot{S}n$	^{119}Sn	1866	469	15550	642

[Ans: 1: $\theta, \phi = 116.2^\circ, 101.9^\circ$; 2: $114.9^\circ, 103.5^\circ$ 3: $113.5^\circ, 105.1^\circ$]

18. The coupling constants for the ortho-, meta- and para protons in $(C_6H_5)_3\dot{C}$ are $(-)$ 0.93, $+$ (0.46) and $(-)$ 0.93G respectively. Calculate the π -spin densities for the respective ring protons. Use $Q = -23.96$.

[Ans: $\rho(o) = +0.039$; $\rho(m) = -0.019$; $\rho(p) = +0.039$]

19. Consider an unpaired electron that interacts with two inequivalent protons ($H-C-OH$). Sketch the electron-spin transitions that occur. How many lines does the EPR spectrum have? Prove the statement in the text that, in general, the number of lines is given by 2^n for an electron that interacts with n inequivalent protons.

[Ans: Four lines of equal intensity]

- **Hint:** For two equivalent protons, number of lines = $(2nI + 1) = (2 \times 1/2 \times 2 + 1) = 3$.

20. By making use of Table 9.5, prove that in a square planar Cu (II) complex, when the electron resides in the $d_{x^2-y^2}$ and d_{z^2} orbitals respectively, the values of $g_{\perp}$ are given by

$$g_{xx} = g_{\perp} = 2.00 - \frac{2\lambda}{E_{d_{x^2-y^2}} - E_{d_{xz}, d_{yz}}}$$

and

$$g_{yy} = g_{\perp} = 2.00 - \frac{6\lambda}{E_{d_{z^2}} - E_{d_{xz}, d_{yz}}}$$

21. (a) Convert the first-derivative spectrum of a free radical shown in Fig. 9.48 (a), into its absorption spectrum.
 (b) Sketched in Fig. 9.48 (b) is the absorption spectrum of some free radical, obtain its first derivative spectrum.

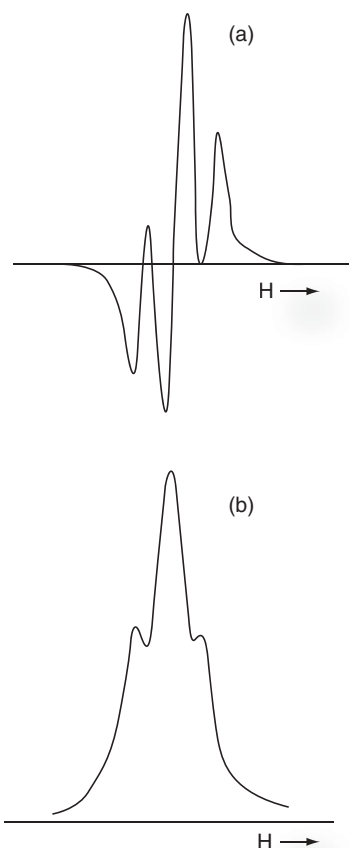
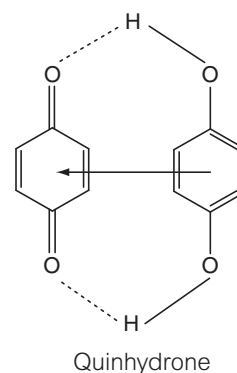


Fig. 9.48 (a) First-derivative ESR spectrum of a free radical, and (b) absorption spectrum of some free radical.

22. (a) When solutions of equimolar compounds of *p*-benzoquinone and hydroquinone are mixed, slightly soluble, nearly black crystals of quinhydrone begin to separate out. Quinhydrone is molecular compound consisting of these two substances, in which the molecules are united through hydrogen bonds and, besides, by charge transfer from hydroquinone to the quinone;

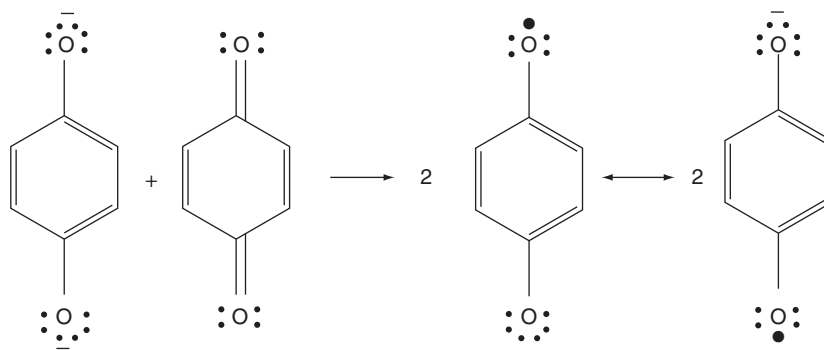


- (b) If we label, say benzoquinone, by introducing deuterium into it, it will turn out that the two halves of the quinhydrone molecule do not inter convert, as might be expected; and

- (c) But if quinhydrone is dissolved in alkali, i.e. if the bonding hydrogen atoms (protons) are removed, the hydroquinone anion will donate one electron to the quinone, and both compounds will be converted into two identical molecules of semiquinone. What spectroscopic techniques might be employed

to study the phenomena occurring in the above cases?

[Ans: (a) IR, NMR, electronic spectroscopy
(b) IR, NMR, electronic spectroscopy (c) EPR.]



CHAPTER 10

MÖSSBAUER
SPECTROSCOPY

The book of nature is written in a mathematical language whose letters are triangles, circles, and other geometrical figures.

—Galileo

10.1 INTRODUCTION

Mössbauer spectroscopy (MBS), also known as γ -ray nuclear resonance fluorescence –, γ -ray recoil free and zero phonon spectroscopy, deals with the study of recoilless nuclear transitions arising due to the absorption or fluorescence of γ -rays by the sample called *target*. The absorption of γ -rays by the sample depends on the electron density around the nucleus and the number of lines obtained in the Mössbauer spectrum are related to the symmetry of the target under investigation. MBS is of fundamental importance in that it provides a means of measuring comparatively weak interactions between nucleus and surrounding electrons. Unlike nuclear magnetic resonance and nuclear quadrupole resonance, which deal with only the ground-state properties of the nucleus, MBS deals with both the excited as well as the ground-state properties of the nucleus. It was discovered in 1958 by Rudolph L Mössbauer, a German scientist working for his PhD degree at Heidelberg University and in 1961, the Nobel prize was awarded to him for researches concerning the resonance absorption of gamma radiation.

10.2 PRE- AND POST-MÖSSBAUER ERA

Before going into the details of the theoretical and practical aspects of **MBS**, let us first review the pre-Mössbauer time during which it was realised on the basis of γ -ray resonance fluorescence experiments that a small overlap between the emission and absorption transitions, as expected, theoretically exists. The phenomenon of γ -ray resonance may occur between two nuclei shown schematically in the ground and excited states in Fig. 10.1. It is pertinent to note that in γ -ray nuclear fluorescence, usually the low-lying nuclear excited states having lifetimes in the range of 10^{-11} – 10^{-4} second are involved. Now when the γ -rays with energy E_γ is emitted by the nucleus (source), it experiences a recoil E_γ such that

$$E_0 - E_R = E_\gamma \quad (10.1)$$

$$E_0 - E_\gamma = E_R$$

where, E_0 is the nuclear transition energy.

Similarly, for the absorption of γ -ray by the nucleus within the absorber (target), we can write,

$$E_0 + E_R = E_\gamma \quad (10.2)$$

$$E_\gamma - E_0 = E_R$$

Accordingly, the separation between the emission and absorption will be $2E_R$ and is shown in Fig. 10.2(a). Here, no overlapping will occur between the absorption and emission lines.

Now, if M_0 is the rest mass of the nucleus it will acquire a velocity v_R by the emission of γ -ray such that

$$E_R = \frac{1}{2} M_0 v_R^2 = \frac{(M_0 v_R)^2}{2M_0} = \frac{P_R^2}{2M_0} \quad (10.3)$$

Here, p_R is the momentum of the recoiling nucleus.

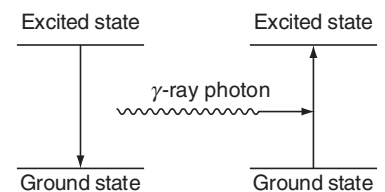


Fig. 10.1 Schematic diagram for the nuclear transition between excited and ground states in two nuclei.

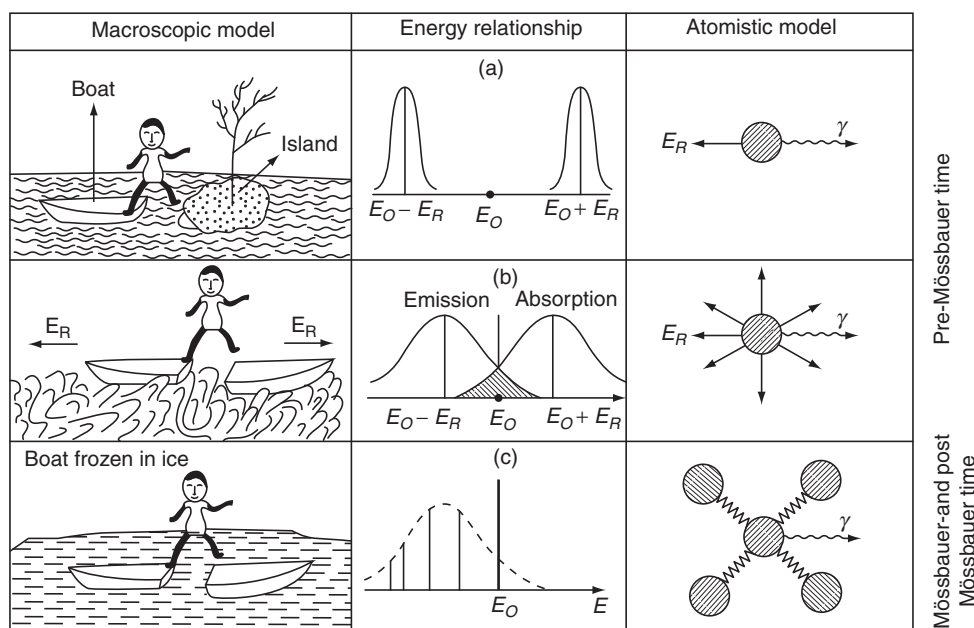


Fig. 10.2 Energy relationship relevant to Mössbauer effect: (a) $2E_R > \Gamma$ (b) $2E_R < \Gamma$ (c) $2E_R = \Gamma$ and macroscopic and atomistic models of the pre-Mössbauer era, MB- and post-Mössbauer era.

We know that the momentum of γ -ray is given by,

$$P_\gamma = \frac{E_\gamma}{c} \quad (10.4)$$

According to law of conservation of momentum, p_R and p_γ are equal in magnitude and opposite in sign. Therefore, for small recoils ($E_R \ll M_0 c^2$), we may write

$$E_R = \frac{P_\gamma^2}{2M_0} = \frac{E_\gamma^2}{2M_0 c^2} = \frac{E_0^2}{2M_0 c^2}$$

or

$$2E_R = \frac{E_0^2}{M_0 c^2} \quad (10.5)$$

For a nucleus with $E_0 = E_\gamma = 10^4$ eV, $M_0 = 50$ amu and lifespan of the excited nuclear state = 10^{-7} second, $E_R = 10^{-3}$ eV

or

$$2E_R = 2 \times 10^{-3} \text{ eV.}$$

The line width Γ of the emitted line is defined as

$$\Gamma = \frac{h}{2\pi} \cdot \frac{1}{\tau} \quad (10.6)$$

where, τ is the mean lifespan of the excited state of the nucleus, τ is related to half life of the state by,

$$\frac{1}{\tau} = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \quad (10.7)$$

If τ is given in electron volts ($1 \text{ eV} = 1.60219 \times 10^{-19} \text{ J} = 96.49 \text{ kJ mole}^{-1}$) and τ in seconds, then Eq. (10.6) reduces to

$$\Gamma = \frac{6.58 \times 10^{-16}}{\tau} \text{ eV} \quad (10.8)$$

Thus for the typical nucleus,

$$\Gamma = \frac{6.58 \times 10^{-16}}{10^{-7}} = 6.58 \times 10^{-9} \text{ eV}$$

This small value of Γ (10^{-9} eV) as compared to $2E_R$ (10^{-3} eV) suggests that there is no possibility of absorption of γ -photon emitted by the nucleus at rest. Thus, it follows from equations (10.5) and (10.6) that resonance absorption will not occur if $2E_R > \Gamma$. For resonance absorption to take place, $2E_R \approx \Gamma$, i.e. resonance absorption will take place only if an overlapping happens between the emission and absorption lines as shown in Fig. 10.2(b).

This is the picture when the nucleus is at rest. Let us now consider the emission of γ -rays from a nucleus moving (due to thermal agitation) with velocity v_N along the direction of γ -rays. The nucleus will now recoil with a new velocity $(v_R + v_N)$ and a total kinetic energy $\frac{1}{2}M_0(v_R + v_N)^2$.

By law of conservation of energy, we can also write,

$$E_0 + \frac{1}{2}M_0v_R^2 = E_\gamma + \frac{1}{2}M_0(v_R + v_N)^2 \quad (10.9)$$

Further, if relative velocity v_s is imposed on the source, the velocity of nucleus, i.e. v_N in Eq. (10.9) should be replaced by $(v_N + v_s)$. Consequently, Eq. (10.9) modifies to,

$$E_0 + \frac{1}{2}M_0v_R^2 = E_\gamma + \frac{1}{2}M_0(v_R + v_N + v_s)^2 \quad (10.10)$$

$$\left[\begin{array}{l} \text{Since } M_0v_s = \frac{E_\gamma}{c} = \frac{E_0}{c} \\ \text{Therefore, } v_s = \frac{E_0}{M_0c} \end{array} \right] \quad (10.11)$$

Eq (10.10) yields

$$E_\gamma = E_0 - \frac{1}{2}M_0(v_N + v_s)^2 - M_0v_R(v_N + v_s) \quad (10.12)$$

If v_s is ignored for the time being, then Eq. (10.12) reduces to

$$E_\gamma = E_0 - \frac{1}{2}M_0v_N^2 - M_0v_Rv_N \quad (10.13)$$

or

$$E_\gamma = E_0 - E_R - E_D$$

where,

$$E_R = -\frac{1}{2}M_0v_N^2 \text{ and } E_D = M_0v_Rv_N$$

It follows from Eq. (10.13) that the energy of the emitted γ -photon is deficient by a recoil kinetic energy $\left(E_R = \frac{1}{2}M_0v_N^2\right)$ which is independent of the initial recoil velocity v_R of the nucleus and the thermal Doppler energy $(E_D = M_0v_Nv_R)$ which is v_R dependent and can therefore be positive or negative.

Thus, in general we may write

$$E_\gamma = E_0 - E_R \pm E_D \quad (\text{emission}) \quad (10.14)$$

$$E_\gamma = E_0 + E_R \pm E_D \quad (\text{absorption})$$

If θ is the angle between the directions of propagation of γ -rays and moving nucleus respectively then

$$E_D = \frac{v_N}{c}E_\gamma \cos \theta \quad (10.15)$$

Applying the law of conservation of momentum to the emission process, we obtain,

$$M_0v_R = M_0(v_R + v_N) + \frac{E_\gamma}{c} \quad (10.16)$$

$\frac{E_\gamma}{c}$ is the momentum of γ -photon and hence the recoil momentum is $-\frac{E_\gamma}{c}$. Thus the recoil energy is expressed as

$$E_R = \frac{E_\gamma^2}{2M_0c^2} \quad (10.17)$$

or

$$E_R = 5.37 \times 10^{-4} \frac{E_\gamma^2}{M_0} \text{ eV}$$

where E_γ is in keV, M_0 is in amu.

It follows from Eq. (10.17) that the recoil energy E_R is directly proportional to the square of the energy of γ -rays and inversely to the mass of the nucleus. E_D depends upon the thermal motion of the nucleus. Nuclear recoil (E_R) and Doppler (E_D) energies are of the order of 10^{-4} – 10^{-2} eV and are compared with some nuclear and chemical interactions in Table 10.1. For nuclei moving isotropically, the energy distribution due to linear Doppler effect to E_γ , i.e. line positioned at E_γ is governed by Maxwell velocity distribution law. The Doppler broadening of energy distribution estimated from the theory of ideal gas is given by

$$D_T = 2\sqrt{E_k E_R} \quad (10.18)$$

where, $E_k = \frac{1}{2} \kappa T = \frac{M}{2\bar{v}_N^2}$ is the mean kinetic translation energy per degree freedom per atom, κ is the Boltzmann

constant and $\bar{v}_N^2$ is the mean square velocity in the direction of observation. Eq. (10.18) reveals that D_T is proportional to the square root of the thermal energy (E_k) and recoil energy (E_R). D_T for a gas made up of atoms with $M_0 = 100$ is about 10^3 eV for 1 keV γ -ray transitions and about 1 eV for 1 MeV transitions. The shift in γ -ray energy due to linear Doppler effect manifests itself in line broadening. This suggests that energy loss because of recoil can be compensated by the linear Doppler effect. Consequently, a small overlap between the emission and absorption distributions takes place as shown in Fig. 10.2(b). It is to be noted that in ultraviolet and optical spectroscopy, the emission and absorption bands overlap to a great extent due to the small recoil energy involved.

This was the situation in the pre-Mössbauer time. During this period, γ -ray resonance fluorescence experiments had already been performed. It was realised that the small overlap between emission and absorption areas, i.e. energy distributions as shown in Fig. 10.2(b) made these experiments possible. The energy loss in the recoil process was compensated by ultracentrifugation, increasing the temperature of the nucleus and (p, γ) nuclear reactions with photon being emitted by the excited nucleus in flight; the Doppler contribution in this case as already mentioned is given the expression:

$$E_D = \frac{E_\gamma}{c} v_N \cos \theta \quad (\text{Eq. 10.15})$$

Hence, it is possible to find an angle θ at which γ -rays are resonantly absorbed. The compensation of the recoil energy loss by Doppler effect was used in 1951 by P B Moon to obtain resonance scattering of the 411 eV transition of ^{198}Hg by ultracentrifugation. Using a rotor to move the ^{198}Au source, which decays to ^{198}Hg and a mercury absorber, he observed that the intensity of the resonantly scattered radiation grows with the velocity of the rotor. Maximum intensity was observed at ≈ 700 m/s in agreement with the relative velocity v_s imposed on the source, i.e. 670 m/s in this case.

Table 10.1 Energies of some nuclear and chemical interactions and energy equivalence.

Interactions	Energy range (kJ mole ⁻¹ /eV)
Mössbauer γ -ray energy (E_γ)	$10^6 - 10^7/10^4 - 10^5$
Chemical bonds and lattice energies	$10^2 - 10^3/1 - 10$
Electronic transitions	$50 - 500/0.5 - 5$
Molecular vibrations	$5 - 50/0.05 - 0.5$
Lattice vibrations	$0.5 - 5/0.005 - 0.05$
Nuclear recoil(E_R) and Doppler(E_D) energies	$10^{-2} - 1/10^{-4} - 10^{-2}$
Nuclear quadrupole coupling constants	$<10^{-3}/<10^{-5}$
Nuclear Zeeman splittings	$<10^{-3}/<10^{-5}$
Heisenberg natural line widths	$10^{-7} - 10^{-4}/10^{-9} - 10^{-6}$
Energy equivalence	
1 atomic mass unit	$= 931 \text{ MeV} = 1.49 \times 10^{-3} \text{ erg} = 3.56 \times 10^{-11} \text{ cal}$
1 electron mass	$= 0.510 \text{ MeV}$
1 MeV	$= 1.07 \times 10^{-3} \text{ amu} = 1.602 \times 10^{-6} \text{ erg}$ $= 3.827 \times 10^{-14} \text{ cal}$
1 eV/molecule	$= 23.06 \text{ kcal/mole}$
1 mm/second	$= 4.807 \times 10^{-8} \text{ eV} = 11.62 \text{ MHz}$

Mössbauer in 1958 while studying the resonance absorption of the 129 keV transition of ^{191}Ir observed that fluorescence becomes stronger at lower temperatures [Fig. 10.2(c)] instead at higher temperatures as expected. The result was interpreted using Lamb's theory for resonance capture of thermal neutrons in crystals. The marked increase in resonance scattering may be because of the emission and absorption of recoil free γ -rays since at low temperatures, the nuclei are fixed. To summarize, Figs 10.2(a) and (b) represent the pre-Mössbauer time and 10.2(c) characterise the Mössbauer discovery, i.e. a recoil-free line exists at E_0 . This line is called the Mössbauer line. The pre-MB era and post-MB era may also be demonstrated by the macroscopic model based on the γ -jumps from a boat with an effort of energy E_0 and atomistic model (Fig. 10.2).

So far we have treated the nucleus to be free at rest or in motion. If the nucleus is bound in a solid, the interaction arising because of the exchange of individual recoil energy among the atoms in the lattice need be considered. The effect of lattice coupling in a recoil nucleus is expressed in terms of a dynamical effective mass M_{eff} given by

$$E_R = \frac{E_\gamma^2}{2M_{\text{eff}}c^2} \quad (10.19)$$

For large values of M_{eff} ; $E_R \ll \Gamma$. The binding energy of an atom in a lattice is about several eV while the recoil energy of the free atom for a 100 keV γ -emission is about hundred times less. This energy is dissipated in altering the vibrational state of the lattice, i.e. by phonon propagation through the crystal lattice. Thus, if phonons are created in the nucleus in the recoil process of it, the energy of the emitted γ -ray will be deficient by

$$\sum_i \frac{h\omega_{E_i}}{2\pi} \text{ or } \sum_i h\nu_{E_i} \text{ and} \\ E_\gamma = E_0 - \sum_i \frac{h\omega_{E_i}}{2\pi} \quad (10.20)$$

or

$$E_\gamma = E_0 - \sum_i h\nu_{E_i}$$

where ω_{E_i} / ν_{E_i} corresponds to the frequency of the phonons. When the factor $\sum_i \frac{h\omega_{E_i}}{2\pi} > \Gamma$, the γ -ray cannot be

resonantly absorbed. But we know that the recoil energy is negligible in a crystal, therefore if no energy is lost by phonon creation, all available energy is emitted in the form of γ -ray. Since the zero phonon process was known from x -ray scattering long before Mössbauer effect and the low energy γ -rays (5–150 keV) and x -rays are basically of the same electromagnetic nature in the same energy region, so the zero phonon process is also possible in Mössbauer effect and hence the effect is also known as zero phonon effect. It is to be noted that in a zero phonon emission, the whole crystal rather than a single nucleus recoils.

Before we proceed further, the characteristic parameters of the MB line, namely position, intensity and bandwidth, and the factors governing these parameters need be defined since they play an important role in the development of theoretical and experimental aspects of MB spectroscopy and are of great value in the study of chemical problems.

10.3 LINE POSITION

It is the most concerned observable to the experimenter and corresponds to the energy difference between the levels of source and absorber. A-MB spectrum may be a single lined, doublet, a six-fingered or a complex one according to the shifting and or splitting of the nuclear levels in the source/absorber excited and ground states due to electric monopole, quadrupole and magnetic interactions. The presence of different lines may also be because of more than one valence state or inequivalent sites. The line position obtained will give the other well-known Mössbauer parameters: isomeric shift quadrupole splitting, Zeeman splitting, temperature shift, pressure shift and or gravitational red shift. The definition, origin and information which one can have from their (of the first three only) numerical estimates will be given in detail when we will discuss the hyperfine interactions.

10.4 INTENSITY OF MÖSSBAUER LINE AND PARAMETERS AFFECTING IT

The relative intensity of MB resonance line, i.e. the probability of recoilless events (emission or absorption) is expressed in terms of recoil-free fraction ' f ' (called Lamb-Mössbauer factor) of γ -rays which is related to the vibrational properties of the crystal lattice. The expression relating ' f ' with the vibrational properties of lattice can be deduced quantum mechanically either from the simple Einstein model or Debye model of the lattice vibrations of the solid.

10.4.1 Einstein Model

In the Einstein model of the solid, the infrequent occurrence of multiphonon processes is ignored and only the mean recoil energy of a single phonon process is considered, i.e. $E_R = (1-f) h\nu_E$. When the recoil energy of γ -rays emitted from an atom bound in a solid is insufficient to displace the atom, a thermal spike is created. Consequently, many high levels in the oscillator will be populated by the thermal excitation. A thermal equilibrium is reached very quickly between this hot spot and the surrounding lattice. When the recoil energy is larger than the separation between the vibrational levels (i.e. $E_R \gg h\nu_E$; ν_E is the frequency of vibrational oscillations of the atoms) of the Einstein solid, the displacement of atoms occur and a thermal spike is created. Low-energy γ -rays (≈ 5 –150 keV) are important for our considerations. The condition $E_R < h\nu_E$ suggests that zero phonon process takes place in the lattice, i.e. emission and absorption processes occur without excitations of phonons in the lattice. Specifically, we select a recoil energy $E_R = \frac{2}{3} h\nu_E = h\theta_E$; where θ_E is the Einstein temperature of the solid.

Accordingly, f , i.e. the number of recoil free γ -ray events divided by the total of γ -ray events is given by

$$f = \exp \left[\frac{-E_R^2 \langle x^2 \rangle}{(hc/2\pi)^2} \right] \quad (10.21)$$

$$\langle x^2 \rangle = \frac{h}{8\pi^2 M \nu} \text{ for the lowest einstein level.}$$

Here, $\langle x^2 \rangle$ is the mean-square vibrational amplitude of the resonating nucleus in the X -direction which is the direction of observation of $\langle x^2 \rangle$, i.e. γ -ray. It is assumed to be an isotropic function and is linearly proportional to temperature. It follows from Eq. (10.21) that (i) the recoil free fraction ' f ' decreases as the energy of γ -rays increases. Due to this very reason, the highest γ -ray energy so far used in the MB effect is the 187 keV transition in ^{190}Os , and (ii) ' f ' will be large for tightly bound atom with small mean square amplitude of vibration.

10.4.2 Debye Model

In this model, the multiphonon processes though occur infrequently but are not ignored, i.e. the large number of vibrational levels in the solid and their energy distribution is taken into account. Each of the levels available has a certain probability to be excited by the recoil energy. The mean energy is transferred to the lattice. E_R and a recoil-free line appears at E_0 . The recoil-free fraction ' f ' according to Debye model of the solid is given by

$$f = \exp \left[\frac{-3E_R}{2\kappa\theta_D} \left\{ 1 + 4 \left(\frac{T}{\theta_D} \right)^2 \int_0^{T/\theta_D} \frac{x}{e^x - 1} dx \right\} \right] \quad (10.22)$$

Here, θ_D is the Debye temperature and is defined as $h\nu_D = \kappa\theta_D$; $h\nu_D$ represents the separation between energy levels of Debye solid. This expression is valid for a monoatomic lattice of identical atoms.

$$\theta_D = \frac{h\nu_m}{\kappa}, \nu_m \text{ is limiting vibrational frequency of a solid.}$$

For $\theta_D \gg T$ or as $T \rightarrow 0$, so we can replace θ_D/T by ∞ . In such a case

$$f = \exp \left[\left(\frac{-E_R}{\kappa\theta_D} \right) \left\{ \frac{3}{2} + \frac{\pi^2 T^2}{\theta_D^2} \right\} \right]$$

$$\text{or} \quad f = \exp \left(\frac{-3E_R}{2\kappa\theta_D} \right) \quad (10.23)$$

For $T > \theta_D$,

$$f = \exp \left(\frac{-6E_R T}{\kappa\theta_D^2} \right) \quad (10.24)$$

It follows from Eqs (10.23) and (10.24) that (i) ' f ' increases as the temperature decreases. This was what observed by Mössbauer with ^{191}Ir , (ii) the higher the value of θ_D of the solid, the larger the value of ' f ' and (iii) the MB effect is limited to relatively low energy γ -ray emission since ' f ' decreases rapidly with the increase in energy. The effect has been observed up to 155 keV γ -radiation. Moreover, it is also known from Eq. (10.21) that recoil

free processes in a solid is solely determined by $\langle x^2 \rangle$. No further specification regarding the solid is necessary. Therefore, the MB spectroscopy is not only applicable to crystalline materials only but also to liquid, amorphous and gaseous materials.

10.5 LINE WIDTH OF MÖSSBAUER LINE AND FACTORS AFFECTING IT

It is well known that the ground state of nucleus is well defined, i.e. it has an infinite lifetime and there is no uncertainty in its energy. However, the excited state is not well defined. The energy 'E' of the level is not sharp, but is spread over a certain range. The width of this range can be obtained from Heisenberg–Bohr uncertainty principle

$$\Delta E \Delta t \geq \frac{h}{2\pi}$$

Here, ΔE is the uncertainty in energy and Δt is the time interval available to measure the energy. The uncertainty in the lifetime of the excited state is expressed in terms of its mean life τ , and the uncertainty in its energy is given by the width of the Mössbauer line at half height, i.e. Γ as indicated in Fig. 10.3.

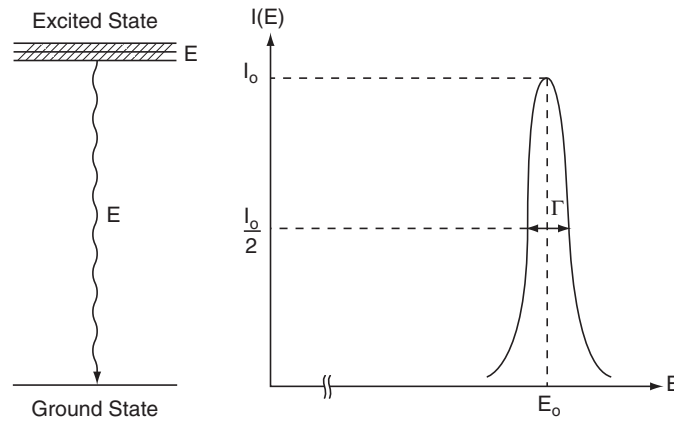


Fig. 10.3 Natural line width for the transition in which energy of the excited state level is spread over a certain energy range.

Thus,

$$\Gamma \tau \geq \frac{h}{2\pi} \quad (\text{Eq. 10.6})$$

τ is related to half-life of the state by

$$\frac{1}{\tau} = \frac{\ln 2}{t_{1/2}} \quad (\text{Eq. 10.7})$$

Thus

$$\Gamma = \left(\frac{h}{2\pi} \right) \frac{1}{\tau} = \left(\frac{h}{2\pi} \right) \frac{\ln 2}{t_{1/2}} = \left(\frac{h}{2\pi} \right) \frac{0.693}{t_{1/2}}$$

Γ is called the natural/inherent/Heisenberg line width of the source emission or absorption line. For a nuclear excited state with $t_{1/2} = 10^{-7}$ second, Γ is of 10^{-9} eV. The ratio of natural line width and energy of the photon is a measure of the resolution of the emitted γ -ray. Thus if energy of the excited state is 45.62 keV, the value of $\Gamma/E_\gamma = 10^{-13}$, i.e. emitted γ -ray will have natural resolution of 1 part in 10^{13} . The maximum resolution obtained in atomic line spectra is only about 1 in 10^8 .

Further, it is to be noted that in the γ -ray emission process, the de-excitation of the system may occur through several mechanisms, namely radiative transition, internal conversion (IC), isomeric transition, i.e. change in the valence or oxidation state (IT) of the atom, etc. All these processes take place independent of each other and decrease the lifetime of the excited state. Consequently, the γ -ray line broadens. Now if the excited state decays in several different ways, the total energy spread of the excited level, Γ is equal to the sum of all the partial widths Γ_i . Thus as the number of modes of decay increases, the lifetime of the excited state also decreases.

Mathematically,

$$\frac{1}{\tau} = \sum \frac{1}{\tau_i} \quad (10.25)$$

or

$$\Gamma = \sum \Gamma_i = \frac{h}{2\pi} \sum \frac{1}{\tau_i}$$

The curve between excitation probability (i.e. observable width) $W(E)$ and energy of resonance radiation is Lorentzian type as shown in Fig. 10.4 and is described by the Breit–Wigner relation

$$W(E) = \frac{\Gamma^2 / 4}{(E - E_0)^2 + \Gamma^2 / 4} \quad (10.26)$$

If in a resonance experiment, an emission line of natural width overlaps the absorption line of the natural width, Γ , the sum of both resonance line widths, 2Γ , will be obtained. The Lorentzian line of such an absorption experiment is given by the total absorption cross-section.

$$\sigma_{\text{abs}} = \sigma_0 \frac{\Gamma^2}{\Gamma^2 + 4(E - E_0)^2} \quad (10.27)$$

With maximum cross-section

$$\sigma_0 = \frac{\lambda^2}{\pi} \frac{2I_e + 1}{2(2I_g + 1)} \cdot \frac{1}{(\alpha_i + 1)} \quad (10.28)$$

where, λ is the wavelength of the γ -ray.

Similarly, the total scattering cross-section is given by

$$\sigma_{\text{scatt}} = \sigma_0 \frac{\Gamma^2}{\Gamma^2 + 4(E - E_0)^2} \quad (10.29)$$

With the maximum cross-section

$$\sigma_0 = \frac{\lambda^2}{\pi} \frac{2I_e + 1}{2(2I_g + 1)} \cdot \frac{1}{(\alpha_i + 1)^2} \quad (10.30)$$

Units of σ_0 are barn ($1 \text{ barn} = 10^{-24} \text{ cm}^2 = 10^{-28} \text{ m}^2$). For σ_0 to be large, both E_0 and α_i should be small. I_e and I_g are the spins of the excited and ground states of the transition respectively, λ is the resonant wavelength, α_i is the total of γ -ray internal conversion coefficient and takes into account the competing mode of transition. Note that not all nuclear γ -transitions produce a physically detectable γ -ray, a proportion eject electrons from the atomic orbitals, giving x-rays and these internal conversion electrons instead. The internal conversion coefficient is thus defined as the ratio of the number of conversion electrons (atomic s-electron) to the number of γ -ray photons emitted. For the most celebrated Mössbauer isotope ^{57}Fe , emitting 14.4 keV γ -ray, α_i is of the order of 10. For high value of α_i it is difficult to observe the MB resonance line, e.g. for ^{73}Ge , emitting 13.5 keV γ -ray, $\alpha_i = 3600$. The values of α_i for ^{57}Fe and ^{73}Ge suggest that in the former σ_0 is reduced by a factor of 100 whereas in the latter by a factor of about 1×10^7 which is very large indeed. The factor 2 in the denominator expresses the multiplicity caused by two possible independent polarisations of the photons. It is to be noted that the expressions (10.28) and (10.30) have been derived on the assumptions that (i) the emission line is very sharp, and (ii) only one absorption or scattering level exists. The characteristic parameters for selected transitions of some Mössbauer nuclei are listed in Table 10.2.

The observed line width of the MB line always differs from the natural line width. The deviation could be due to Doppler broadening of an improper functioning of Mössbauer apparatus (oscillation) or saturation effects in the absorber or in the source (self-absorption, i.e. resonance). In addition, a number of inherent physical processes such as diffusion and Brownian motion of the atoms or molecules, relaxation processes, spin-flip process, super paramagnetism, fluctuations near the critical temperature (magnetic) ferroelectric and other phase transitions, etc., could cause line broadening.

The Doppler broadening due to the thermal agitation of the emitting and absorbing systems being temperature dependent is given by

$$\Delta\Gamma = v_0 \sqrt{\frac{2\kappa T}{M_0 c^2}} \log 2, \Delta\Gamma > \Gamma \quad (10.31)$$

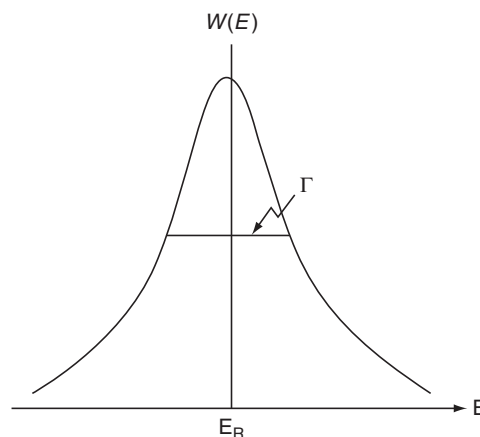


Fig. 10.4 A plot between excitation probability and energy of resonance radiation.

Table 10.2 Mössbauer Isotopes and relevant parameters for the selected Mössbauer transitions.

Isotope	Isotope	Nuclear decay	α_t	E/E_0	$t_{1/2}$	I_g	I_e	μ_g
μ_e (nm)	abundance (%) σ_0 (10^{-20} cm ^{2})	2Γ (mm/s)	E_R (10^{-3} eV)	keV	(ns)	(Q_g barn)	(Q_e barn)	(nm)
^{57}Fe	2.19	^{57}Co (EC 270d)	8.17	14.4125	97.81	$\frac{1}{2}-$	$\frac{3}{2}-$	0.0902
-0.1547	256.6	0.194	1.957			(0)	(0.2)	
^{57}Fe	2.19	^{57}Co (EC 270d)	0.14	136.46	8.7	$\frac{1}{2}-$	$\frac{5}{2}-$	0.0902
(-)	4.3	0.2304	175.4			(0)	(-)	
^{61}Ni	1.25	$^{61}\text{Co}(\beta^- 99\text{m})$	0.12	67.4	5.06	$\frac{3}{2}-$	$\frac{5}{2}-$	-0.7487
0.47	72.12	0.8021	39.99			(+0.162)	(-0.3)	
^{119}Sn	8.58	$^{119\text{m}}\text{Sn}$ (IT 250d)	5.12	23.871	17.75	$\frac{1}{2}+$	$\frac{3}{2}+$	-1.041
0.67	140.3	0.6456	2.571			(0)	(-0.08)	
^{121}Sb	57.25	$^{121\text{m}}\text{Sn}(\beta^- 76\text{y})$	~ 10	37.15	3.5	$\frac{5}{2}+$	$\frac{7}{2}+$	3.359
2.35	19.7	2.104	6.124			(-0.26)	(-0.36)	
^{125}Te	6.99	^{125}I (EC 60d)	12.7	35.46	1.48	$\frac{1}{2}+$	$\frac{3}{2}+$	-0.8872
0.6	26.56	5.212	5.401			(0)	(-0.2)	
^{127}I	100	$^{127\text{m}}\text{Te}(\beta^- 109\text{d})$	3.7	57.6	1.9	$\frac{5}{2}+$	$\frac{7}{2}+$	2.809
2.02	21.37	2.5	14.03			(-0.79)	(-0.71)	
^{129}I	nil (radioactive)	$^{129\text{m}}\text{Te}(\beta^- 33\text{d})$	5.3	27.77	16.8	$\frac{7}{2}+$	$\frac{5}{2}+$	2.617
2.84	40.32	0.5863	3.21			(-0.55)	(-0.68)	
^{129}Xe	26.44	$^{129}\text{I}(\beta^- 1.7 \times 10^7\text{y})$	11.8	39.58	1.01	$\frac{1}{2}+$	$\frac{3}{2}+$	-0.7769
0.68	23.31	6.843	6.521			(0)	(0.41)	
^{149}Sm	13.83	^{149}Eu (EC 106d)	~ 12	22.5	7.12	$\frac{7}{2}-$	$\frac{5}{2}-$	-0.665
-0.620	7.106	1.708	1.824			(≤ 0.06)	(0.4)	
^{151}Eu	47.82	^{151}Gd (EC 120d)	29	21.64	9.7	$\frac{5}{2}+$	$\frac{7}{2}+$	3.465
2.587	11.42	1.303	1.665			(+1.16)	(+1.51)	
^{161}Dy	18.88	$^{161}\text{Tb}(\beta^- 6.9\text{d})$	~ 2.5	25.65	28.1	$\frac{5}{2}+$	$\frac{5}{2}+$	-0.472

(Continued)

Table 10.2 Mössbauer Isotopes and relevant parameters for the selected Mössbauer transitions—Cont'd

Isotope	Isotope	Nuclear decay	α_t	E_λ/E_0	$t_{1/2}$	I_g	I_e	μ_g
0.59	95.34	0.3795	2.194			(+1.35)	(+1.36)	
^{169}Tm	100	$^{169}\text{Er} (\beta^{-19.4\text{d}})$	220	8.42	3.9	$\frac{1}{2}+$	$\frac{3}{2}+$	-0.231
0.5	21.17	8.33	0.2253			(0)	(-1.30)	
^{182}W	26.41	$^{182}\text{Ta}(\beta^{-115\text{d}})$	3.2	100.102	1.37	0+	2+	(0)
0.532	25.17	1.995	29.56			(0)	(1)	
^{189}Os	16.1	$^{189}\text{Ir}(\text{EC } 13.3\text{d})$	8.2	69.59	1.64	$\frac{3}{2}-$	$\frac{5}{2}-$	0.6565
0.988	8.419	2.397	13.76			(+0.91)	(-)	
^{193}Ir	62.7	$^{193}\text{Os}(\beta^{-131\text{h}})$	~ 6	73.028	6.3	$\frac{3}{2}+$	$\frac{1}{2}+$	0.1589
0.47	3.058	0.5946	14.84			(+1.50)	(0)	
^{197}Au	100	$^{197}\text{Pt}(\beta^{-118\text{h}})$	4	77.35	1.9	$\frac{3}{2}+$	$\frac{1}{2}+$	0.1449
0.419	3.857	1.861	16.31			(+0.56)	(0)	
^{237}Np	nil (radioactive)	$^{241}\text{Am}(\alpha 458\text{y})$	1.06	59.537	68.3	$\frac{5}{2}+$	$\frac{5}{2}+$	2.8
1.5	32.55	0.06727	8.031			(+4.1)	(+4.1)	

EC-electron capture, β^{-1} -beta-decay, IT-isomeric transition, α -alpha decay, E_λ/E_0 -nuclear transition energy, $t_{1/2}$ -half-life period, I_e and I_g -nuclear spin quantum numbers excited (e) and ground (g) states respectively, μ_g and μ_e -nuclear magnetic moments, σ_0 -maximum resonance cross-section in barn,

Γ -Heisenberg line width, E_R -recoil energy. The following derivations can be used for the determination of 2Γ , E_R and σ_0 ; $2\Gamma = \frac{273.8}{E_\gamma t_{1/2}}$ mm/sec (E_γ in keV,

$$t_{1/2} \text{ in ns, } E_R = 5.36942 \times 10^{-4} \frac{(E_\gamma)^2}{M} \text{ eV (} E_\gamma \text{ in keV, } M \text{ in amu) and } \sigma_0 = \left[\frac{2.446 \times 10^{-15}}{(E_\gamma^2)} \right] \cdot \left[\frac{2I_e + 1}{2I_g + 1} \right] \cdot \left[\frac{1}{1 + \alpha_t} \right] \text{ cm}^2 \text{ (} E_\gamma \text{ in keV)}$$

where ν_0 is the frequency of harmonic vibrator. The MB spectral line is no more Lorentzian but becomes Gaussian. The effective Doppler scattering cross-section is given by

$$\sigma_{\text{scatt}}^D = \sigma_0 \left(\frac{\Gamma \sqrt{\pi}}{2\Delta\Gamma} \right) \exp \left[- \left(\frac{E - E_0}{\Delta\Gamma} \right)^2 \right], \Delta\Gamma > \Gamma \quad (10.32)$$

The maximum Doppler scattering cross-section is then expressed as

$$\sigma_{\text{max,scatt}}^D = \frac{\sigma_0 \Gamma^2}{\Delta\Gamma^2} \cdot \frac{1}{(1 + \alpha_t)^2} \quad (10.33)$$

The corresponding maximum Doppler absorption cross-section will be

$$\sigma_{\text{max,abs}}^D = \frac{\sigma_0 \Gamma}{\Delta\Gamma} \cdot \frac{1}{(1 + \alpha_t)} \quad (10.34)$$

The line broadening due to diffusive motion of atoms could be explained by the sudden jump and continuous diffusion models of Singwi and Sjolander. The diffusion in solids would be approximated by the first model while in liquids by the second model.

According to sudden jump model, the atom or ion does not stick to a particular site in the lattice. This is possible in two ways. In the first, an electron may hop from the resonant atom (within the Mössbauer lifetime) to

another atom on a neighbouring site and in the second, the resonant nucleus itself changes its lattice site by jump diffusion. When the jump frequency of the resonant atom matches with the reciprocal of the mean lifetime of the excited state, $\frac{1}{\tau}$, line broadening occurs. For either model, the diffusion broadening $\Delta\Gamma$ is expressed as

$$\frac{\Delta\Gamma}{\Gamma} = \sigma(K^2\tau)D \quad (10.35)$$

where, D is the diffusion coefficient,

$$K = \frac{2\pi}{h} \cdot \frac{E_\gamma}{c}, \quad \sigma = 12 / f_c r_0^2 K^2 = 0.04$$

in the sudden jump model and $\sigma = 2$ in the continuous diffusion model, ' f_c ' is a factor which describes the correlation in a direction between successive jumps of one and the same atom and r_0 is the jump distance.

The simple jump model predicts a line broadening of $\frac{h}{\pi\tau}$ whereas the Lorentzian full width predicted by the Singwi and Sjolander continuous diffusion model is given by

$$\Delta\Gamma = \frac{h}{2\pi}(\Gamma + 2\alpha\beta) = \frac{h}{2\pi}(\Gamma + 2K^2D) \quad (10.36)$$

$\alpha \ll 1$, $K^2 \ll \frac{\beta}{D}$ and

$$\Delta\Gamma = (\Gamma + 2\alpha\beta) \left[\left(\frac{\Gamma + 2\alpha\beta}{\Gamma + 2\alpha\beta + 2\beta} \right)^2 + 1 \right]^{-1/2}; \quad \alpha < 1 \quad (10.37)$$

where, $\beta = \frac{6\pi\eta a}{m}$, the quantity β^{-1} is called the characteristic or relaxation time. For atomic motion, β^{-1} is of the order of 10^{-12} – 10^{-20} second. For particles, β^{-1} is of the order of lifetime of the nucleus in the excited state, $\alpha = \frac{K^2D}{\beta}$; α is a dimensionless number connecting the γ -ray energy with relaxation time of the liquid and the diffusion constant D , ' a ' is the size of the particle and η is coefficient of viscosity.

The Gaussian full width is then given by

$$\Delta\Gamma = 2 \left(\frac{\lambda}{2\pi} \right) [\beta(\Gamma + 2\alpha\beta) \log 2]^{1/2} \quad (10.38)$$

It has been observed that when $\alpha > 1$, (i) the width of resonance line varies as $\sqrt{T/\eta}$ rather than as T/η , and (ii) the line is always narrower than $\frac{h}{2\pi}(\Gamma + 2\alpha\beta)$. However, on the basis of experimental data, it is seen that the type of linear relationship between the experimental Mössbauer line broadening and T/η depends upon the system under diffusion studies in liquids, i.e. (i) $\Delta\Gamma \propto \frac{T}{\eta}$ (ii) $\log \Delta\Gamma \propto \log \left(\frac{T}{\eta} \right)$ with slope < 1 , and (iii) $\Delta\Gamma \propto \sqrt{\frac{T}{\eta}}$.

The broadening of the Mössbauer resonance line due to diffusion of iron and in copper and gold corresponds to $\frac{h}{2\pi\tau}$ but not $\frac{h}{\pi\tau}$ as expected on the basis of simple jump model. Diffusion of different-sized nuclei say ^{57}Fe ($a = 0.08 \mu$), ^{119}Sn ($a = 0.22 \mu$) and ^{127}I ($a = 1.28 \mu$) and $\beta = 0.1 \times$ natural width in a liquid of $\eta = 1\text{P}$ (say machine oil) gives

$$\frac{\Delta\Gamma(^{119}\text{Sn})}{\Delta\Gamma(^{57}\text{Fe})} = 2.754 \quad \text{and} \quad \frac{\Delta\Gamma(^{127}\text{I})}{\Delta\Gamma(^{57}\text{Fe})} = 16.00$$

on the basis of continuous diffusion model. The respective ratios from Eq. (10.37) are 2.509 and 10.74.

Further, it is interesting to note that resonance lines narrower than the natural line width could also be observed. Line narrowing could take place due to delay coincidence measurements and thermal spike. In both the cases,

the resonant γ -rays come from excited states with apparently longer mean lifetimes which results in narrowing the line width. In the former case, the foregoing decay to the nuclear excited state can be used as signal in delay coincidence experiment. In the following transition to the ground state, only γ -rays from long-lived excited states is selected. By this mechanism, the mean lifetime has artificially been increased and line width decreased. In the latter case, the foregoing decay is associated with the creation of thermal spike because of which even high oscillation levels will be occupied. In the transition from $^{57}\text{Co} \rightarrow ^{57}\text{Fe}$, more than 3 keV energy is dissipated. The probability of following recoil-free emission becomes a function of time for which the nucleus has been excited during the thermalisation process with decrease of $\langle x^2 \rangle$. Thus the resonant γ -rays come from excited states with apparently longer lifetimes. The Heisenberg principle is not violated in both the situations. The relaxation processes cause, a decrease/increase in the lifetime of the excited state, consequently the broadening/narrowing of MB line occurs.

10.6 HYPERFINE INTERACTIONS

Many of the applications of MB spectroscopy are based on the fact that the line widths encountered are small compared to the characteristic energy of interaction of nuclei with their surroundings. The interactions arise due to the coupling of nuclear magnetic dipole moment with an appropriate electronic or atomic property and are called hyperfine interactions. The hyperfine-coupling mechanisms provide a wealth of information pertaining to electron and spin-density distribution. The temperature dependence of these interactions also provide valuable chemical information. The three main hyperfine interactions corresponding to the nuclear moments determining the nuclear levels are electric monopole interaction (eo)–nuclear isomeric/chemical shift; magnetic dipole interaction (m_1)–magnetic hyperfine interaction/nuclear Zeeman effect and electric-quadrupole interaction (e_2)–nuclear quadrupole coupling.

The theoretical treatment of these interactions is based on the following three assumptions: (i) The nuclear dimensions are infinite and the electrostatic potential sensed by the electrons is different inside and outside the nucleus, (ii) The nuclear charge distribution is nonspherical and therefore the nucleus possesses an electric quadrupole eQ . Q is a measure of the deviation of the nuclear charge from spherical symmetry. (iii) All the three effects may occur together, but only the magnetic and quadrupole interactions are directional and thus have a complicated inter-relationship. The behaviour of isomer shift is independent of the other two interactions.

10.6.1 Centre Shift

The shift of the transition energy of the nucleus in an absorber (source) relative to the source (absorber) is known as centre shift and is denoted by δ_c . This energy difference actually consists of two parts one of which is the physical, i.e. second-order Doppler shift whereas the other is the chemical, i.e. isomeric shift. The former arises due to the difference between the mean square velocity of the Mössbauer probe in the absorber and in the source. This is expressed as

$$\delta_{SOD} = \frac{h\nu}{2c^2} \left[\langle v_{\text{abs}}^2 \rangle - \langle v_{\text{so}}^2 \rangle \right] \quad (10.39)$$

Here, ν is the apparent frequency of the emitted photon and v is the apparent velocity of the absorber and the source. The latter, i.e. isomeric shift results, because of the difference in the electrostatic interaction between the positively charged nucleus density and the s -electron density at the nucleus in the source and the absorber respectively. This is given by

$$\delta_{\text{IS}} = \frac{2}{5} \pi Z e^2 \left(\underbrace{R_e^2 - R_g^2}_{\text{Nuclear term}} \right) \left(\underbrace{|\psi_s(0)_{\text{abs}}|^2 - |\psi_s(0)_{\text{so}}|^2}_{\text{Chemical term}} \right) \quad (10.40)$$

Here, R_e and R_g are the radii of the nuclei in the excited and the ground states respectively, $(-e) |\psi_s(0)_{\text{abs}}|^2$ and $(-e) |\psi_s(0)_{\text{so}}|^2$ are the s -electron densities at the nucleus in the absorber and the source respectively, Z is the atomic number of the nucleus. The values of $1s$, $2s$, $3s$ Hartree–Fock wave functions and s -electron densities at the iron nucleus have been recorded in Table 10.3(a) and (b) respectively.

Table 10.3(a) Values of 1s, 2s, 3s restricted Hartree–Fock wave functions and s-electron densities (in atomic units; electrons per cubic Bohr radius) at the iron nucleus (at $r = 0$) for various 3d electron configurations of the iron atom.

Configuration	1s	2s	3s
Fe ^I (d ⁸)	259.9656	−78.78302	+29.10285
Fe ^{II} (d ⁷)	259.9656	−78.77200	+29.16182
Fe ^{III} (d ⁶)	259.9572	−78.77200	+29.26054
Fe ^{IV} (d ⁵)	259.9572	−78.77020	+29.49279
Fe ^V (d ⁴)	259.9504	−78.77805	+29.49729
Fe ^{VI} (d ³)	259.9423	−78.79529	+30.040612

Table 10.3(b) Electron densities at $r = 0$ for various configurations.

	$ \psi_{1s}(0) ^2$	$ \psi_{2s}(0) ^2$	$ \psi_{3s}(0) ^2$	$ \psi_{4s}(0) ^2$	$2\sum \psi_{ns}(0) ^2_{r=0}$
3d ⁸	5378.005	493.953	67.524		11878.9
3d ⁷ (Fe ⁺)	5377.973	493.873	67.764		11879.2
3d ⁶ (Fe ²⁺)	5377.840	493.796	68.274		11879.8
3d ⁵ (Fe ³⁺)	5377.625	493.793	69.433		11881.7
3d ⁶ 4s ² (free atom)	5377.873	493.968	68.028	3.024	11885.8

Partial electron densities $|\psi_{ns}|^2_{r=0} = \frac{1}{4\pi n} \sum |R_{ns}(r)|^2_{r=0}$ for the configuration 3dⁿ ($n = 5, 6, 7, 8$) and 3d⁶4s².

The centre shift may thus be written as

$$\delta_c = \delta_{\text{SOD}} + \delta_{\text{IS}} \quad (10.41)$$

When the source and the target are at the same temperature, i.e. room temperature, the centre shift becomes equal to isomer shift since under this condition, the second order Doppler shift, i.e. δ_{SOD} is zero.

10.6.2 Second-Order Doppler Shift (δ_{SOD})

The emitting or absorbing nucleus is not at rest but is vibrating on its lattice site. The frequency of vibration is smaller than the reciprocal of the MB lifetime, so the average displacement and velocity are effectively zero but the mean-square values of the velocity, $\langle v^2 \rangle$ are finite. $\langle v^2 \rangle$ depends on temperature, and pressure, Debye temperature of the surrounding matrix and lattice defects, etc.

The relativistic expression for the Doppler effect on the apparent frequency ν of the emitted photon as recorded at the absorbing nucleus is

$$\nu = \nu_0 \left(1 - \frac{v}{c} \cos \theta \right) \left(1 - \frac{v^2}{c^2} \right)^{-1/2} \quad (10.42)$$

Here, ν_0 is the frequency of the nucleus at rest, v is the apparent relative velocity of the emitting nucleus along the direction making an θ with the direction of propagation of γ -ray.

The mean value of $\langle v \rangle$ is zero for a vibratory motion but the second-order term $\langle v^2 \rangle$ being finite can influence the Mössbauer resonance.

$$\nu = \nu_0 \left(1 + \frac{\langle v^2 \rangle}{2c^2} \right) \quad (10.43)$$

This gives rise to shift in MB line.

$$\frac{\nu - \nu_0}{\nu_0} = \frac{\Delta \nu}{\nu_0} = -\frac{\langle v^2 \rangle}{2c^2} = \frac{\delta E}{E_\gamma}$$

$$\text{or} \quad \delta E = -\frac{\langle v^2 \rangle}{2c^2} \cdot E_\gamma \quad (10.44)$$

It is obvious that $\langle v^2 \rangle$ grows with temperature. Accordingly, the MB line moves to more negative velocity as the temperature is increased. The second-order Doppler shift is smallest at absolute zero but will have finite value because of zero point motion of the nucleus.

In the high-temperature region,

$$\frac{\Delta v}{v_0} = \frac{3\kappa T}{2m_i c^2}, \quad \left[\text{Since } \langle v^2 \rangle = \frac{3\kappa T}{m_i} \right] \quad (10.45)$$

where, m_i is the mass of the i^{th} atom.

Differentiating (10.45) with respect to temperature, we obtain

$$\frac{\partial(\Delta v)}{\partial T} = \frac{3v_0 \kappa}{2m_i c^2} \quad (10.46)$$

Since, $N_A \kappa = R$

$$\text{therefore,} \quad \frac{\partial(\Delta v)}{\partial T} = v_0 \cdot \frac{3R}{2N_A m_i c^2} = \frac{3R v_0}{2M_0 c^2} \quad (10.47)$$

The behaviour of fractional shift, $\frac{\Delta v}{v_0}$ with temperature is shown in Fig. 10.5.

The second-order Doppler shift in the temperature limit $T > \frac{\theta_D}{3}$ is given by,

$$\frac{\delta_{\text{SOD}}(T)}{E_\gamma} = \frac{-3\kappa T}{2M_0 c^2} \left(1 + \frac{\theta_D^2}{20T^2} \right) \quad (10.48)$$

The shift of the resonance line by a temperature-governed second-order Doppler effect is termed a *thermal red shift*. At temperatures, $T \gg \theta_D$, the value of $\delta_{\text{SOD}}(T)$ for ^{57}Fe estimated from Dulong Petit's law is 7×10^{-4} mm (second K). The second-order Doppler shift enables one to calculate the isomeric shift accurately and is being discussed under temperature effect on isomer shift.

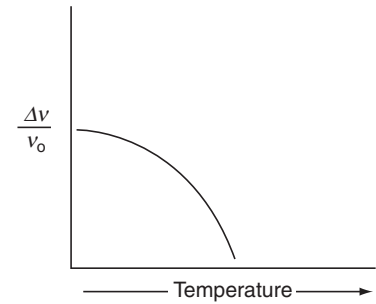


Fig. 10.5 A plot between fractional shift ($\Delta v/v_0$) and temperature.

10.6.3 Nuclear Isomer Shift and Factors Affecting It

The nuclear isomer shift arises because of the electrostatic interaction between the nuclear charge (Ze) distribution over a finite radius R and the s -electron charge density at the nucleus ($-e$) $|\psi_s(0)|^2$. The energy shift due to the charge of potential inside a sphere of radius R is given by

$$\delta E = \frac{2\pi}{5} Ze^2 R^2 |\psi_s(0)|^2 \quad (10.49)$$

Here, $\Psi_s(0)$ is the wave function at $r = 0$. This relation is based on the assumption that the radial distance r , i.e. the distance between the positive and negative charges, is greater than R , i.e. $r \gg R$. Since the size of the nucleus in the ground and excited states is different, so the electrostatic shift δE will also be different in each nuclear state. Thus in a transition from a nucleus in the excited to the ground state, the change in energy of γ -ray due to this 'volume' effect will be

$$\begin{aligned} \Delta E &= (\delta E)_e - (\delta E)_g \\ &= \frac{2\pi}{5} Ze^2 |\psi_s(0)|^2 (R_e^2 - R_g^2) \end{aligned} \quad (10.50)$$

It is frequently written as

$$\Delta E = \frac{4\pi}{5} Z e^2 R^2 \frac{\delta R}{R} |\psi_s(0)|^2 \quad (10.51)$$

The nuclear radius R (cm) = 1.4×10^{-13} (mass number) $^{1/3}$.

The value of $\frac{\delta R}{R}$ is characteristic of each transition and is of the order of 10^{-4} . It can either be positive or negative. A positive sign signifies that the nucleus shrinks on de-excitation.

The Mössbauer experiment compares the difference in the energy of γ -ray between the nuclear transitions in the source and the absorber (Fig. 10.6). In such a situation, the chemical isomer shift is given by

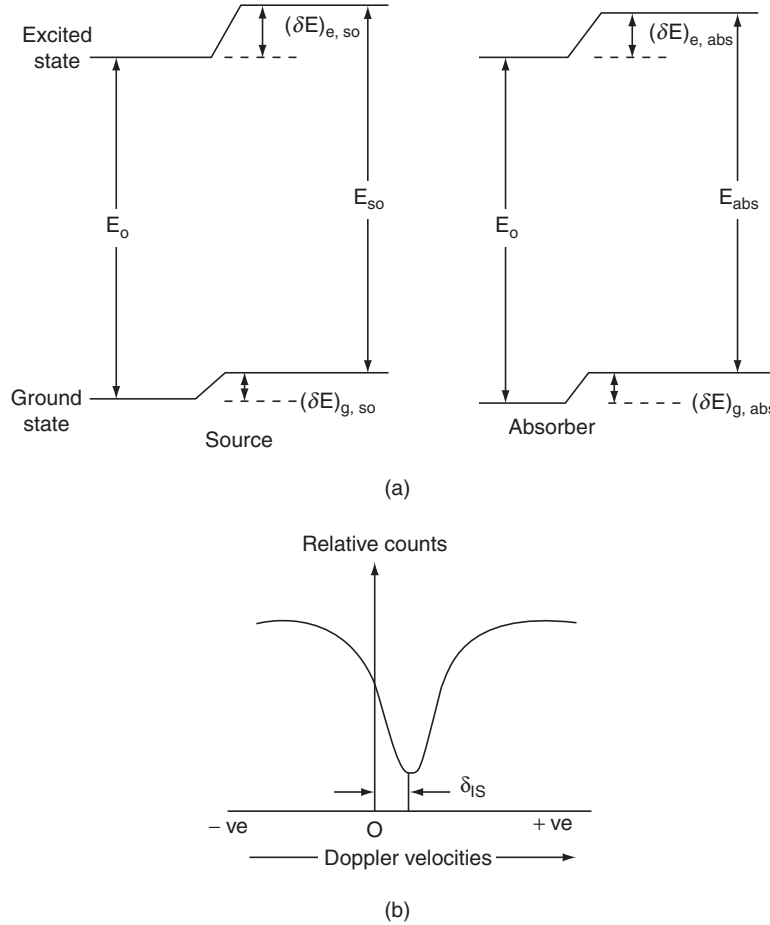


Fig. 10.6 (a) Shift of the nuclear levels due to the monopole coulombic interaction between the nuclear and electronic charges inside the nucleus. (b) Theoretical MB spectrum of Fig. 10.6 (a) above. ($\delta_{IS} = E_{abs} - E_{so}$).

$$\delta_{IS} = \underbrace{\frac{4\pi}{5} Z e^2 R^2}_{\text{Nuclear term}} \cdot \underbrace{\frac{\delta R}{R} (|\psi_s(0)_{abs}|^2 - |\psi_s(0)_{so}|^2)}_{\text{Chemical term}} \quad (10.52)$$

The theoretical shift δ_{IS} is related to the measured shift in the Doppler velocity units v (mm/s) by

$$v_{IS} = \left(\frac{c}{E_\gamma} \right) \delta_{IS} \quad (10.53a)$$

$$v = \left(\frac{c}{E_\gamma} \right) \Gamma \text{ cm/s} \quad (10.53b)$$

Thus, from Eqs (10.52) and (10.55), we write

$$v_{IS} = \frac{4\pi c Z e^2 R^2}{5 E_\gamma} \cdot \frac{\delta R}{R} (|\psi_s(0)_{abs}|^2 - |\psi_s(0)_{so}|^2) \quad (10.54)$$

In Eq. (10.54) appears two interesting quantities, the radius of the nucleus and the total electron density at the nucleus. The first information is useful for testing of different nuclear models whereas the second is of interest for the molecular structure and magnetic properties of solids. If $\frac{\delta R}{R}$ is positive, δ_{IS} is positive, i.e. s -electron density at the absorber is greater than at the source. For negative value of $\frac{\delta R}{R}$, the reverse is true. The chemical isomer shifts of two different isotopes in the same series of compounds could be explained by the difference in $\frac{\delta R}{R}$, e.g. ^{127}I and ^{129}I spectra of $\text{Na}_3\text{H}_2\text{IO}_6$ (Fig. 10.7). The source matrix is zinc telluride in each case but contains ^{127}Te and ^{129}Te respectively. These isotopes undergo β decay to populate the 57.6 keV state of ^{127}I and the 27.7 keV state of ^{129}I . The absorption occurs at positive and negative velocities because $\frac{\delta R}{R}$ is negative in ^{127}I and positive in ^{129}I whereas the s -electron density at the nucleus is greater in the source than in the absorber. The relative magnitude of the shift also differs because $\left[\frac{\delta R}{R}({}^{127}\text{I})\right] / \left[\frac{\delta R}{R}({}^{129}\text{I})\right] = -0.65$.

The line widths are also different for two isotopes, i.e. $2\Gamma({}^{127}\text{I}) = 2.54$ and $2\Gamma({}^{129}\text{I}) = 0.5863$ mm/s. We know that all the occupied s -electron orbitals in the atom contribute to $|\Psi_s(0)|^2$. In addition, it is also affected by the changes which occur in the outer valence shells. Although the values of $|\Psi_s(0)|^2$ for p -, d -, and f -electron are zero, nevertheless, these orbitals indirectly interact with the nucleus via interpenetration shielding of the s -electrons, e.g. $3d^5 4s^1$ configuration have larger value of $|\Psi_s(0)|^2$ as compared to $3d^6 4s^1$ since in the latter case the extra d -electrons shields the $4s$ electron from the nucleus. The difference in the electron density at the nucleus in different chemical environments influences the mean lifetime of the radioactive decay by the relation

$$\frac{\Delta \frac{1}{\tau}}{\frac{1}{\tau}} = \frac{\alpha_s}{\alpha_t + 1} \cdot \frac{\Delta |\psi_s(0)|^2}{|\psi_s(0)|^2} \quad (10.55)$$

The internal coefficients α_s are proportional to the s -electron densities of the various corresponding shells. The chemically induced change in the mean lifetime, i.e. ' $\Delta \frac{1}{\tau}$ ', can be used as a tool for calibrating ^{57}Fe and other isomer shifts and in principle, the Mössbauer line width should indicate the effect according to Eq. (10.6).

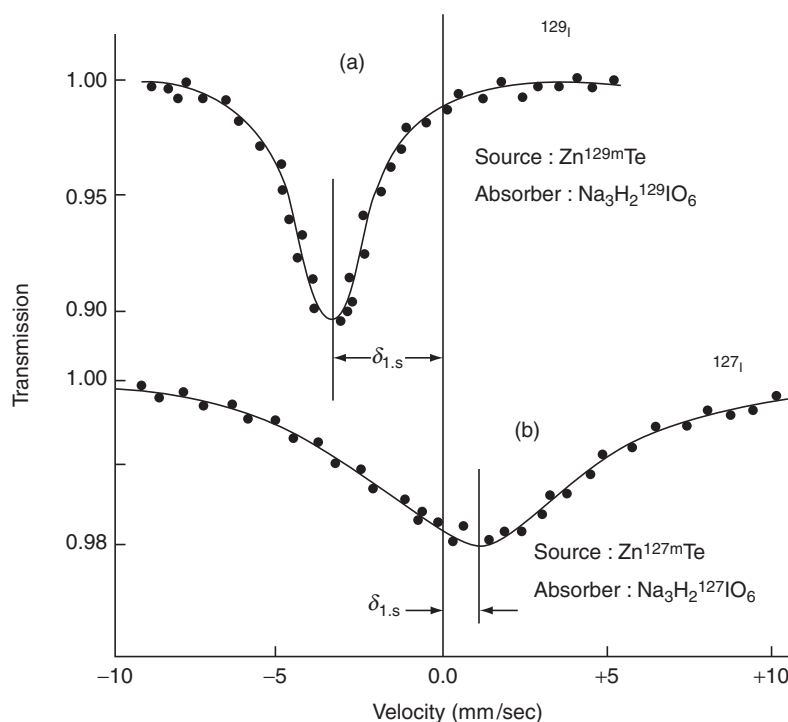


Fig. 10.7 Chemical isomer shifts of (a) ^{129}I and (b) ^{127}I in the Mössbauer spectra of $\text{Na}_3\text{H}_2^{129}\text{IO}_6$ and $\text{Na}_3\text{H}_2^{127}\text{IO}_6$ respectively.

It should be kept in mind that the MB spectra of a particular material measured in different sources under constant conditions will have different isomer shifts because $|\Psi_s(0)|^2$ changes with chemical environment of the MB nucleus. Therefore, isomer shift data must be reported with respect to some standard material. The standard can be the Mössbauer source used in a particular experiment or any absorber material, e.g. in ^{57}Fe MB spectroscopy ^{57}Co in metal foils of Pd, Pt, Cr, Cu and standard steels used as source will show different isomer shifts. The commonly used standards in this spectroscopy are metallic α - ^{57}Fe foil and sodium nitroprussidedihydrate; $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, (SNP); but the metallic iron spectrum is popular as a reference standard for calibration of chemical isomer shifts. Metallic iron spectrum has six hyperfine fingers (Fig. 10.8) because of which the linearity of the MB spectrometer can be checked in a better way as compared to SNP spectrum which has only two peaks (Fig. 10.9) with large separation. Moreover, the zero chemical shift is defined on the basis of metallic iron spectrum. The advantage of adopting SNP as standard is that nearly all the ^{57}Fe chemical isomer shifts are positive in sign. Chemical isomer shifts and quadrupole splitting for α - ^{57}Fe and SNP standards are:

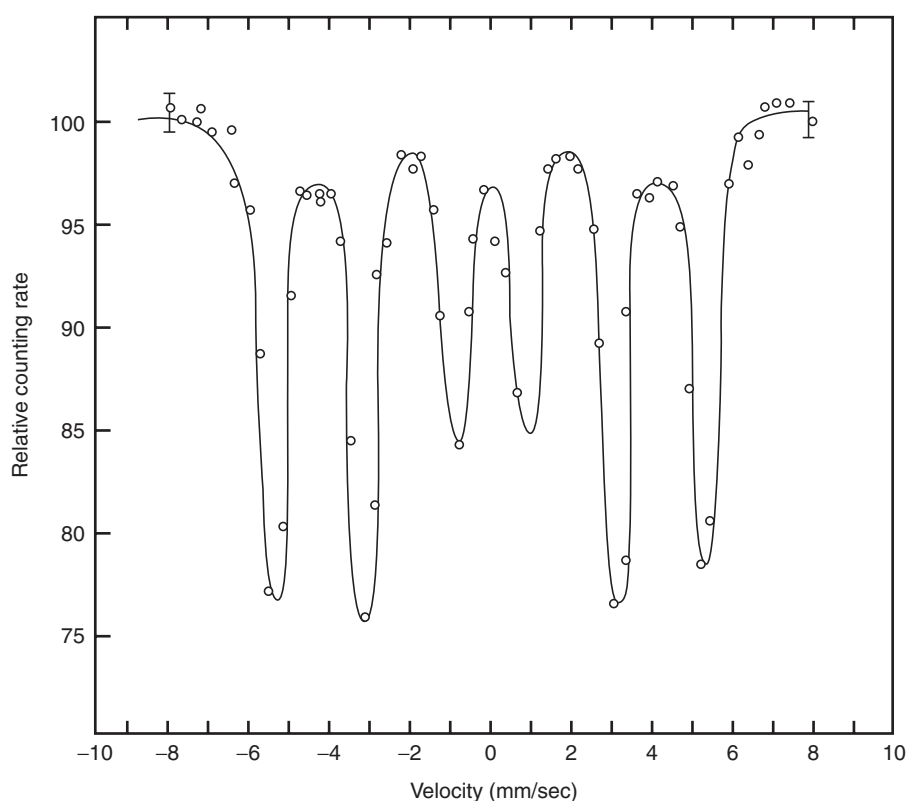


Fig. 10.8 Mössbauer absorption spectrum of ^{57}Fe in metallic iron showing the magnetic hyperfine structure.

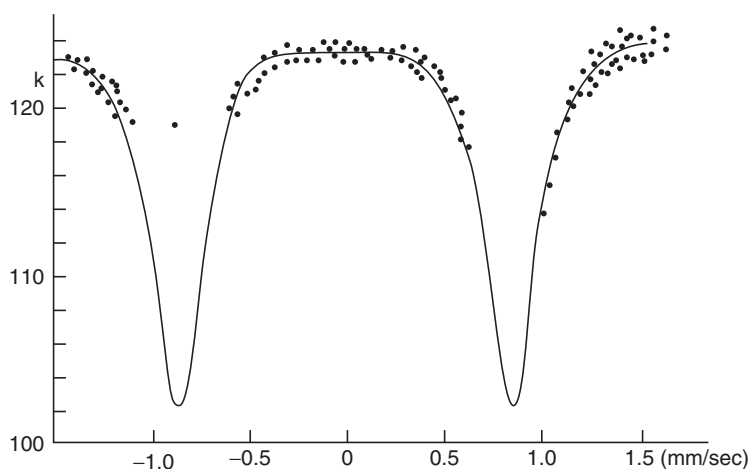


Fig. 10.9 Mössbauer spectra of single crystal of sodium nitroprusside cut parallel to the bc plane $[100]$.

$^{57}\text{Co}/\alpha\text{-}^{57}\text{Fe}$ or SNP; $\delta_{\text{is}} = 0.000$ mm/sec. $\Delta = 0.000$ mm/sec. For other standards, i.e. $^{57}\text{Co}/\text{Cu}$: SNP: $\delta_{\text{is}} = -0.4844 \pm 0.0010$ mm/sec; $\Delta = 1.7048 \pm 0.0025$ mm/sec. $\alpha\text{-}^{57}\text{Fe}$ is preferred by physicists whereas SNP is adopted by chemists.

The reference standard material for Sn is SnTe and BaSnO_3 , I is CsI, Ir is Ir and Zn is ZnS.

Let us now see how the observed chemical shift is influenced by ligands and coordination number and by temperature and pressure and what do these effects do?

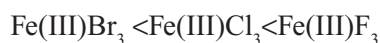
(a) Effect of Ligands and Coordination Number With high-spin complexes, s-electron density increases for $\text{L} \rightarrow \text{M}\sigma$ electron transfer while in low-spin complexes it increases for the $\text{M} \rightarrow \text{L}\pi$ -back transfer of electron. Both these processes helps to interpret isomer shift changes. The other two processes $\sigma_{\text{M} \rightarrow \text{L}}$ and $\pi_{\text{M} \rightarrow \text{L}}$ do not play significant role neither in bonding nor in isomer shift changes. The isomer shift decreases as the covalent character of the ligand increases, i.e. $-\text{H}_2\text{O} > -\text{Cl}^- > -\text{O}_2^{2-} > -\text{S}^{2-} > -\text{CN}^-$, etc. The isomer shifts of some inorganic compounds have been listed in Table 10.4.

Table 10.4 Effect of ligands and coordination number on Isomer shift (in mm/sec) of Some inorganic compounds. Measured at 77 K, relative to iron metal at 290 K.

Ion	Spin	Coordination	Compound	Ligands	Isomer shift (mm/s)
Fe^{2+} (High spin)	2	Octahedral	$\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$	$6\text{H}_2\text{O}$	1.42
			$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	$4\text{H}_2\text{O}, 2\text{Cl}^-$	1.34
			$\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$	$2\text{H}_2\text{O}, 4\text{Cl}^-$	1.24
			FeCl_2	6Cl^-	1.20
		Tetrahedral	$(\text{NMe}_4)_2\text{FeCl}_4$	4Cl^-	1.05
			$\text{FeBaSi}_4\text{O}_{10}$	4O^{2-}	0.87
Fe^{3+} (High spin)	$\frac{5}{2}$	Octahedral	FeCl_3	6Cl^-	0.53
			Fe_2O_3	6O^{2-}	0.50
			Fe-tris-dtc	6S^{2-}	0.50
		Tetrahedral	$(\text{NMe}_4)\text{FeCl}_4$	4Cl^-	0.30
Fe^{2+} (Low spin)	0	Octahedral	$\text{K}_4\text{Fe}(\text{CN})_6$	6CN^-	0.06
Fe^{3+} (Low spin)	$\frac{1}{2}$	Octahedral	$\text{K}_3\text{Fe}(\text{CN})_6$	6CN^-	-0.03

The isomer shifts are also related to the electronegativity of the ligands, i.e.,

Isomer shift $\leftarrow$



$\rightarrow$ Electronegativity

Isomer shift $\leftarrow$

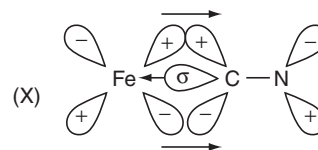


Electronegativity $\leftarrow$

$^{119}\text{Sn X}_4$ (where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) shows that as electronegativity increases, isomer shift also increases as expected. This behaviour is consistent with the fact that Sn is sp^3 hybridised. Quadrupole splitting has been observed only in case of SnF_4 which exists as a polymer in which Sn is octahedrally bounded to four bridging and two neighbouring fluorine atoms.

In $[\text{Fe}(\text{CN})_6]^{4-}$ complexes π and σ bonds exist between metal atom and the ligand. The cyanide group donates a pair of electrons to iron atom via σ -bond and some of the d -electron density is donated back to the ligand via $d_{\pi} - p_{\pi}$ interaction as shown below (X). Thus replacement of one of the cyanide groups by a group which cannot form π -bonds, leads to higher value of isomer shift. This is due to the increase in d -electron density on iron and hence, decrease in s -electron density. The metal ligands σ -bond has little effect on isomer shift in this case.

Thus, as the π -bond strength of ligand decreases, the isomer shift increases, i.e. π -decrease: $\leftarrow \pi$ bond strength $\text{NO}^+ > \text{CO} > \text{CN}^- > \text{SO}_3^{2-} > \text{Ph}_3\text{P} > \text{NO}_2^- > \text{NH}_3$. Isomer shift $\rightarrow \text{NO}^+$ is a good π -acceptor ligand.



$[\text{Fe(II)}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ (0.31), $[\text{Fe(II)}(\text{CN})_5\text{NH}_3]^{3-}$ (0.26) $\sim$ $[\text{Fe(II)}(\text{CN})_5\text{NO}_2]^{4-}$ (0.26) $>$ $[\text{Fe(II)}(\text{CN})_5\text{SO}_3]^{5-}$ (0.22) $>$ $[\text{Fe(II)}(\text{CN})_5(\text{CO})]^{3-}$ (0.15) $>$ $[\text{Fe(II)}(\text{CN})_5\text{NO}]^{2-}$ (0.00)
 $\rightarrow \pi$ -bond strength

In general, on the basis of molecular orbital theory, we can say that in series of $[\text{Fe(II)}(\text{CN})_5\text{X}^{n-}]^{(3+n)-}$ compounds, both $\sigma_{\text{L} \rightarrow \text{M}}$ and $\pi_{\text{M} \rightarrow \text{L}}$ processes increases the $|\Psi_s(O)|^2$ and since $\delta R/R$ is negative for $^{57}\text{Fe}-\delta_{\text{IS}}$ becomes more negative with increasing $\sigma_{\text{L} \rightarrow \text{M}} + \pi_{\text{L} \rightarrow \text{M}}$ in the order $\text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2 < \text{SO}_3^{2-} < \text{CO} \ll \text{NO}^+$. H_2O is a rather weak σ -donor ligand with negligible π -acceptor capability. CO and NO^+ , however, are known to be strong π -acceptor ligands. For the $[\text{Ru(II)}(\text{NH}_3)_5\text{X}^{n-}]^{(n-2)-}$ compounds δ_{IS} becomes more positive with increasing $(\sigma_{\text{L} \rightarrow \text{M}} + \pi_{\text{M} \rightarrow \text{L}})$ in the order $\text{NH}_3 < \text{SO}_2 < \text{CO} \ll \text{NO}^+$ (note that $\delta R/R$ is positive for ^{99}Ru series). Similarly in the $[\text{RuX}_5(\text{NO})]^{2-}$ series δ_{IS} changes in a more positive direction with increasing $(\sigma_{\text{L} \rightarrow \text{M}} + \pi_{\text{M} \rightarrow \text{L}})$ in the order $\text{X} = \text{Br}^- < \text{Cl}^- < \text{NCS}^- < \text{CN}^-$. It is to be noted that, there is close correlation with the ranking of these ligands in the spectrochemical chemical series.

Thus, isomer shift can be fixed as a criterion to study the nature of chemical bond in complexes.

Although the isomer shifts depend upon the oxidation state and degree of covalency of the iron, it is not always possible to use them to measure the oxidation state in proteins. However in many cases, the information regarding the oxidation state of iron can be obtained from the data recorded in Table 10.4.

(b) Effect of Temperature As we have already pointed out that the observed line shift is not solely caused by the chemical isomer shift but by SOD shift also. The isomer shift is not temperature dependent whereas SOD shift is temperature dependent because $\langle v^2 \rangle$ changes with temperature. However, in the high-temperature region, δ_{IS} becomes temperature dependent due to the thermal expansion of the electron charge density at the nucleus. At such temperatures,

$$\delta_{\text{IS}}(T) = \delta_{\text{IS}}(0) + \alpha T \quad (10.56)$$

where, $\delta_{\text{IS}}(T)$ is the isomer shift at T K. The coefficient α can be estimated from the pressure dependence of isomer shift.

Lumping together Eqs (10.41), (10.48) and (10.56), we obtain

$$\frac{\delta_c(T)}{E_\gamma} + T \left(\frac{3\kappa}{2M_0 c^2} - \frac{\alpha}{E_\gamma} \right) = \frac{\delta_{\text{IS}}(0)}{E_\gamma} - \frac{3\kappa\theta_D^2}{40M_0 c^2 T} \quad (10.57)$$

or

$$\frac{c\delta_c(T)}{E_\gamma} + T \left(\frac{3\kappa}{2M_0 c} - \frac{\alpha c}{E_\gamma} \right) = \frac{\delta_{\text{IS}}(0)c}{E_\gamma} - \frac{3\kappa\theta_D^2}{40M_0 c T}$$

The plot between the left-hand side of Eq. (10.57) against $1/T$ will be a straight line. From the intercept $\frac{\delta_{\text{IS}}(0)}{E_\gamma}$, one can determine the value of isomer shift at 0 K and from the slope, the value of θ_D , the Debye temperature can be estimated. Once $\delta_{\text{IS}}(0)$ is known, one can determine accurately, the value of chemical shift at any temperature from Eq. (10.56), δ_{SOD} from Eq. (10.48) and $\delta_c(T)$ from Eq. (10.41).

The plots between (i) isomer shift and temperature ($^\circ\text{C}$), and (ii) left-hand side of Eq. (10.57) and $1/T$ (K^{-1}) are shown in Figs (10.10) and (10.11) respectively. The sudden change in the isomer shift (Fig. 10.10) and centre shift (Fig. 10.11) at the Curie temperature (T_c) (ferromagnetic substances become paramagnetic at this temperature). $T_c < T_m$ (i.e. melting point) may be due to (i) sudden change in volume at T_c or phase transition, i.e. change in

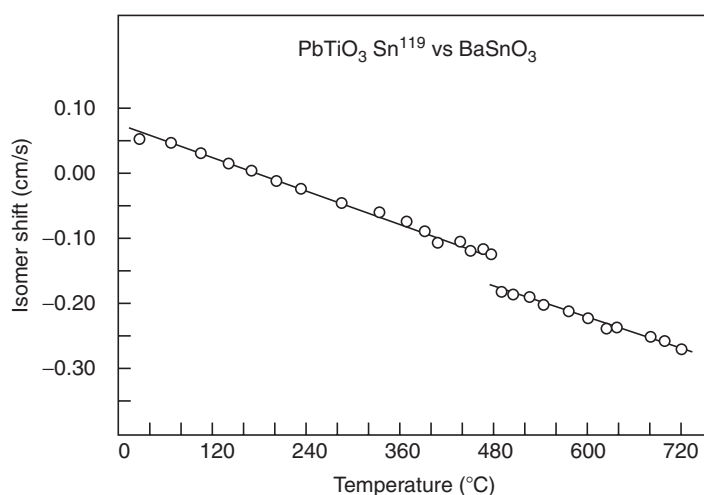


Fig. 10.10 Isomer shift in PbTiO₃: ⁵⁷Fe Mössbauer spectrum as a function of temperature, 0–800°C.

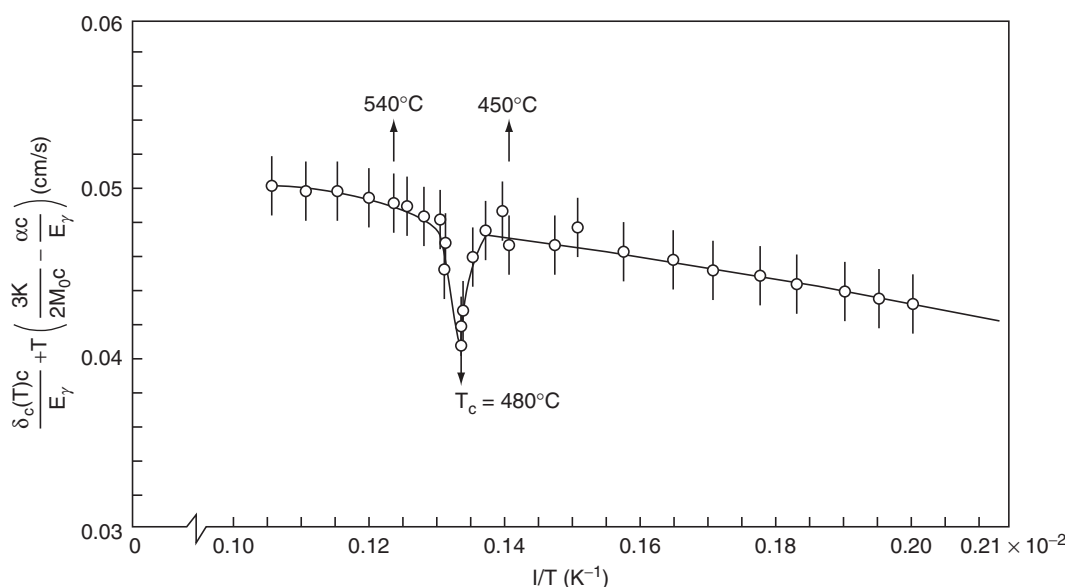


Fig. 10.11 Plot of $\frac{\delta_c(T)_c}{E_\gamma} + T \left(\frac{3K}{2M_0c} - \frac{\alpha_c}{E_\gamma} \right)$ against $\frac{1}{T}$ for PbTiO₃ probed with ⁵⁷Fe.

nature of chemical bond, and (ii) change in the Debye temperature (θ_D) occurring at the transition or disappearance of Cochrane-type soft mode at T_c . (Transverse optical mode in ferroelectrics is anharmonic in nature and is called Cochrane type soft mode. Because of this mode, the crystal becomes unstable). Further, it follows from Fig. (10.11), that the Debye temperature falls from ~ 500 K above T_c to 225 K below T_c . The curve also exhibits a discontinuous change of about 0.075 mm/s in the vicinity of the Curie temperature. Assuming that the sudden break in the curve is due to the change in volume at T_c , we may express the behaviour as

$$\frac{\partial E_\gamma / E_\gamma}{\partial V / V} = (5.37 + 0.07) \times 10^{-12} \left(1 - \frac{\Delta V}{V} \right) \quad (10.58)$$

where, $\frac{\Delta V}{V}$ is the relative change in volume. It is estimated that sudden change in isomer shift at transition temperature is about 0.01 mm/s. The change in isomer shift due to change in nature of the chemical bond at T_c is also expected to be very small in view of the pseudo cubic transformation at T_c . Thus the origin of discontinuous in δ_c at T_c may be due to some other factors rather than isomer shift. The three factors which can result in a discontinuous change in δ_c close to T_c are (i) change in Debye temperature on two sides of T_c , (ii) Cochrane-type mode is temperature dependent, and (iii) the transverse acoustic energy is temperature dependent. It is possible to estimate the change in δ_c because of the change in θ_D . The observed changes in θ_D below and above T_c give rise to change

in δ_c of about 0.012 mm/s. These results reveal that the observed sudden change in δ_c at T_c is due to (i), disappearance of soft mode or, and (ii) the transverse acoustic energy depends upon temperature. However it is difficult to estimate the contributions due to these two factors.

(c) Effect of Pressure The chemical isomer shift decreases with the growth of pressure. Extreme pressures (up to 200,000 atmospheres; 1 atm = 1.01325×10^5 Pa = 1.01325 bar) will compress the material (in the context of ^{57}Fe), as a consequence the overlap between the inner s -shells of iron and the valence orbitals of the ligands will increase. The induced overlap due to pressure results in increase in s -electron density (i.e. decrease in volume) at the nucleus and a decrease in the chemical isomer shift. The decrease in isomer shift with increase of pressure has been observed in a large number of compounds and the effect is fully reversible on release of the pressure. Theoretically, the effect has been fully confirmed on the basis of wave function calculations in the case of KFeF_3 . The behaviour of isomer shift with volume is given by

$$\frac{\partial \delta_{\text{is}}(P)}{\partial (V/V_0)} = 0.14 \text{ cm/s} \quad (10.59)$$

The plot between isomer shift for ^{57}Fe in Fe and pressure is shown in Fig. 10.12 and can be predicted from Eq. (10.59).

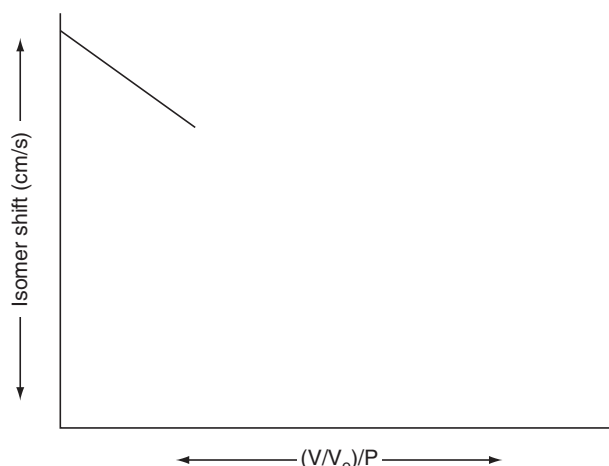


Fig. 10.12 Isomer shift of ^{57}Fe in Fe as a function of volume.

It is to be noted that at low pressures, iron has bcc structure and is ferromagnetic. At about 130 kb occurs a first-order phase transition to non ferromagnetic hcp structure. However, the behaviour of isomer shift as a function of volume for ^{57}Fe embedded in nickel, copper and palladium which have fcc structure and ^{57}Fe in hcp phases in titanium, cobalt and iron cannot be predicted from Eq. (10.59). The predicted value is comparatively more than the expected one as shown in Fig. 10.13.

The most interesting aspect of pressure studies is that iron in many compounds shows a change in oxidation state or electronic configuration at high pressures. Only a fraction of total iron is changed and the effect is fully reversible on the release of pressure, e.g. high-spin iron (III) in $\text{Fe}_2(\text{SO}_4)_3$ and FePO_4 shows a partial conversion to high-spin iron (II); low-spin iron (III) in $\text{K}_4\text{Fe}(\text{CN})_6$ can change to low spin iron (II). The change in oxidation state occurs because of electron transfer from ligand to metal, i.e. $\text{L} \xrightarrow{e^-} \text{M}$.

The foregoing treatment of chemical shift indicates that it depends on the electronic environment as well as the parameters, viz., temperature, pressure, etc., influencing the electronic environment around the nucleus. Thus, it provides very useful information about the bond properties, valency and oxidation state of a Mössbauer atom.

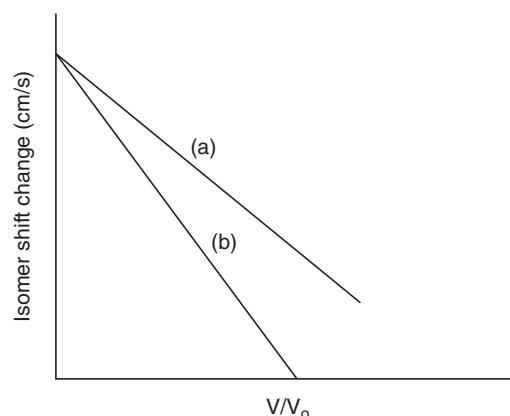


Fig. 10.13 The behaviour of isomer shift for ^{57}Fe in nickel, copper and palladium with volume, (a) experimental, and (b) theoretical.

10.6.4 Partial Isomer Shift

The concept of partial isomer shift (p.i.s.) stemmed from the observations that (i) isomer shifts vary linearly with average electronegativities of surrounding ligands. This has been observed in many iron and tin compounds. (ii) There exists a characteristic bonding distance between the metal atom and a given ligand in a variety of related compounds.

The partial isomer shift is an additive property. The isomer shift of a Mössbauer atom in a given compound is the sum of the p.i.s. values of all coordinated ligands, i: $\delta_{\text{IS}} = \sum_i (\text{p.i.s.})_i$. The concept of p.i.s. holds good for Fe(II) and Sn(IV) compounds. p.i.s. for ligands in low-spin Fe(II) compounds is listed in Table 10.5. With these values and using the model,

$$\delta_{\text{IS}} = 0.16 + \sum_{i=1}^6 (\text{p.i.s.})_i \quad (10.60)$$

the isomer shift for low-spin Fe(II) compounds can be predicted. This model is partially useful for predicting the isomer shifts of low-spin Fe(II) compounds which only exist as unstable intermediates. Alike isomer shifts in Fe(II) compounds, p.i.s. also decrease as the σ -bonding and π -back bonding increase.

Table 10.5 Partial Isomer Shift (in mm/s) values (with respect to sodium nitroprusside at 295 K) for ligands in low-spin Fe(II) compounds.

Ligand	p.i.s.	Ligand	p.i.s.	Ligand	p.i.s.
NO ⁺	−0.20	CN [−]	0.01	phen/2*	0.07
H [−]	−0.08	SnCl ₃ ^{−1}	0.04	py*	0.07
SiH ₃ [−]	−0.05	Pc/2*	0.05	NH ₃	0.07
ArNC*	0.00	NCS [−]	0.05	N ₃ [−]	0.08
MeNC	0.00	NCO [−]	0.06	H ₂ O	0.10
EtNC	0.00	depe/2*	0.06	Cl [−]	0.10
CO	0.00	bipy/2*	0.06	Br [−]	0.13
				I [−]	0.13

ArNC $\doteq$ *p*-methoxyphenylisocyanide; pe $\doteq$ phthalocyanine; depe $\doteq$ bis(diethylphosphino) ethane; bipy $\doteq$ 2, 2'-bipyridyl, phen $\doteq$ 1, 10-phenanthroline; py $\doteq$ pyridine

Problem 10.1: Using the data in Table 10.5 on p.i.s., predict the isomer shifts for *cis*-FeCl₂ (ArNC)₄ and Na₃[Fe(CN)₅NH₃].H₂O and *trans*-FeCl (SnCl₃) (depe)₂.

Solution The ligands in *cis*-FeCl₂ (ArNC)₄ are Cl[−] and ArNC. From Table 10.5, we write

$$\text{Cl}^- = 0.10 \text{ mm/s, ArNC} = 0.00 \text{ mm/s.}$$

From Eq. (10.60) we obtain

$$\begin{aligned} \delta_{\text{IS}} &= 0.16 + \sum_{i=1}^2 (\text{p.i.s.})_i = 0.16 + 2 \text{ Cl}^- + 4 \times \text{ArNC} \\ &= 0.16 + 2 \times 0.10 = 0.36 \text{ mm/s } (\delta_{\text{IS}} \text{ (obs)} = + 0.28 \text{ mm/s}) \end{aligned}$$

Similarly, for Na₃[Fe(CN)₅NH₃].H₂O

$$\begin{aligned} \delta_{\text{IS}} &= 0.16 + 5 \times \text{CN}^- + 1 \text{NH}_3 \\ &= 0.16 + 5 \times 0.01 + 0.07 = 0.28 \text{ mm/s } (\delta_{\text{IS}} \text{ (obs)} = 0.26 \text{ mm/s}) \end{aligned}$$

and for *trans*-FeCl(SnCl₃)(depe)₂

$$\delta_{\text{IS}} = 0.16 + \text{Cl}^{-1} + \text{SnCl}_3 + 2 \text{ depe}$$

$$= 0.16 + 0.10 + 0.04 + 2 \times 0.12 = 0.54 \text{ mm/s } (\delta_{\text{IS}}(\text{obs}) = 0.55 \text{ mm/s})$$

10.7 INTERNAL OR EFFECTIVE MAGNETIC FIELD

The effective magnetic field acting on the nucleus arises from the atom's own electrons and is termed as internal magnetic field, H_{int} . The main contributions to the internal magnetic field are (i) the interaction between the nucleus and electron density of the unpaired *s*-electrons, i.e. Fermi contact interaction, e.g. an unpaired electron in the atomic environment generates a local magnetic field of about 2T, and (ii) orbital magnetic moment on the resonant atom. In the high-spin Fe²⁺ compounds the contribution because of this factor varies from +20T to +60T and is opposite in sign to Fermi contact interaction contribution. (iii) Doppler interaction of the electron spin moment of the atom with the nucleus. In high-spin Fe²⁺ iron, the contribution due to this interaction is in the range 0–8T and is zero in cubic symmetry. The relative contributions of these interactions depend on the electron configuration of the atom. The most important contribution is because of Fermi contact interaction. It is to be noted that unpaired spin density appears even in *s*-shells of transition metal ions. This is so because the exchange interaction between the spin-up polarized *d* shell and a spin-up *s*-electron is attractive whereas the interaction between the *d*-shell and a spin down *s*-electron is repulsive. Consequently, the radial parts of the two *s*-electron wave functions are distorted, one being pushed closer to the nucleus and the other being pulled further out.

10.7.1 Effect of Temperature on Internal Magnetic Field

The internal magnetic field is influenced significantly by temperature. The behaviour of internal magnetic field with temperature in case of FeF₂ is shown in Fig. 10.14. There is a steep growth of field at first with the decreasing temperature and a saturation value is attained at absolute zero. In the neighbourhood of Neel temperature, the hyperfine effective magnetic field is given by the usual function, $H_T = H_0 D(1 - T/T_N)^\beta$. For FeF₂, $D = 1.36 \pm 0.03$, $\beta = 0.325 \pm 0.005$ and the hyperfine field at absolute zero $H_0 = 329 \pm 2 \text{ kG}$. $T_N = 78.12 \text{ K}$.

10.7.2 Effect of Pressure on Internal Magnetic Field

The total spin-density imbalance is also affected by change in volume, so that there is a small effect on an internal magnetic field. The behaviour of internal magnetic field of ⁵⁷Fe in iron, cobalt and nickel as a function of pressure

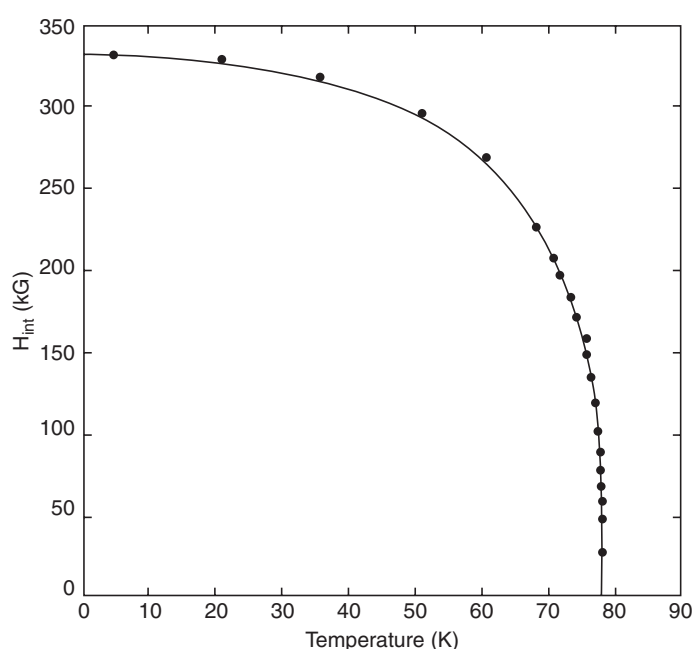


Fig. 10.14 The internal magnetic field in FeF₂ as a function of temperature. Note that the MB spectrum of FeF₂ exhibit more than six Zeeman lines. This implies that the Zeeman levels are no longer pure $M_I >$ eigen-states, so the $\Delta M_I = \pm 2$ transitions are weakly allowed. At 4.2 K where the magnetic field is considerably greater than the quadrupole coupling, the spectrum approximates to a six line pattern.

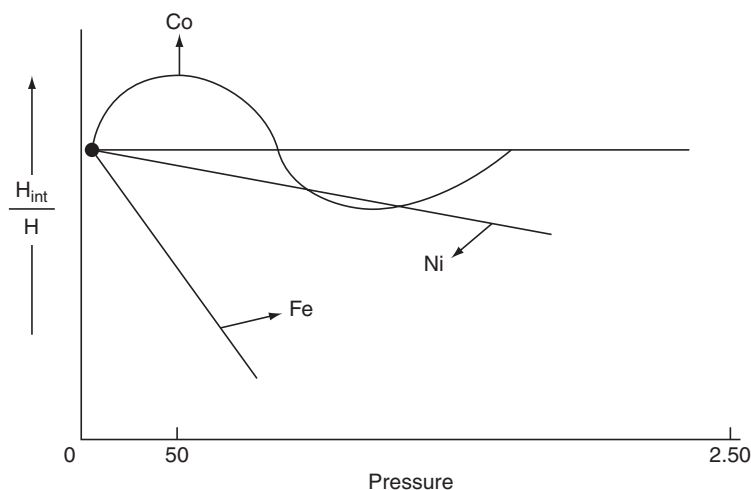


Fig. 10.15 Internal magnetic field of ^{57}Fe in Fe, Ni and Co as a function of pressure.

is shown in Fig. 10.15. The decrease in internal magnetic field with pressure for iron agrees well with NMR measurements. In case of nickel, the decrease is at a smaller rate as compared to iron. In case of Co, the internal field first increases and then decreases with rise of pressure.

10.7.3 Effect of External Magnetic Field

The field at the nucleus is parallel (+) or anti-parallel (−) to the direction of external magnetic field. Thus, the total field experienced by the nucleus in the former case will be $H + H_{\text{int}}$ and $H_{\text{int}} - H$ in the latter case.

10.8 MAGNETIC HYPERFINE INTERACTION

The splitting of the nuclear state with spin I ($I > 0$) into $(2I + 1)$ sublevels because of the interaction of nuclear magnetic dipole moment μ with a magnetic field (internal or external) at the site of the nucleus is called the nuclear Zeeman effect.

The hyperfine Hamiltonian operator for a magnetic interaction of nuclear level with spin angular momentum I and magnetic field H is given by

$$H_m = -g_N \beta_N \hat{I} \hat{H} \quad (10.61)$$

Here, g_N is the nuclear Landé splitting factor $\left[g_N = \frac{\mu_I}{\hat{I} \beta_N} \right]$; β_N is the nuclear Bohr magneton $\left(\frac{eh}{4\pi m_p} = 5.04929 \times 10^{-27} \text{ Am}^2 \text{ or } \text{J T}^{-1} \right)$, H is the strength of magnetic field. If the magnetic field is acting along Z -axis, it becomes

$$H_m = -g_N \beta_N \hat{I} \hat{H}_z \quad (10.62)$$

The resulting Hamiltonian matrix is diagonal with $(2I + 1)$ eigenvalues, given by

$$E_m = -g_N \beta_N H \cdot M_I \text{ (or } -\mu_I H M_I / I) \quad (10.63)$$

Here, M_I is the magnetic quantum number and can take on values; $I = I - 1, I - 2, \dots, -I$. E_m corresponds to minimum value of μH which is negative.

It can readily be shown that the sublevels are equally spaced with a separation of $g_N \beta_N H$. In case of ^{57}Fe , $I_g = \frac{1}{2}$ for the ground state and $I_e = \frac{3}{2}$ for the 14.4 keV first excited state. For this isotope $\mu_g = +0.0902 \text{ nm}$ and $\mu_e = -0.1547 \text{ nm}$. Thus $\frac{\mu_e}{\mu_g} = -1.7145$.

The magnetic splitting in mm/s of ^{57}Fe ground state and first excited state are $g_g = 3.9098$, $g_e = 2.2342$ at 298 K and $g_g = 4.0117$, $g_e = 2.2931$ at 4.3 K. For ^{119}Sn , $I_g = \frac{1}{2}$, $I_e = \frac{3}{2}$, $\mu_g = -1.047 \text{ nm}$ and $\mu_e = +0.67 \text{ nm}$. The ground

state splits into two $\left(2 \times \frac{1}{2} + 1 = 2\right)$ sublevels separated by an amount $\beta = \Delta E_{m(g)} = g_g \beta_N H$ and the excited state splits into four $\left(2 \times \frac{3}{2} + 1 = 4\right)$ sublevels with an equal separation of $\alpha = \Delta E_{m(e)} = g_e \beta_N H$. According to the dipole radiation selection rule, $\Delta M_I = 0, \pm 1$, the number of permissible transitions are restricted to six at the most, and the energy of each transition is listed in Table 10.6.

Table 10.6 Relative energy positions and intensities for various allowed transitions in ^{57}Fe .

Transition	ΔM_I	Relative energy with respect to E_0	Total intensity	Angular dependence
$-\frac{1}{2} \rightarrow -\frac{3}{2}$	-1	$-\frac{1}{2}(\beta + 3\alpha)$	3	$\frac{9}{4}(1 + \cos^2 \theta)$
$-\frac{1}{2} \rightarrow -\frac{1}{2}$	0	$-\frac{1}{2}(\beta + \alpha)$	2	$\frac{3}{2}\sin^2 \theta$
$-\frac{1}{2} \rightarrow +\frac{1}{2}$	+1	$-\frac{1}{2}(\beta - \alpha)$	1	$\frac{3}{4}(1 + \cos^2 \theta)$
$+\frac{1}{2} \rightarrow -\frac{1}{2}$	-1	$+\frac{1}{2}(\beta - \alpha)$	1	$\frac{3}{4}(1 + \cos^2 \theta)$
$+\frac{1}{2} \rightarrow +\frac{1}{2}$	0	$+\frac{1}{2}(\beta + \alpha)$	2	$\frac{3}{2}\sin^2 \theta$
$+\frac{1}{2} \rightarrow +\frac{3}{2}$	+1	$+\frac{1}{2}(\beta + 3\alpha)$	3	$\frac{9}{4}(1 + \cos^2 \theta)$

The magnetic hyperfine splitting and the resultant spectrum is shown in Fig. 10.16. The separation between the outermost two lines, $3\alpha + \beta$ or 4.715α is found to be 10.64 mm/s, which corresponds to an effective magnetic field of 330 kG. The selection rule for magnetic quantum number (i.e. $\Delta M_I = 0, \pm 1$), if written in the following fashion, constitutes the polarization values for Zeeman lines.

(a) View Perpendicular to the Field $\Delta M_I = \pm 1$, plane polarised parallel to the magnetic field direction; π -components: $\Delta M_I = 0$, plane polarized, perpendicular to the magnetic field direction; σ -components.

(b) View Parallel to the Field $\Delta M_I = \pm 1$, circularly polarised, π -components.

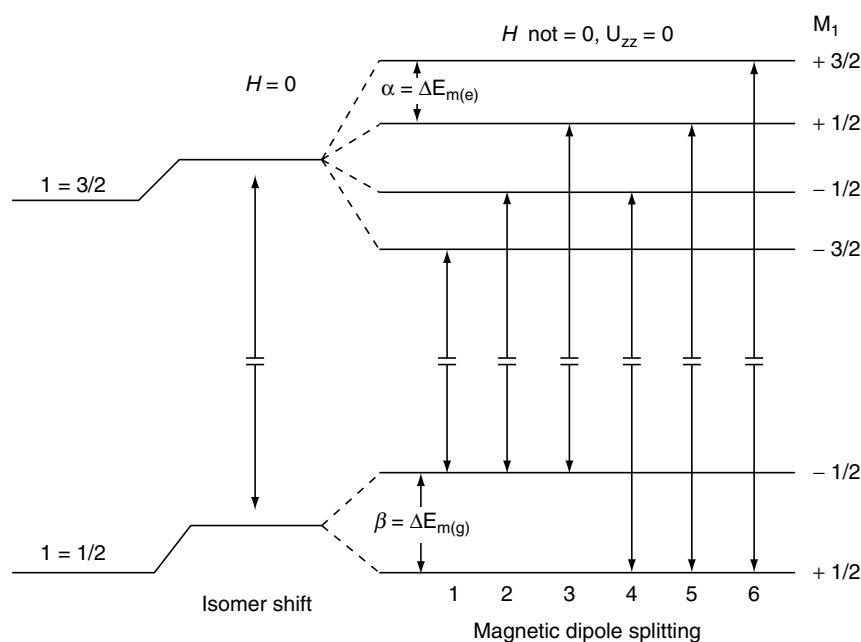
(c) Right Circularly Polarised Spin of γ -ray lies in the direction of γ -emission.

(d) Left Circularly Polarised Spin of γ -ray lies in the opposite direction of γ -emission. $\Delta M_I = 0$; forbidden, σ components.

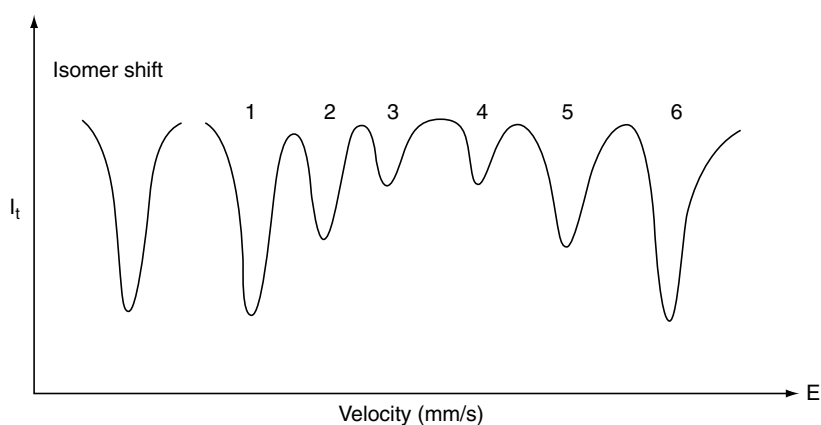
These conventions pertaining to polarization in MB spectroscopy are opposite to the one in optical spectroscopy.

Accordingly, for random orientation of H with respect to the γ -ray direction, the radiation is unpolarized. For a perpendicular magnetic field $H(\theta = 90^\circ)$, the six lines are observed with linear polarization $\parallel, \perp, \parallel, \parallel, \perp, \parallel$. For axial field (i.e. $\theta = 0$), the radiation is circularly polarized with $\Delta M_I = 0$ transition missing and the remaining four lines are observed with polarization left, right, left, right.

The nuclear magnetic moment of the ground and excited states of ^{57}Fe are of opposite signs, i.e. positive for the ground state and negative for the excited state. This change in sign of magnetic moment results in relative inversion of the multiplets. The lines are not of equal intensity but have 3:2:1:1:2:3 ratio. However, the spectrum is symmetrical about the centroid. Such spectra have been observed in polycrystalline samples of ^{57}Fe .



(a)



(b)

Fig. 10.16 Magnetic dipole splitting ($H \neq 0$, $U_{zz} = 0$) without electric quadrupole (a), and the resultant theoretical spectrum (b) of ^{57}Fe .

and ^{119}Sn . Combined magnetic and quadrupole splittings are also possible in some samples. However to negate the impact of quadrupole splitting, the source material is selected to give a single-line spectra, e.g. when ^{57}Co is embedded in metallic chromium, no net electric field gradient and magnetic fields are present at the cobalt nucleus.

10.8.1 Intensity of Hyperfine Lines

The intensity of a particular hyperfine transition between sublevels is determined from the interaction of two nuclear angular momentum states. It is expressed as the product of two terms which are angular dependent and angular independent. The angular-dependent term averages to unity when all the orientations are equally probable, e.g. in a randomly oriented polycrystalline sample. The intensity of the angular-dependent term is given by the square of the appropriate Clebsh–Gordan coefficient, i.e.

$$\text{intensity} \propto \langle I_g J - m_1 m | I_e m_2 \rangle^2 \quad (10.64)$$

where the two nuclear spin states I_g and I_e have I_z values of m_1 and m_2 and their coupling obeys the vector sum $J = I_e + I_g$ and $m = m_1 - m_2$. J is called the *multipolarity* of the transition and the intensity is greater if J is small.

$J = 1$ for dipole transition and $J = 2$ for quadrupole transition. If there is no change in parity during the decay it is classified as magnetic dipole (M_1) or electric quadrupole (E_2) and for a change in parity, the transition is classified as electric dipole (E_1). The angular-dependent term $\theta(J, m)$ is expressed as the radiation probability in a direction at an angle θ to the magnetic field axis. θ is the angle between the direction of the magnetic field at the nucleus and the direction of propagation of γ -ray. The angular-dependent probability functions $\theta(J, M)$ are given in the tabular form as foot note (2) under Table 10.8.

The intensity for polycrystalline samples is obtained by integration over all orientations to obtain average

$$\overline{\theta(J, m)}, \text{ e.g. } \frac{3}{2} \overline{\sin^2 \theta} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi \left(\frac{3}{2} \sin^2 \theta \right) \sin \varphi d\theta d\varphi = 1 \quad (10.65)$$

and the total emitted radiation given by $\sum_{m_1 m_2} \langle I_1 J - m_1 m | I_2 m_2 \rangle^2 \overline{\theta(J, m)}$ is independent of θ i.e. the γ -ray emission is isotropic and is normalised to unity, i.e.

$$\sum_{m_1 m_2} \frac{1}{4} \langle I_1 J - m_1 m | I_2 m_2 \rangle^2 \overline{\theta(J, m)} = 1 \quad (10.66)$$

The Clebsch–Gordan coefficients and angular-dependence functions needed to compute the relative intensities of hyperfine lines for $\frac{3}{2} - \frac{1}{2}$ and $\frac{7}{2} - \frac{5}{2}$ transitions with M_1 multipolarity have been given in Tables 10.7 and 10.8 respectively.

Table 10.7 Relative probabilities for a $\frac{3}{2}, \frac{1}{2}$ transition.

Magnetic spectra (M_1)							
m_2	$-m_1$	m	C (1)	C^2 (2)	$\theta(J, m)$ (2)	$\theta_2 = 0^\circ$ $C^2 \theta$ (3)	$\theta = 90^\circ$ $C^2 \theta$ (3)
$+\frac{3}{2}$	$+\frac{1}{2}$	+1	1	$\frac{1}{4}$	$\frac{3}{4}(1 + \cos^2 \theta)$	6	3
$+\frac{1}{2}$	$+\frac{1}{2}$	0	$\sqrt{2/3}$	$\frac{1}{6}$	$\frac{3}{2} \sin^2 \theta$	0	4
$-\frac{1}{2}$	$+\frac{1}{2}$	-1	$\sqrt{1/3}$	$\frac{1}{12}$	$\frac{3}{4}(1 + \cos^2 \theta)$	2	1
$-\frac{3}{2}$	$+\frac{1}{2}$	-2	0	0	0	0	0
$+\frac{3}{2}$	$-\frac{1}{2}$	+2	0	0	0	0	0
$+\frac{1}{2}$	$-\frac{1}{2}$	+1	$\sqrt{1/3}$	$\frac{1}{12}$	$\frac{3}{4}(1 + \cos^2 \theta)$	2	1
$-\frac{1}{2}$	$-\frac{1}{2}$	0	$\sqrt{2/3}$	$\frac{1}{6}$	$\frac{3}{2} \sin^2 \theta$	0	4
$-\frac{3}{2}$	$-\frac{1}{2}$	-1	1	$\frac{1}{4}$	$\frac{3}{4}(1 + \cos^2 \theta)$	6	3

Quadrupole spectra (M_J) when $\eta = 0$				
Transition	C^2 (2)	$\theta(J, m)$ (2)	$\theta = 0^\circ$ $C^2\theta(3)$	$\theta = 90^\circ$ $C^2\theta(3)$
$\pm\frac{1}{2}, \pm\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2} + \frac{3}{4}\sin^2\theta$	$\frac{1}{4}$	$\frac{5}{8}$
$\pm\frac{3}{2}, \pm\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{4}(1 + \cos^2\theta)$	$\frac{3}{4}$	$\frac{3}{8}$

Table 10.8 Relative probabilities for a $7/2, 5/2$ transition.

Magnetic spectra (M_J)							
m_2	$-m_1$	m	C (1)	C^2 (2)	$\theta(J, m)$ (2)	$\theta = 0^\circ$ $C^2\theta(3)$	$\theta = 90^\circ$ $C^2\theta(3)$
$+\frac{7}{2}$	$+\frac{5}{2}$	+1	1	21	$1 + \cos^2\theta$	42	21
$+\frac{5}{2}$	$+\frac{3}{2}$	+1	$\sqrt{\frac{5}{7}}$	15		30	15
$+\frac{3}{2}$	$+\frac{1}{2}$	+1	$\sqrt{\frac{10}{21}}$	10		20	10
$+\frac{1}{2}$	$-\frac{1}{2}$	+1	$\sqrt{\frac{2}{7}}$	6		12	6
$-\frac{1}{2}$	$-\frac{3}{2}$	+1	$\sqrt{\frac{1}{7}}$	3		6	3
$-\frac{3}{2}$	$-\frac{5}{2}$	+1	$\sqrt{\frac{1}{21}}$	1	$2 \sin^2\theta$	2	1
$+\frac{5}{2}$	$+\frac{5}{2}$	0	$\sqrt{\frac{2}{7}}$	6		0	12
$+\frac{3}{2}$	$+\frac{3}{2}$	0	$\sqrt{\frac{10}{21}}$	10		0	20
$+\frac{1}{2}$	$+\frac{1}{2}$	0	$\sqrt{\frac{4}{7}}$	12		0	24
$-\frac{1}{2}$	$-\frac{1}{2}$	0	$\sqrt{\frac{4}{7}}$	12		0	24
$-\frac{3}{2}$	$-\frac{3}{2}$	0	$\sqrt{\frac{10}{21}}$	10		0	20
$-\frac{5}{2}$	$-\frac{5}{2}$	0	$\sqrt{\frac{2}{7}}$	6		0	12

Table 10.8 Relative probabilities for a 7/2, 5/2 transition—Cont'd.

<i>Magnetic spectra (M_I)</i>							
m_2	$-m_1$	m	C	C^2	$\theta(J, m)$	$\theta = 0^\circ$	$\theta = 90^\circ$
			(1)	(2)	(2)	$C^2 \theta(3)$	$C^2 \theta(3)$
$+\frac{3}{2}$	$+\frac{5}{2}$	-1	$\sqrt{\frac{1}{21}}$	1	$1 + \cos^2 \theta$	2	1
$+\frac{1}{2}$	$+\frac{3}{2}$	-1	$\sqrt{\frac{1}{7}}$	3		6	3
$-\frac{1}{2}$	$+\frac{1}{2}$	-1	$\sqrt{\frac{2}{7}}$	6		12	6
$-\frac{3}{2}$	$-\frac{1}{2}$	-1	$\sqrt{\frac{10}{21}}$	10		20	10
$-\frac{5}{2}$	$-\frac{3}{2}$	-1	$\sqrt{\frac{5}{7}}$	15		30	15
$-\frac{7}{2}$	$-\frac{5}{2}$	-1	1	21		42	21

<i>Quadrupole spectra (M_I)</i>				
<i>Transitions</i>	C^2	$\theta(J, m)$	$\theta = 0^\circ$	$\theta = 90^\circ$
	(2)	(2)	$C^2 \theta(3)$	$C^2 \theta(3)$
$\pm\frac{5}{2}, \pm\frac{7}{2}$	21	$1 + \cos^2 \theta$	42	21
$\pm\frac{5}{2}, \pm\frac{5}{2}$	6	$2\sin^2 \theta$	0	12
$\pm\frac{5}{2}, \pm\frac{3}{2}$	1	$1 + \cos^2 \theta$	2	1
$\pm\frac{3}{2}, \pm\frac{5}{2}$	15	$1 + \cos^2 \theta$	30	15
$\pm\frac{3}{2}, \pm\frac{3}{2}$	10	$2\sin^2 \theta$	0	20
$\pm\frac{3}{2}, \pm\frac{1}{2}$	3	$1 + \cos^2 \theta$	6	3
$\pm\frac{1}{2}, \pm\frac{3}{2}$	10	$1 + \cos^2 \theta$	20	10
$\pm\frac{1}{2}, \pm\frac{1}{2}$	18	$\frac{2}{3} + \sin^2 \theta$	12	30

1. The Clebsch-Gordon coefficient: For $\langle \frac{3}{2} \frac{1}{2} m_2 m_1 | 2m \rangle$ is $\langle \frac{1}{2} 2 - m_1 m | \frac{3}{2} m_2 \rangle = (-)^{\frac{1}{2} + m_1} \sqrt{\frac{4}{3}}$

$\langle \frac{3}{2} \frac{1}{2} m_2 m_1 | 2m \rangle$. For $\langle \frac{7}{2} \frac{5}{2} m_2 m_1 | 1m \rangle$ is $\langle \frac{5}{2} 1 - m_1 m | \frac{7}{2} m_2 \rangle = (-)^{\frac{5}{2} + m_1} \sqrt{\frac{8}{3}} \langle \frac{7}{2} \frac{5}{2} m_2 m_1 | 1m \rangle$.

2. The angular dependent probability functions $\theta(J, M)$ are

$m \setminus j$	0	± 1	± 2
1	$\frac{1}{2} \sin^2 \theta$	$\frac{1}{4} (1 + \cos^2 \theta)$	—
2	$\frac{3}{8} \sin^2 2\theta$	$\frac{1}{4} (\cos^2 \theta + \cos^2 2\theta)$	$\frac{1}{4} (\sin^2 \theta + \sin^2 2\theta / 4)$

3. C^2 and $\theta(J, m)$ are the angular independent and angular dependent terms normalized to a total radiation probability of

$$\sum_{m_1, m_2} C^2 \theta(J, m) = 1$$

4. Relative intensities are observed at 0° and 90° to the principal axis: normalisation is arbitrary.

The theoretical stick spectra for $\frac{1}{2} \rightarrow \frac{3}{2}$ transition deduced from $(2I + 1)$ multiplicity rule; $\Delta M_I = 0, \pm 1$ selection rule and the probability of the transition given in Table 10.7 are shown in Figs 10.17(a)–(c) whereas, the observed experimental spectra for $\frac{1}{2} \rightarrow \frac{3}{2}$ transition for α -Fe foil at room temperature with hyperfine magnetic field of $H_{int} = 330$ kOe are shown in Fig. 10.18(a)–(c).

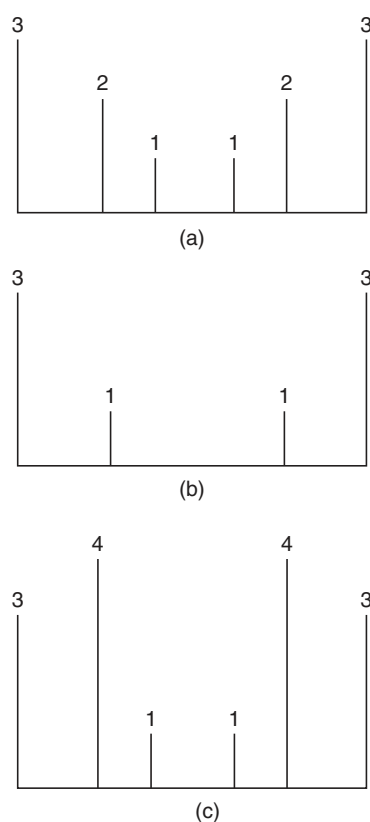


Fig. 10.17 MB stick spectra (a) for a randomly oriented crystalline sample, when no external field is applied, (b) $\theta = 0$, a magnetic field is applied parallel to the direction of the internal magnetic field of the sample, and (c) $\theta = 90^\circ$, a magnetic field is applied perpendicular to the direction of the internal magnetic field of the sample.

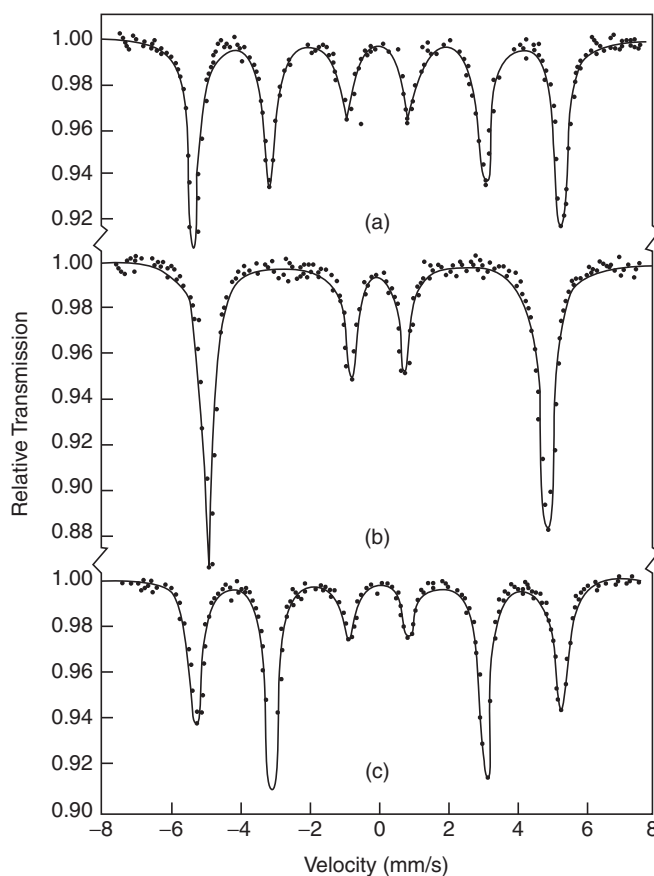


Fig. 10.18 Experimentally observed MB spectra of α - ^{57}Fe foil at room temperature (a) $H = 0$, Random (b) $H = 50$ kOe, $\theta = 0$ and (c) $H = 3.5$ kOe, $\theta = 90^\circ$.

Further, at very low temperatures, $T \ll 1$ K, the magnitude of magnetic hyperfine splitting and the thermal energy kT are of the same order. Thus, the populations of the nuclear levels are governed by Maxwell–Boltzmann distribution law. Accordingly, the higher levels will be thinly populated and transitions from these levels will be less frequent. Consequently, the spectra become asymmetric with respect to relative line intensity. This effect is observed for the parent isotope ^{57}Co ($I = 7/2$) which has a large magnetic moment and the polarisation is maintained through the decay to ^{57}Fe .

10.8.2 Sign of Nuclear Zeeman Interaction and Internal Magnetic Field

The spectrum in Fig. 10.18(b) reveals that when large magnetic field is applied perpendicular to the foil plane ($\theta = 0$) in excess of the demagnetisation field (≈ 21 kOe), the splitting is reduced by the applied field. This indicates that hyperfine interaction has a negative sign, i.e. atomic moment and the magnetic field at the nucleus (H_{int}) are in opposite directions, e.g. ^{57}Fe in most alloys and ferrites. Thus, the sign of internal magnetic field can be determined by applying external magnetic field ($H = 30 - 50$ kG). When the internal field is aligned parallel to external field, i.e. magnetization, the internal field is increased to $H_{\text{int}} + H$, then the sign of the internal field is positive. In the antiparallel alignment, i.e. demagnetisation, a field of $H_{\text{int}} - H$ indicates a negative sign. However, this method fails when magnetic interaction anisotropy of the matrix is so large that it prevents the rotation of the internal field into the direction of the applied field, i.e. it prevents complete polarisation of the ordered spins by the external field.

10.8.3 Relaxation Effects in Relation to Magnetic Hyperfine Splitting

Further it is to be noted that the magnetic hyperfine interaction depends upon the magnetic nature of the sample, viz., paramagnetic, ferromagnetic or antiferromagnetic. For paramagnetic samples, the time lag τ_f elapsed between two successive flips of the electron spin needs to be considered. The flips could be because of electronic relaxation or above Curie point, due to exchange coupling between neighbouring electron spins. When the frequency $\frac{1}{\tau_f}$ of the flips is $\gg$ than the Larmor frequency $\frac{1}{\tau_L}$ of the nuclear spin in the internal field, there will be no magnetic hyperfine pattern, since the value of the internal field experienced by the nucleus averages out to zero over the time of the frequency of the nuclear spin. On the other hand, if the electron-flips frequency is $\ll$ than the frequency of the nuclear spin, the spectrum will exhibit a magnetic hyperfine structure, e.g. Fe and rare earth Mössbauer nuclei. When the relaxation time of the electron spin (spin-spin and spin-lattice) $\tau_f = \tau_L$, complicated spectra with broad lines are observed, which enables us to determine the electron relaxation time. The line broadening in the Mössbauer–Zeeman pattern is closely connected to the motional narrowing in NMR. In case of ferro-, ferri-, and antiferromagnetic substances, the electron s - s interaction is $\gg$ than the nuclear Zeeman splitting, consequently the nuclear spin interacts with the average value of the internal magnetic field and the MB spectrum exhibits a magnetic hyperfine pattern. From the foregoing description, it is pertinent to note that magnetic dipole interactions are rarely encountered in chemical applications of Mössbauer spectroscopy. Metallic iron is an exception. However, the magnetic dipole interactions provide a technique for the study of magnetically ordered materials, sublattice magnetisation, Curie or Neel temperature and atomic magnetic moments can be deduced from the magnetic hyperfine field.

The magnetic hyperfine pattern in paramagnetic substances serves as a tool for the study of spin relaxation time and the nuclear Lande g -factor. The two parameters which give information on the magnetic properties of the material under study are (i) the position of the six fingers gives information on the splitting of the excited and ground states, and (ii) the relative intensity of the lines gives information on the polarisation. The magnetic splitting in α -iron (in mm/s) is determined from the appropriate first differences of line positions.

The ground state splitting is

$$\begin{aligned}\Delta E_{m(g)} &= g_g = v_4 - v_2 \\ &= v_5 - v_3;\end{aligned}\tag{10.67a}$$

and the excited-state splitting is

$$\begin{aligned}\Delta E_{m(e)} &= g_e = v_3 - v_2 \\ &= v_5 - v_4\end{aligned}\tag{10.67b}$$

$$\delta_{\text{is}}(\text{mm/s}) = \frac{1}{2} \left[\frac{1}{2} (v_1 + v_6) + \frac{1}{4} (v_2 + v_3 + v_4 + v_5) \right] \quad (10.68)$$

Problem 10.2: For ^{57}Fe , $\mu_e = -0.15 \text{ nm}$, $I_e = 3/2$, $\mu_g = 0.09 \text{ nm}$ and $I_g = \frac{1}{2}$. Prove that the separation between any two consecutive excited magnetic hyperfine levels is small as compared to their counter parts in the ground state.

Solution We know that

$$E_m = - \frac{\mu_l H M_l}{I} \quad (10.69)$$

Let α and β be the separations between any two consecutive Zeeman levels in the excited and ground states respectively.

Applying the selection rule for permissible transitions, i.e. $\Delta M_l = 0, \pm 1$, we get

$$\begin{aligned} \alpha &= + \frac{\mu_e H}{I_e} \\ \beta &= + \frac{\mu_g H}{I_g} \\ \frac{\alpha}{\beta} &= \left(\frac{\mu_e}{\mu_g} \right) \left(\frac{I_g}{I_e} \right) \end{aligned} \quad (10.70)$$

Substituting the values of the respective parameters, we get

$$\frac{\alpha}{\beta} = \left(\frac{-0.15(\text{nm})}{0.09(\text{nm})} \right) \left(\frac{1}{2} \times \frac{2}{3} \right) = \frac{-5}{9} = -0.55$$

or

$$\begin{aligned} \alpha &= -0.55 \beta \\ \beta &> \alpha \end{aligned}$$

Problem 10.3: Prove that in the ground state of ^{57}Fe (14.4 keV), the hyperfine magnetic field is given by

$$H = \left(\frac{E_\gamma}{c\beta_N} \right) \left(\frac{-g_g I_g}{\mu_g} \right)$$

Solution We know that

$$E_m = -\mu H \frac{M_l}{I} \quad (\text{Eq. 10.63})$$

For ground state of ^{57}Fe , $I_g = \frac{1}{2}$.

Therefore, $M_l = \pm \frac{1}{2}$

Thus, the energy difference between the Zeeman levels corresponding the ground state is

$$\Delta E_{m(g)} = g_g = \frac{-\mu_g H}{I_g} \quad (10.71)$$

$$H = - \frac{I_g g_g}{\mu_g} \quad (10.72)$$

If g_g is in mm/s then $g_g \frac{E_\gamma}{c}$ is in ergs, also if μ_g is in units of nuclear magneton, β_N .
Then

$$H = \left(\frac{E_\gamma}{c\beta_N} \right) \left(\frac{-g_g I_g}{\mu_g} \right) \quad (10.73)$$

Now,

$$E_\gamma = 14.4125 \text{ keV}$$

$$\beta_N = 5.04929 \times 10^{-27} \text{ J T}^{-1}$$

$$1 \text{ eV} = 1.6021 \times 10^{-9} \text{ J}$$

Substituting these values in Eq. (10.73), we get

$$H = - (15.250 \text{ kOe s/mm nm}) \left(\frac{g_g I_g}{\mu_g} \right) \quad (10.74)$$

The hyperfine field could also be derived from the excited state splitting g_e . Since this method is inherently less accurate and non-independent, g_e is not used to calculate H .

10.9 ELECTRIC QUADRUPOLE INTERACTION

Recall from Chapter 8 on nuclear quadrupole resonance spectroscopy that when a crystal has low symmetry or its high symmetry is broken locally, an electric field gradient $U_{zz} = \frac{\partial^2 U}{\partial z^2} = eq$ will result at the site of the nucleus and interact with the electric quadrupole moment eQ of the probe isotope nucleus, causing a splitting of the nuclear state into substates, e.g. in case of ^{57}Fe a double peak spectrum will appear when the crystal is paramagnetic, and an asymmetric six-line pattern is observed in case of ferromagnetic ordering. The electric quadrupole coupling in MB spectroscopy is similar to that in nuclear quadrupole resonance spectroscopy. The main difference is that the latter deals with radio-frequency transitions within hyperfine multiplets of a nucleus in the ground state whereas the former is a γ -ray transition between hyperfine multiplets of the nucleus in the ground and excited states.

The classical expression for the quadrupole interaction is given by

$$H_Q = \frac{e^2 q Q}{6} \left[1 - \frac{1}{2} \frac{U_{xx} + U_{yy}}{U_{zz}} \right] \quad (10.75)$$

where terms which are independent of nuclear orientation have been neglected.

The quantum mechanical analogue of the classical quadrupole Hamiltonian is

$$H_Q = \frac{eQ U_{zz}}{4I(2I-1)} \left[3I_z^2 - I^2 + \eta(I_+^2 + I_-^2)/2 \right] \quad (10.76)$$

where, $\hat{I}_z$ is the Z -component of the nuclear spin operator $\hat{I}$ and $\hat{I}_+$ and $\hat{I}_-$ are the raising and lowering operators defined as

$$\hat{I}_\pm = \hat{I}_x \pm i \hat{I}_y.$$

The eigen value of the operator $\hat{I}^2$ is $I(I+1)$

The eigen values of the Hamiltonian H_Q , i.e. the energies of the sublevels are given by

$$E_Q = \frac{eQ U_{zz}}{4I(2I-1)} \left[3M_I^2 - I(I+1) \right] \left(1 + \frac{\eta^2}{3} \right)^{1/2} \quad (10.77)$$

where the nuclear magnetic spin quantum number M_I can take on $(2I+1)$ values of $I, I-1, I-2, \dots, -I$. Here the substates can't be distinguished by the sign of M_I , since Eq. (10.77) contains only the second power of M_I . Therefore, the nuclear substates arising from nuclear quadrupole splitting remain doubly degenerate and are denoted by $|I, \pm M_I\rangle$. The two-fold degeneracy of substates can only be removed by magnetic perturbation. For spherically symmetric fields ($U_{xx} = U_{yy} = U_{zz}$) degeneracy corresponding to M_I is not removed and no resonance can take place. For axial symmetrical fields ($I = 3/2, 5/2, 7/2, \dots$) the energy level splits into a series of Kramer's doublet by $\left(I + \frac{1}{2} \right)$ rule and for integral spins, i.e. $I = 1, 2, 3, \dots$, the number of sublevels is given by $I+1$. It is to be noted

that only those transitions among the substates are allowed for which $\Delta M_I = 0, \pm 1$. A lack of axial symmetry in the EFG introduces matrix elements which are off diagonal with $\Delta M_I = \pm 2$. For ^{57}Fe and ^{119}Sn , $I_e = 3/2$ and $I_g = 1/2$. The excited state will split into two doubly degenerate sublevels whereas the number of sublevels corresponding to the ground state will be one only. The nuclear ground state $\left(I_g = \frac{1}{2}\right)$ is not split, because $Q = 0$. Accordingly, for ^{57}Fe ,

the energy difference ΔE_Q between the two substates $\left|\frac{3}{2}, \pm\frac{3}{2}\right\rangle$ and $\left|\frac{3}{2}, \pm\frac{1}{2}\right\rangle$ can be worked out as follows.

From Eq. (10.77), we write

$$E_Q\left(\pm\frac{3}{2}\right) = 3eQ \frac{U_{zz}}{12} \left(1 + \frac{\eta^2}{3}\right)^{1/2} \quad \text{for } I = \frac{1}{2}, M_I = \pm\frac{3}{2}$$

$$E_Q\left(\pm\frac{1}{2}\right) = -3eQ \frac{U_{zz}}{12} \left(1 + \frac{\eta^2}{3}\right)^{1/2} \quad \text{for } I = \frac{3}{2}, M_I = \pm\frac{1}{2}$$

Thus, the quadrupole transition energy is given by

$$\begin{aligned} \Delta E_Q &= E_Q\left(\pm\frac{3}{2}\right) - E_Q\left(\pm\frac{1}{2}\right) \\ &= \left(\frac{eQU_{zz}}{2}\right) \left(1 + \frac{\eta^2}{3}\right)^{1/2} \end{aligned} \quad (10.78)$$

$$\Delta E_Q (\text{mm/s}) = \frac{1}{2} \left(\frac{c}{E_\gamma}\right) e^2 q Q \left(1 + \frac{\eta^2}{3}\right)^{1/2}$$

For $\eta = 0$, Eq. (10.78) becomes

$$\Delta E_Q = \frac{eQU_{zz}}{2} = \frac{eQeq}{2} = \frac{e^2 Qq}{2} \quad (10.79)$$

$$\Delta E_Q (\text{mm/s}) = \frac{1}{2} \left(\frac{c}{E_\gamma}\right) e^2 q Q$$

Note that ΔE_Q is half the quadrupole coupling constant defined in *NQR* spectroscopy. Further, it is always better to refer to the sign of $e^2 q Q$ or of q since in the term eq , it is not always mentioned whether e is taken the charge of electron or the proton. The observed sign of $e^2 q Q$ may be an important factor in deciding the origin of the EFG. As we know that the quadrupole moment Q for ^{57}Fe is positive so the quadrupole coupling constant $\frac{e^2 q Q}{2}$ will be positive or negative according as q , the Z-component of EFG, is positive or negative. In these two possible situations, the excited-state sublevels interchange. The energy-level diagram for ^{57}Fe $\left(I_e = +\frac{3}{2}\right)$ exhibiting the quadrupole splitting and the resultant Mossbauer spectrum under different possible situations is shown in Fig. 10.19.

10.9.1 Intensity of Nuclear Quadrupole Doublet

The quadrupole split spectrum of ^{57}Fe consists of two lines. The intensity of the lines can be predicted from the Clebsch-Gordon coefficients and angular dependence functions listed in Table 10.7. The angular dependence of intensity ratio when field gradient is axially symmetric, i.e. $\eta = 0$ is given by

$$\frac{I_{\pm 1/2, \pm 3/2}}{I_{\pm 1/2, \pm 1/2}} = \frac{I_{\parallel}}{I_{\sigma}} = \left(\frac{1 + \cos^2 \theta}{\frac{2}{3} + \sin^2 \theta} \right) \quad (10.80)$$

where, θ is the angle between the U_{zz} axis and direction of γ -emission.

The intensity ratio ranges from 3 ($\theta = 0^\circ$) to 0.6 ($\theta = 90^\circ$).

It may be pointed out that the above expression does not include the effect of vibrational anisotropy (Goldanskii–Karyagin effect) and thus for any meaningful interpretation one should give proper consideration

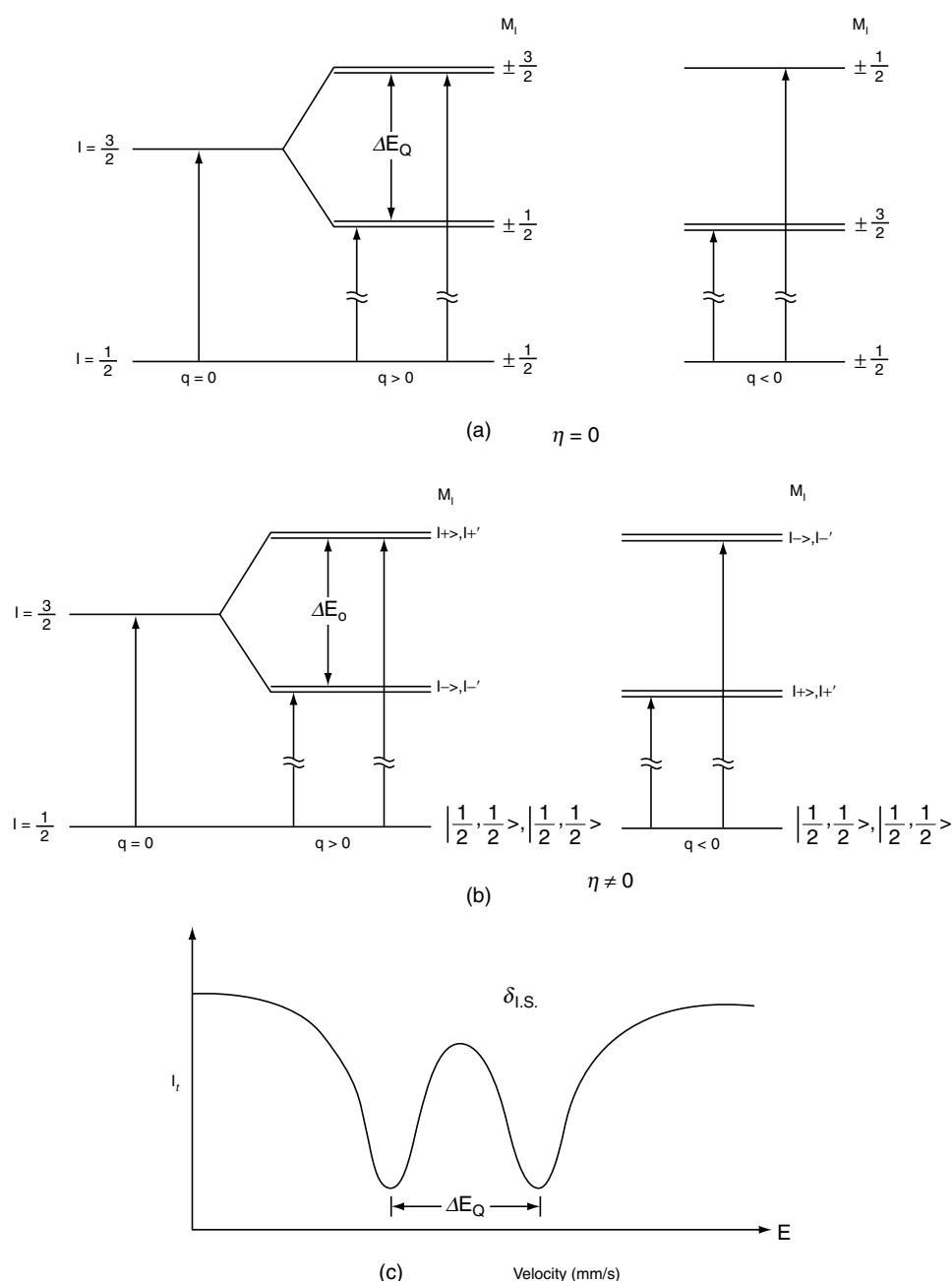


Fig. 10.19 An energy-level diagram illustrating the quadrupole splitting for ^{57}Fe nucleus under different situations (a) axially symmetric field gradient $\eta = 0$ ($q > 0$ and $q < 0$). (b) asymmetry parameter $\eta \neq 0$ ($q > 0$ and $q < 0$, and (c) theoretical Mössbauer spectrum.

while comparing intensities. Further it is interesting to note that for polycrystalline sample the intensity ratio is unity.

Note that for $\theta = 54^\circ 44'$, Eq. (10.80) yields an intensity ratio of unity. Thus, the presence or absence of any asymmetry parameter is not evident from any ordinary MB spectrum of a powdered sample.

10.9.2 Magnitude and Sign of Quadrupole Interaction

The magnitude of the quadrupole interaction is a product of two factors: (i) eQ which is a nuclear constant for the resonant MB isotope, and (ii) eq which is a function of chemical environment. For a $3/2-1/2$ transition, it is not possible to determine the sign of e^2qQ or the magnitude of η from the line positions alone. However, for higher spin states, the sign of e^2qQ can be determined from unequally spaced lines. If both I_e and I_g are greater than $1/2$ then eq can be estimated because the ground state quadrupole moment can be determined from other measurements, i.e. NQR. If $I_g = 0$ or $\frac{1}{2}$, then Q for the excited state is calculated from estimated values eq in chemical compounds. Although e^2qQ and η can be evaluated from a MB spectrum, it is difficult to relate these parameters to electronic structure which generates them.

10.10 COMBINED MAGNETIC AND QUADRUPOLE INTERACTIONS

As has already been discussed in Chapter 8 on nuclear quadrupole resonance spectroscopy, when both magnetic and quadrupole interactions (both are directional effects) exist simultaneously, their respective principal axes may or may not be in the same direction because of which the resulting behaviour may be complex. Consequently, the general interpretation of the spectrum can be quite complex. The combined effects may cause a change in the line positions and/or in the relative line intensities or width of the hyperfine pattern. The combined effects can operate in different ways, either the magnetic hyperfine interaction is perturbed by an electric quadrupole interaction or the quadrupole interaction is perturbed by magnetic dipole interaction, for instance by an applied external magnetic field. In case the quadrupole interaction is very weak as compared to magnetic hyperfine interaction (i.e. $e^2qQ \ll \mu H$), it may cause a perturbation of the magnetic hyperfine interaction. The resultant energy level for such cases is given by

$$E_{QM} = -g_N \beta_N H M_I + (-1)^{|M_I|+\frac{1}{2}} \frac{e^2qQ}{4} \left(\frac{3\cos^2\theta - 1}{2} \right) \quad (10.81)$$

Here, θ is the angle between magnetic axis and the major axis (Z-axis) of EFG. For the transition $\frac{3}{2} - \frac{1}{2}$, all the magnetic hyperfine levels in the excited state and hence the lines in the resultant MB spectrum are shifted by the quantity.

$$|\varepsilon| = \frac{e^2qQ}{4} (3\cos^2\theta - 1) \quad (10.82)$$

The symbol ε is often used if θ is unknown. For a positive EFG (α -Fe foil), ε is positive for $M_I = \pm \frac{3}{2}$ and negative for $M_I = \pm \frac{1}{2}$, which implies that the substates with $M_I = \pm \frac{3}{2}$ will be raised by amount ε while those with $M_I = \pm \frac{1}{2}$ will be lowered by the same amount. On the other hand, for a negative EFG (naturally occurring chalcopryrite) the substates with $M_I = \pm \frac{3}{2}$ are lowered by an amount ε and those with $M_I = \pm \frac{1}{2}$ are raised by the same amount. The schematic diagram showing the splitting of the excited ($3/2$) and ground state ($1/2$) levels in the combined action of internal magnetic field and quadrupole interaction and the resultant six-fingered MB spectrum for positive EFG is shown in Fig. 10.20. The angle θ and value of e^2qQ cannot be determined separately from the

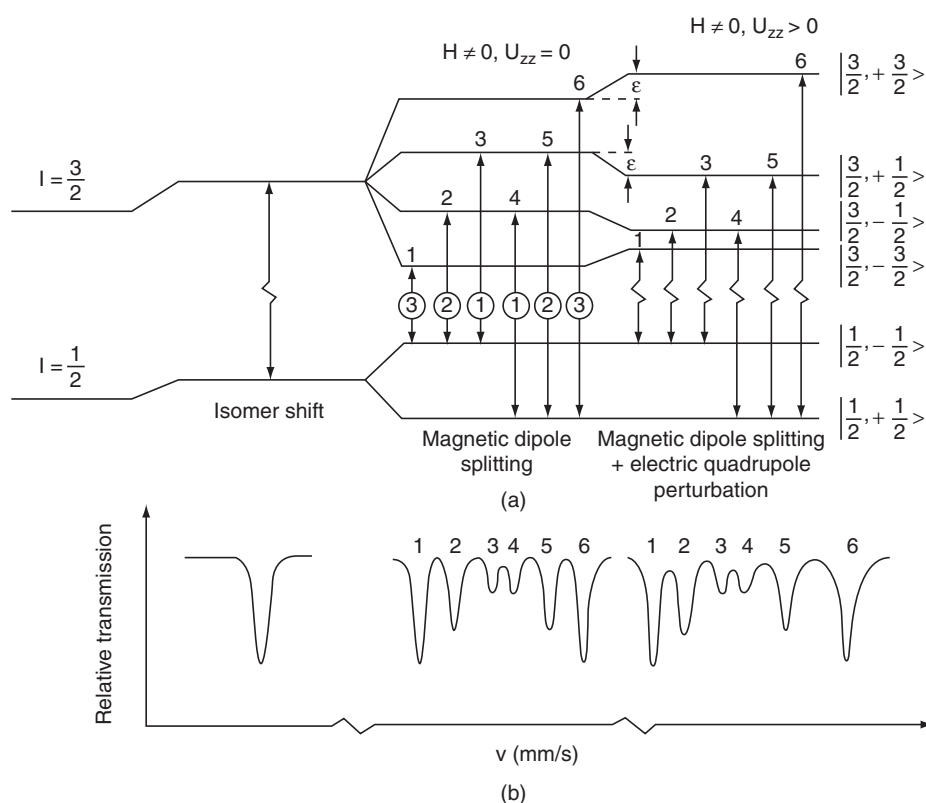


Fig. 10.20 Magnetic dipole splitting without ($H \neq 0, U_{zz} = 0$) and with electric quadrupole splitting ($H \neq 0, U_{zz} > 0$) (a) and the resultant spectra (b) of Fe^{57} .

position of the lines. The asymmetrical nature of the spectrum about the centroid is an evidence for the presence of quadrupole perturbation in the $\frac{3}{2} - \frac{1}{2}$ magnetic hyperfine splitting. However, if $\cos \theta = \frac{1}{\sqrt{3}}$, the second term of

Eq. (10.81) will vanish and the spectrum resembles with that of an unperturbed magnetic hyperfine splitting.

The ground state (g_g) and excited state (g_e) splittings can be determined from Eqs (10.67) and (10.68) respectively while the isomer shift from Eq. (10.69), i.e.

$$g_g = v_4 - v_2 = v_5 - v_3 \quad (\text{Eq. 10.67})$$

$$g_e = v_3 - v_2 = v_5 - v_4 \quad (\text{Eq. 10.68})$$

and

$$\delta_{\text{IS}} = \frac{1}{2} \left[\frac{1}{2} (v_1 + v_6) + \frac{1}{4} (v_2 + v_3 + v_4 + v_5) \right] \quad (\text{Eq. 10.69})$$

The quadrupole coupling, eQU_{zz} is never between $4\varepsilon(\theta = 0^\circ)$ and $-8\varepsilon(\theta = 90^\circ)$. Twice the difference between the centres of gravity of lines 1 and 6 and lines 2–5 gives the best value of 4ε :

$$4\varepsilon = 2 \left[\frac{1}{2} (v_1 + v_6) + \frac{1}{4} (v_2 + v_3 + v_4 + v_5) \right] \quad (10.83)$$

Thus the following quantities can be estimated from the hyperfine interactions (i) magnetic moment ratio, $\mu_e/\mu_g = 3g_e/g_g$, (ii) first excited-state magnetic moment, $\mu_e = \mu_g (3g_e/g_g)$ provided the value of the ground state magnetic moment μ_g is known from other source, and (iii) hyperfine magnetic field using the expressions (10.76) or (10.77), i.e.

$$H = - (15.250 \text{ kOe s/mm nm}) \left(\frac{g_g I_g}{\mu_g} \right) \quad (10.84)$$

Hyperfine magnetic field ratio $\frac{H(T_1 K)}{H(T_2 K)}$ and temperature shift $\delta_{\text{IS}}(T_1 K) - \delta_{\text{IS}}(T_2 K)$ can also be estimated by performing the experiment at two different temperatures T_1 and T_2 say $T_1 = 298 \text{ K}$ and $T_2 = 4.3 \text{ K}$.

In case of naturally occurring chalcopyrite, the observed spectra at 300, 373 and 448 K (Fig. 10.21) conform to the energy-level diagram shown in Fig. 10.22. This implies a negative EFG, i.e. ε . The magnetic interaction

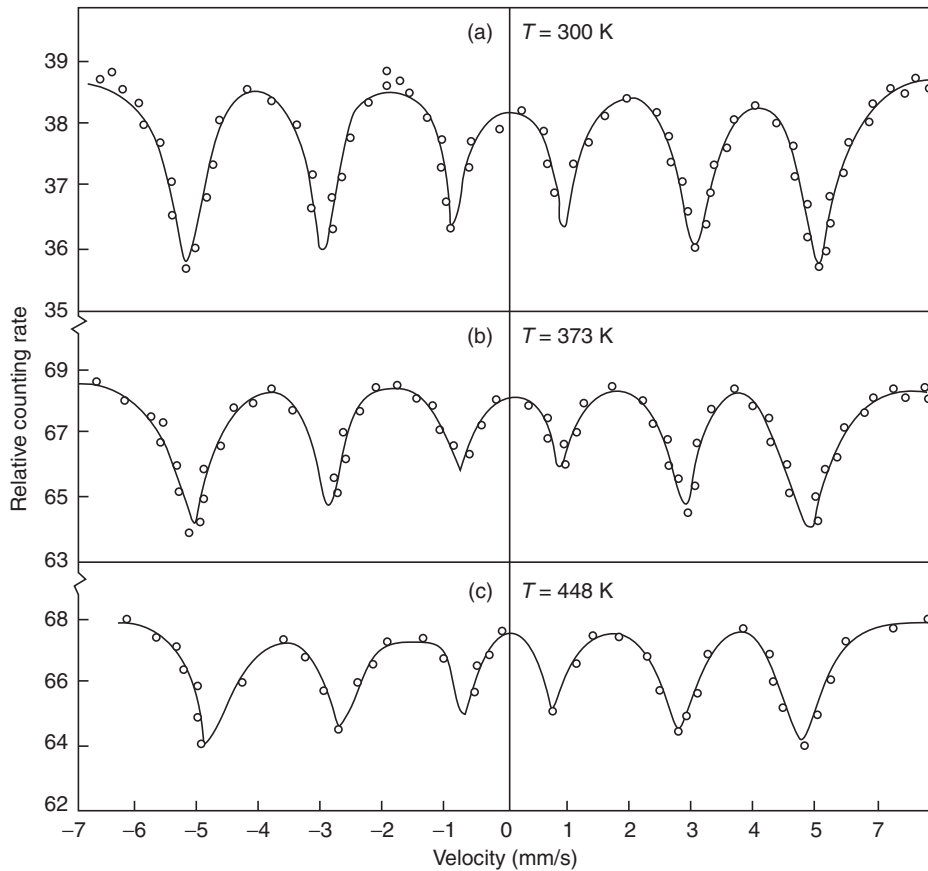


Fig. 10.21 The observed Mössbauer spectra of naturally occurring chalcopyrite at (a) 300, (b) 373, and (c) 448 K.

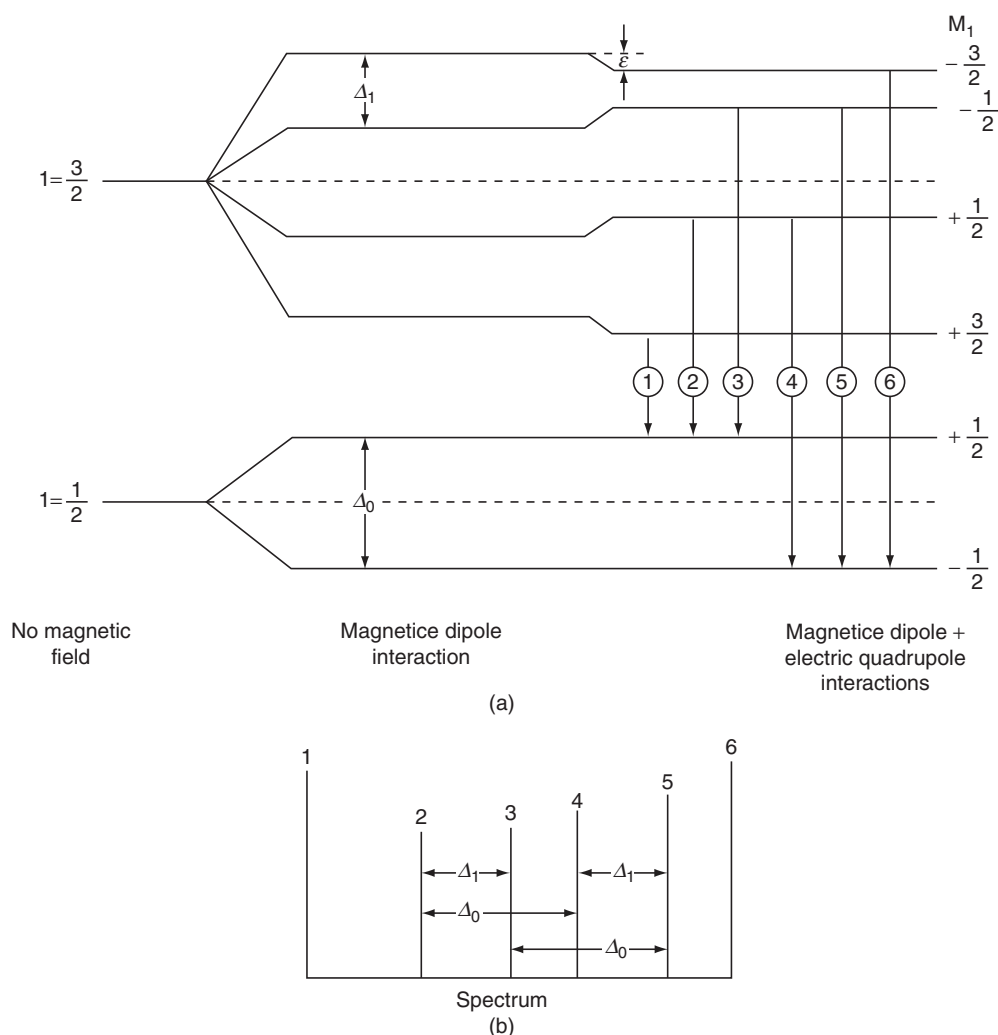


Fig. 10.22 (a) Schematic splitting of ^{57}Fe levels of excited and ground states under the combined interaction of magnetic dipole and electric quadrupole. (b) The six-fingered spectrum to a first approximation.

first leads to the splitting of the ground state and the first excited state of ^{57}Fe characterised by $\Delta E_{m(g)}$ and $\Delta E_{m(e)}$. The substates of the excited state with $M_I = \pm \frac{3}{2}$ are then displaced to lower and those with $M_I = \pm \frac{1}{2}$ raised by the electric quadrupole interaction, i.e. ϵ . The six possible transitions with their Doppler energies required to have the observed spectrum have been listed in Table 10.9.

Table 10.9 Six possible transitions and their Doppler energies.

Transition (Number)	ΔM_I	Doppler energy E_{QM} required for resonance
$+\frac{3}{2} \rightarrow +\frac{1}{2}(1)$	-1	$\delta_{IS} - \frac{\Delta E_{m(g)}}{2} - \frac{3\Delta E_{m(e)}}{2} - \epsilon$
$+\frac{1}{2} \rightarrow +\frac{1}{2}(2)$	0	$\delta_{IS} - \frac{\Delta E_{m(g)}}{2} - \frac{\Delta E_{m(e)}}{2} + \epsilon$
$-\frac{1}{2} \rightarrow +\frac{1}{2}(3)$	+1	$\delta_{IS} - \frac{\Delta E_{m(g)}}{2} + \frac{\Delta E_{m(e)}}{2} + \epsilon$
$+\frac{1}{2} \rightarrow -\frac{1}{2}(4)$	-1	$\delta_{IS} + \frac{\Delta E_{m(g)}}{2} - \frac{\Delta E_{m(e)}}{2} + \epsilon$
$-\frac{1}{2} \rightarrow -\frac{1}{2}(5)$	0	$\delta_{IS} + \frac{\Delta E_{m(g)}}{2} + \frac{\Delta E_{m(e)}}{2} + \epsilon$
$-\frac{3}{2} \rightarrow -\frac{1}{2}(6)$	+1	$\delta_{IS} + \frac{\Delta E_{m(g)}}{2} + \frac{3\Delta E_{m(e)}}{2} - \epsilon$

These Doppler energies are the respective positions of lines in the observed spectra. Now the determination of the parameter δ_{IS} , ϵ , $\Delta E_{m(g)}$, i.e. g_g and $\Delta E_{m(e)}$, i.e. g_e is feasible in the following manner. δ_{IS} is obtained as the mean values of the positions of the lines at ν_1 , ν_2 , ν_5 and ν_6 or ν_1 , ν_3 , ν_4 and ν_6 as the sum of the energies of interactions E_{QM} for the four excited substates must be zero in the absence of any isomer shift. Further defining S_1 as the difference in E_{QM} for the lines ν_1 and ν_2 and S_2 as the difference in E_{QM} for the lines ν_5 and ν_6 we see that

$$|S_1 - S_2| = |\nu_2 - \nu_1| - |\nu_6 - \nu_5| = 4\epsilon$$

i.e. ϵ , the quadrupole interaction energy given by Eq. (10.83) is one quarter the difference in splitting of the outer pairs of the six-line spectra. $\Delta E_{m(g)}$ as shown in Fig. 10.22 is the difference in E_{QM} of the lines ν_2 and ν_4 or ν_3 and ν_5 , i.e. $\nu_4 - \nu_2$ or $\nu_5 - \nu_3$. Similarly, $\Delta_1 = \nu_3 - \nu_2$ or $\nu_5 - \nu_4$. The value of the internal magnetic field can be estimated from Eq. (10.74) provided the value of magnetic moment in the ground state (μ_g) is known. Alternatively the measured value $\Delta E_{m(g)}$, i.e. g_g for the specimen may be correlated with the corresponding $\Delta E_{m(g)}$ for Fe which has been determined from precise measurements related to $H_{\text{int}} = 330$ kOe. The values of δ_{IS} , ϵ , and internal magnetic field for naturally occurring chalcopyrite are given in Table 10.10.

Table 10.10 Isomer shift, quadrupole splitting and internal magnetic field in chalcopyrite at various temperatures.

Temperature (K)	δ_{IS} (mm/s)	ϵ (mm/s)	H_{int} (kG)
300	-0.03 ± 0.02	0.05 ± 0.02	325 ± 10
373	-0.03 ± 0.03	0.05 ± 0.03	312 ± 10
448	-0.04 ± 0.02	0.04 ± 0.02	290 ± 10

10.10.1 Effect of Pressure on Quadrupole Splitting

The behaviour of quadrupole splitting with pressure in ^{57}Fe in CoCl_2 (rhombohedral structure) and ^{57}Fe in hcp cobalt is shown in Figs 10.23 (a) and (b) respectively. Theoretically, quadrupole splitting varies as $1/R_{I-L}^3$ where R_{I-L} is the ion-ligand distance. The shape of curves in Fig. 10.23 follows the theoretical behaviour. This is expected because as the pressure grows, the ion-ligand distance decreases.

10.10.2 Effect of Temperature on Quadrupole Splitting

The effect of temperature on quadrupole splitting depends on the nature of the compound. Quadrupole splitting in several ferrous compounds, e.g. FeF_2 , FeSO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ grows very slowly and then also decreases very slowly in the temperature range 0–350 K. The dependence of quadrupole splitting on temperature is usually small for Fe^{3+} ions since EFG arises only from lattice contributions. The temperature dependence of quadrupole splitting (in the temperature range 0–400 K) for both Fe^{3+} sites for three compositions of the $(\text{Mn}_{1-x}\text{Fe})_2\text{O}_3$ where $x = 0.028, 0.060$ and 0.082 , system indicates little temperature dependence in the high-temperature region (>250 K, for $x = 0.028$, >150 K for $x = 0.060$), as expected for Fe^{3+} containing materials. However, for the specimens with $x = 0.028$ and 0.060 , the variation of ΔE_Q with temperature increases markedly below specific temperatures (i.e. below 250 K for $x = 0.028$ and <150 K for $x = 0.060$). The inflexion at 250 K for $x = 0.028$ and 150 K for $x = 0.060$ suggests the phase transition from

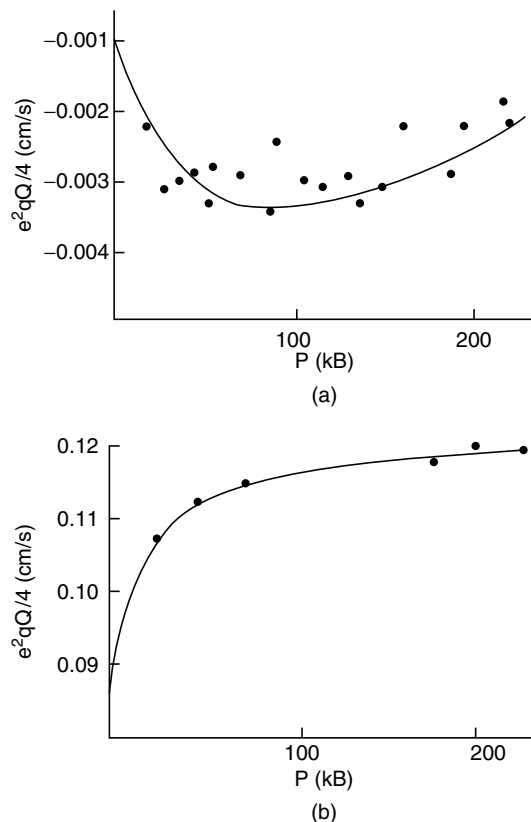


Fig. 10.23 (a) Quadrupole splitting of ^{57}Fe in CoCl_2 as a function of pressure (b) Quadrupole splitting of ^{57}Fe in hcp cobalt as a function of pressure.

Table 10.11 Effect of temperature on various configurations of iron.

Configuration	Symmetry	$(\Delta E_Q)_0$	Temperature dependence
Fe^{2+} (high spin)	$\left. \begin{matrix} O_h \\ T_d \end{matrix} \right\}$	large	yes
Fe(II) (low spin)	$\left. \begin{matrix} O_h \\ T_d \end{matrix} \right\}$	large	$\left. \begin{matrix} \text{no} \\ \text{yes} \end{matrix} \right\}$
Fe^{3+} (high spin)	$\left. \begin{matrix} O_h \\ T_d \end{matrix} \right\}$	small	no
Fe(III) (low spin)	$\left. \begin{matrix} O_h \\ T_d \end{matrix} \right\}$	Intermediate	yes

cubic to orthorhombic. Samples with $x = 0.082$ remain cubic to below 55 K. It should be borne in mind that not all paramagnetic configurations of iron exhibit a temperature-dependent quadrupole splitting as evident from Table 10.11.

However, in the second- and third-row transition metals, the spin-orbit coupling is much larger because of which an almost temperature independent or much reduced quadrupole splitting below 300 K is observed.

For tetrahedral environment, the relation between ΔE_Q and temperature is given by

$$\Delta E_Q = (\Delta E_Q)_0 \frac{1 - e^{-\Delta_1/\kappa T}}{1 + e^{-\Delta_1/\kappa T}} \quad (10.85)$$

where $(\Delta E_Q)_0$ is the value of quadrupole splitting at absolute zero, i.e. $(\Delta E_Q)_{T \rightarrow 0} = (\Delta E_Q)_0$. Δ_1 is the energy difference between two d_γ lines. At high temperature $\Delta E_Q \rightarrow 0$, i.e. two d_γ levels have equal electron population when $\kappa T \gg \Delta_1$.

10.11 SIGN OF QUADRUPOLE INTERACTION

The determination of sign of quadrupole constant and hence U_{zz} is important because it plays an important role in studies of electronic and molecular structure of compounds containing MB nuclides, e.g. since for ^{57}Fe , $Q = +0.18$ barn, a positive value of e^2qQ suggests that $U_{zz} > 0$. The MB effect makes it possible to determine the sign of quadrupole interaction. A number of methods are reported in the literature but only the three are being described here.

The sign of quadrupole coupling constant can be determined in a single crystal by studying the angular variation of area ratios. The increase of area ratios as a function of angular variation suggests negative sign for quadrupole interaction and vice versa.

The second method due to Ruby and Flinn is based on the perturbation of quadrupole doublet by the strong external magnetic field. When a strong external magnetic field is applied, the doublet of the quadrupole spectra (in paramagnetic or diamagnetic state), split into a triplet and a doublet provided the value of η is small. For positive e^2qQ , the doublet will be on the higher energy side while on the lower energy side for negative e^2qQ . This method fails if η deviates significantly from zero. The doublet/triplet observation is then not applicable. The doublet/triplet observation in case of ferrocene and butadiene iron tricarbonyl is shown in Figs 10.24 and 10.25 respectively.

The third method to determine the sign of quadrupole interaction in case of a powdered sample is based on the simultaneous presence of magnetic dipole and electric quadrupole interaction. The structure of the hyperfine multiplet depends upon whether the EFG is parallel to the direction of the hyperfine magnetic field, i.e. direction of propagation of γ -ray beam or perpendicular to it. Thus from the splitting pattern, it is possible to determine the magnitude as well as the sign of quadrupole interaction. When splitting is reduced on the application of external magnetic field parallel to the direction of the internal magnetic field, the sign of quadrupole splitting will be negative. The sign of quadrupole interaction is also obtained by comparing the splitting pattern of hyperfine multiplet of unknown absorber with the hyperfine structure of a system with known sign of quadrupole interaction.

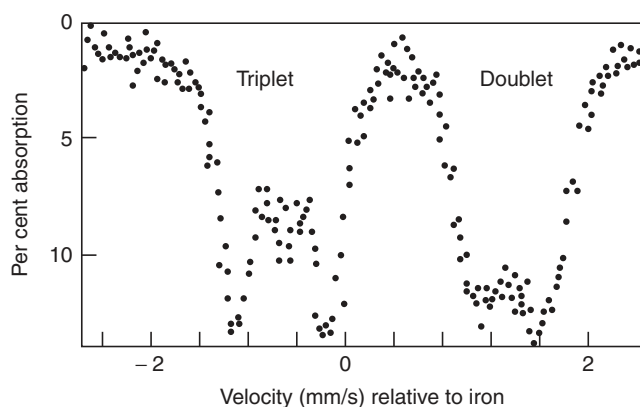


Fig. 10.24 Mössbauer absorption spectrum of ferrocene at 4.2 K and 40 kOe. U_{zz} is positive here.

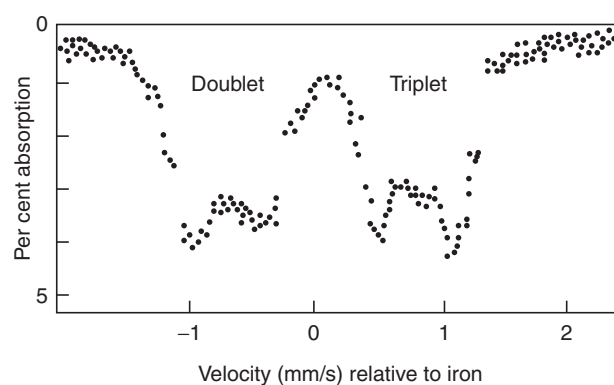


Fig. 10.25 Mössbauer absorption spectrum of butadiene iron tricarbonyl at 4.2 K and 26 kOe. U_{zz} is negative here.

10.12 GOLDANSKII-KARYAGIN (G-K) > (G-K) EFFECT (LATTICE VIBRATION ANISOTROPY)

The phenomenon of induction of angular independent asymmetry in the intensity of the magnetic and/ or quadrupole hyperfine pattern by anisotropic lattice vibrations of the crystallite or anisotropic recoil free fraction of γ -ray is called Goldanskii-Karyagin effect.

At high temperature, the mean-square displacement $\langle x_i^2 \rangle$ of the atom in the lattice is linearly proportional to temperature. Therefore, the straight line plot of $\langle x^2 \rangle$ against temperature should pass through the origin. Such a behaviour has been observed in hydrated sodium hexacyanoferrate (II). However, in case of potassium hexacyanoferrate (II), the line intercepts the vertical axis. This suggests the presence of anisotropy in the lattice vibrations. Large mean-square displacements have been observed even at low temperatures, e.g. low temperature anharmonicity has been observed in FeCl_2 ; potassium hexacyano ferrate(II) becomes ferroelectric below 251 K because of which frequencies of some of the optical modes of the lattice vibrations change.

Now, if we define three principle components of $\langle x_i^2 \rangle$ in the coordinate system X, Y, Z such that 'i' is defined by the polar angles θ and ϕ , then

$$\langle x_i^2 \rangle = [\langle x_x^2 \rangle \cos^2 \phi + \langle x_y^2 \rangle \sin^2 \phi] \sin^2 \theta + \langle x_z^2 \rangle \cos^2 \theta \quad (10.86a)$$

In case of axial symmetry,

$$\langle x_x^2 \rangle = \langle x_y^2 \rangle \text{ and } \phi = 0; \text{ Thus Eq. (10.85) becomes}$$

$$\langle x_i^2 \rangle = \langle x_x^2 \rangle \sin^2 \theta + \langle x_z^2 \rangle \cos^2 \theta \quad (10.86b)$$

It is the convention to write

$$\langle x_z^2 \rangle \text{ as } \langle x_{\parallel}^2 \rangle \text{ and}$$

$$\langle x_x^2 \rangle \text{ as } \langle x_{\perp}^2 \rangle, \text{ so Eq. (10.86b) is written as}$$

$$\langle x_i^2 \rangle = [\langle x_{\parallel}^2 \rangle - \langle x_{\perp}^2 \rangle] \cos^2 \theta + \langle x_{\perp}^2 \rangle \quad (10.87)$$

We already know that the recoilless fraction of γ -rays is related to $\langle x^2 \rangle$ by the expression (10.21), i.e.

$$f = \exp \left[\frac{-E_{\gamma}^2 \langle x^2 \rangle}{(hc/2\pi)^2} \right] \quad (\text{Eq. 10.21})$$

Here, $\langle x^2 \rangle$ is assumed to be an isotropic function which of course is not always true. The isotropic concept is valid when absorber is a random microcrystalline sample with single MB resonance line and an average value

of $\langle x^2 \rangle$ can be defined. However, the vibrations of an atom at the lattice site of noncubic symmetry are in general anharmonic. This anharmonicity of lattice vibrations induces anisotropy in the recoilless fraction of γ -rays and has been observed in single crystal samples, e.g. anisotropic recoilless emission has been noticed in experiments using ^{57}Co source doped in a single crystal of zinc metal. The crystal is cut at an angle of 45° to the c -axis. At room temperature, the values of $f_{\perp} = 0.64$ and $f_{\parallel} = 0.41$ reflect large anisotropy in vibrations of Co impurity atom. In view of it, the expression (10.21) should be written as,

$$f(\theta) = \exp \left[\frac{-\langle x_{\perp}^2 \rangle}{(hc/2\pi E_{\gamma})^2} \right] \exp \left[\frac{-x_{\parallel}^2 + \langle x_{\perp}^2 \rangle}{(hc/2\pi E_{\gamma})^2} \cos^2 \theta \right]$$

or

$$f(\theta) = \exp \left\{ \left[\frac{-\langle x_{\perp}^2 \rangle}{(hc/2\pi E_{\gamma})^2} \right] - \left[\frac{\langle x_{\parallel}^2 \rangle - \langle x_{\perp}^2 \rangle}{(hc/2\pi E_{\gamma})^2} \right] \cos^2 \theta \right\} \quad (10.88)$$

Let us now see how the anisotropic recoilless fraction of γ -rays influences the intensity of the hyperfine quadrupole doublet corresponding to $3/2 - 1/2$ transition. The intensity $I_{3/2}/I_{1/2}$ of the lines involving $\pm 3/2 >$ and $\pm 1/2 >$ levels of the excited state depends upon the angle θ between the direction of propagation of γ -ray and principal Z-axis of the EFG and is expressed as,

$$\frac{I_{3/2}(\theta)}{I_{1/2}(\theta)} = \frac{1 + \cos^2 \theta}{\frac{2}{3} + \sin^2 \theta} \quad (10.89)$$

For a random polycrystalline samples the averaged value of intensity ratio is obtained by integrating over all the orientations, i.e.

$$\frac{I_{3/2}(\theta)}{I_{1/2}(\theta)} = \frac{\int_0^{\pi} (1 + \cos^2 \theta) \sin \theta d\theta}{\int_0^{\pi} \left(\frac{2}{3} + \sin^2 \theta \right) \sin \theta d\theta} = 1 \quad (10.90)$$

These formulae hold good only for axial symmetry and become more complex for non-axial field gradient because of state mixing. The above argument is valid provided the probability for recoilless event (emission or absorption) is equal in all directions. However if the recoilless radiation is anisotropic, the recoil free fraction ' f ' for a thin absorber is a function of θ , then Eq. (10.90) modifies to,

$$\frac{I_{3/2}}{I_{1/2}} = \frac{\int_0^{\pi} (1 + \cos^2 \theta) f(\theta) \sin \theta d\theta}{\int_0^{\pi} \left(\frac{2}{3} + \sin^2 \theta \right) f(\theta) \sin \theta d\theta} \neq 1 \quad (10.91)$$

Thus, an anisotropic recoilless fraction of γ -rays generates an angular independent asymmetry in the $\frac{3}{2} - \frac{1}{2}$ quadrupole doublet. This is termed as the Goldanskii-Karyagin effect and in case of a iron silicate glass is shown in Fig. 10.26, e.g. the value of $I_{3/2}/I_{1/2}$ determined from the hyperfine quadrupole split spectrum of Me_2SnF_2 at room temperature has been found to be 0.78. The root mean square amplitudes of vibration of tin deduced from x-ray come out to be 13.7 pm along the Sn-F bonds and 2.10 along the Sn-C bonds. By making use of Eq. (10.91) and the known values for $\langle x_{\perp}^2 \rangle$ and $\langle x_{\parallel}^2 \rangle$, given above, the intensity ratio comes out to be 0.72 which is in agreement with the experimental value, i.e. 0.78.

It is pertinent to note that the main features of asymmetry, because of vibrational anisotropy in polycrystalline materials are identical to the effects of partial orientation of crystallites, molecules or spins (texture). Texture has a sensitive effect on the relative line intensities of a quadrupole hyperfine pattern. It is difficult to differentiate experimentally between G-K and texture effects. So, it is to be checked whether the possibility of orientation has been eliminated by checking for the angular dependence of spectra. The safest method of preparing unoriented absorbers is by grinding the sample with large bulk of an abrasive powder such as Al_2O_3 or quartz glass.

The principle of G-K effect is also applicable to magnetic hyperfine spectra and to isotopes with higher spin states and in all cases deviation from the predicted line intensities have been noticed.

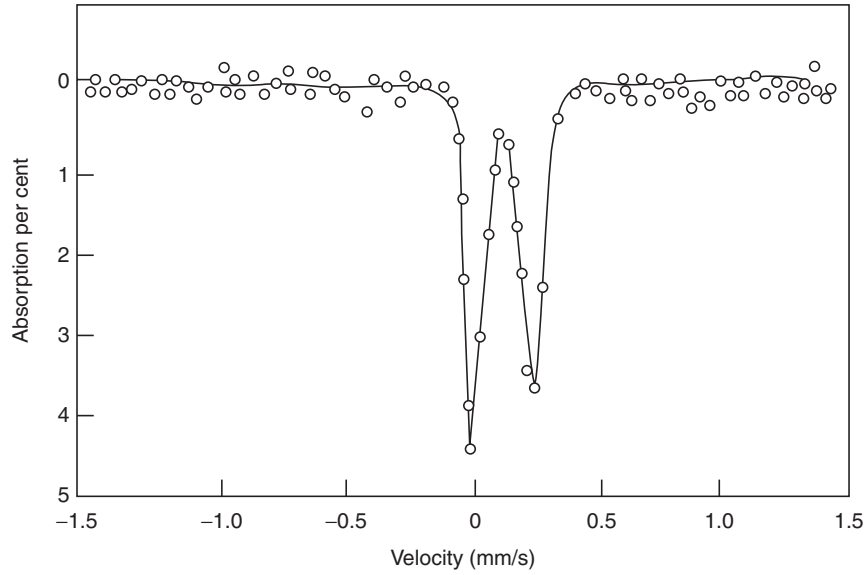


Fig. 10.26 Goldanskii-Karyagin effect in the Mössbauer spectrum of an iron silicate glass.

In case of magnetic hyperfine interactions, the intensities of the $\Delta M_I = 0$ lines (I_2, I_5) and the inner $\Delta M_I = \pm 1$ lines (I_3, I_4) are defined by the ratio,

$$\frac{I_{2,5}}{I_{3,4}} = \frac{\sin^2 \theta}{\frac{1}{4}(1 + \cos^2 \theta)}$$

So

$$\frac{I_{2,5}}{I_{3,4}} = \frac{\int_0^\pi \sin^2 \theta f(\theta) \sin \theta d\theta}{\int_0^\pi \frac{1}{4}(1 + \cos^2 \theta) f(\theta) \sin \theta d\theta} \quad (10.92)$$

The G-K effect may be employed to deduce the sign of U_{zz} in both ^{57}Fe and ^{119}mSn spectra.

The dependence of intensity ratio upon $(\langle x_{\parallel}^2 \rangle - \langle x_{\perp}^2 \rangle)$ may be employed to identify the lines (i.e. π and σ components), thus the sign of U_{zz} can be determined if the sign of $(\langle x_{\parallel}^2 \rangle - \langle x_{\perp}^2 \rangle)$ is known. Conversely, the sign of vibrational anisotropy factor can be determined, if sign of U_{zz} is known. In Fe and Sn, the $M_I = \pm 3/2$ line is the more intense for negative values of the anisotropy parameter $(\langle x_{\parallel}^2 \rangle - \langle x_{\perp}^2 \rangle)$ and is less intense for positive values. $\langle x_{\parallel}^2 \rangle = 1.76 \times 10^{-18} \text{ cm}^2$ and $\langle x_{\perp}^2 \rangle = 0.48 \times 10^{-18} \text{ cm}^2$.

10.13 PARTIAL QUADRUPOLE SPLITTING (PQS)

Similar to partial centre shifts (p.c.s.); quadrupole splitting is also an additive property. The resultant quadrupole splitting could be expressed as an algebraic sum of partial quadrupole splitting. For any low-spin iron (II) compound of the type FeA_2B_4 or FeAB_5 , ΔE_Q can be expressed as

$$\Delta E_Q (\text{trans}) = +4 (p.q.s.)_A - 4(p.q.s.)_B \quad (10.93)$$

$$\Delta E_Q (\text{cis}) = -2(p.q.s.)_A + 2(p.q.s.)_B \quad (10.94)$$

$$\Delta E_Q (\text{FeAB}_5) = +2(p.q.s.)_A - 2(p.q.s.)_B \quad (10.95)$$

The partial quadrupole splitting for various ligands are listed in Table 10.12.

Table 10.12 Tentative partial quadrupole splitting values (mm/s) for some ligands.

Br ⁻	-0.32	depb	-0.02
I ⁻	-0.31	depe	+0.02
Cl ⁻	-0.30	dmpe/2	+0.07
N ₃ ⁻	-0.22	RNC	+0.09
SnCl ₃ ⁻	-0.17	CO	+0.16
NCO ⁻	-0.10	SiH ₃ ⁻	+0.40
NCS ⁻	-0.11	H ⁻	+0.44
CN ⁻	-0.06	NO ⁺	+0.91

Problem 10.4: Using the data on p.q.s. in Table 10.12, calculate the quadrupole splitting for (a) $\text{cis-}[\text{FeCl}_2(\text{ArNC})_4]$ (b) $\text{trans-}[\text{FeCl}_2 \text{ Ar}(\text{NC})_4]$ (c) $\text{cis-}[\text{Fe}(\text{CN})_2(\text{CNEt})_4]$, (d) $\text{trans-}[\text{Fe}(\text{CN})_2 (\text{CNEt})_4]$ and (e) $[\text{FeCl}(\text{ArNC})_5] (\text{ClO}_4)$.

Solution (a) $\text{cis-}[\text{FeCl}_2(\text{ArNC})_4]$ is of the type FeA_2B_4 . So by Eq. (10.94)

$$\begin{aligned}\Delta E_Q(\text{cis}) &= -2(\text{p.q.s.})_{\text{Cl}} + 2(\text{p.q.s.})_{\text{ArNC}} \\ &= -2(-0.30) + 2(0.09) \\ &= 0.60 + 0.18 = 0.78 \text{ mm/s} \quad (\text{obs: } -0.78 \text{ mm/s})\end{aligned}$$

(b) For $\text{trans-}[\text{FeCl}_2 \text{ Ar}(\text{NC})_4]$;

$$\Delta E_Q(\text{trans}) = 4(-0.30) - 4(0.09) = -1.20 - 0.36 = -1.56 \text{ mm/s} \quad (\text{obs: } +1.55 \text{ mm/s})$$

(c) For $\text{cis-}[\text{Fe}(\text{CN})_2(\text{CNEt})_4]$;

$$\Delta E_Q = -2(-0.06) + 2(0.09) = 0.12 + 0.18 = 0.30 \text{ mm/s} \quad (\text{obs: } +0.29 \text{ mm/s})$$

(d) For $\text{trans-}[\text{Fe}(\text{CN})_2 (\text{CNEt})_4]$;

$$\Delta E_Q = 4(-0.06) - 4(0.091) = -0.24 - 0.36 = -0.60 \text{ mm/s} \quad (\text{obs: } -0.60 \text{ mm/s})$$

(e) For $[\text{FeCl}(\text{ArNC})_5] (\text{ClO}_4)$

$$\Delta E_Q = 2(-0.30) - 2(0.09) = -0.60 - 0.18 = 0.78 \text{ mm/s} \quad (\text{obs. } +0.70 \text{ mm/s})$$

10.14 MÖSSBAUER SPECTROMETER

Basically, there are four elements of MB-spectrometer (i) Mössbauer drive to provide controlled and well-defined relative velocity to source or absorber for Doppler tuning, (ii) Mössbauer source, (iii) Mössbauer absorber (or scatterer), and (iv) a suitable counting assembly for detecting the transmitted or scattered γ -beam intensity. The elements and their functions are shown in Fig. 10.27.

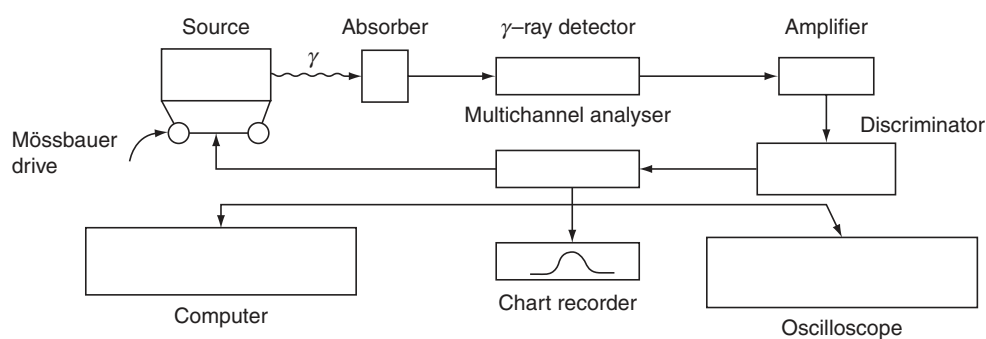


Fig. 10.27 A block diagram of a Mössbauer spectrometer.

Several additional auxiliary systems (e.g. cryostat, furnace, arrangement for pressure variation, etc.) may be necessary to perform a particular experiment.

(a) Mössbauer Drive Systems The desired velocity to the source is imparted by the system called the MB drive. It is of two types.

(i) Constant Velocity Drive In the constant velocity mode either the source or target is moved with a controlled constant velocity for the pre-set time during which the transmitted γ -ray counts are recorded. With this drive system, we record the whole spectrum point by point. One can select a particular velocity of interest for specific investigations, e.g. measuring the resonance signal as a function of temperature (thermal scan). A change in count rate might indicate (Curie, Neel and Morin temperatures phase transitions, etc.) which can be determined with high accuracy by this method. The limitation of this drive system is that the range of velocities covered is of about 10 or 20 mm/s. This limitation makes these drives useful only for ^{57}Fe and ^{119}Sn isotopes.

(ii) Constant Acceleration Drive In the constant acceleration mode, the velocity of the source is changed continuously from $-v$ to $+v$ in one cycle. The main advantage of this method over constant velocity method is that in this method the count rate for each velocity over the entire range is made in each and every cycle so that drifts in the count rate do not affect the observed spectrum and very small MB effects can be measured. Moreover velocities up to 1000 mm/s can be attained by this method. This method is disadvantageous to constant velocity method because the velocity measurements in this method are not direct, one has to calibrate the drives often.

(b) Mössbauer Source and Mössbauer Isotopes The Mössbauer source is a system which emits a fraction of recoil-free γ -rays. There is no unique method for the preparation of good source. However, a good source should have long life, a narrow line width, high Lamb MB factor, etc.

Generally, MB source is a solid matrix called 'host matrix' containing the excited nuclei of a suitable isotope. The selection of a suitable host matrix is very important from experimental point of view. For the sources, mostly high melting metallic matrices with high coordination symmetry are chosen in which the parent isotopes are diffused, implanted, Coulomb excited, or produced by nuclear reaction. The metals have a number of advantages over other materials, viz., nonmagnetic cubic metals (*bcc/fcc*) with low impurity concentration produce single-line emission spectra, i.e. complexity in the spectra due to hyperfine splitting does not occur, the Lamb MB factor is relatively high for most metals and the electronic relaxation process are extremely fast as compared to the lifetime of the excited state of the MB nuclei. High-melting refractory oxides of cubic structure are also very popular host matrices. e.g. host for $^{119\text{m}}\text{Sn}$ is the oxide BaSnO_3 .

Although these days, MB sources are commercially available, the two alternate methods used to populate the 14.4 keV MB transition in ^{57}Fe are illustrated by Figs 10.28 and 10.29. In the first method, ^{57}Co with half life of 270 days is prepared by the (*d, p*) reaction on ^{57}Fe . The carrier free ^{57}Co isotope is plated on a base; such metals like Pt, Pd, Cu, Cr, Rh, etc., and alloys like some of the stainless steels. The plated isotope is then diffused into the base metal by heating at $\sim 700^\circ\text{C}$ in an inert atmosphere or better, 'in a reducing atmosphere of hydrogen. Certain stainless steels, give a single line, but these are broader than the Heisenberg width due to self-resonant absorption. ^{57}Co : Cr and ^{57}Co : Pd sources have been found to be the best. These source matrices are not self-resonant and yield high recoilless fraction of γ -rays with no significant line broadening of the natural width. The Lamb MB factor for ^{57}Co :Cr source is 0.81 at room temperature and MB effect can be studied with this source up to very high temperatures. In the second

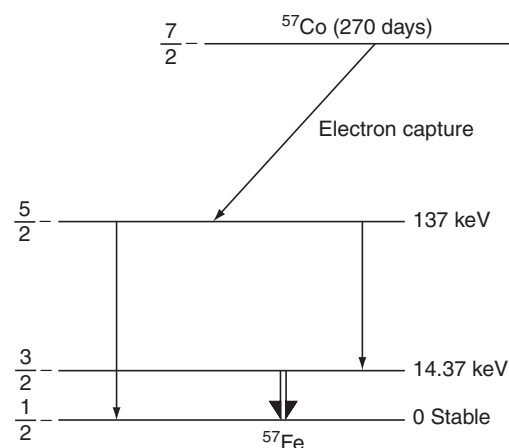


Fig. 10.28 Decay scheme of ^{57}Co leading to 14.37 keV γ -ray photons from ^{57}Fe .

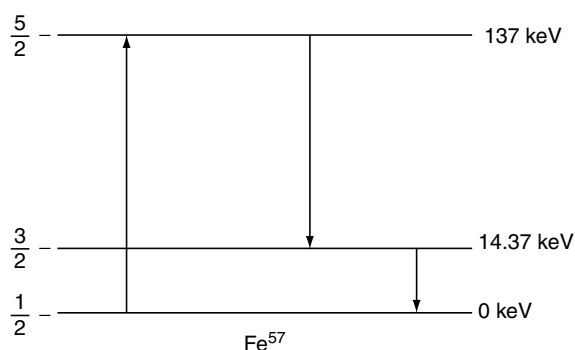


Fig. 10.29 Decay scheme of ^{57}Fe leading to 14.37 keV Mössbauer transition of ^{57}Fe .

method, EC is produced by the 1.5 μA beam from 3 MeV α -particle Vande Graaff accelerator. The target and absorber are 1.9 mg/cm^2 of 91 per cent enriched ^{57}Fe . The recoilless emission is observed following Coulomb excitation of the 137 keV level. The 14.4 keV is detected in coincidence with the 122 keV γ -ray in order to reduce the background of x-ray and bremsstrahlung. It may be pointed out that in the (d, p) (n, γ) , etc., reactions produced sources there is radiation damage, which results into a recoil-free fraction ' f '. The variety of host matrices, mostly of metallic form are not without limitations. Pt which is chemically inert and gives large room temperature recoilless fraction, ' f ', is not well suited because of large photoelectric and Compton scattering due to its high atomic number, as the latter will make the diffusion requirements for such a source extremely stringent. On the other hand, Cu matrices, while having large recoil-free fraction at room temperature and low atomic number, are chemically unstable, since unprotected sources tend to react with atmospheric oxygen and sulphides which may be present in the ambient environment. Pd though is a reasonable compromise between the various characteristics, which in addition also gives a narrow line has also one disadvantage of having an x-ray of 21 keV falling near the 14.4 keV MB γ -ray level, which may increase nonresonant background (in case of scintillation detector). A very good 23.8 keV γ -ray source (^{119}Sn) is made using Mg_2Sn or KSnO_3 lattices. The Mg_2Sn sources have to be sealed or kept in dry atmosphere, otherwise they will decompose. The line width of these sources is 12 times the natural line width and the Lamb MB factor is also very high. The other sources of ^{119}Sn are Pd-Sn; Ag-Sn.

The decay scheme of some typical MB nuclei, viz., ^{57}Fe leading to 14.40 keV, ^{193}Ir leading to 73.00, 138.9 keV, ^{129}I leading to 27.8 keV, ^{127}I leading to 57.6 eV and ^{119}Sn leading to 23.9 keV MB transitions are shown in Figs. 10.30–10.34 respectively. Inspection of the decay schemes indicates that the radiations emitted from the source are complex, and mostly consist of (i) recoil-free resonant γ -rays from the same transition, (ii) nonrecoil free nonresonant γ -rays from the same transition, (iii) radiation from all other transitions, and (iv) secondary radiation produced in the matrix mainly x-ray by conversion electrons. Except the recoil-free resonant γ -rays which cause the MB effect, all the other radiations contribute to the background and produces complications especially when the energy of the background radiation is close to that of MB γ -ray, e.g. in ^{119}Sn one gets 26 keV x-rays and are filtered by Pd filter of suitable thickness.

In order that the MB resonance is observed easily, the MB isotope should qualify the following requirements: (i) The energy of γ -ray must lie between 10–150 keV preferably less than 50 keV, since the Lamb MB factor ' f ' and resonant cross-section ' σ_0 ' both decrease as E_γ grows. Consequently, isotopes higher than ^{40}K do not show

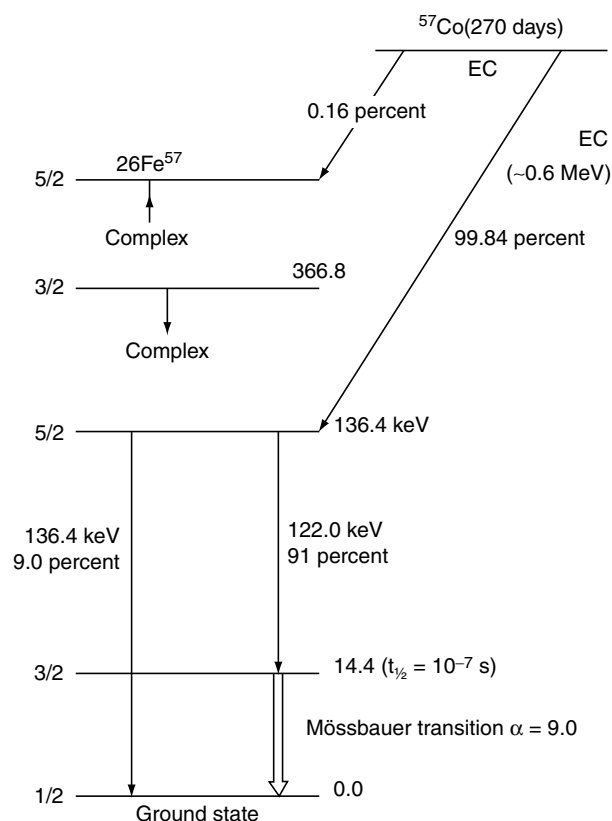


Fig. 10.30 Decay scheme of ^{57}Co showing 14.4 keV Mössbauer transition of ^{57}Fe .

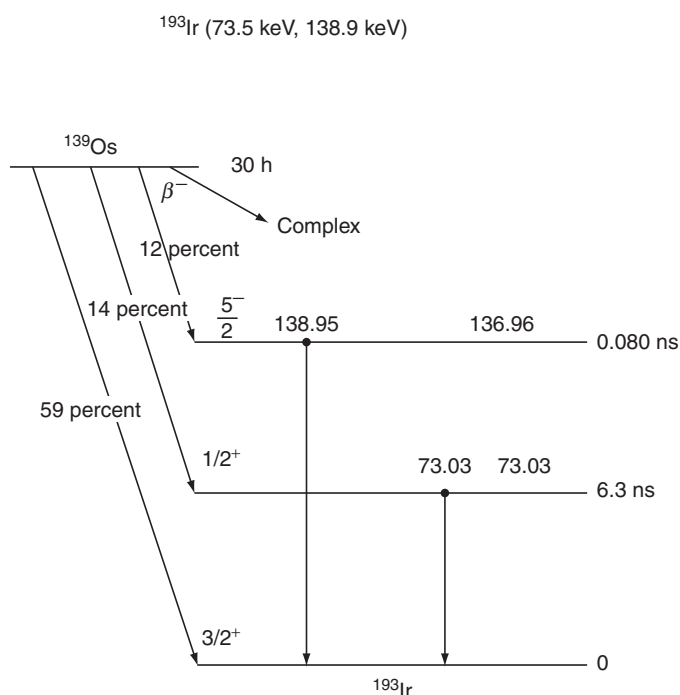


Fig. 10.31 Decay scheme of ^{139}Os leading to 73.03 and 138.95 keV Mössbauer transitions from ^{193}Ir .

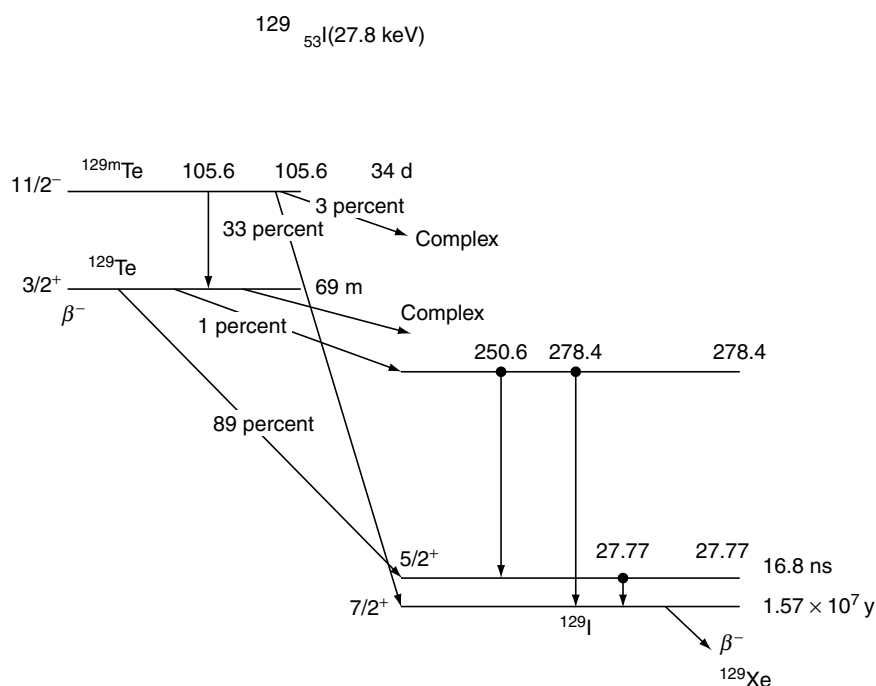


Fig. 10.32 Decay scheme of $^{129\text{m}}\text{Te}$ showing 27.8 keV Mössbauer transition from ^{129}I .

MB effect because of high energy of emitted γ -rays. (ii) The half-life of the first excited level of MB nuclei which determines the line width Γ should be between 1 and 100 ns. If $t_{1/2}$ is very long, T becomes so narrow that resonance overlapping is destroyed and for short $t_{1/2}$, Γ becomes so broad that hyperfine interactions can't be resolved and detected. (iii) The internal conversion factor α_i should be <10 , otherwise the probability of detection of γ -ray decreases. (iv) The ground-state isotope should be stable and have a high natural abundance so that isotopic enrichment may not be required. (v) The precursor (i.e. the isotope which decays by β -decay, electron capture or isomeric transitions) should have longer life, otherwise the population of the required excited level will not be maintained.

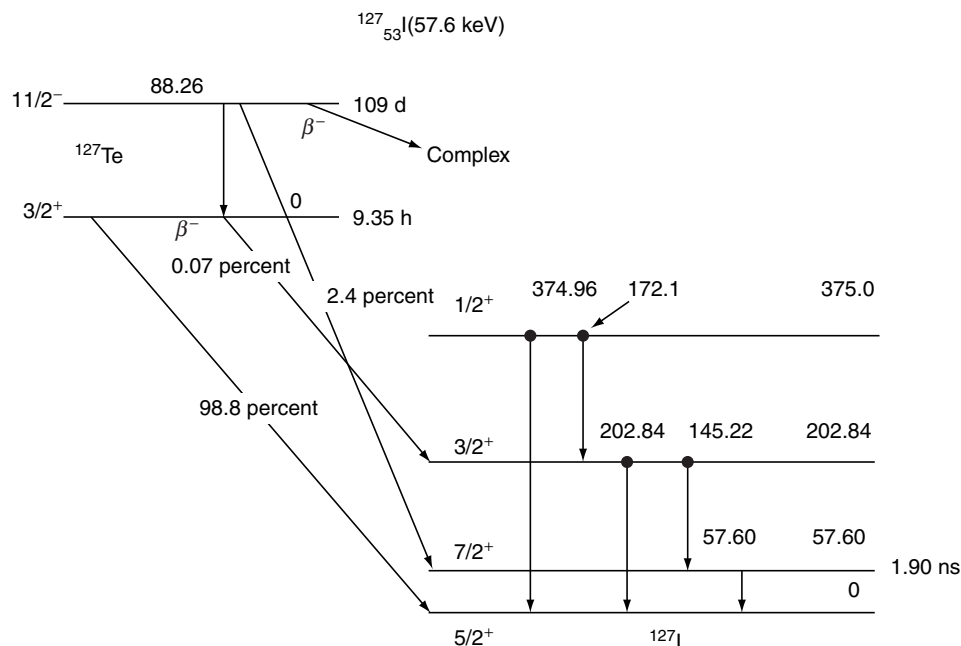


Fig. 10.33 Decay scheme of ^{127}Te leading to 57.60 keV Mössbauer transition of ^{127}I .

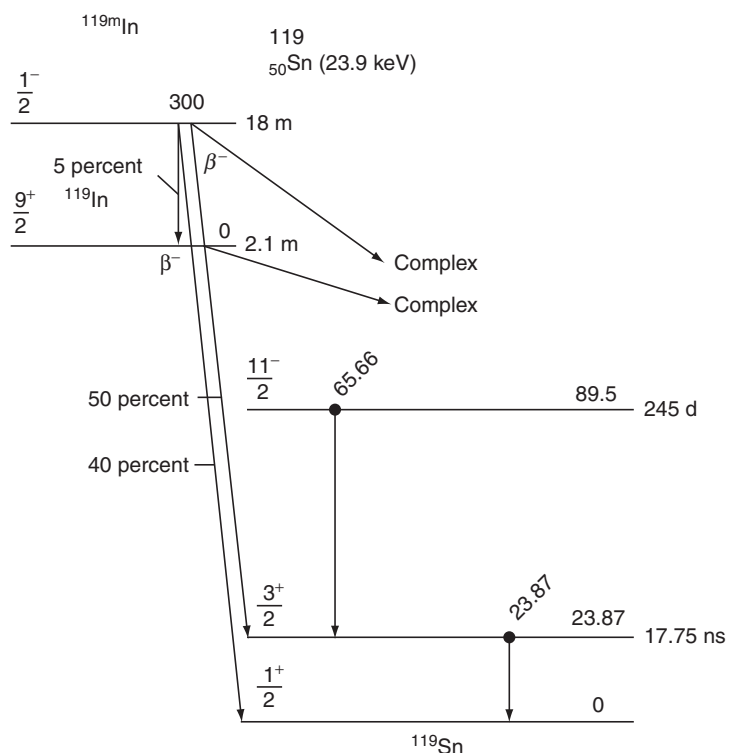
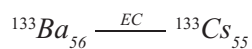
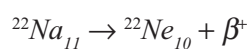


Fig. 10.34 Decay scheme of $^{119\text{m}}\text{In}$ showing 23.87 keV Mössbauer transition from ^{119}Sn .

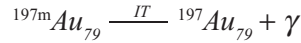
Electron capture: A nucleus emits no particles but decreases in Z by one unit by capturing an orbital electron, most frequently from the K shell; e.g.



This is an alternative process to positron (β^+) emission.



Isomeric transition: A nuclide in a metastable nuclear state passes to a nuclear state of low energy, with emission of a γ -ray; e.g.



Conversion electron: Internal photoelectric effect which takes place in the excited nuclear state of the atom gives rise to electrons called conversion electrons

In spite of these limitations, an MB effect has been observed in 100 transitions of 83 different isotopes in 44 elements. Some of the typical MB isotopes along with their characteristics parameters are listed in Table 10.2.

(c) Mössbauer Absorber (or Scatterer or Sample) Just like the source, the standard reference absorber should be stable and should not undergo any chemical or physical change that may affect the MB spectra. It should have narrow line width and large Lamb MB factor. Metallic α - ^{57}Fe foil (i.e. Fe at room temperature) and single crystal of sodium nitropruside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]2\text{H}_2\text{O}$ have been accepted as standard reference absorbers for Mössbauer nuclei ^{57}Fe .

The absorber contains the same MB isotope as the source, in its ground state. In most of the cases, the absorber is the material to be studied. It may be pointed out that the absorber mounting materials must be MB-isotope free as otherwise even in traces it may sometimes complicate the whole MB spectra.

The absorber physical thickness t_a , plays a significant role in the quantitative analysis of the spectra. The effective thickness of an absorber is defined by a dimensionless parameter,

$$T_a = f_a \sigma_0 n_a t_a a_a \quad (10.96)$$

where, f_a is the Lamb MB factor in the absorber, n_a is the number of resonant atoms/cm³ of the particular element, t_a is the physical thickness of the absorber in cm, σ_0 is the maximum absorption coefficient (cm²) and a_a is the isotopic abundance of the MB isotope.

The following relations exist between apparent width Γ_{app} and effective absorber thickness T_a .

$$\frac{\Gamma_{\text{app}}}{\Gamma_{\text{nat}}} = 2.00 + 0.27 T_a, \quad 0 \leq T_a \leq 5 \quad (10.97)$$

$$\frac{\Gamma_{\text{app}}}{\Gamma_{\text{nat}}} = 2.02 + 0.29 T_a - 0.005 T_a^2, \quad 4 \leq T_a \leq 10 \quad (10.98)$$

Γ_{nat} is the natural line width.

Further, the absorption is defined as

$$A = \frac{(I_\infty - I_0)}{I_\infty} \quad (10.99)$$

Here, I_0 is the transmitted intensity at the resonance maximum, I_∞ is the transmitted intensity at the large Doppler velocity where the absorption is zero.

The absorption is related to the effective thickness by the expression

$$A = f_s [1 - e^{-\frac{T_a}{2}} J_0(i T_a / 2)] \quad (10.100)$$

where, f_s is the recoilless fraction of the source. $J_0(i T_a / 2)$ is the zero-order Bessel function, i.e.

$$J_0(x) = 1 + \left(\frac{x}{2}\right)^2 + \frac{\left(\frac{x}{2}\right)^4}{1^2 \cdot 2^2} + \frac{\left(\frac{x}{2}\right)^6}{1^2 \cdot 2^2 \cdot 3^2} + \dots$$

The plot between A/f_s and T_a shown in Fig. 10.35 reveals that the absorption shows a saturation with thickness. Therefore, an appropriate value of thickness should be used to obtain adequate absorption. If $T_a \ll 1$, the intensities of resonance lines are small. The line can be approximated to Lorentzian curves. If $T_a \gg 1$, the

shape of the absorption curve is nearly of Lorentzian type but with a broadened width 2Γ , given by

$$\frac{2\Gamma}{\Gamma_{\text{nat}}} = 2 + 0.27 T_a \quad (10.101)$$

provided $T_a < 5$.

(d) γ -ray Detectors Sodium iodide, NaI (Tl), scintillation counters, proportional counters and lithium-drifted germanium and silicon detectors may be used for registration of γ -rays. Photographic emulsion can also be used in special cases. The pulses from the detector are amplified and passed through a discriminator which filters out most of the nonresonant background radiation. The resonant radiation is then fed to a multichannel analyser which is synchronised with an MB drive. The stored data in the multichannel analyser is traced in the recorder. A γ -ray emitted along the axis of motion of the source has a Doppler shift relative to the absorber of $\frac{E_\gamma v}{c}$, but any γ -ray which travels to the detector along the path at an angle θ to the axis has an effective Doppler shift of only $E_\gamma v \cos \theta / c$. This cosine effect of solid angle causes a spread in the apparent Doppler energy of the γ -rays and hence line broadening. The cosine effect can be reduced by maintaining an adequate separation between source and absorber or by collimation of γ -ray beams. Pulse height spectra from ^{57}Co source is shown in Fig. 10.36(a-c). Inspection of Fig. 10.36 indicates that resolution depends on the type of γ -ray detector. However, the poor resolution of a detector is counter balanced by the high count rate which can be achieved. It may be pointed out that the relatively low γ -photon flux density necessitates much longer counting times to achieve significant counting statistics than for example in optical spectroscopy. The statistical behaviour of γ -emission results in a standard deviation of $\sqrt{n}$ for a number of n registered counts. Hence the standard deviation in 10,000 counts is 100(1 per cent), in 1,000,000 counts is 1000(0.1 per cent). The longer the counting time, the better the definition of resonance line, but the improvement to be gained must be balanced against the experimental time required and the long-term stability or reproducibility of the apparatus. Efficiency, resolution, count rate and price of the γ -ray detector must be considered before its selection.

10.14.1 MÖSSBAUER SPECTRUM

A Mössbauer experiment can be performed either in a transmission geometry or scattering geometry. The scattering geometry experiments have some outstanding and special advantages over the transmission geometry but require high source strength (as the scattering cross-section is less than absorption cross-section by a factor of $\frac{1}{(1 + \alpha_r)} [= \frac{\sigma_0(\text{scatt})}{\sigma_0(\text{abs})}]$) and careful attention to geometry and shielding makes this technique less attractive. To find maximum energy at which MB effect can still be observed, we consider the case where source and scatterer are at low temperatures. The Debye–Waller factor is then given by

$$f(T = 0) = \exp \left[- \frac{3E_\gamma^2}{4M_0 c^2 \kappa \theta_D} \right] \quad (10.102)$$

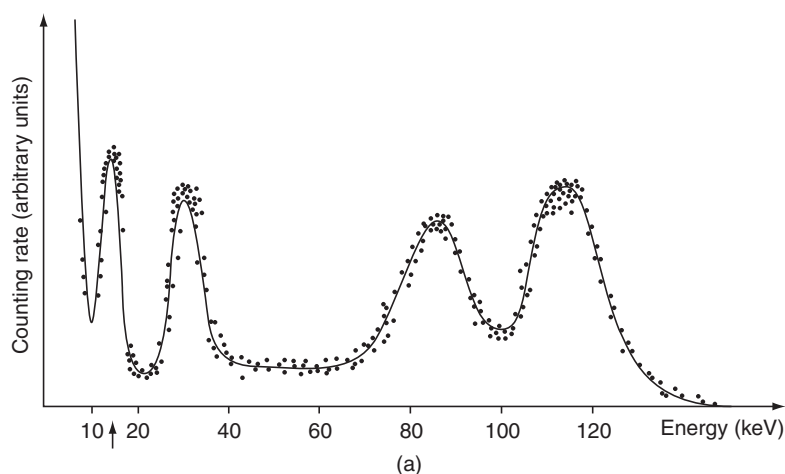
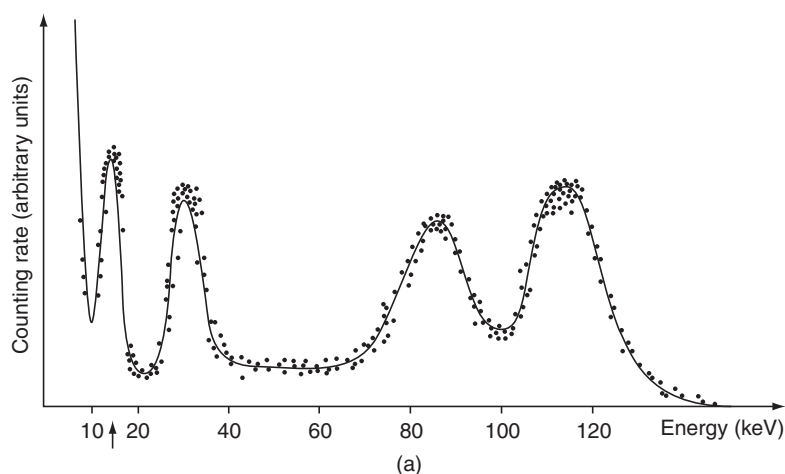


Fig. 10.35 The behaviour of absorption with effective thickness (T_a) of the absorber.



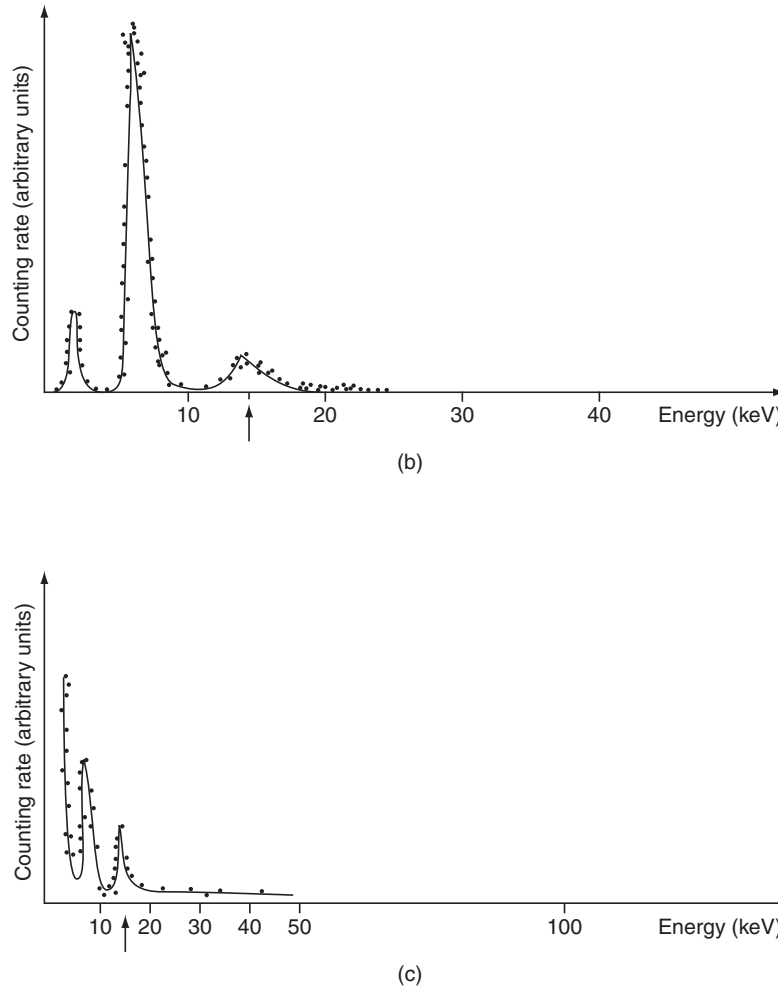


Fig. 10.36 Pulse height spectra (of ^{57}Fe from ^{57}Co source) of γ -ray detectors: (a) Proportional counter (b) NaI (Tl) scintillation counter (c) Solid state Si (Li) Detector.

Mössbauer scattering have been observed with recoil-less fractions as small as 5×10^{-3} and it seems feasible to lower the limit even further. For a given f_{crit} , a critical γ -ray energy, E_{crit} can be calculated from Eq. (10.102):

$$E_{\text{crit}} = \left[\frac{4}{3} M_0 c^2 \kappa \theta_D \ln \left(\frac{1}{f_{\text{crit}}} \right) \right]^{1/2}$$

$$\text{or} \quad E_{\text{crit}} = 0.33 \left[\text{Mass number} \times \theta_D \times \ln \left(\frac{1}{f_{\text{crit}}} \right) \right]^{1/2} \quad (10.103)$$

for $f_{\text{crit}} = 5 \times 10^{-3}$, we get for E_{crit} ,

$$E_{\text{crit}} (f = 5 \times 10^{-3}) = 0.76 [\text{Mass number} \times \theta_D]^{1/2} \quad (\text{E in keV, } \theta_D \text{ in } K) \quad (10.104)$$

In the scattering technique, the re-emission (scattering) of resonant γ -radiation in the target is detected. Further, in many Mössbauer isotopes, the γ -radiation is internally converted into an x -ray and conversion electron. In such cases, the different competing radiation (i.e. nonresonant γ -rays, x -rays, conversion electrons) accompanying the resonant γ -nuclear transitions with their characteristic penetration depth can be used for detecting the MB effect. Because of the low power of re-emitted secondary radiations, only atoms near the surface of the target ($0.1\text{--}1 \mu\text{m}$) will contribute to the observed resonance effect. For ^{57}Fe , the x -ray energy is 6.3 keV and 7.3 keV for conversion electron. The geometry for back scattering is shown in Fig. 10.37. The x -ray and conversion electron Mössbauer back scattering spectra for ^{57}Fe are shown in Figs. 10.38 and 10.39 respectively. For Fe, the internal conversion coefficient is 9, and hence the detection of the 14.4 keV radiation is insufficient. x -ray fluorescence by the 122 keV precursor increases the noise for x -ray detection. In proportional counter, with 2π back scattering geometry an argon–10 per cent methane gas is most efficient for x -ray detection [Fig. 10.40(a)], while the conversion electrons can be detected by a helium–10 per cent methane mixture without x -ray interference [10.40(b)]. MB nuclei suitable for scattering experiments are ^{57}Fe (136 keV), ^{190}Os (187 keV), ^{192}Os (206 keV), ^{139}La (163 keV), ^{101}Ru (127 keV),

^{123}Te (159 keV) and ^{175}Lu (114 keV). Scattering is particularly useful for (a) surface analysis, (b) very thick samples, and (c) small Mössbauer effects due to the sample size or low ' f ' factor. By this technique, material of nearly any shape can be investigated in the original condition, '*in situ*', e.g. painting, locomotive boilers, etc. Corroded surfaces less than 1000 Å can be studied.

In order to obtain the MB spectrum either in the transmission mode or scattering mode, the source is moved towards the target by the MB drive system. And, the number of resonant γ -rays passing through the target are counted by a γ -ray detector as a function of velocity of source, i.e. the source is moved towards the target until the velocity at which the maximum absorption/minimum transmission, i.e. dip of γ -rays occurs, is determined. It is to be noted that the transmitted γ -rays from the absorber are scattered in the 4π solid angle because of which a very small amount of these rays reaches the detector. Consequently, the number of secondary events recorded at the detector in a collimated transmission experiment is few and are usually neglected. The sign convention is that the positive velocity is defined as the motion of the source towards the target and vice versa, whereas the negative velocity is defined, as the movement of the source away from the target and vice versa.

The MB spectrum is then obtained by plotting the counts on the vertical axis as a function of Doppler velocity on the horizontal axis. A hypothetical spectrum in both the geometries is shown in Fig. 10.41, whereas shapes of some typical experimentally observed spectra are shown in Figs 10.42(a–d). It is to be noted that (i) the energy of a photon emitted by a moving source is displaced by an amount $(v/c)E_\gamma$ (Eq. 10.15). If the source is moved with a constant velocity v , the emitted photons will have an energy $= E_\gamma \left(1 + \frac{v}{c}\right)$. What does this energy shift, i.e. $E_\gamma \frac{v}{c}$ do?

Emission and absorption lines both show a Lorentzian shape with width Γ . If their centres coincide, the absorption will be maximized. If one of the lines is shifted, the overlap will be smaller, the absorption will be smaller, and the

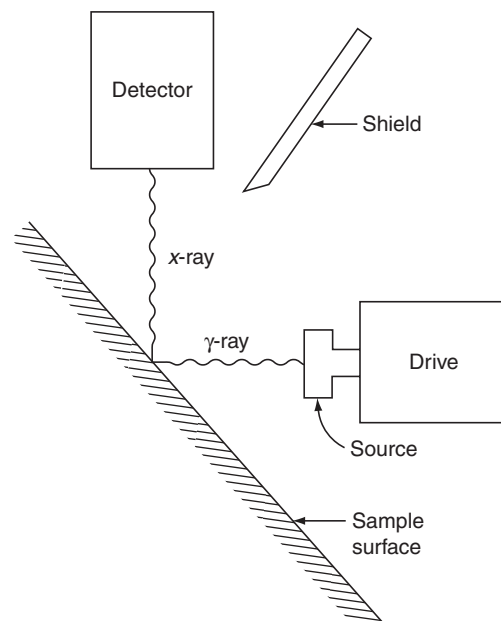


Fig. 10.37 Schematic representation of geometry for back scattering.

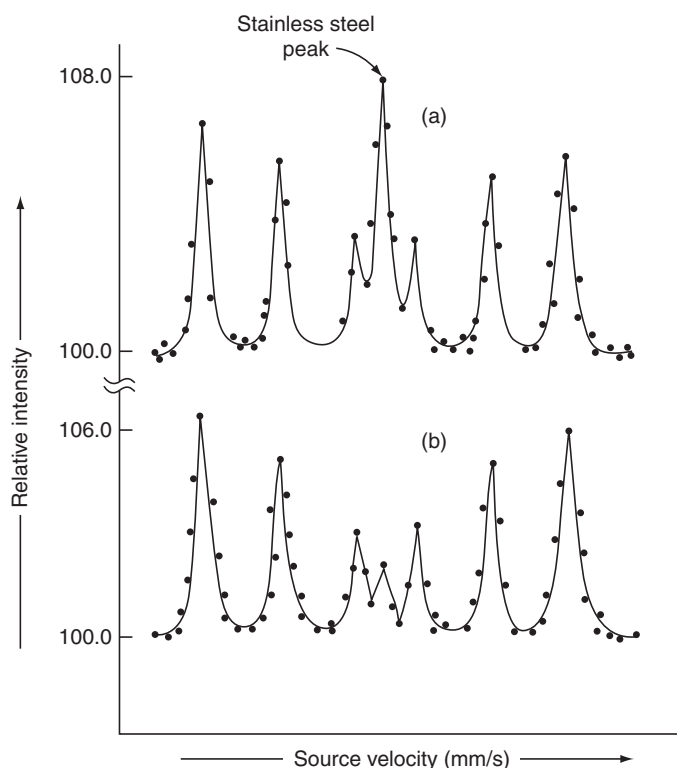


Fig. 10.38 x-ray Mössbauer back-scattering spectra for (a) 0.2 mil, and (b) 0.5 mil thick iron foils in stainless steel foil. (1 mil = 0.0254 mm).

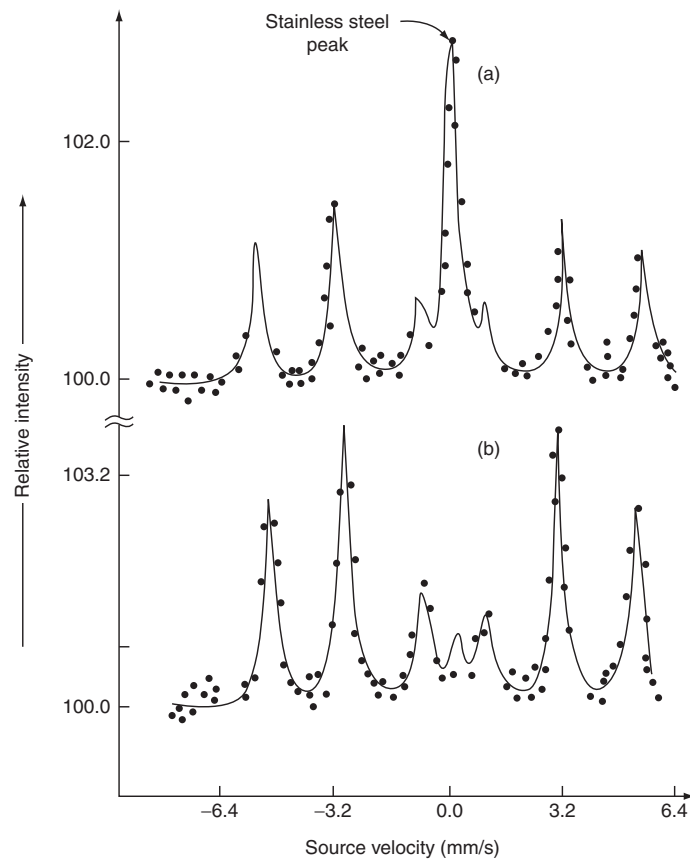


Fig. 10.39 Conversion electron Mössbauer back-scattering spectra for (a) 600 Å, and (b) 3000 Å thick vacuum-deposited iron on stainless steel.

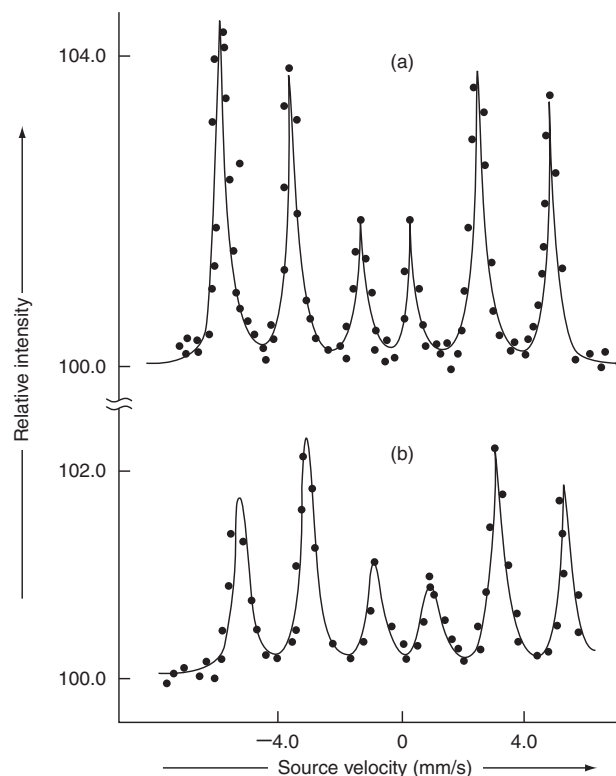


Fig. 10.40 x-ray and conversion electron Mössbauer back scattering spectra for iron foil using (a) argon—10 per cent methane, and (b) helium—10 percent methane respectively on a proportional counter with 2π back-scatter geometry.

counting rate in the detector will increase. The resulting transmission line is again a Lorentzian, but with width 2Γ . These lines are shown in Fig. 10.43. (ii) The doppler velocity needed to obtain a spectrum is in the order of the line width or of the hyperfine splitting. It is related to the Heisenberg width Γ of the emitted γ -photon by.

$$\frac{v}{c} = \frac{2\Gamma}{E_\gamma} \quad (10.105)$$

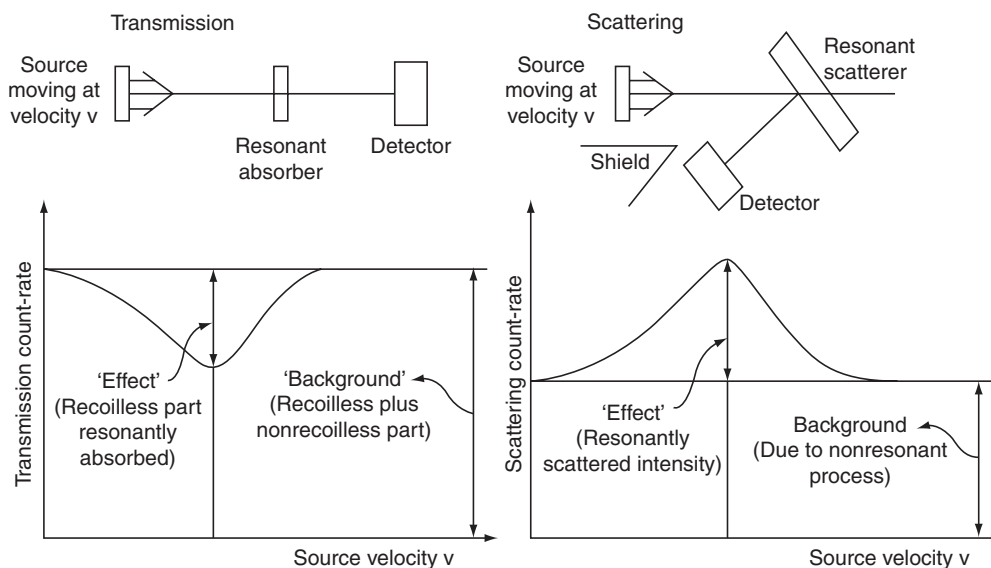


Fig. 10.41 Comparison of transmission and scattering geometries and hypothetical spectra in both the geometries.

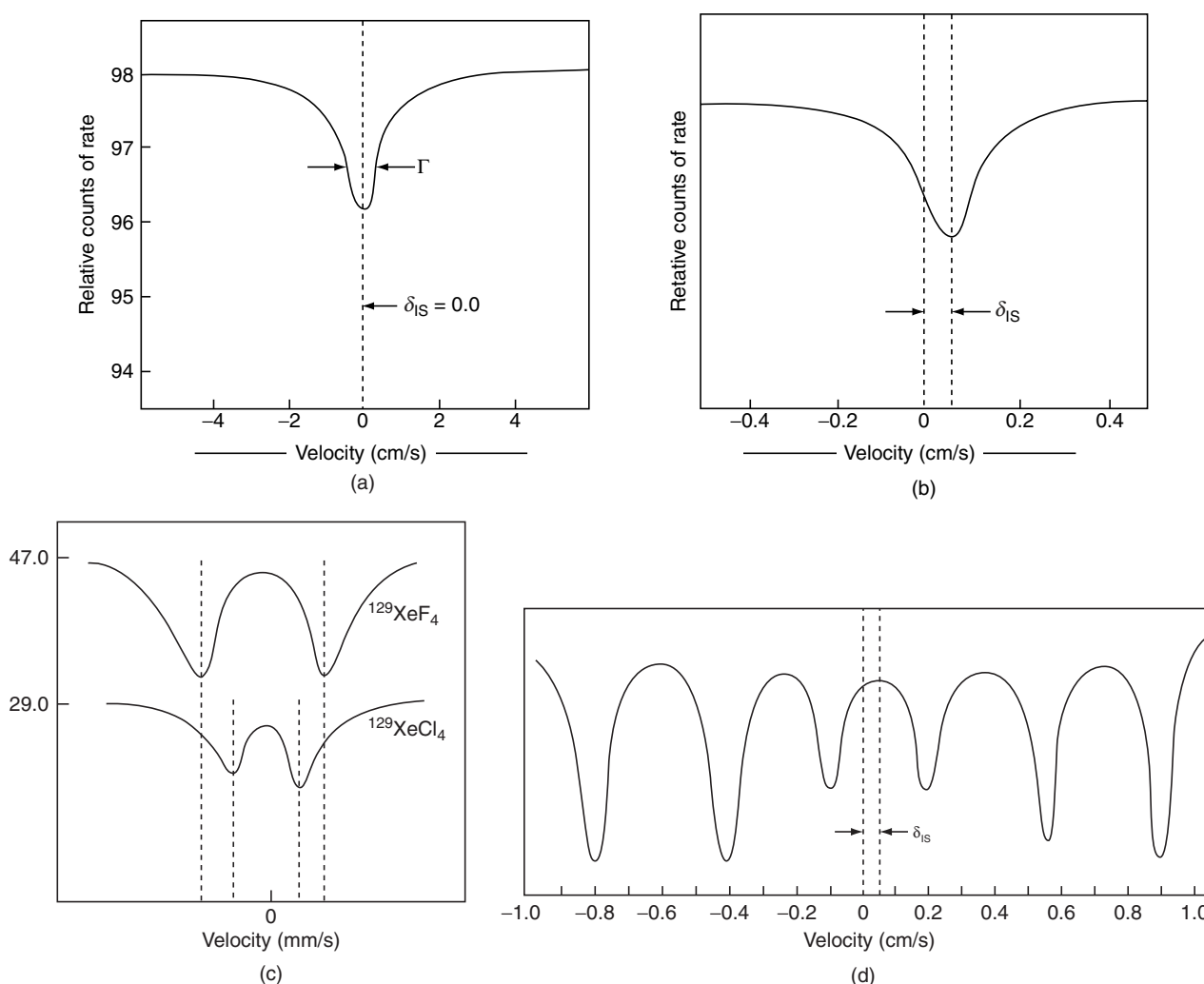


Fig. 10.42 Various shapes of Mössbauer spectrum: (a) ^{99}Ru at 85K (90 keV transition, metallic source and absorber) (b) Ferricinium bromide (c) $^{129}\text{XeF}_4$ and $^{129}\text{XeCl}_4$ (40 keV-transition) (d) ^{57}Fe (14.4 keV transition).

and (iii) the Doppler velocity given to the source relative to the target is not to compensate the recoil-energy loss but to compensate the energy difference between the MB transition states of the source and the target due to the difference in the electronic environment.

For the transitions with large recoil-less fractions, the numbers $N(R)$ and $N(NR)$ of resonantly and nonresonantly scattered γ -rays can be determined by analysing the resonantly scattered radiation by a resonant absorber rather than by a source. A typical arrangement for such a measurement and the data obtained with it are shown in

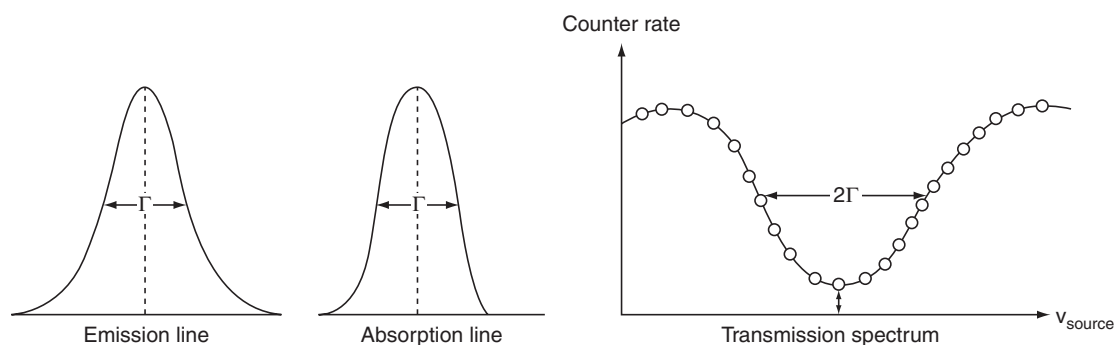


Fig. 10.43 Emission, absorption and transmission lines in a simple Mössbauer arrangement.

Fig. 10.44. With source and scatterer off resonance, the background level 'B' is measured. If the source and scatterer are on resonance, the transmission through a black absorber on and off resonance is given by

$$T(0) = B + N(NR) \quad (10.106)$$

$$T(\infty) = B + N(NR) + N(R)$$

For a thin scatterer, the MB Lamb factor for the absorber is given by

$$\frac{f_{\text{abs}}}{(1 - f_{\text{abs}})} = \frac{T(\infty) - T(0)}{T(0) - B} \quad (10.107)$$

It should be noted that an MB spectrum resembles UV, IR and NMR spectra that the intensity is plotted against energy of radiation.

10.14.2 Data Computation

Position, width, intensity and splitting are the parameters characterising the MB line. In order to locate the centre of gravity of the spectrum with respect to zero velocity, it is necessary to analyse the spectrum and do the line fitting very carefully. It is presumed that the spectrometer is calibrated for velocity. This is normally done by taking standard spectra for ^{57}Fe such as $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (single line), Fe_2O_3 (magnetically split), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (quadrupole split) and checking the results with the reported values for isomer shift, magnetic hyperfine splitting and quadrupole splitting. In the absence of computing facilities, the analysis of the experimental data is done by fitting the experimental points with theoretically computed Lorentzians. The curves may be computed using the expression

$$I = \frac{I_0}{1 + \frac{3}{4} \left(\frac{v}{\Gamma} \right)^2 + \frac{1}{4} \left(\frac{v}{\Gamma} \right)^4} \quad (10.108)$$

Here, I_0 and Γ are the intensity and full width of the experimental line respectively.

These days a number of softwares which synthesize spectra from assumed interaction parameters, viz., the isomer shift δ , the hyperfine magnetic field H_{int} , the principle component of the electric field gradient, U_{zz} , the polar and azimuthal angles relating the direction of H_{int} and the direction of propagation of γ -ray to the principle axes (X, Y, Z) of EFG and the asymmetry parameter η are available and are being used for the analysis of the spectra, i.e. experimental data in terms of line positions and relative line intensities.

10.15 APPLICATIONS OF MÖSSBAUER SPECTROSCOPY

The applications of Mössbauer spectroscopy are based on the MB parameters, namely line width, isomer shift, magnetic and quadrupole hyperfine interactions, and factors influencing them. A wealth of information about

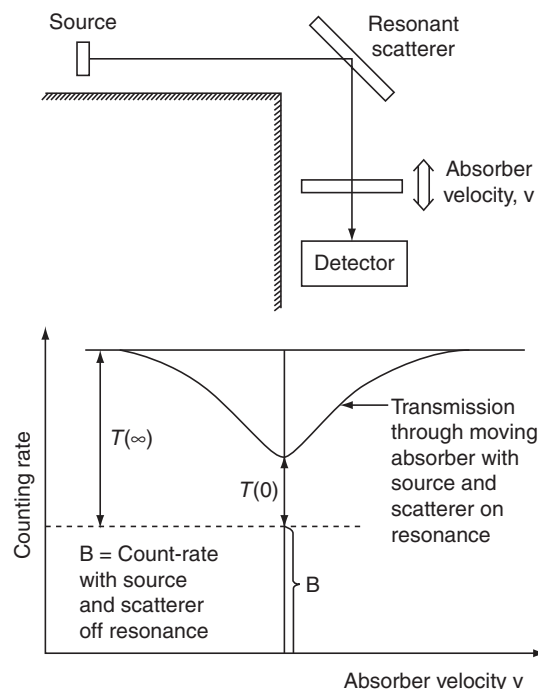


Fig. 10.44 Geometry for measurement of resonantly and nonresonantly γ -photons and the resultant hypothetical spectrum.

the physical and chemical properties of the MB nuclei in the materials can be obtained from these parameters. For instance, nuclear physical properties in the excited state, i.e. Lande splitting g factor, magnetic dipole moment, lifetime, internal conversion coefficient, etc., and physical phenomena such as diffusion and gravitational red shift are studied by this technique. Further, this technique is routinely applied to study the electronic configuration and nature of chemical bond not only of coordinated and organometallic compounds but also of molecular complexes and oxidation and corrosion phenomena on surfaces as well. This technique has also made deep inroads to the field of biological sciences. It not only enables us to understand the electronic structure of biological molecules *in vivo* and *in vitro* but also about their coordinating behaviour.

Furthermore, MB spectroscopy has made a unique contribution to the study of conformational changes of organometallic compounds resulting from the change of environment. Such studies are important because of the ambiguity in the structural information derived from x -ray diffraction data on single crystal and from NMR and IR measurements on solutions. Since MB spectrum can be recorded both on neat solids and frozen solutions, this tool bridges the gap between x -ray diffraction and spectroscopic, i.e. IR, NMR measurements to resolve the ambiguity in structural information so derived.

10.15.1 Lifetime of the Excited State

The relation between apparent width, Γ_{app} (sum of the emission and absorption half-widths, i.e. 2Γ and effective absorber thickness T_a is expressed by the equation (10.97), i.e.

$$\frac{\Gamma_{\text{app}}}{\Gamma_{\text{nat}}} = 2.00 + 0.27 T_a, \quad 0 \leq T_a \leq 5 \quad (10.109)$$

The expression indicates that

$$\left(\frac{\Gamma_{\text{app}}}{\Gamma_{\text{nat}}} \right)_{T_a \rightarrow 0} \approx 2 \quad (10.110)$$

Thus, from the plot of Γ_{app} , as a function of T_a , it is possible to obtain the true value of $\Gamma_{\text{nat}} = \frac{\Gamma_{\text{app}}}{2} (T_a \rightarrow 0)$.

The lifetime of the excited state is then obtained from Eq. (10.8), i.e.

$$\tau(\text{s}) = \frac{6.58 \times 10^{-16}}{\Gamma_{\text{app}}(\text{eV})} \quad (\text{Eq. 10.8})$$

The method only provides a lower limit to lifetime as the possibilities of intrinsic broadening from unresolved hyperfine effects cannot be eliminated.

10.15.2 Determination of Quadrupole Moment Ratio Q_e/Q_g

Since the quadrupole hyperfine structure in the MB spectrum arises because of the transitions between the sublevels of the excited state and the ground state of the MB nucleus, so it is possible to determine only the ratio Q_e/Q_g but not the values Q_e and Q_g separately.

We know that for axial symmetric fields (i.e. $\eta = 0$),

$$E_Q = \frac{e^2 Q q}{4I(2I-1)} [3M_I^2 - I(I+1)] \quad (\text{Eq. 10.77})$$

Since the MB nucleus experiences this interaction in both its ground and excited states, Eq. (10.77) for the ground and excited states is expressed as

$$E_Q(g) = \frac{e^2 q Q_g}{4I_g(2I_g-1)} [3M_{I_g}^2 - I_g(I_g+1)] \quad (10.111a)$$

$$E_Q(e) = \frac{e^2 q Q_e}{4I_e(2I_e-1)} [3M_{I_e}^2 - I_e(I_e+1)] \quad (10.111b)$$

Thus, the energy of γ -ray for a transition from the ground state sublevel M_{I_g} to the excited state-sublevel M_{I_e} will be given by

$$E_\gamma(g \rightarrow e) = E_0 + \frac{\delta}{c} E_0 + \frac{e^2 q}{4} [Q_e C(I_e, M_{I_e}) - Q_g C(I_g, M_{I_g})] \quad (10.112)$$

where $C(I, M_I) = \frac{[3M_I^2 - I(I+1)]}{I(2I-1)}$, and $\frac{\delta}{c} E_0$ is the isomer shift-energy term.

The positions of the quadrupole hyperfine lines in the MB spectrum can now be represented as

$$\begin{aligned}\Delta E_Q(g \rightarrow e) &= E_\gamma(g \rightarrow e) - E_0 \\ &= \frac{\delta}{c} E_0 + \frac{e^2 q}{4} [Q_e C(I_e, M_{I_e}) - Q_g C(I_g, M_{I_g})]\end{aligned}$$

or

$$\delta(g \rightarrow e) = \frac{ce^2 q Q_g}{4E_\gamma} \left[\frac{Q_e}{Q_g} C(I_e, M_{I_e}) - C(I_g, M_{I_g}) \right] + \delta_{\text{IS}} \quad (10.113)$$

Here, $\delta(g \rightarrow e)$ in (mm/s) represents the shift of the transition from the ground state level $|I_g, M_{I_g}\rangle$ to the excited-state level $|I_e, M_{I_e}\rangle$, δ_{IS} is the isomer shift of the MB nucleus with respect to the source.

Equation (10.113) shows that the line positions change as a function of Q_e/Q_g . The ratio Q_e/Q_g and isomer shifts δ_{IS} can be obtained from the observed values of $\delta(e \rightarrow g)$ for the lines by least square fit to Eq. (10.113), which represents a straight line with slope Q_e/Q_g and an intercept δ_{IS} . Further, from the ratio Q_e/Q_g , the quadrupole moment Q_e can be determined provided the ground-state quadrupole moment Q_g is known from other experiments.

Note that for MB nuclei with $\eta \neq 0$, Eq. (10.113) becomes complex, i.e. nonlinear due to the term η and the fitting of the observed line positions to the differences in energy for the sublevels of the ground and excited states becomes cumbersome, e.g. MB spectra of ^{129}I in solid I_2 ($\eta = -0.16$) gives $Q_e/Q_g = 1.232 \pm 0.004$ and 1.237 ± 0.002 .

Problem 10.5: (a) The MB spectrum of ^{129}I in KIO_3 (Fig. 10.45) ($\eta = 0$, $I_e = 5/2$, $I_g = 7/2$, ZnTe source) consists of eight quadrupole hyperfine lines (left to right) with relative intensity ratios:

$$\begin{aligned}1\left(\pm\frac{3}{2}-\pm\frac{5}{2}\right), 6\left(\pm\frac{5}{2}-\pm\frac{5}{2}\right), 21\left(\pm\frac{7}{2}-\pm\frac{5}{2}\right), 3\left(\pm\frac{1}{2}-\pm\frac{3}{2}\right), 10\left(\pm\frac{3}{2}-\pm\frac{3}{2}\right), \\ 15\left(\pm\frac{5}{2}-\pm\frac{3}{2}\right), 18\left(\pm\frac{1}{2}-\pm\frac{1}{2}\right), 10\left(\pm\frac{3}{2}-\pm\frac{1}{2}\right).\end{aligned}$$

The observed position of lines yield $Q_e/Q_g = \pm 1.23$ and $\delta_{\text{IS}} = 0.156$ cm/s. If the measured (at 80 K) $\text{K}^{127}\text{IO}_3$ quadrupole coupling constant is 996.7 MHz and the observed quadrupole moment ratio $\frac{Q_{129}}{Q_{127}} = +0.70121$, what will be the value of eqQ_e (129)?

(b) A comparison of the MB spectra of ^{129}I in KIO_3 ($\eta = 0$) and I_2 ($\eta = -0.16$) indicates that the two spectra are approximately inverted from right to left. If in the former, eqQ is positive and the quadrupole moments of both the ground state and the 26.8 keV excited state are negative, what will be the signs of q in case of KIO_3 and I_2 ?

Solution (a) From,

$$eq Q_{127} = 996.7 \text{ MHz}$$

and

$$\frac{Q_{129}}{Q_{127}} = 0.70121$$

we obtain the $\text{K}^{129}\text{IO}_3$ ground-state coupling constant

$$eq Q_{129} = 0.70121 \times 996.7 \text{ (MHz)} = 698.9 \text{ MHz}$$

Further, since the quadrupole moments ratio

$$\frac{Q_e}{Q_g} = 1.23$$

Therefore, the $\text{K}^{129}\text{IO}_3$ excited state coupling constant

$$eqQ_e = eqQ_g \times 1.23 = 698.9 \text{ (MHz)} \times 1.23 = 859.6 \text{ MHz}$$

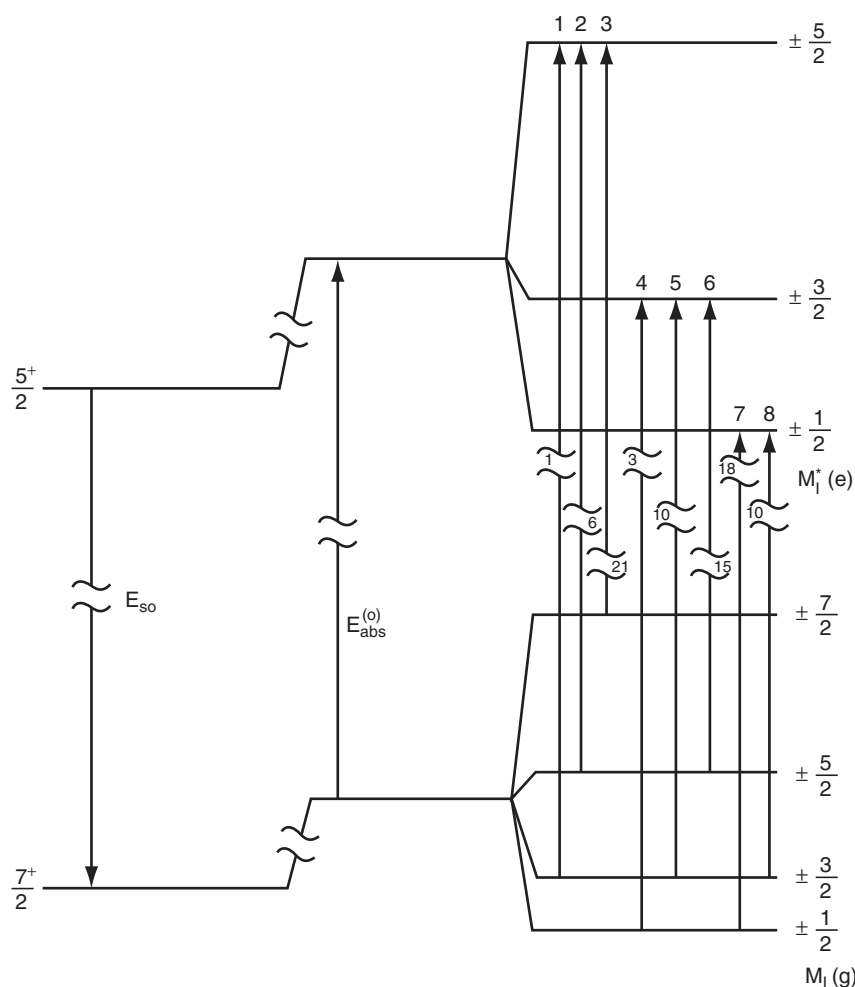


Fig. 10.45 A nuclear energy-level diagram illustrating the quadrupole splitting for ^{129}I in KIO_3 .

(b) In case of KIO_3 , eqQ is positive since both Q_e and Q_g are negative and therefore q should always be negative for eqQ to be positive. The inversion suggests that the sign of eqQ should be negative in case of I_2 with the result q is positive in I_2 . Further since the field gradient at the iodine nucleus is due to a p -electron vacancy which behaves like a positive charge, we expect a positive value of q , i.e.

$$U = +\frac{e}{r} \text{ and } \frac{\partial^2 U}{\partial r^2} = +\frac{2e}{r^3}.$$

10.15.3 Determination of g -Factors and Nuclear Magnetic Dipole Moments

Just like quadrupole hyperfine lines in the MB spectrum, the magnetic hyperfine pattern is also caused by the transitions between the sublevels of the excited state and the ground state of the MB nucleus because of which it is possible to determine only the ratio μ_e/μ_g but not the values of μ_e and μ_g separately.

Now, in order to determine μ_e/μ_g we are to work out a relationship between μ_e/μ_g and the position of the magnetic hyperfine lines. This is done as follows.

The magnetic hyperfine Hamiltonian for a nuclear magnetic dipole μ_I in a magnetic field H is given by

$$H_m = -\mu_I H = -g_N \beta_N \hat{I} \hat{H} \quad (\text{Eq. 10.61})$$

and the energy of the magnetic substates is expressed as

$$E_m = -g_N \beta_N H M_I \quad (\text{Eq. 10.63})$$

where the terms and symbols have their usual meanings. It can be readily proved that the $2I + 1$ magnetic substates are equally spaced with a separation of $g_N \beta_N H$ between the substates.

Further since the MB nucleus experiences this interaction in both its excited and ground states, so Eq. (10.63) for the ground state and the excited state is expressed as

$$E_{m(g)} = -g_g \beta_N H M_{I_g} \quad (10.114)$$

$$E_{m(e)} = -g_e \beta_N H M_{I_e} \quad (10.115)$$

Thus, the energy of γ -ray for a transition from the excited state sublevel M_{I_e} to the ground-state sublevel M_{I_g} will be

$$E_\gamma(e \rightarrow g) = E_0 + \frac{\delta}{c} E_0 - g_g \beta_N H M_{I_g} + g_e \beta_N H M_{I_e} \quad (10.116)$$

where, $\frac{\delta}{c} E_0$ is the isomer shift-energy term.

Note that the NMR spectroscopy measures the energy differences between the magnetic substates of the ground state.

$$\Delta E = g_N \beta_N H, [M_I (=I-1) - M_I (=I)] \quad (\text{Eq. 7.16})$$

The position of the magnetic hyperfine lines in the MB spectrum can be expressed as

$$\Delta E_m(e \rightarrow g) = E_\gamma(e \rightarrow g) - E_0 = \frac{\delta}{c} E_0 - \beta_N H g_g \left(M_{I_g} - \frac{g_e}{g_g} M_{I_e} \right)$$

or
$$\delta(e \rightarrow g) = \frac{c \beta_N H g_g}{E_\gamma} \left(\frac{g_e}{g_g} M_{I_e} - M_{I_g} \right) + \delta_{IS} \quad (10.117)$$

Here, $\delta(e \rightarrow g)$ in mm/s represents the shift of the transition from the excited state level $|I_e, M_{I_e}\rangle$ to the ground-state level $|I_g, M_{I_g}\rangle$, δ_{IS} is the isomer shift of the MB nucleus with respect to the source.

Equation (10.117) shows that the line positions change as a function of g_e/g_g and isomer shift can be obtained from the measured values of $\delta(e \rightarrow g)$ for the lines by least square fit to Eq. (10.117) which represents a straight line with slope g_e/g_g and an intercept δ_{IS} .

Once g_e/g_g is known, one can readily obtain the magnetic dipole moment ratio $\frac{\mu_e}{\mu_g}$ from the relation

$$\frac{\mu_e}{\mu_g} = \frac{g_e I_g}{g_g I_e} \quad (\text{Eq. 10.70})$$

Unlike the quadrupole case, the ground state g -factors and the magnetic dipole moments μ_g are well known since they can be determined very accurately from NMR measurements, i.e.

$$g_N = \frac{\Delta E}{\beta_N H} \text{ and } \mu_g = I g_g \beta_N$$

By using the known ground-state value of μ , i.e. μ_g , one can determine the value of μ_e from Eq. (10.70), as well as the field strength H ; $H = \frac{-g_g I_g}{\mu_g}$.

Further, it is to be noted that for the $2^+ \rightarrow 0^+$ even-even nuclei, the magnetic interaction in the ground state will not exist, and the hyperfine splitting will only be from the excited state. The magnetic measurements will then only give a value for $g_e \beta_N H$. Thus in order to obtain the value of g_e or H , one must know that value of H or g_e from another measurement.

10.15.4 Determination of Internal Conversion Coefficient

The intensity or area of an absorption line is a function of the various parameters involved in the effective thicknesses T_a

$$\left[= n \sigma_0 f_a t_a a_a (10.96) \text{ where } \sigma_0 = \frac{\lambda^2}{2\pi(1 + \alpha_t)} \cdot \frac{(2I_e + 1)}{(2I_g + 1)} (10.28) \right] \text{ of a Mössbauer absorber.}$$

Thus the internal conversion coefficient α_i can be determined from the area of an absorption line which is given by

$$A = f_s \int_{-\infty}^{+\infty} dE \left[1 - \exp(-\sigma(E) f_a t_a n a_a) \right] \quad (10.118)$$

where,

$$\sigma(E) = \frac{\sigma_0 \Gamma^2}{4(E - E_0)^2 + \Gamma^2} \quad (10.119)$$

By evaluating the transmission integral and by measuring the ratios of the areas in order to eliminate the recoil-free fraction of source, f_s , one can determine σ_0 and hence from Eq. (10.28), the internal conversion coefficient α_i . If absorbers of varying thickness are used, the amount of photoelectron absorption from atomic electrons will vary from absorber to absorber. This results in an inaccurate values of area, and hence the value of α_i . Such an effect can be eliminated by using a series of absorbers having the same thickness of MB atoms but whose density of atoms varies.

10.15.5 Determination of $\delta R/R$ or Nuclear Radius Changes from Mössbauer Isomer Shift

We know that isomer shift is a product of nuclear term, $\frac{\delta R}{R}$ and chemical term, $|\psi_s(0)_{\text{abs}}|^2 - |\psi_s(0)_{\text{so}}|^2$. So, if either of the two factors is determined independently by some method, the other can be determined from the isomer shift. The chemical term suggests that isomer shift is proportional to the difference in the total s -electron density at the source and the absorber nuclei. Thus the change in the radius, $\delta R/R$ can't be determined independently of the chemical environment, which means that electron density has to be estimated by molecular orbital methods in at least two compounds before a value of $\frac{\delta R}{R}$ can be estimated. The values of electron densities for $1s$, $2s$; $3s$, $4s$ electrons for different $3d^n$ configurations of the MB celebrated iron atom computed by Hartree Fock method have already been listed in Table 10.3. $\frac{\delta R}{R}$ for a number of nuclei, namely ^{57}Fe , ^{119}Sn , ^{121}Sb , ^{127}I , ^{129}I , etc., have been estimated from the isomer-shift data. It is found that the values of $\delta R/R$ determined from chemical isomer shift data are sensitive to the various methods of computation of $|\psi_s(0)|^2$. It appears, therefore, that isomer shift is not an ideal parameter to determine $\delta R/R$. It is better to determine $\delta R/R$ values independently and then use these values to interpret $|\psi_s(0)|^2$, the s -electron density at the nucleus and hence the nature of chemical bond. $\delta R/R$ can be determined by measuring internal conversion coefficients for valence electrons as a function of the chemical state of the element. $\delta R/R$ values in deformed nuclei have been estimated from the energy shifts of muonic x -rays. For ^{57}Fe (14.4 keV), the value of $\delta R/R$ determined from MB isomer shift is -1.28×10^{-3} . The values of $\delta R/R$ determined by molecular orbital and density calibration methods lie in the range -0.4 to -5.4×10^{-4} . The negative value of $\delta R/R$ indicates that radius of the 14.4 keV excited state ($I = 3/2$) of ^{57}Fe is smaller than the radius of the ground state ($I = 1/2$). On the other hand, in case of divalent ^{119}Sn , the value of $\delta R/R$ determined by different methods (lie in the range $0.3 - 3.5 \times 10^{-4}$) and from isomer shifts 9.21×10^{-5} . The positive sign of $\delta R/R$ in case of divalent ^{119}Sn shows that the radius of the excited state ($I = 3/2$) is larger than its counterpart in the ground state ($I = 1/2$). The values of $\delta R/R$ in ^{57}Fe and ^{119}Sn are likely to be changed if their relativistic correction factors $S(Z)$ are taken into account. The values of $S(Z)$ for some MB isotopes are $\text{Fe}(26) = 1.29$; $\text{Ni}(28) = 1.33$, $\text{Zn}(30) = 1.39$, $\text{Sn}(50) = 2.30$, $\text{I}(53) = 2.53$.

The discrepancies in the values of ($\delta R/R$) obtained from the isomer shift data are attributed to the inadequate knowledge of the charge density of an ion when it is situated in a lattice. This difficulty is solved by making ratios of the δR values from the isomer shift data obtained from two different Mössbauer levels.

$$\frac{(\delta R/R)_2}{(\delta R/R)_1} = \frac{E_{\gamma_2}}{E_{\gamma_1}} \cdot \frac{\delta_2}{\delta_1} \cdot \frac{Z_1 R_1^2}{Z_2 R_2^2} \cdot \frac{S(Z_1)}{S(Z_2)} \cdot \frac{\Delta\psi^2(Z_1)}{\Delta\psi^2(Z_2)} \quad (10.120)$$

For the case of two excited states in the same nucleus, e.g. the 97.4 and 103.2 keV levels in ^{153}Eu , Eq. (10.120) reduces to

$$\frac{(\delta R/R)_2}{(\delta R/R)_1} = \frac{E_{\gamma_2}}{E_{\gamma_1}} \cdot \frac{\delta_2}{\delta_1} \quad (10.121)$$

For the case of two different isotopes of the same element, e.g. the 57.5 keV level in ^{127}I and the 27.7 keV level in ^{129}I , Eq. (10.120) becomes

$$\frac{(\delta R/R)_2}{(\delta R/R)_1} = \frac{E_{\gamma_2}}{E_{\gamma_1}} \cdot \frac{\delta_2}{\delta_1} \cdot \frac{R_1^2}{R_2^2} \quad (10.122)$$

This method can also be extended to isoelectronic compounds, e.g. the ratios of nuclear radii for nuclei from tin, $Z = 50$, to Xe, $Z = 54$; i.e. for isoelectronic pairs such as $(^{129}\text{I O}_4)^-$ vs $(^{129}\text{XeO}_4)$, $^{129}\text{I}^-$ vs $^{129}\text{Xe}^0$ and $\text{K}_2^{125}\text{Te O}_4$ vs $\text{K}^{129}\text{IO}_4$, etc. The calculations with Hartree–Fock self-consistent field wave functions show that the ratio of electron densities for any pair of iso-electronic compounds is approximately a constant $\Delta\psi^2(Z+1)/\Delta\psi^2(Z) = 5/4$ for the various $5s^m 5p^n$ configurations.

Problem 10.6: The isomer shift for Fe^{3+} ions has been observed at about 0.5 mm/s and around 1.2 mm/s for Fe^{2+} ions. (a) Account for the different values of isomer shifts of Fe^{2+} and Fe^{3+} ions. Using the required data from Table 10.3, determine the (b) contribution of chemical term to isomer shift, (c) contribution of nuclear term to isomer shift, and (d) effect of relativistic term on the nuclear term.

Solution (a) The electronic configuration of iron in the various oxidation states is Fe (metallic): $[\text{Ar}] 3d^7 4s^1$, Fe^{2+} , Fe^{++} : $[\text{Ar}] 3d^6$, Fe^{3+} : $[\text{Ar}] 3d^5$. Normally s -electron density at the nucleus of Fe^{3+} ion in a salt is expected to be the same as that at the nucleus of Fe^{2+} ion. The difference in the isomer shifts of Fe^{2+} and Fe^{3+} ions suggests that the shielding effect of $3d^6$ electrons of Fe^{2+} ion and $3d^5$ of Fe^{3+} ion on the respective $3s$ electrons is different.

(b) The contribution of chemical term to isomer shift is determined from the expression

$$|\psi_{3s}(0)|^2 = |\psi_{3s}(0)_{2+}|^2 - |\psi_{3s}(0)_{3+}|^2$$

From Table 10.3, we write

$$|\psi_{3s}(0)_{2+}|^2 = 68.274 \text{ au}$$

$$|\psi_{3s}(0)_{3+}|^2 = 69.433 \text{ au}$$

Thus,

$$\begin{aligned} |\psi_{3s}(0)|^2 &= (68.274) - (69.433) \\ &= -1.159 \text{ au.} \end{aligned}$$

(c) $\frac{\delta R}{R}$ can be determined from the relation

$$v_{\text{IS}} = \frac{4\pi c Z e^2 R^2}{5E_\gamma} \left(\frac{\delta R}{R} \right) |\psi_{3s}(0)|^2 \quad (\text{Eq. 10.54})$$

$$= \frac{4 \times 3.14 \times 3 \times 10^{10} \times 26 \times (4.8 \times 10^{-10})^2 \times [1.4 \times 10^{-13} \times (57)^{1/3}]^2}{5 \times 14.4 \times 10^3 \times 1.602 \times 10^{-12} \times (0.53 \times 10^{-8})^3} \times \left(\frac{\delta R}{R} \right) |\psi_{3s}(0)|^2 \text{ (mm/s)}$$

$$\text{or} \quad v_{\text{IS}} = 381.9 \left(\frac{\delta R}{R} \right) |\psi_{3s}(0)|^2 \text{ (mm/s)}$$

Now,

$$v_{\text{IS}} = v_{\text{IS}}(\text{Fe}^{2+}) - v_{\text{IS}}(\text{Fe}^{3+}) = 1.20 - 0.50 = 0.70 \text{ mm/s}$$

and from Part (b), $|\psi_{3s}(0)|^2 = -1.159 \text{ au}$.

Substituting these values in the above expression, we obtain

$$\frac{\delta R}{R} = \frac{0.70}{381.9 \times (-1.159)} = -1.58 \times 10^{-3}$$

The negative value of $\delta R/R$ indicates that the radius of 14.4 keV excited state (3/2) of ^{57}Fe is smaller than the radius of the ground state.

(d) For ^{57}Fe ($Z = 26$), the relativistic correction factor $S(Z) = 1.29$

Therefore,

$$\left| \psi'_{3s}(0) \right|^2 = \left| \psi_{3s}(0) \right|^2 \times S(Z) = -1.159 \times 1.29 = -1.495$$

and

$$\frac{\delta R}{R} = \frac{0.70}{-1.495 \times 381.9} = -1.23 \times 10^{-3}$$

The increase in the value of $\frac{\delta R}{R}$ indicates that the increase in radius of 14.4 keV excited state of ^{57}Fe is relatively more than that of the ground state when the relativistic correction factor is taken in consideration.

10.15.6 Determination of Gravitational Red Shift

The change in energy of γ -ray photon travelling between source and absorber of different gravitational field is termed *gravitational red shift* and is expressed as

$$\begin{aligned} \delta_g &= g_\gamma \cdot d \text{ mass of } \gamma\text{-photon} \\ &= g_\gamma d \cdot \left(\frac{E_\gamma}{c^2} \right) \end{aligned} \quad (10.123)$$

Here, g_γ is the acceleration of the photon in the gravitational field and d is the distance between the source and the absorber.

This effect was first predicted by Einstein in 1907. The magnitude of the shift is very small (i.e. 1.1 parts in 10^{-16} m^{-1}).

The experiments were performed using the isotope ^{57}Fe (14.4 keV) over a distance of $d = 22.5 \text{ m}$. The source is mounted at a distance d above the absorber so that the photon travels through the gravitational field which would introduce an acceleration of g_γ in the atom, if it is free to fall. The γ -photon interacts with the gravitational field and a change in the γ -ray energy occurs and thus a change in position of the MB resonance line. The shift has been found to be 0.9970 ± 0.0076 at a height separation of 22.5 m. For a shift of full line width, $d \approx 3000 \text{ m}$, the experiments become unfeasible. Other isotopes like ^{181}Ta can be used because of their very small natural line widths.

10.15.7 Diffusion in Solids and Liquids

The MB resonance of hydrated iron (III) sulphate in glycerol (in the temperature range -100 to 0°C) shows the presence of Fe^{2+} and Fe^{3+} ions at -100°C at which temperature the matrix is frozen. The resonance becomes broadened with the growth in temperature and at 0°C when the sample becomes liquid, the very broad lines (Fe^{2+} doublet + Fe^{3+} singlet) have been observed. The relationship between viscosity of the liquid and the broadening of the MB line can be thought to be related to the relative importance of jump and continuous/Brownian types of diffusion processes.

MB spectroscopy can be used to study diffusion and related processes in solid systems since the appearance of spectrum depends upon the lifespan of the motion executed by the resonant atom. If the nucleus is vibrating harmonically about a fixed position at a frequency which is high compared with the inverse of excited state lifetime then the intensity of resonance line decreases without any line broadening. The decrease in the MB Lamb factor is given by the Debye–Waller formula

$$f = e^{-4\pi^2 x^2 / \lambda_\gamma^2} \quad (10.124)$$

where, x^2 is the mean square amplitude of oscillation in the direction of observation of γ -ray, λ_γ is the wavelength of the γ -photon. This means that the value of x of the order of 10 pm can be measured with MB isotopes with excited state lifespans similar to those of ^{57}Fe or ^{119}Sn .

In continuous diffusion, the broadening of MB line without reduction in overall recoil-less factor and change in the shape of the basic Lorentzian line occurs. The increase in experimental line width at half height is given by

$$\Delta\Gamma_{\text{exp}} = 2h \left(\frac{2\pi}{\lambda_\gamma} \right)^2 D_c \quad (10.125)$$

Here, D_c is the self-diffusion coefficient. D_c value of the order of $10^{-15} \text{ m}^2\text{s}^{-1}$ gives broadening of the order of natural line width for ^{57}Fe or ^{119}Sn sources.

At elevated temperatures, the relaxation time for diffuse jumps of the resonance atoms is in the same order of magnitude as the mean lifetime of the excited state. The line broadening without any change in intensity and Lorentzian line shape for random jumps of a diffusing MB atom is given by

$$\Delta\Gamma_{\text{exp}} = \frac{h}{\pi\tau_0} (1 - \alpha_g) \quad (10.126)$$

where, τ_0 is the mean stay time of an atom at a lattice site ($1/\tau_0$ is the jump frequency), values of τ_0 equal to 280 ns and 53 ns give broadening equal to natural line width for ^{57}Fe and ^{119}Sn respectively. α_g is a geometric factor. The diffusion coefficient is given by

$$D_j = \frac{1}{6\tau_0} d_j^2 f_c \quad (10.127)$$

where, d_j is the jump distance and f_c is a factor which describes the correlation in direction between successive jumps of one and the same atom. Lumping together Eqs (10.126) and (10.127), we obtain

$$\Delta\Gamma_{\text{exp}} = \frac{6h}{d_j^2 f_c} D_j (1 - \alpha_g) \quad (10.128)$$

The diffusion coefficient (and jump frequency) and jump direction can be determined from this expression. This unique feature of the Mössbauer effect is very useful in the study of diffusion mechanism especially for the anisotropic diffusion including surface diffusion. Diffusion phenomena of Fe in β -Ti have been studied by MB technique. Tracer measurements for the diffusion in β -Ti indicate an anomaly in the log D versus $1/T$. The observed diffusional broadening could be analysed in terms of an appropriate diffusion mechanism for this alloy system. A $^{57}\text{Co}/\text{Cu}$ source or a $^{57}\text{Fe}/\text{Cu}$ absorber shows line broadening between 1000–1060°C due to solid state diffusion, although data show deviation from simple diffusion jump model.

10.15.8 Study of Surfaces

MB spectroscopy represents an important addition to other surface spectroscopy tools like LEED (Low-Energy Electron Diffraction), ESCA (electron spectroscopy by chemical analysis) and Auger electron spectroscopy and can provide information which classical methods can't. Because of its sensitivity to strength and angular distribution of binding, to magnetic and electric fields, and to the s -electrons density at the nucleus, this tool can be used to study surfaces. The fraction of recoil-free γ -rays emitted depends on the mean square displacement of the emitting nucleus from its equilibrium position. The displacement will be different on surfaces than in the bulk of a crystal and will depend on the direction of the γ -ray emission. The structure of the MB line will depend on the magnetic fields and on the electric-field gradient at the surface. The various components of a line split by a quadrupole interaction will have different directional distributions with respect to the field axis. An anisotropy in the binding at the surface may result in isomer shift. The difference between the mean square velocity of surface and bulk atoms will lead to a second-order Doppler effect. For experimental studies, ultra-high vacuum should be maintained, the surface must be checked and the radioactive material must be deposited in less than a monolayer. The surface temperature should be kept below the room temperature, otherwise the tracer atoms may rapidly diffuse to a crack or a surface imperfection and lead to erroneous results.

Before discussing some of the experimental facts, let us first describe briefly the basic aspects of the theory related to the MB effect on surfaces.

The fraction ' f ' of recoil-less emitted γ -rays is expressed as

$$f = \exp \left[\frac{-E_\gamma^2 \langle x^2 \rangle}{(hc/2\pi)^2} \right] \quad (\text{Eq. 10.21})$$

The three typical positions of a nucleus undergoing, an MB transition have been shown in Fig. 10.46.

According to Eq. (10.21), the recoil-less fraction ' f ' is smallest in the direction of the largest excursion for the emitting nucleus. Thus, in a cubic crystal, f will be isotropic for a nucleus C residing in the bulk. The fraction ' f ' will be smaller parallel to the normal $\vec{n}$ than perpendicular to it, when the nucleus B resides in the surface whereas reverse will be true for the nucleus A on the surface. Furthermore, f_C will be greater than either f_A or f_B .

Further, if we assume that for a periodic lattice in the high-temperature region, all frequencies contribute equally to the calculation of ' f ' then on the basis of Einstein model of a solid, it is found that a single typical frequency related to the fraction f of γ -rays emitted without recoil is given by

$$\nu_{\text{typical}} = \frac{1}{\sqrt{3}} \nu_{\text{max}} \quad (10.129)$$

or equivalently,

$$\theta_E = \frac{1}{\sqrt{3}} \theta_D \quad (10.130)$$

Accordingly, a nucleus in a crystal can be considered as a single particle of mass m located in an anisotropic harmonic potential with force constants k_1 , k_2 and k_3 .

In the high-temperature limit, the recoilless fraction f is expressed as

$$f = \exp \left[- \left(\frac{h}{\lambda} \right)^2 \frac{T}{\kappa m} \left\{ \frac{1}{\theta_{E(1)}^2} \sin^2 \theta \cos^2 \varphi + \frac{1}{\theta_{E(2)}^2} \sin^2 \theta \sin^2 \varphi + \frac{1}{\theta_{E(3)}^2} \cos^2 \theta \right\} \right] \quad (10.131)$$

where λ is the wavelength of the γ -ray. For surface studies θ is assumed to be the angle between the surface normal and the direction of the emitted γ -ray. $\theta_E(i)$ is an Einstein temperature defined by

$$\theta_E(i) = \frac{h}{2\pi\kappa} \left(\frac{k_i}{m} \right)^{1/2} \quad (10.132a)$$

Moreover,

$$\langle x_\gamma^2 \rangle \propto \frac{i}{\theta_{E(\gamma)}^2} \propto \frac{1}{k_\gamma} \quad (10.132b)$$

where k_γ is the effective force constant in the direction of the γ -ray emission.

The isomer shift is given by

$$\delta_{\text{IS}} = \frac{2}{5} \pi Z e^2 (R_e^2 - R_g^2) \cdot \left[|\psi_s(0)_{\text{abs}}|^2 - |\psi_s(0)_{\text{so}}|^2 \right] \quad (\text{Eq. 10.40})$$

where the terms and symbols have their conventional meanings.

A given MB transition investigated on surfaces and in the bulk of a crystal will give information about the electronic functions in the various situations. This effect will be temperature independent provided a crystal phase transition does not take place.

The second-order Doppler shift is given by

$$\delta_{\text{SOD}} = \frac{E_\gamma}{2c^2} \langle v^2 \rangle \quad (\text{Eq. 10.44})$$

Here,

$$\langle v^2 \rangle = \frac{3\kappa T}{m} + \frac{(h/2\pi)^2 (k_1 + k_2 + k_3)}{12\kappa T m^2} \quad (10.133)$$

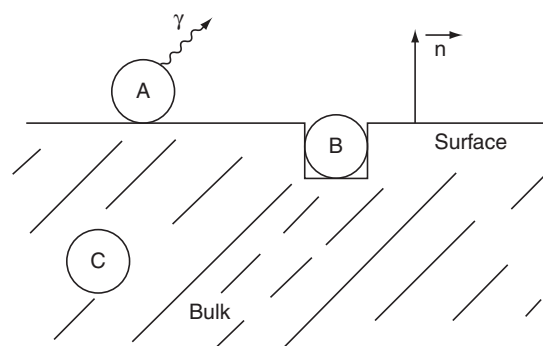


Fig. 10.46 Three typical positions of an MB nucleus adsorbed on a surface.

Let $k_1 + k_2 + k_3 = k_{\text{eff}}$ where k_{eff} for atoms in the direction of the emitted γ -rays in the bulk, in the surface and on the surface of a single cubic lattice have been approximated to be in the ratio 3 : 2 : 1.

Lumping together Eqs (10.44) and (10.134) we obtain

$$\delta_{\text{SOD}} = \frac{E_\gamma}{2c^2} \left[\frac{3\kappa T}{m} + \frac{(h/2\pi)^2 k_{\text{eff}}}{12\kappa T m^2} \right] \quad (10.134)$$

The central line shift δ_c is

$$\delta_c = \delta_{\text{IS}} + \delta_{\text{SOD}} \quad (10.135)$$

If we assume δ_{IS} to be independent of temperature and plot $\delta_c - \frac{3\kappa T E_\gamma}{2mc^2}$ against $\frac{1}{T}$, the slope of Eq. (10.135) will be equal to $\frac{(h/2\pi)^2 k_{\text{eff}}}{12\kappa m^2}$. Thus from the slope one can determine the value of k_{eff} , i.e. the effective force

constant which gives us information about the details of surface lattice binding.

The effect of adsorption on quadrupole coupling constant can be estimated from the electric field splitting of the nuclear energy levels as follows.

We know that for axial symmetric fields,

$$E_Q = \frac{e^2 q Q}{4I(2I-1)} [3M_I^2 - I(I+1)], [\because U_{zz} = eq] \quad (\text{Eq. 10.77})$$

For ^{57}Fe ,

$$\begin{aligned} \Delta E_Q &= E_Q \left(\pm \frac{3}{2} \right) - E_Q \left(\pm \frac{1}{2} \right) \\ &= \frac{e^2 q Q}{2} = \frac{1}{2} e Q \frac{\partial^2 U}{\partial z^2} \left[\because U_{zz} = \frac{\partial^2 U}{\partial z^2} = eq \right] \end{aligned} \quad (\text{Eq. 10.79})$$

The actual splitting is larger because of polarisation of the d -electrons by external field gradient. The polarisation is taken into account by multiplying Eq. (10.79) by Sternheimer antishielding factor, γ_∞ .

The order of magnitude of a field gradient on a surface is estimated by assuming a charge $-e$ placed at a typical lattice spacing ' a ' above the surface, simulating a missing positively charged ion. We then obtain

$$\frac{\partial^2 U}{\partial z^2} = \frac{-2e}{a^3} \quad (10.136)$$

Assuming, $a = 3 \times 10^{-8}$ cm, Sternheimer antishielding factor for Fe = 15, quadrupole moment $eQ = 0.2$ b, we get from Eq. (10.79),

$$\Delta E_Q \approx 10^{-8} \text{ eV}$$

Since the natural width of the MB line in ^{57}Fe is about 10^{-8} eV, surface field gradients may be observable.

The field gradient at a surface is expected to have a well-defined axis. The two components that result from the splitting of the ^{57}Fe 14 keV line by quadrupole interaction will exhibit different directional behaviour. The directional dependence of intensities of the two lines is

$$\frac{I_{\pm 1/2, \pm 3/2}}{I_{\pm 1/2, \pm 1/2}} = \frac{I_\pi}{I_\sigma} = \frac{1 + \cos^2 \theta}{\left(\frac{2}{3} + \sin^2 \theta \right)} \quad (\text{Eq. 10.80})$$

Thus, the direction of the field gradient can be obtained from the intensities of a quadrupole split MB line in different directions.

Let us now examine the MB spectra of ^{57}Fe on the surface of polycrystalline tungsten (in the temperature range 100–500 K) and at angles of 0° and 60° relative to the surface normal. The spectra as deduced from least square fit computer analysis consists of three unresolved lines. The middle line conforms to the measured spectra of ^{57}Fe in the bulk of tungsten and the outer two lines are attributed to the surface effects. MB spectrum of a single crystal surface showed no central peak substantiating there by the assumption that the central line is due to diffusion of ^{57}Fe into the bulk of tungsten.

The asymmetry of the surface spectra, the angular dependence of shape and the magnitude of splitting of the two lines are attributed to the surface quadrupole splitting. EFG at the nucleus is -3.6×10^{17} V/cm² perpendicular

to the surface for quadrupole moment $= 0.2 \times 10^{-28} \text{ m}^2$ of the $3/2$ state in ^{57}Fe . The average ratios of the intensities of the two lines are 2.1 at 0° and 1.4 at 60° . The expected ratios with corrections for experimental facts are between 2.5 and 1.9 at 0° and between 0.9 and 1.0 at 60° . The discrepancies at 60° may be attributed to the difficulties in the analysis of the three unresolved lines.

The intensity of the central component of the unresolved line depends on temperature and θ_D has been found to be $403 \pm 70 \text{ K}$ whereas MB spectrum of ^{57}Co diffused into polycrystalline tungsten gives a value of $\theta_D = 406 \pm 12 \text{ K}$. The value of θ_D as determined from the combined intensity of the outer components of the line is $340 \pm 30 \text{ K}$ perpendicular to the surface and, $273 \pm 30 \text{ K}$ at 60° from the normal. It is to be noted that solid angle has not been taken into account while calculating these values. When solid angle is considered, the effective value of $\theta_D = 354 \pm 30 \text{ K}$ perpendicular to the surface and $255 \pm 30 \text{ K}$ parallel to the surface. It can easily be shown by Eq. (10.132b) that these results correspond to the following mean square displacement ratios (recall that the mean square displacement in the high temperature limit is inversely proportional to the square of the effective Debye temperature).

$$\frac{\langle x_{\parallel}^2 \rangle}{\langle x_{\perp}^2 \rangle} = 1.9 \pm 0.4, \quad (1.2)$$

$$\frac{\langle x_{\perp}^2 \rangle}{\langle x_{\text{bulk}}^2 \rangle} = 1.3 \pm 0.2 \quad (2) \quad (10.137)$$

and

$$\frac{\langle x_{\parallel}^2 \rangle}{\langle x_{\text{bulk}}^2 \rangle} = 2.5 \pm 0.5 (\sim 2.5)$$

The quantities with in braces are because of an extension of the ‘bond counting’ analysis to an atom on the surface of a body-centred cubic lattice such as tungsten. More sophisticated assumptions about the effective bonding in various directions need to be made to have good agreement with the experimental data.

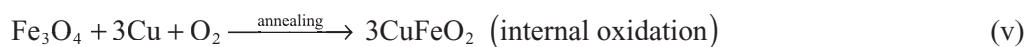
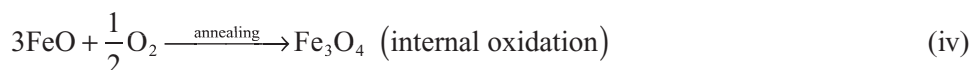
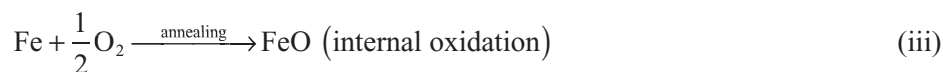
The isomer shift relative to iron at 300 K is $0.0151 \pm 0.0002 \text{ cm/s}$ in bulk and $0.018 \pm 0.002 \text{ cm/s}$ on the surface. The position of the central component matches with that of the bulk measurement.

This tool is also suitable to study oxidation and corrosion phenomena on surfaces, the initial states of internally oxidised atoms, and internally oxidised phases. The isomer shift of internally oxidised Sn atoms of an Ag–Sn alloy showed that the ionization state is close to +4 and that most of the oxidised Sn has been precipitated as SnO_2 particles.

The internal oxidation of Fe to FeO and subsequently to Fe_3O_4 and CuFeO_2 which occurs by heat treatments of Cu–Fe samples in a relatively low partial pressure atmosphere of O_2 , can be followed by MB spectroscopy. Although FeO has the cubic NaCl structure, it exhibits, at room temperature, a quadrupole split spectrum with an isomer shift characteristic of divalent Fe. The removal of the local cubic symmetry in the iron deficient compound ($\text{Fe}_{0.87-0.95}\text{O}$) could be the reason for the presence of the electric field gradient at the site of the nucleus.

Fe_3O_4 exhibits, at room temperature, two superimposed six-line Zeeman spectra. The two patterns are because of Fe^{3+} at tetrahedral sites ($H_{\text{int}} = 492 \pm 5 \text{ kOe}$) and Fe^{2+} and Fe^{3+} with rapid charge exchange at octahedral sites ($H_{\text{int}} = 464 \pm 5 \text{ kOe}$). The terminal oxidation product has been identified as CuFeO_2 , which occurs naturally as mineral delafossite and in copper smelter furnace slags. The isomer shift observed is characteristic of trivalent iron which provides evidence of ionic charge state of delafossite: $\text{Cu}^+\text{Fe}^{3+}\text{O}_2$ (not $\text{Cu}^{2+}\text{Fe}^{2+}\text{O}_2$). A magnetic transition has been found with a Neel temperature of 190 K.

The following reactions have been summarised in the Cu–Fe system.



10.15.9 Structure of Coordination Compounds

The tool of MB spectroscopy is routinely employed these days to study the structure of coordination compounds. Besides iron, MB investigations have been made with coordination compounds of Ni, Ru, Os, Ir, Pt, Au, Eu and Np among the transition elements, and of Sn, Sb, Te, I, Xe and Kr among the nontransition elements. The importance of this technique regarding structural elucidation of coordination compounds is demonstrated with some representative examples cited here.

(a) Crystalline Structure The MB spectrum of polycrystalline hydrated ferrous formate ($\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$) at 6, 77 and 298 K consists of four equally sharp lines. The inner and outside lines are attributed to two quadrupole doublets arising from different electric field gradients corresponding to two inequivalent sites. The results are listed in Table 10.13. The smaller quadrupole splitting is expected to be associated with the more symmetrical site. The nearest-neighbour symmetry at the two sites is O_h and D_{4h} respectively and is shown in Fig. 10.47. These MB spectral observations conform to *x*-ray diffraction data.

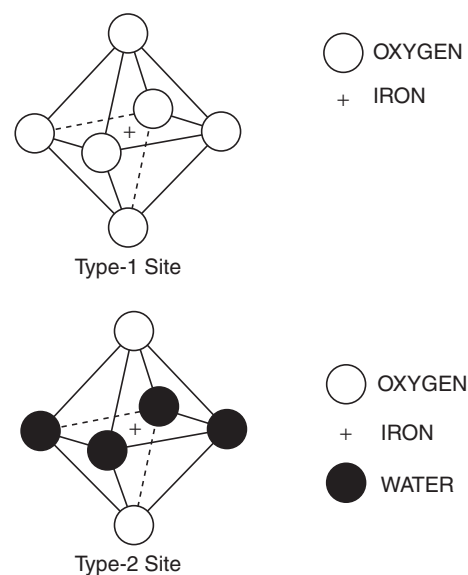


Fig. 10.47 Models of the approximate nearest neighbour symmetry at the two ferrous ion sites in hydrated ferrous formate.

Table 10.13 Isomer shifts (mm/s) and quadrupole splittings (mm/s) of ferrous formate.

Temperature (K)	ΔE_Q	$\delta_{IS}(\text{Cr})$	$\delta_{IS}(\text{Fe})$
298	0.59	1.34	1.19
	2.97	1.39	1.24
77	1.37	1.56	1.41
	3.42	1.56	1.41
6	1.48	1.48	1.33
	3.36	1.53	1.38

(b) Complex Isomerism Compounds having the same stoichiometric composition but different arrangement of ligands are called isomers. The MB spectrum may be of help to decide about the correct structure of the isomer, e.g. hydrated ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) may have an iron ion surrounded by an octahedral environment of water molecules as shown in Fig. 10.48. However, the MB spectrum of this molecule exhibits much quadrupole splitting ($\Delta E_Q = 0.91$ mm/s, $\delta_{IS}(\text{Pd})/\delta_{IS}(\text{Fe}) = 0.42/0.53$ mm/s at 77 K, and $\Delta E_Q = 0.97$ mm/s, $\delta_{IS}(\text{Pd})/\delta_{IS}(\text{Fe}) = 0.27/0.45$ mm/s at 300 K), suggesting that the symmetry around the ferric ion should be lower than octahedral. The *x*-ray diffraction studies have then shown that this molecule has a *trans* octahedral arrangement 2Cl^- and $4\text{H}_2\text{O}$ around the iron atom as shown in Fig. 10.49.

This result is of interest in understanding the properties of aqueous solutions of the ferric ion in the presence of chloride ions, since the different complexes which are formed are derived from this basic distorted structure.

(c) Cis-trans Isomerism The differences in ligand should induce different values of the electric field gradient at the central ion. In the *trans* case there is an axial symmetry (D_{4h}), which is absent in the *cis* case (C_{2v}). Based on the point charge model, the field gradient is given by Fig. 10.50.

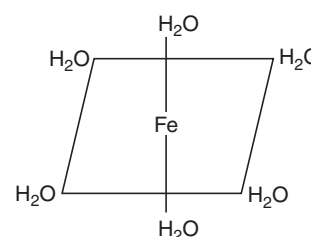


Fig. 10.48 Model of the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion with octahedral structure.

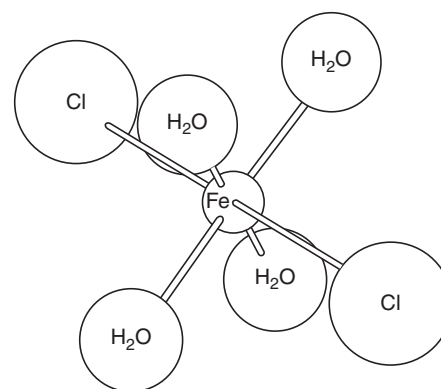


Fig. 10.49 Model of the $[\text{FeCl}_2(\text{H}_2\text{O})_4]^+$ ion.

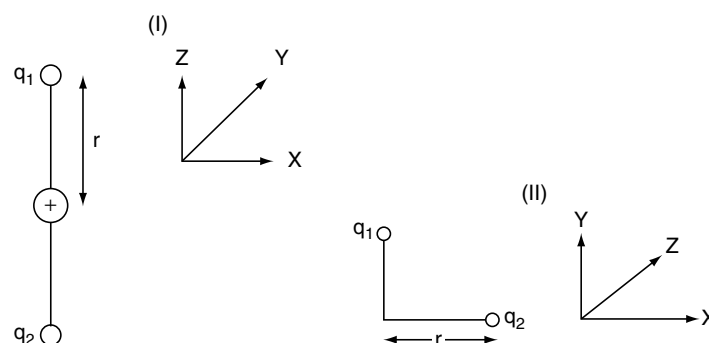


Fig. 10.50 The EFG in a point charge model for cis and trans isomers.

(I) Transcase (D_{4h}): $\theta = 0$

$$[q]_{\text{trans}} = (1 - \gamma_{\infty}) 4q / r^3 \quad (10.138)$$

(II) Cis case (C_{2v}): $\theta = \pi/2$

$$[q]_{\text{cis}} = (1 - \gamma_{\infty}) 2q / r^3 \quad (10.139)$$

In general,

$$q = (1 - \gamma_{\infty}) \left[\sum_i q_i (3 \cos^2 \theta_i - 1) / r_i^3 \right] \quad (10.140)$$

where terms and symbols have their usual meanings. q_i is the magnitude of the i th charge whose coordinates are r_i and θ_i .

Since $\theta = 0$ for *trans* case and $\theta = \frac{\pi}{2}$ for the *cis* case, so the ratio of quadrupole splittings is

$$\frac{E_Q(\text{trans})}{E_Q(\text{cis})} = 2:1 \quad (10.141)$$

This procedure can be used to identify which is the *cis* and which is the *trans* isomer, e.g. $\Delta E_Q / \delta_{\text{IS}}$: $\text{cis-Fe}(\text{CNMe})_4(\text{CN})_2 = 0.24/0.18$ and $\text{trans-Fe}(\text{CNMe})_4(\text{CN})_2 = 0.44/0.18$ mm/s. $\Delta E_Q / \delta_{\text{IS}}$: $\text{cis-Fe}(\text{CN Et})_4(\text{CN})_2 = 0.29/0.23$ mm/s. δ values are with respect to SNP.

(d) Ligand Linkage Isomerism The *x*-ray structure of metal ferrocyanides (the Prussian blue and similar compounds, e.g. $\text{K}_2\text{NiFe}(\text{CN})_6$) shows that one metal is bound to the nitrogen and the other to the carbon atom, i.e. $\text{Fe}-\text{C} \equiv \text{N}-\text{Ni}$. The carbon end of the cyanide linkage creates a strong field and tends to form low-spin complexes, whereas the nitrogen end is a weak field ligand and usually gives high-spin complexes. The phenomenon of cyanide linkage isomerism has been studied in iron (II) hexacyanochromate. This complex with composition $\text{Fe}_3^{\text{II}}(\text{Cr}^{\text{III}}(\text{CN})_6)$ exhibits linkage isomerism. At room temperature it changes spontaneously from form (I) to form (II) as shown in Fig. 10.51. Because of the difference in strength of ligand field induced by carbon and nitrogen ends of the cyanide ligand, the high-spin $S = 2$, Fe^{2+} is expected in form (I) and a low-spin $S = 0$ $\text{Fe}(\text{II})$ complex in form (II). The MB spectra of form (I) show indeed the typical isomer shift and quadrupole splitting of the high-spin Fe^{2+} whereas form (II) exhibits low values of isomer shift and quadrupole splitting corresponding to low-spin ferrous ion configurations. The MB observations find support from *x*-ray powder diffraction, infrared and magnetic susceptibility studies on this complex.

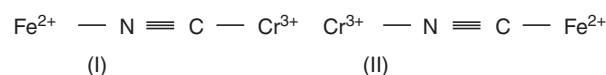


Fig. 10.51 Ligand linkage isomerism in iron hexacyanochromate.

(e) Structure of Complex Coordinated Molecules Structure of complicated complex molecules can be accomplished from MB parameters, namely intensity, isomer shift, quadrupole splitting, internal magnetic field, etc., since they are sensitive to the electron configuration of the molecules. Let us first examine whether quadrupole splitting alone is competent enough to rule out the possible structures of a particular compound or not. This is demonstrated here by taking the example of $\text{Fe}_3(\text{CO})_{12}$. The MB spectrum of $\text{Fe}_3(\text{CO})_{12}$: Cr (^{57}CO) at 78 K

consists of three lines. Three structures shown in Fig. 10.52 are possible corresponding to formula $\text{Fe}_3(\text{CO})_{12}$. In one of the structures (a) the three iron atoms may be equivalent. In such a situation, the MB spectrum should exhibit an unexpected two-line spectrum. Thus such a structure is ruled out. In the other two structures (b) and (c), two of the three atoms may be equivalent. In one of these structures (b), if the two atoms are irregularly octahedrally arranged and the third one is not, the spectrum would consist of four lines due to quadrupole splittings which is contrary to the expected spectrum. On the other hand, if the two equivalent atoms are irregularly octahedrally arranged and the third one is nearly octahedral as shown in Fig. 10.52(c), the spectrum would consist of three lines as expected, the central line is because of nearly octahedral Fe atom and the other two lines are due to quadrupole splitting at two equivalent Fe atoms.

The other structural problem which demonstrates the potential of MB tool is that of Prussian and Turnbull's blues. Prussian blue is prepared by mixing the solutions of an iron (III) salt (in excess for insoluble Prussian blue) ($\text{Fe}_2(\text{SO}_4)_3$) and potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) and Turnbull's blue by mixing the solutions of ferrous salt (FeCl_2) and potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$). Now the problem arises as to (i) what are the electronic configurations of iron in these three compounds: ferric ferrocyanide $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$, ferrous ferricyanide $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ or a more complex configuration, and (ii) whether soluble Prussian blue, insoluble Prussian blue and Turnbull's blue have the same formula or not.

However, before discussing these aspects, it will be more appropriate to report the MB spectra of potassium ferrocyanide and potassium ferricyanide. Ferrocyanides exhibit a single-line spectra because of the octahedral ligand symmetry and the lack of a nonbonding $3d$ electron contribution to EFG, e.g. $\text{K}_4\text{Fe}(\text{CN})_6$ at 143 K: $\delta_{\text{IS}}(\text{Fe}) = +0.04$; $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ at 298 K: $\delta_{\text{IS}}(\text{Fe}) = -0.047$.

Further, a decrease of chemical shift and broadening of line occurs under the influence of applied pressure. This is attributed to an increase in s -electron density at the nucleus and a possible distortion of octahedron. High pressures at above 100°C on $\text{M}_2\text{Fe}(\text{CN})_6$ where $M = \text{Cu}, \text{Ni}$ and Zn , cause a partial change into high spin ($S = 2$) Fe^{2+} species. The process is reversible but with hysteresis.

A small quadrupole splitting of 0.28 mm/s has been observed in $\text{H}_4\text{Fe}(\text{CN})_6$. This is attributed to H-bond structure which has a symmetry lower than octahedral.

On the other hand, the MB spectra of $\text{K}_3\text{Fe}(\text{CN})_6$ in the temperature range 4.2–300 K, consist of a doublet: $\Delta E_Q = 0.28$ mm/s, and $\delta_{\text{IS}}(\text{Fe}) = -0.124$ mm/s. However, below Neel's temperature at 0.025–0.04 K, a six-line pattern has been observed with $H_{\text{int}} = 193$ kG. Moreover, the increase of quadrupole splitting, together with the appearance of a third peak in the spectrum which has isomer shift value similar to that of ferrocyanide has been observed with the increase of pressure. This may be either due to an increase in the degree of back donation from $3d$ orbitals to the empty ligand π^* -antibonding orbitals or a change in the $4s$ -admixture in the binding or both. Near 50 kilobar (kb), there is a phase transition which causes discontinuity in the isomer shift-pressure curves for both the ferrocyanide and ferricyanide components and at the same time produces a partial reversion to the oxidation species. All these changes are fully reversible on the release of pressure. $\text{M}_2\text{Fe}(\text{CN})_6$ also shows a reduction to ferrocyanides with increasing pressure. At elevated temperatures, a second change to high spin ($S = 2$) $\text{Fe}(\text{II})$ is also observed.

Let us now describe the two methods which are employed to identify and confirm the oxidation states of iron in the three blue complexes. The natural abundance of ^{57}Fe is only 2.17 per cent. The first method is based on the MB studies on samples prepared from reactants containing unenriched iron whereas the second is based on the samples prepared from reactants containing enriched iron.

(i). All the three complexes become ferromagnetic below 5.5 K and the MB spectra at 1.6 K consist of a well-resolved six-line pattern typical of ferric iron and a superimposed singlet owing to diamagnetic ferrocyanides

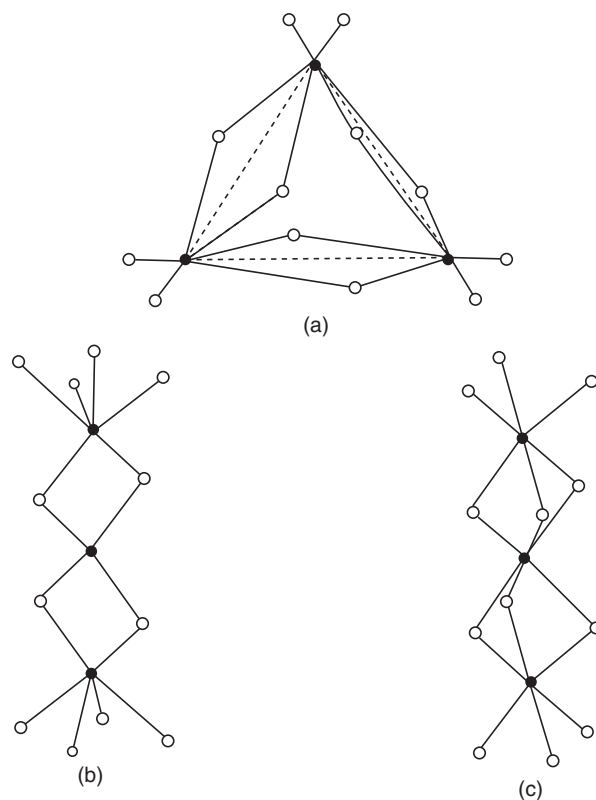


Fig. 10.52 Three possible structures of $\text{Fe}_3(\text{CO})_{12}$, ● – Fe, O – CO.

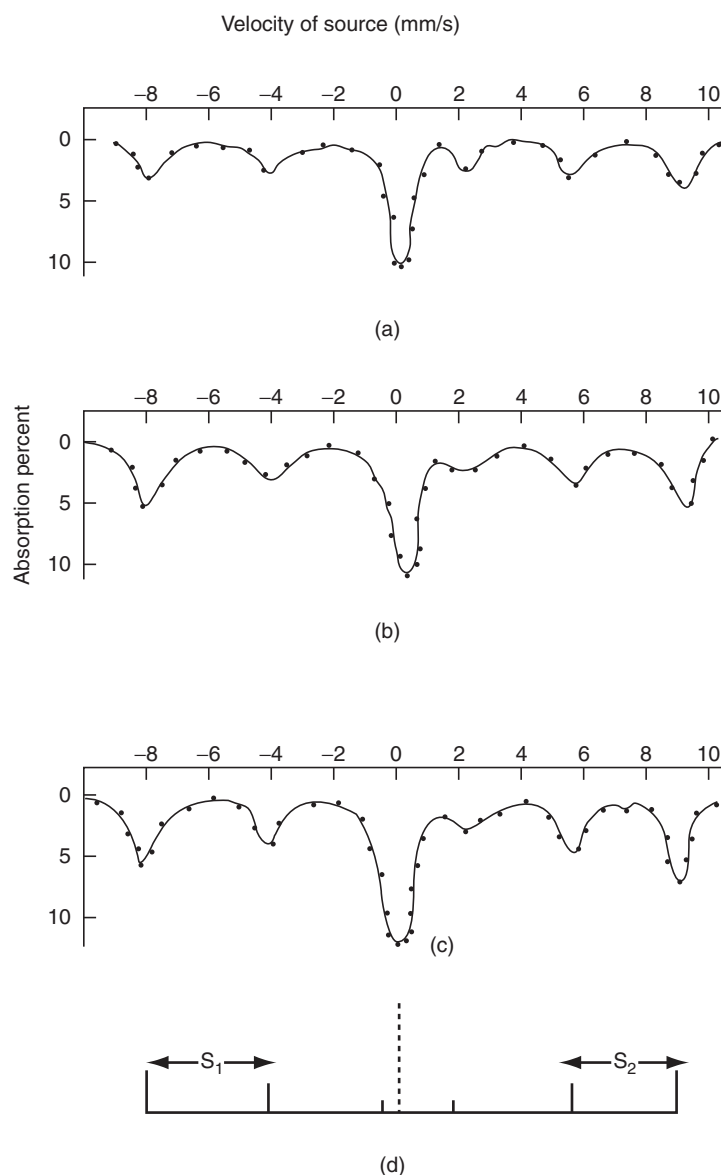


Fig. 10.53 The Mössbauer spectra at 1.6 K for (a) soluble Prussian blue, (b) insoluble Prussian blue, and (c) Turnbull's blue. The line positions for the two kinds of iron are indicated in (d) with solid lines and dashed line. The ferric six lines spectrum shows a quadrupole splitting $S_1 - S_2 = \frac{1}{2} e^2 q Q (3 \cos^2 \theta - 1)$.

Table 10.14 Mössbauer Parameters for Iron Ferro/Ferricyanides.

Parameter	Prussian blue				Turnbull's blue	
	Soluble		Insoluble		Fe ³⁺	Fe(II)
	Fe ³⁺	Fe(II)	Fe ³⁺	Fe(II)	Fe ³⁺	Fe(II)
δ_{IS} (SNP)/	0.84/0.57	0.33/0.06	0.84/0.57	0.31/0.04	0.83/0.56	0.27/0.0
δ_{IS} (Fe) mm/s						
$S_1 - S_2$ (mm/s)	0.37	0	0.48	0	0.52	0
H_{int} (kOe)	536 ± 20	0 ± 10	541 ± 20	0 ± 10	543 ± 20	0 ± 10

$$S_1 - S_2 = \frac{1}{2} e^2 q Q (3 \cos^2 \theta - 1)$$

(because of octahedral ligand symmetry and the lack of non bonding 3d electron contribution to EFG) (Fig. 10.53). The results obtained are listed in Tables 10.14 and 10.15 and are compared with characteristic values of MB parameters for the various states of iron recorded in Table 10.16.

Table 10.15 Intensity ratio between two kinds of Iron, Fe^{3+} and Fe(II) , for Prussian Blue and Turnbull's Blue.

	$\text{Fe}^{3+}/\text{Fe(II)}$ (observed) ^a	$\text{Fe}^{3+}/\text{Fe(II)}$ (normalised) ^b
Soluble Prussian blue	1.39	1.00
Insoluble Prussian blue	1.78	1.28
Turnbull's blue	1.84	1.32

(a) $\text{Fe}^{3+}/\text{Fe(II)}$ observed with the absorbers containing iron of about 20 mg/cm² (b) Normalised to the thin absorber.

Table 10.16 Characteristic Mössbauer parameters for various charge states of iron.

	Fe^{3+} (ionic)	Fe^{2+} (ionic)	$\text{Fe(III)} (\text{CN})$	$\text{Fe(II)} (\text{CN})$
$\delta_{\text{IS}}(\text{SNP})$ (mm/s)	~ 0.7	~ 1.6	~0	~ 0
ΔE_Q	~ 0.5	1.0 – 3.4	≤1.0	~0
H_{int} (kOe)	500 ~ 600	0 ~ 300	170 ~ 270*	0

* The value of internal magnetic field of low-spin Fe(III) combined with $(\text{CN})_6$ are for $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{M}_3[\text{Fe}(\text{CN})_6]_2$ (M : Mn, Co, Ni, Cu).

The internal magnetic fields of 540 kOe and zero kOe are typical of high-spin $S = 5/2$, ferric iron and low-spin $S = 0$ ferrous iron respectively. The isomer shift and quadrupole splitting for each iron moities also conform to typical value for Fe^{3+} and Fe(II) respectively. Thus these compounds exist in the Fe^{3+} ionic and covalent Fe(II) electronic states. It is to be noted that blue colour is still retained at 1.6 K, which confirms the charge transfer model and discards the valence oscillation or resonance between structures (i.e. $\text{Fe(II)} (\text{CN})_6\text{Fe}^{3+} \rightleftharpoons \text{Fe(III)} (\text{CN})_6\text{Fe}^{2+}$) at 1.6 K because the charged states are stable for at least for 10^{-7} s or at least occurs much more rapidly than 10^{-8} s; time of Larmor's precession of the ^{57}Fe nucleus. The preparation of Turnbull's blue, therefore, involves a mutual redox reaction.

Almost the same value of quadrupole splittings in the three compounds suggests that the electronic structure of these compounds is the same from the MB spectral point of view. Therefore, in Turnbull's blue, the charge transfer from Fe^{2+} (high spin) to Fe(III) (low spin) or flipping of the CN ligand by 180° should occur at the instant of combination.

The intensity ratios of the MB spectra are consistent with the stoichiometric formula $\text{KFe}(\text{Fe}(\text{CN})_6)_3$ for soluble Prussian blue (the electronic spectra of soluble Prussian blue could be interpreted in terms of a $\text{KFe}^{3+}[\text{Fe(II)}(\text{CN})_6]$ formulation with a charge transfer excitation to the unstable $\text{KFe}^{2+}[\text{Fe(III)}(\text{CN})_6]$ alternative) and $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ for insoluble Prussian blue and Turnbull's blue. Thus, from the comparison of the MB spectra, the basic information on the structure of these coordinated complexes has been obtained.

(ii) The MB spectrum of Prussian blue at 77 K prepared from enriched ^{57}Fe , $\text{Fe}_2(\text{SO}_4)_3$ and unenriched $\text{K}_4\text{Fe}(\text{CN})_6$ exhibits a dominant feature of iron (III) quadrupole doublet [Fig. 10.54(a)]. There is little or no transfer of enriched iron to the low-spin moities. The equivalent Turnbull's blue preparation $^{57}\text{Fe} \text{Cl}_2$ and unenriched ferricyanide also gives the enhanced iron (III) spectrum [Fig. 10.54(b)], thereby confirming the redox reaction. In both spectra the weaker singlet

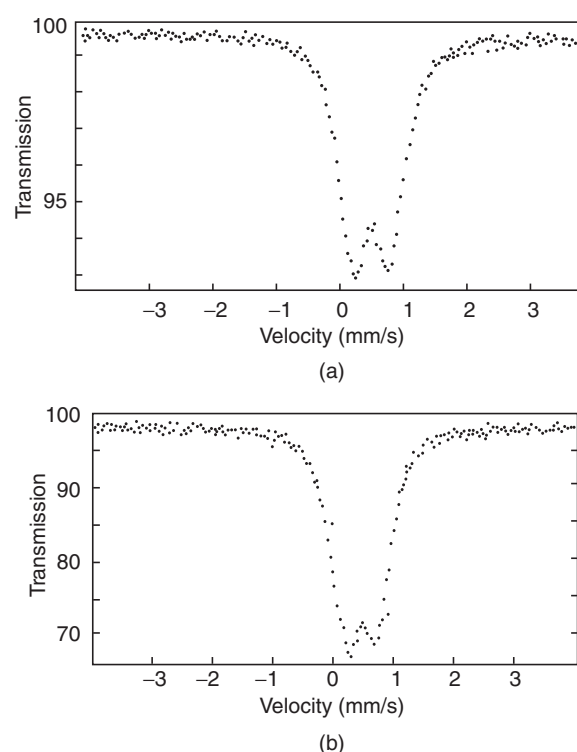


Fig. 10.54 Mössbauer spectrum at 77 K for Prussian blue prepared by mixing: (a) $^{57}\text{Fe}_2(\text{SO}_4)_3$ and unenriched $\text{K}_4[\text{Fe}(\text{CN})_6]$, and (b) $^{57}\text{FeCl}_2$ and unenriched $\text{K}_3[\text{Fe}(\text{CN})_6]$.

component arising from the unenriched ferrocyanide is obscured within the unresolved central portion of the spectra.

Application of pressure to insoluble Prussian blue causes considerable reversible reduction of high-spin ferric iron to high spin ferrous iron.

10.15.10 Spin-State Equilibria

The MB spectra of iron (II)-bis-(1, 10-phenanthroline) at 293 and 77 K exhibit quadrupole doublet respectively. The MB parameters: $\Delta E_Q = 2.67$ mm/s, δ_{IS} (SNP)/(Fe) = 0.34/0.98 mm/s at 293 K correspond to high-spin $S = 2$, $\text{Fe}^{2+}({}^5T_2)$ configuration whereas $\Delta E_Q = 0.34$ mm/s, δ_{IS} (SNP)/Fe = 0.62/0.37 mm/s at 77 K correspond to low-spin, $S = 0$ $\text{Fe}^{2+}({}^1A_1)$ configuration. However, the more extensive measurements over this temperature range show lines due to both the spin states in the vicinity of transition region (133–173 K). This shows that the interconversion takes place on a time scale, greater than 10^{-7} s, a factor also common to other ${}^5T_2 - {}^1A_1$ transitions. Thus the variation of hyperfine parameters as a function of temperature from the range of values of high-spin to low-spin configuration of the ferrous ion reveals the coexistence at a given temperature of different configurations of ferrous ion in the complex as expected on the basis of magnetic susceptibility measurements on transition metal ions. Thus, this data provides evidence for the existence of spin-state equilibria between equienergetic ${}^5T_2$ and ${}^1A_1$ states and is the first reported quintet-singlet equilibrium in a transition metal complex.

$\text{Fe(phen)}_2(\text{NCSe})$ also exhibit spin-state equilibria. The MB parameters for this complex are: $\Delta E_Q = 2.52$ mm/s, $\delta_{IS}(\text{Fe}) = 1.03$ mm/s at 293 K for ${}^5T_2$ configuration and $\Delta E_Q = 0.18$ mm/s, $\delta_{IS}(\text{Fe}) = 0.35$ mm/s at 77K for ${}^1A_1$ configuration.

10.15.11 Structure of Organometallic Compounds

The MB spectroscopy is used to study the structure, bonding, conformational changes with the change in environment; and symmetry in organometallic compounds. The solvents play a key role in such studies. They should have good solvating power and should be inert and glass formers at low temperatures (so that the solvent accommodates the structure of the solute rather than imposing a crystalline environment on the latter), they should have a high lattice temperature (so that the resonance effects are large at the temperature of the measurement, usually liquid nitrogen temperature). For the study of cyclooctatetraene iron tricarbonyl [COTFe(CO)_3] problem, these criteria are met by methyltetrahydrofuran (MTF) and ethanol + 1 propanol + diethyl ether (EPA 16 : 42 : 42). The correlation diagram (δ_{IS} vs ΔE_Q) for the several iron tricarbonyl compounds [RFe(CO)_3] as neat solids and as frozen solution samples is shown in Fig. 10.55. Figure 10.55 reveals that the quadrupole splitting parameter

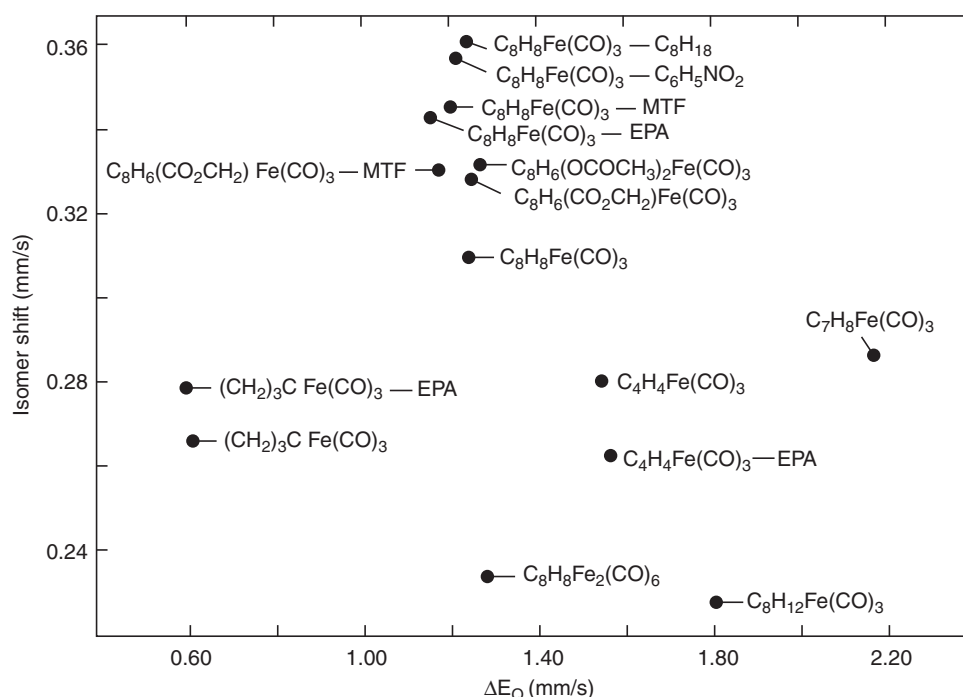


Fig. 10.55 Correlation diagram between isomer shift and quadrupole splitting for several iron tricarbonyl compounds as neat solids and as frozen solution samples. Metal in these complexes is bonded to a C_4H_4 fragment. Data is relative to SNP at 294 K.

(which is most sensitive to variations in the structures that are being considered) of COT $\text{Fe}(\text{CO})_3$ is the same in the solid and in EPA, nitrobenzene, MTF (methyl tetra hydrofuran), *n*-octane and identical to the quadrupole splitting in the binuclear complex $\text{COT}[\text{Fe}(\text{CO})_3]_2$. Moreover, this parameter i.e. ΔE_Q in the COT complexes (i) is markedly different from the value observed for $\text{C}_8\text{H}_{12}\text{Fe}(\text{CO})_3$ a compound which from other evidence is found to be a 1, 5-diene complex of iron tricarbonyl, and (ii) is much smaller compared to ΔE_Q value observed for norbornadienyl iron tricarbonyl $[\text{C}_7\text{H}_8\text{Fe}(\text{CO})_3]$ in which pseudooctahedral structure is not realised.

The MB data on COT $\text{Fe}(\text{CO})_3$ show that the configuration of this compound in solid and solution phases is the same as that observed by *x*-ray techniques for the solid. NMR and IR measurements also confirm this observation. PMR spectrum of this compound in solution phase at room temperature consists of a single peak. Accordingly, all the eight protons in the complex should be equivalent. This is possible provided the complex is an 'open-faced sandwich' with cyclooctatetraene ring approximately planar and symmetrically bonded to the $\text{Fe}(\text{CO})_3$ moiety.

On the other hand, the *x*-ray diffraction data show that in the solid state, the COT $\text{Fe}(\text{CO})_3$ molecule has a pseudo-octahedral structure, i.e. the $\text{Fe}(\text{CO})_3$ moiety is asymmetrically situated above the C_4H_4 fragment of the ring and the remaining hydrocarbon framework is separated by distances which preclude a direct bonding interaction. The ambiguity in the room temperature NMR and *x*-ray diffraction results has been resolved from low-temperature NMR spectrum which exhibits a splitting of proton resonance into two structured peaks symmetrically displaced from the resonance peak at room temperature. Note that at low temperature, the frequency of rotation of eight protons around the bond becomes large compared to NMR time-scan, i.e. 10^{-6} s. This results in eight equivalent protons. The low-temperature NMR spectra may be interpreted in terms of bonding of the $\text{Fe}(\text{CO})_3$ fragment to (a) a biplanar COT ring acting as a 1, 3-diene, (b) a tub shaped COT ring acting as a 1,3-diene and (c) a tub-shaped COT ring acting as a 1, 5-diene. The unwanted structure of the low-temperature solution conformation has been ruled out from MB measurements on neat solids and on frozen solution samples of the COT $\text{Fe}(\text{CO})_3$ complex and related molecules. Quadrupole splitting parameter of COT $\text{Fe}(\text{CO})_3$ is same in both the phases (1.16–1.24 mm/s) and is also identical to the quadrupole splitting of binuclear complex, COT $[\text{Fe}(\text{CO})_3]_2$. This parameter of COT complex is different from the value observed for $\text{C}_8\text{H}_{12}\text{Fe}(\text{CO})_3$ (1.8 mm/s) which is known from other evidence to be a 1, 5,-diene complex of iron tricarbonyl and is also much smaller compared to that of norbornadienyl iron tricarbonyl $[\text{C}_7\text{H}_8\text{Fe}(\text{CO})_3]$ ($\Delta E_Q = 2.15$ mm/s in which pseudo octahedral structure is not realised).

Further, the possible, conformational changes in other, organometallic compounds when these are subjected to changes in environment can also be followed by MB spectroscopic tool, e.g. the ^{119}Sn (relative to SnO_2 , $\delta_{\text{is}} = 0$) MB resonance (Sn) spectrum of neat $[(\pi - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnCl}_2$ consists of a sharp doublet ($\delta_{\text{is}} = 1.95$ mm/s and $\Delta E_Q = 2.38$ mm/s). However, the spectrum (Sn) in frozen solution in poly (methylmethacrylate) matrix becomes broad and can be resolved into two quadrupole doublets of essentially identical quadrupole splitting but different isomer shifts, (i.e. $\Delta E_Q = 2.25/2.29$ mm/s and $\delta_{\text{is}} = 1.96/1.31$ mm/s), Fe(SNP): Neat/2-methylfuran: $\Delta E_Q = 1.68/1.68$ mm/s and $\delta_{\text{is}} = 0.36/0.36$ mm/s. The two doublets suggest the presence of two different tin (Sn) atoms which are associated with two rotational conformers of this molecule in solution. These results provide confirmation of the speculation based on infrared spectral data.

$\{\text{Me}_2\text{Sn}[\text{Fe}(\text{CO})_4]\}_2$ Sn also exhibits rotational isomerism as is evident from the MB data indicated below in the tabular form.

^{57}Fe		$^{119}\text{Sn}(\text{SnO}_2)$	
ΔE_Q	δ_{is}	ΔE_Q	δ_{is}
0.30	-0.10	1.24	1.45
		—	2.20

80 K and values for δ_{is} (Fe) converted from SNP. Parameters are in mm/s.

10.15.12 Electronic Structure and Bond Nature of Charge Transfer Complexes

The change in the MB parameters namely, quadrupole coupling constant and chemical shift of MB nucleus present either in the donor or acceptor in the donor-acceptor systems may be fixed a criterion for the charge-transfer complexation between the donor and the acceptor. From the number of quadrupole splitting patterns in the MB spectrum, one can infer about the chemical species of MB nuclei present in the molecular complex. Further, it is also possible to estimate the charge densities on the chemical species of MB nuclei and the bond nature in the charge-transfer complex provided a relationship exists between the MB parameters and the bond parameters.

For instance, the MB spectrum of ^{129}I (at 16 K in CS_2 , relative to ZnTe source) of pyridine–iodine complex exhibits two quadrupole splitting patterns say A and B ; the pattern A is more intense than pattern B and the MB parameters corresponding to these patterns in the pyridine– I_2 system are (A/B) : e^2qQ (MHz) = $-2631/1439$, δ (mm/s) = $1.82/0.39$. For I_2 (in CS_2): e^2qQ (MHz) = -2242 ; δ (mm/s) = 0.93 , η (per cent) = 11 . (The quadrupole coupling constant (e^2qQ) is converted to I^{127}). The MB data indicate that there are two chemical species (say I_A and I_B) containing two electronic charge states of the MB nucleus in the complex (in the inert solvent). This fact may suggest that the iodine molecule lies along the symmetry axis of the donor molecule resulting in a linear $N-I_A-I_B$ arrangement. The large absorption intensity of A as compared to that of B lends support to the assignment of I_A to the bridged iodine atom and I_B to the terminal iodine atom. In order to determine the charge densities on the atoms involved in charge-transfer complexation and the nature of chemical bond formed, use is made of the following relations between MB parameters and bond parameters.

The number of the unbalanced p -electrons is given by

$$U_p = \frac{-e^2Qq_{\text{obs}}}{e^2Qq_{\text{atom}}} = 1 - s^2 \pm i - \pi \quad (10.142)$$

where s^2 is the amount of s hybridisation of the σ bond, i is the ionic charge, and π is the double-bond character and/or the intermolecular bond. The atomic iodine quadrupole coupling constant for ^{127}I $e^2Qq_{\text{atom}} = 2293$ MHz.

Thus, from the observed values of e^2qQ and Eq. (10.142), we get

$$U_p(I_A) = \frac{-2631 \text{ (MHz)}}{-2293 \text{ (MHz)}} = 1.147$$

$$U_p(I_B) = \frac{-1439 \text{ (MHz)}}{-2293 \text{ (MHz)}} = 0.627$$

Assuming that s^2 and π are negligible with respect to the quantity i , we obtain

$$1 \pm i_A = 1.147$$

and

$$1 \pm i_B = 0.627$$

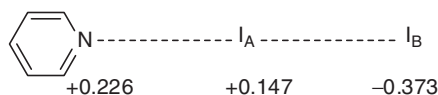
Thus,

$$i_A = +0.147,$$

$$i_B = -0.373,$$

and

$$i_N = +0.226$$



These values are reasonable compared to the values obtained from the far infrared spectroscopy and the measurement of the dipole moment.

The correctness of the assumption that the chemical bond of the bridging iodine atom is formed by only pure $5p_\sigma$ orbital can be checked from the correlation between δ_{Is} value and the charge density on the iodine atoms.

$$\delta_{\text{Is}} \text{ (mm/s)} = -9.2 h_s + 1.5 h_p - 0.54 \text{ (ZnTe source)} \quad (10.143)$$

where, h_s and h_p are the number of s - and p -electrons removed from the $5s^25p^6$ (I^-) configuration respectively.

Assuming that there is no s hybridisation in the $\text{I}-\text{I}$ bond, we obtain from observed value of δ_{Is} and Eq. (10.143), the values of charge densities on the terminal and the bridged iodine atoms as follows:

$$0.39 = 1.5 h_p - 0.54$$

or

$$h_p = \frac{0.39 + 0.54}{1.5} = \frac{0.93}{1.5} = 0.620$$

Thus,

$$i_B = 0.620 - 1 = -0.38$$

Similarly, we get, $h_p = 1.573$ and $i_A = 0.573$.

The agreement between the values of i_B obtained from quadrupole coupling constant and δ_{IS} values respectively shows that the I–I bond in the pyridine-iodine complex consists of mainly a pure σ bond of the p -electrons. On the other hand, the unexpected large value of $h_p(I_A)$ compared to $U_p(I_A)$ suggests that the intermolecular charge-transfer bond cannot be described by only a pure σ bond of the $5p$ electrons. The s hybridisation of the σ bond does not contribute to the CT bond since it greatly increases the h_p value and slightly decreases U_p . The discrepancy of $h_p(I_A)$ and $U_p(I_A)$ may be due to the presence of π bond which arises due to the donation of $5p_\pi$ electrons by iodine to the donor molecule. Based on this assumption the π -bond character can readily be obtained from the following expressions:

$$h_p = 6 - (N_x + N_y + N_z) \quad (10.144)$$

$$U_p = \frac{1}{2} (N_x + N_y) - N_z \quad (10.145)$$

where, N_x , N_y and N_z are the number of $5p$ electrons along the X , Y , and Z -axes, respectively.

Substituting the values of $h_p(I_A)$ and $U_p(I_A)$ into the respective expressions we obtain

$$1.15 = \frac{1}{2} (N_x + N_y) - N_z \quad (10.146)$$

$$1.57 = 6 - (N_x + N_y + N_z) \quad (10.147)$$

From the solution of the equations represented by (10.146) and (10.147), we get

$$N_z = 0.71, N_x + N_y = 3.72.$$

The π -bond character comes out to be about 14 per cent which of course is unreasonably high. In other words we can say that the bridging iodine atom (I_A) has abnormally high positive charge, i.e. + 0.573.

The unreasonably high value of charge density on the bridged iodine atom may be due to the non consideration of $4d$ electrons contribution partially to the formation of the CT bond between the nitrogen atom in the donor molecule and the bridging iodine atom. The calculations on the basis of $d_\sigma p_\sigma$ hybridisation in which the $4d_\sigma$ electrons promote to the $5p_\sigma$ orbital yield $I_A = +0.11$, $I_B = -0.38$ and $4d$ electron defect on the iodine atom = 0.33. Further, the low value of η (10 per cent) for the bridged iodine atom rules out the contribution due to back donation of $4d_\pi$ electrons in this complex although this donation causes an increase in the isomer shift greatly and the quadrupole coupling constant slightly.

It is interesting to note that unlike pyridine $-I_2$ complex the observed spectra of benzene, mesitylene and hexamethylbenzene, $-I_2$ complexes exhibit only one type of quadrupole splitting pattern suggesting thereby that only one chemical species of iodine is present in these complexes. The correlations between MB parameters and bond parameters also exist in these type of complexes. They, being complicated, are not treated here.

10.15.13 Studies of Lunar Soil

An interesting problem is the oxidation state of iron in the constituents of the soil, namely earthly soil, lunar soil, Martian soil etc. The primary aim has been to study the amount of iron in the soil, distribution of iron over the soil constituents and the particular valence states. Such type of studies on earth is important because plants take Fe^{2+} form of iron but not Fe^{3+} from the soil. These days due to soil pollution, soils may become Fe^{2+} deficient, consequently the growth of plant kingdom may be retarded. As an example, sandy soil being Fe^{2+} deficient is not recommended for the cultivation of paddy. Thus for survival of mankind in the future, it is important to study the composition and characteristics of soil from other planets also.

The constituents of the lunar soil are of complex nature. Since the first landing on the moon in July 1969, a large number of physical techniques, viz., x-ray diffraction, electron microscopy, and x-ray emission microanalysis and chemical methods have been employed to study lunar samples returned in the course of the Apollo and Luna missions. The main constituents include glassy agglomerates with a wide range of colour and transparency, and with angular, ellipsoidal, or spherical shapes, or formed like dumb-bells. Some glass particles show devitrification or inclusions of partially molten crystals. Additional components of the soil are isolated mineral particles of plagioclase (Na, Ca) $[(Al, Si)_4O_8]$, pyroxene $[(Ca, Mg, Fe)SiO_3]$, the minerals of this group are augite $[Ca_{0.15-0.4}(Mg, Fe)_{0.85-0.6}SiO_3]$, pigeonite $[Ca_{0.5-0.15}(Mg, Fe)_{0.95-0.85}SiO_3]$, and orthopyroxene $[(Mg, Fe)SiO_3]$; ilmenite $(FeTiO_3)$, and olivine $[(Mg, Fe)_2SiO_4]$. The soil also contains small amounts of alloys with

compositions close to metallic iron. The principal elements which form more than 99 per cent of the lunar surface are, in order of decreasing abundance oxygen, silicon, aluminium, iron, calcium, titanium, sodium and potassium. The aluminium and calcium show higher concentrations in the terra regions or highlands whereas iron and titanium in the mare regions. In view of the chemical composition of the lunar surface, applications of the MB effect have naturally been restricted to iron which is one of the four most abundant elements. The MB effect has made a modest, more or less descriptive contribution to the study of composite samples and separated mineral phases from the moon. MB spectroscopy of ^{57}Fe has been used mainly as a complement to various other techniques to characterise the soil fraction with a grain size smaller than about one mm. Even analytical data regarding the amount and properties of iron in grain sizes less than $1\ \mu\text{m}$, not easily obtainable by other techniques such as x -ray emission-microprobe analysis can be obtained by MB technique. Here, we shall be concentrating on the study of lunar soil by this technique since earthly soils have already been well characterised and documented.

The MB absorption spectra of the bulk fines represent remarkable ‘fingerprints’ of the landing sites, e.g. the resonant absorption spectrum of ^{57}Fe (295K) in lunar soil from Apollo landing site at Mare Tranquillitatis is shown in Fig. 10.56. The spectrum consists primarily of the superimposed resonant absorption patterns of ^{57}Fe in the silicate minerals, silicate glasses, ilmenite (FeTiO_3), metallic iron and troilite (stoichiometric FeS). The absorption in the range between 0 and 0.3 mm/s arises primarily from iron in silicate-glass, pyroxene, and olivine whereas the peaks at lower and higher velocities are attributed to metallic iron. The MB spectra of ^{57}Fe (at 295 and 77 K) in glass separated from Apollo 11 soil with 1 mm grain size shown in Figs 10.57 (a) and (b) did not exhibit any signal corresponding to Fe^{3+} ions with a detectability limit of ± 1 per cent. The doublet due to ilmenite (FeTiO_3) results from inclusions whereas the doublets 1 and 2 are because of Fe^{2+} ions in two distinct coordination polyhedra sites similar to that in pyroxene suggesting a high degree of devitrification. The temperature dependence of the doublets 1 and 2 is also similar to that of pyroxene.

MB hyperfine spectrum of ^{57}Fe in plagioclase separated from grained basalt of the Apollo 11 landing site at Mare Tranquillitatis consists of an apparent three-line pattern as shown in Fig. 10.58. The three-line pattern has been ascribed to two overlapping quadrupole split doublets of Fe^{2+} ions at tetrahedrally coordinated Al^{3+} sites and at the Ca^{2+} site. Though plagioclase did not show any signal corresponding to Fe^{3+} ions, the presence of these ions in lunar plagioclase crystals has been confirmed by ESR. However, the MB spectrum of ^{57}Fe (295K) in augite from a terrestrial volcanic rock, exhibits in addition to an intense doublet because of Fe^{2+} ions, a weak peak which is assigned to Fe^{3+} ions. (Fig. 10.59). The total iron content in the bulk fines of Apollo-11 soil as estimated from the total resonant absorption is about 10–12 mass per cent. MB parameters in glasses from lunar soils have been compared with synthetic glasses in Table 10.17.

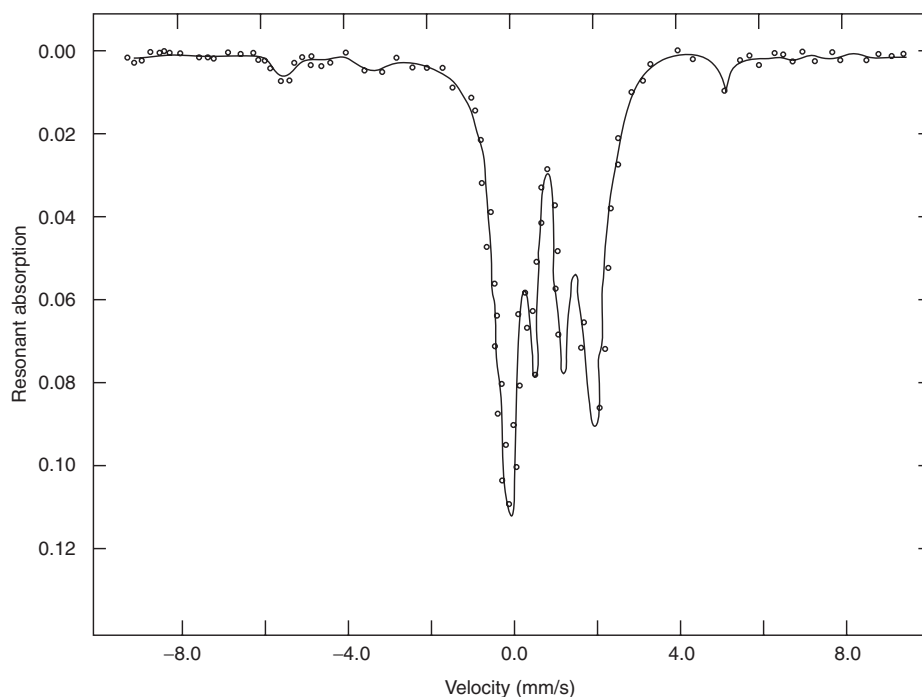


Fig. 10.56 Mössbauer spectrum of Fe^{57} at 295 K in lunar soil from the Apollo 11 landing site at Mare Tranquillitatis.

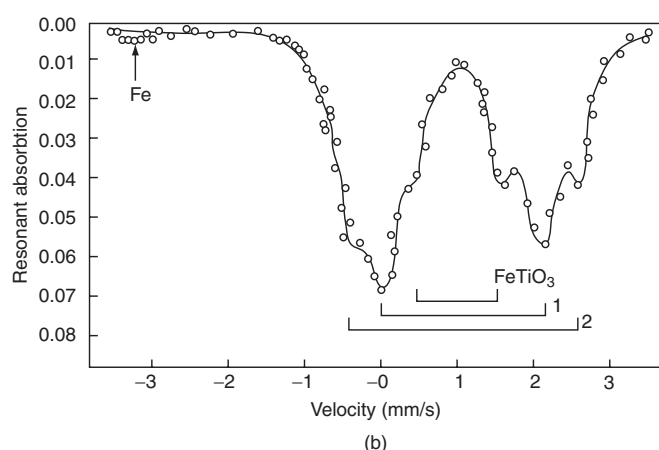
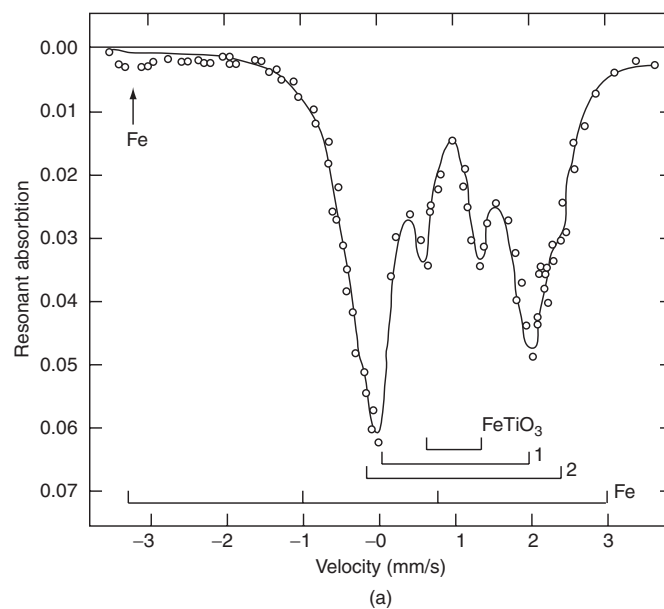


Fig. 10.57 Mössbauer spectra of ^{57}Fe (a) at 295 K in glass particles separated from Apollo 11 soil and (b) at 77 K of the glass particles.

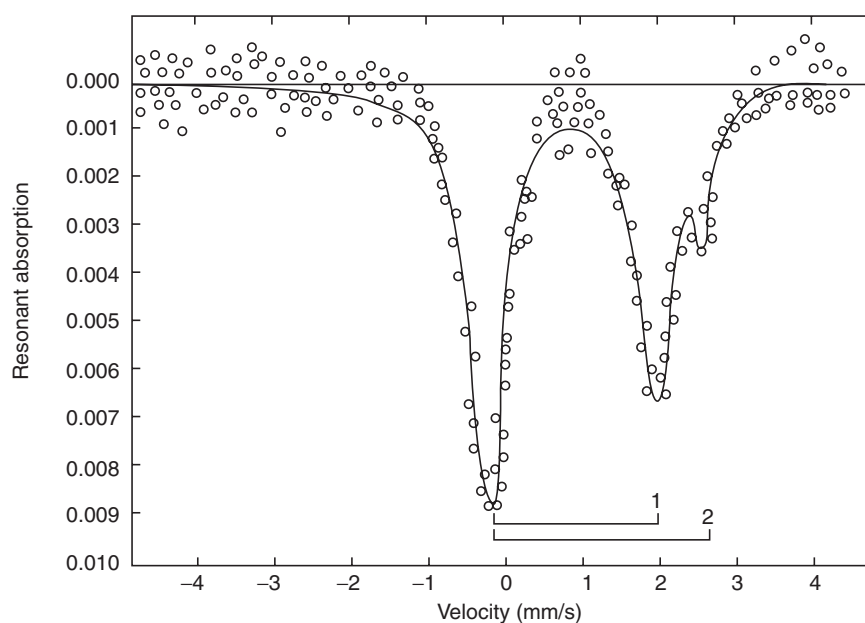


Fig. 10.58 Mössbauer spectrum of ^{57}Fe in plagioclase isolated from a coarse grained basalt of the Apollo 11 landing site at Mare Tranquillitatis. 2: doublet due to Fe^{2+} at the Ca^{2+} sites; 1: doublet due to Fe^{2+} ions at tetrahedrally coordinated Al^{3+} sites.

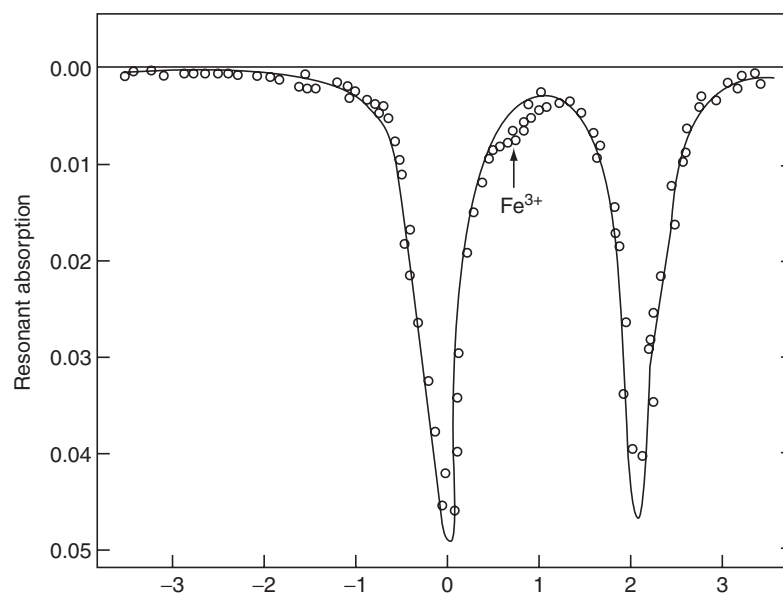


Fig. 10.59 Mössbauer spectrum of ^{57}Fe (295 K) in augite from a terrestrial volcanic rock of the Apollo 11 landing site at Mare Tranquillitatis. The weak Fe^{3+} peak is a part of doublet which includes approximately ten per cent of the total resonant absorption.

Table 10.17 Isomer Shifts, Quadrupole Splittings and Line Widths in Glasses from Lunar Soils and Synthetic Glasses at Room Temperature.

Sample	State of iron	Average $\delta_{\text{I.S.}}$ (a) (mm/s)	Average ΔE_Q (mm/s)	Line-width Lower position (mm/s)	Linewidth Upper position (mm/s)
Apollo 11 doublet 1 ^(b)	2+	1.16	2.72	0.27	0.37
doublet 2 ^(b)	2+	1.17	1.87	0.49	0.64
Apollo 17					
Orange glass ^(c)	2+	1.05	1.99	0.64	0.78
Synthetic glass prepared at 1335 °C	2+	1.04	1.97	0.57	0.72
Synthetic glass prepared at 1500 °C	3+	0.32	1.15	0.66	0.58

(a) With respect to metallic iron absorber, (b) area ratio $\frac{1}{1+2} = 0.15$. Additional peaks due to ilmenite inclusions are not tabulated. (c) Apollo 17 orange

glass is separated from orange soil collected at the Apollo 17 landing site in the Taurus Mountains–Littrow region, on the rim of Shorty Crater. Apollo 17 landed on 11 December, 1972.

10.16 BIOLOGICAL APPLICATIONS

The most celebrated MB nucleus ^{57}Fe , is present in many biological molecules, so most of the interesting and stimulating applications of MB spectroscopy are in the field of biosciences. Earlier the state of transition metal ions in biological molecules has been accomplished by magnetic susceptibility and ESR techniques, both of which deal with the bulk properties of the system. One of the major advantages of MB tool over these techniques is that it is site specific. Moreover, proteins containing diamagnetic iron which could not be studied by ESR technique can be measured by MB method. The measurements are made on frozen aqueous solutions of protein which have been precipitated and separated in solid form using ultra centrifuge. Care is also taken that in the separation process, the denaturation of protein does not take place. However, the possibility of a conformational change in the solid cannot be ruled out, and consequently the active solution form is not observed. On the basis of observations, it is found that frozen solutions of protein concentrates give satisfactory results. Further, since natural iron contains

only 2 per cent of MB isotope, comparatively a weak MB resonance is observed in biological molecules. So in order to obtain a strong MB resonance line in biological molecules, the natural samples need be enriched in ^{57}Fe . This is achieved either by growing organisms on a diet enriched in ^{57}Fe or by incorporating ^{57}Fe in the samples by chemical exchange, i.e. in some proteins it is possible to remove iron and then to reconstitute the protein with enriched ^{57}Fe without affecting the biological activity. The growing method requires more ^{57}Fe and is more reliable than exchange method since in the latter, the proton may be modified in the exchange process.

MB resonance studies in biological molecules are carried out to have information on (i) the electronic structure of iron in these molecules, (ii) location and site symmetry of iron in them, and (iii) the role of iron in biochemical transformations in which these molecules participate.

^{57}Fe is present in biological systems such as (i) haemoproteins, i.e. haemoglobin, myoglobin, cytochromes, peroxidases, catalases. The latter three are also known as haeme enzymes, (ii) iron-sulphur proteins, i.e. rubredoxins (1-iron/molecule), ferredoxins (a) plant type (2-iron/molecule) (b) bacterial (8-iron/molecule), high potential iron proteins (HPIP) (4-iron/molecule), conjugated iron-sulphur proteins (8 or more iron/molecule), i.e. xanthine oxidase; iron-molybdenum proteins, iron-zinc proteins, superoxide dismutase contain Cu-Zn and Fe-Zn proteins which control the aging process in living systems by reducing the accumulation of superoxide-free radicals (O_2^-) formed in many redox reactions, and (iii) iron storage and transport proteins such as ferritin, transferrins and hemosiderin. The latter two types are nonhaeme proteins. The haeme proteins have many different kinds of functions: oxygen transport (haemoglobin), electron transport (cytochrome), catalysis (peroxidase), etc. The iron-sulphur proteins which are found in many diverse organisms, in plants, animals and bacteria are involved in oxidative electron transfer in photosynthesis, nitrogen fixation, digestion, respiration, vision, etc. It is to be noted that the function of haeme proteins is governed by the haeme group present in such proteins. Haeme is a small planar stable molecule in which iron is coordinated to four nitrogen atoms which belong to the porphyrin ring and the remaining two sites of iron may be occupied by two ligands above and below the plane of the four nitrogen ligands. The structure of haeme is shown in Fig. 10.60. Haemoglobin contains four haeme groups in each of which the fifth coordination site of iron is attached to globin through a nitrogen atom in an imadizole of histidine residue below the plane of four nitrogen ligands. The sixth coordination site, i.e. X of iron is occupied by an exchangeable ligand (L) such as CO , NO , O_2 , etc., and the state of iron varies with the nature of the labile ligand. Myoglobin differs from haemoglobin in that it contains only one haeme group. Haemoglobin is the biological molecule, the structure of which is established by x-ray diffraction tool.

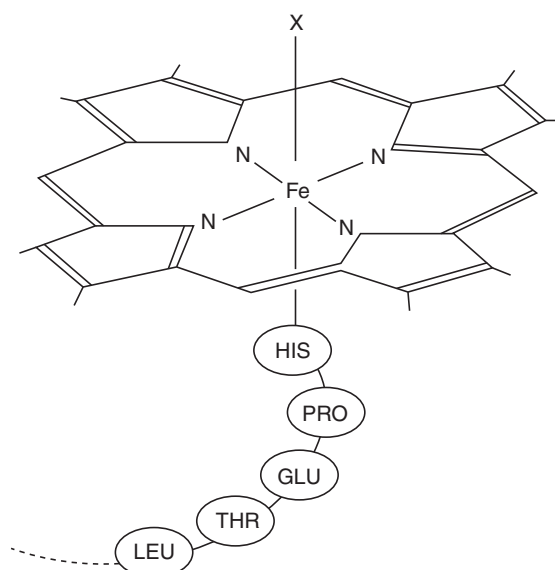


Fig. 10.60 Structure of haeme group.

Iodine, though controls all the metabolic processes in the body, but iodine MB effect has no significant applications in biological sciences because (i) although the natural linewidth of ^{129}I is 0.59 mm/s, its natural abundance is zero and one has to use radioactive ^{129}I obtained as a fission by-product and replace natural ^{129}I -partially or wholly. (ii) ^{127}I has 100 per cent abundance, but the MB spectrum for ^{127}I is hard to observe because of high energy of γ -ray it emits (57 keV) and the accompanied x-rays. The effect is observed at liquid nitrogen temperature. Moreover, due to large natural linewidth (2.54 mm/s), the small quadrupole interactions cannot be resolved and detected.

Let us now examine how MB spectra of haemoglobin and its complexes are valuable in understanding the role of iron in biological processes.

10.16.1 Studies of Haemoglobin and its Derivations

The ^{57}Fe Mössbauer spectral studies of haemoglobin and its derivations are important in order to differentiate between healthy ($S = 0$, Fe(II) in HbO_2 and $S = 2$, Fe(II) in Hb) and unhealthy ($S = 1/2$, Fe(III) in HbCN , HbN_3 , HbOH and $S = 5/2$, Fe(III) in HbH_2O , i.e. methaemoglobin), HbF bloods. MB data on Hb and its derivatives have been summarised in Table 10.18.

Table 10.18 Isomer Shifts (δ_{is} in mm/s) and Quadrupole Splittings (ΔE_Q in mm/s) for haemoglobin and its Derivatives.

Compound	Temperature(K)	δ_{is}	ΔE_Q	Configuration
Hb	195	0.90	2.40	High spin $S = 2$, Fe(II)
	4	0.91	2.40	
HbO ₂	195	0.20	1.89	
		(0.00)	(1.89)	
	77	0.26	2.19	
		(0.06)	(2.19)	
	1.2	0.24	2.24	Low spin $S = 0$, Fe(II)
		(0.04)	(2.24)	
HbCO	195	0.18	0.36	Fe(II)
	4	0.26	0.36	
HbCN	195	0.17	1.39	Low spin $S = 1/2$, Fe(III)
HbN ₃	195	0.15	2.30	
HbOH	195	0.18	1.57	
	77	0.20	1.90	
HbNO	195–1.2	Magnetically broadened		
HbH ₂ O	195	0.20	2.00	High spin $S = 5/2$, Fe(III)
HbF	195–1.2	0.43	(0.67)	
		Magnetically broadened		

The values within parenthesis are for rat HbO₂.

(a) Deoxy/Reduced Haemoglobin (Hb) It is present in arterial and venous blood. Magnetic susceptibility data show that Hb is high spin $S = 2$, iron (II) compound in the solution phase whereas its magnetic susceptibility in powder form is less than 2. The data also revealed that iron atom in this compound lies out of the plane of the haeme group.

The MB spectrum of Hb consists of a quadrupole doublet with MB parameters $\Delta E_Q = 2.4$ mm/s and $\delta_{\text{is}} = 0.90$ mm/s at 195 K (Table 10.18). Data reveal that Hb is a high spin $S = 2$, ferrous Fe(II) compound even though the value of isomer shift is less than the expected value for high-spin ionic ferrous compounds (Table 10.4). Magnetic hyperfine splitting is not observed in the zero field. The broadening of the quadrupole doublet at low temperatures (4 K) in the presence of strong external magnetic field (7.5 and 30 kG) perpendicular to the direction of observation may be because of anisotropy of ferrous ions. The applied field produces a large internal field which is different for each of the random orientations of the haeme plane and which broadens the spectrum. The absence of internal magnetic field hyperfine interaction may be due to the fact that an ion with even number of electrons will have $(2S + 1)$ spin degeneracy removed completely by a small crystal field provided the crystal-field symmetry is low, i.e. the electron spin-lattice relaxation time for ferrous is rapid compared to the life of the MB excited state even at low temperatures so that the magnetic field at the nuclei averages to zero.

(b) Oxygenated Haemoglobin (HbO₂) Just like reduced haemoglobin, HbO₂ also occurs in arterial as well as in venous blood and the iron atom in HbO₂ lies in the plane of the haeme group. Magnetic susceptibility data show that iron exists as low spin $S = 0$ ferrous (II) state in HbO₂. This also rules out the possibility of oxygen lying perpendicular to the plane of haeme group.

MB spectrum of HbO₂ at 195 K consists of a quadrupole doublet with MB parameters, $\Delta E_Q = 1.89$ mm/s, $\delta = 0.2$ mm/s (Table 10.18). It is difficult to assign low-spin ferrous or ferric state from the isomer shift and ΔE_Q data (Table 10.18). However, the spectrum of HbO₂ under the influence of external magnetic field (30 kOe at 4.2K) shows that the total field at the nucleus equals the applied field suggesting no magnetic hyperfine field, i.e. H_{int} , as expected for low-spin $S = 0$, ferrous (II) state. The applied field also suggests that the sign of e^2qQ is negative.

One interesting feature of HbO₂ spectrum is that the quadrupole splitting is unusually temperature dependent for a diamagnetic configuration (Table 10.18), e.g. the quadrupole splitting at 4.2 K is 2.24 mm/s and decreases to

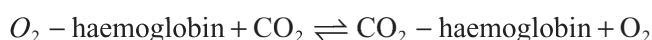
1.89 mm/s on warming to 195 K. This may be attributed to the existence of low-lying excited state, i.e. paramagnetism which of course is not observed. However, it could be because of a possible libration motion of the oxygen molecule at higher temperatures.

The sharp decrease in δ_{IS} in going from Hb (0.90 mm/s at 195 K) to HbO₂ (0.20 mm/s at 195 K) suggests some d -orbital and π -bond interaction between iron and oxygen in the HbO₂ molecule. There may be an electron transfer from iron to oxygen or one or more d -electrons are back donated. However the interaction between the metal d_{yz} -orbital and the π^* -antibonding orbitals of oxygen responsible for the loss of oxygen molecule's paramagnetism and the covalent bonding effectively removes an electron from the d_{yz} orbital. This conforms to the negative sign of e^2qQ measured by the applied magnetic field which suggests an electron hole in the d_{yz} orbital. The scheme for geometrical arrangement and bonding of molecular orbitals in HbO₂ is shown in Fig. 10.61. The molecular orbital

$\frac{(d_{yz} + \pi_z^*)}{\sqrt{2}}$ has only one-half character of d_{yz} orbital.

(c) Haemoglobin–Carbon Monoxide (HbCO) The MB spectrum of HbCO consists of a small quadrupole doublet ($\Delta E_Q = 0.36$ mm/s) at 195 K (Table 10.18). The quadrupole splitting has little temperature dependence, and there is a complete absence of magnetic interactions. The value of $\Delta E_Q = 0.36$ mm/s and $\delta_{\text{IS}} = 0.18$ mm/s at 195 K in HbCO conforms to low spin $S = 0$, Fe(II) configuration as expected (Table 10.4).

Let us now examine the ^{57}Fe MB spectrum of red blood cells in the light of the following exchange reaction occurring in such cells.



MB spectra of human and rat blood cells enriched to 35 per cent ^{57}Fe exhibit two doublets, a weak one and a strong one. These are attributed to O₂-haemoglobin and CO₂-haemoglobin. An additional weak single resonance line is

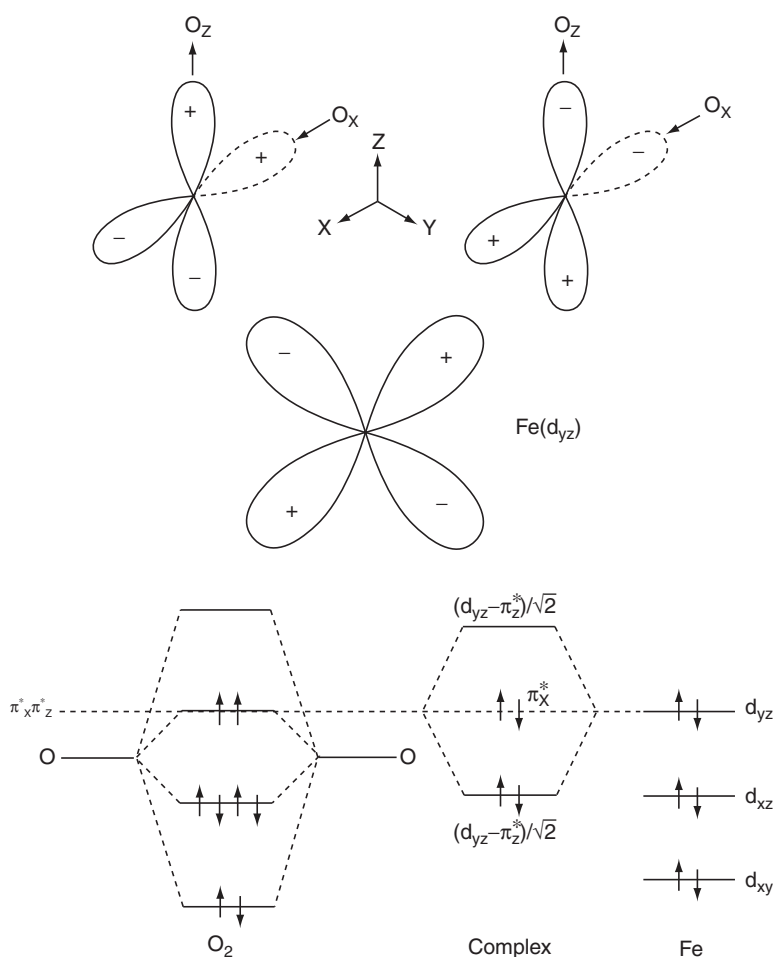


Fig. 10.61 Schematic diagram of the bonding in oxyhaemoglobin showing how the interaction between oxygen π_z^* molecule orbital and the iron d_{yz} orbital removes the degeneracy and causes spin pairing on the oxygen molecule.

also observed in MB spectrum of human blood. However CO_2 in CO_2 -haemoglobin is not attached to iron but to another part of haemoglobin since the spectra of blood which is exposed separately to an atmosphere of nitrogen and carbon dioxide are the same. It is known that terminal amine groups produced in muscles bind CO_2 for transport to the lungs. Thus, site 6 of iron may be either vacant or loosely bound to a molecule of water.

(d) Haemoglobin Cyanide (HbCN), Haemoglobin Azide (HbN_3) and Haemoglobin Hydroxide (HbOH) In all the three compounds, a symmetrical (with respect to width and intensity) hyperfine quadrupole doublet is observed at high temperature, i.e. 195 K. The values of quadrupole splitting and isomer shifts. (Table 10.18) lie within the expected range for the low spin $S = 1/2$, Fe(III) compounds (Table 10.4). This observation complements the results obtained from ESR and magnetic susceptibility measurements on these compounds. The marked low value of isomer shift in these compounds compared to reduced haemoglobin (Table 10.18) suggests that $-\text{CN}$, $-\text{N}_3$ and $-\text{OH}$ groups are attached to the site 6 of iron atom.

The doublet at 195 K becomes broadens on cooling the sample and is illustrated in case of HbCN in Fig. 10.62. Inspection of Fig. 10.62 reveals that at 77 K, the wing of the doublet on the low-velocity side is more intense compared to its counterpart on the high-frequency side of the spectrum. The broadening at 77 K relative to 195 K is due to slower spin relaxation rate which is responsible for the lack of magnetic splitting at higher temperatures. The asymmetry in the spectrum is attributed to the anisotropy of the magnetic hyperfine interaction. At 4.2 K, the relaxation is so slow that the hyperfine pattern is well resolved, but complex and asymmetrical because of the reason reported above.

(e) Haemoglobin Nitric Oxide (HbNO) MB spectrum of HbNO exhibits paramagnetic broadening at all temperatures between 195 and 1.2 K (Fig. 10.63). The magnetic hyperfine structure suggests a strong covalent bonding and a large spin transfer from the paramagnetic NO molecule to iron. The broadening is so strong that it is not possible to define the state of iron (ferrous or ferric) with certainty. This inference from Mössbauer studies is compatible with the reports in the literature that some haemoglobin compounds previously assumed to be ferrous contain ferric ions also.

(f) Haemoglobin Fluoride (HbF) and Methaemoglobin (HbH_2O) In both the compounds, ferric being in a ^6S state has zero orbital magnetic moment. This results in very slow $s-l$ relaxation rates and isotropic magnetic properties. The zero field MB spectrum of HbF exhibits magnetic broadening' even at high temperature (195 K) because of which it becomes difficult to obtain accurate values of quadrupole splitting and isomer shift. The zero-field spectrum remains unresolved even at low temperatures because of coupling of electron spin (transferred hyperfine interaction) with the magnetic moment of the neighbouring fluorine nucleus and to a lesser extent with a nitrogen nuclei in the haeme group. However, under the influence of a very small external magnetic field (≈ 100 Oe) perpendicular to the ligand field axis (i.e. γ -ray beam), an almost symmetrical six-finger splitting is observed. This marked change in spectrum is due to the decoupling by the external magnetic field

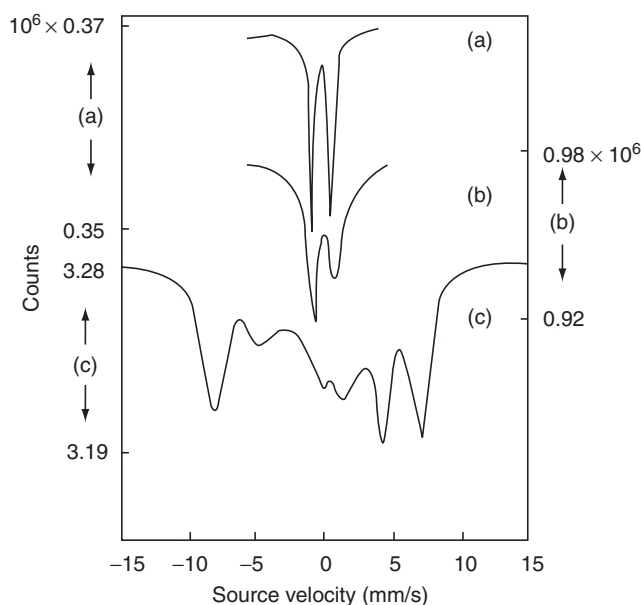


Fig. 10.62 Mössbauer spectra of haemoglobin cyanide at (a) 195 K, (b) 77 K, and (c) 4.2 K.

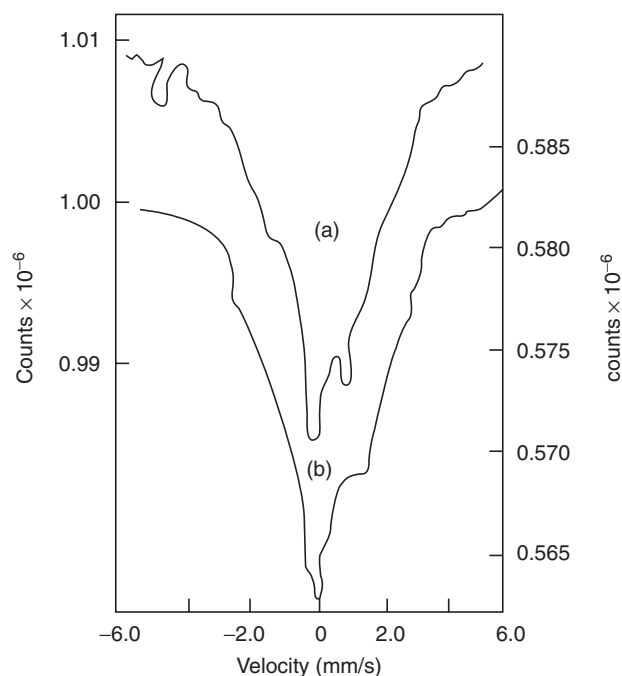


Fig. 10.63 Mössbauer spectra of haemoglobin nitric oxide at (a) 195 K, and (b) 77 K.

of electron spin from the nuclear spins of ^{57}Fe , ^{19}F and ^{14}N nuclei. The small quadrupole splitting and six sharp fingers are characteristic of the high spin $S = 5/2$, ferric (III) configuration. This inference is compatible with the ESR studies of HbF.

The MB spectra of this compound at 4 K and under external magnetic fields of 30, 15 and 7.5 kOe look like a superposition of two six-line spectra caused by different effective magnetic fields of the upper and lower members of the magnetically split $|M_s > \pm \frac{1}{2}$ doublet. Under the influence of high external magnetic field, the higher ligand field states get mixed with the ground state $|M_s = \pm 1/2 >$ in such a way that the effective field for the $|M_s = -1/2 >$ state increases while that of the $|M_s = +1/2 >$ state decreases. The observed value of effective magnetic field which is governed by ligand and field is about 300 kOe is consistent with that of 500 kOe usually found when $M_s = \frac{5}{2}$.

In HbH_2O , H_2O is in sixth coordination position. ESR spectra and magnetic susceptibility are consistent with high spin $S = 5/2$, Fe(III) configuration.

MB behaviour of this compound is similar to that of HbF, though (i) the temperature dependence of magnetic hyperfine spectra shows that the spin-lattice relaxation is much faster than what could be expected on the basis of pure s -state ion, and (ii) the quadrupole splitting observed in this compound is large (2.00 mm/s) compared to HbF (0.67 mm/sec). Both the points suggest that there is considerable mixing in of orbital moment into the ferric states by the ligand field.

10.16.2 Studies of Peroxidase and Its Derivatives

The MB spectrum of the peroxidase enzyme is of special interest because iron in these compounds can exist in a higher oxidation state than Fe(III). The MB data on Japanese radish peroxidase-a (JRP-a) enriched in Fe and its derivatives are compared with their respective derivatives of hemoglobin in Table 10.19.

10.16.3 Studies of Iron–Sulphur Proteins

Fe in these proteins is not bound in a stable basic structural unit as in the case of haemoglobin. It is held loosely in the chain of amino acids via sulphur atoms. The MB effect has been able to observe directly the antiferromagnetic coupling between the pair of iron atoms in such proteins.

(a) Ferredoxins (*Scenedesmus* is Involved in Plant Photosynthesis) (2-iron Proteins) Ferredoxin from plants contains two atoms of iron and two atoms of inorganic sulphur. The MB spectra of oxidised and reduced

Table 10.19 MB Data on JRP-a and its Derivatives.

Compound	T (K)	ΔE_Q (mm/s)	$\delta_{is}(Fe)$ (mm/s)	Configuration	Remarks
JRP-a	243–77	1.67–2.20	0.3 1–0.37	$S = \frac{5}{2}$, Fe(III)	Large quadrupole splitting which is temperature dependent, splitting is asymmetrical below 120 K. This behaviour is similar to methaemoglobin.
JRP - a OH	243–120	1.84–2.36	0.27–0.22	$S = \frac{1}{2}$, Fe(III)	All the three show similar behaviour but more magnetic broadening in hydroxide and azide as compared to cyanide because of longer relaxation times. Behaviour is similar to respective haemoglobin derivatives.
JRP - a N ₃	120	2.22	0.31		
JRP - a CN	195–77	1.61–1.81	0.11–0.15		
Reduced JRP-a	243–77	1.79–2.32	0.79–0.81	$S = 2$, Fe(II)	Spectrum is analogous to reduced haemoglobin
JRP-a CO	77	0.21	0.32	$S = 0$, Fe(II)	Spectrum is analogous to HbCO.
JRP-a F	195–4.2	Magnetically broadened		$S = \frac{5}{2}$, Fe(III)	Substantial magnetic broadening between 105–4.2 K. Behaviour is similar to HbF
JRP-a H ₂ O ₂ (I)	77	1.33	0.10	$S = 1$, Fe(IV) with two unpaired electrons	All the three give sharp quadrupole splitting which is small and temperature dependent. Compounds I and II can't be distinguished from isomer shifts since $\delta_{is}(I) \approx \delta_{is}(II)$. Compound III is similar to oxyhaemoglobin.
JRP-a H ₂ O ₂ (II)	77	1.46	0.11	$S = 1$, Fe(IV) with two unpaired electrons	
JRP-a H ₂ O ₂ (III)	77	2.37	0.29	$S = 0$, Fe(II)	

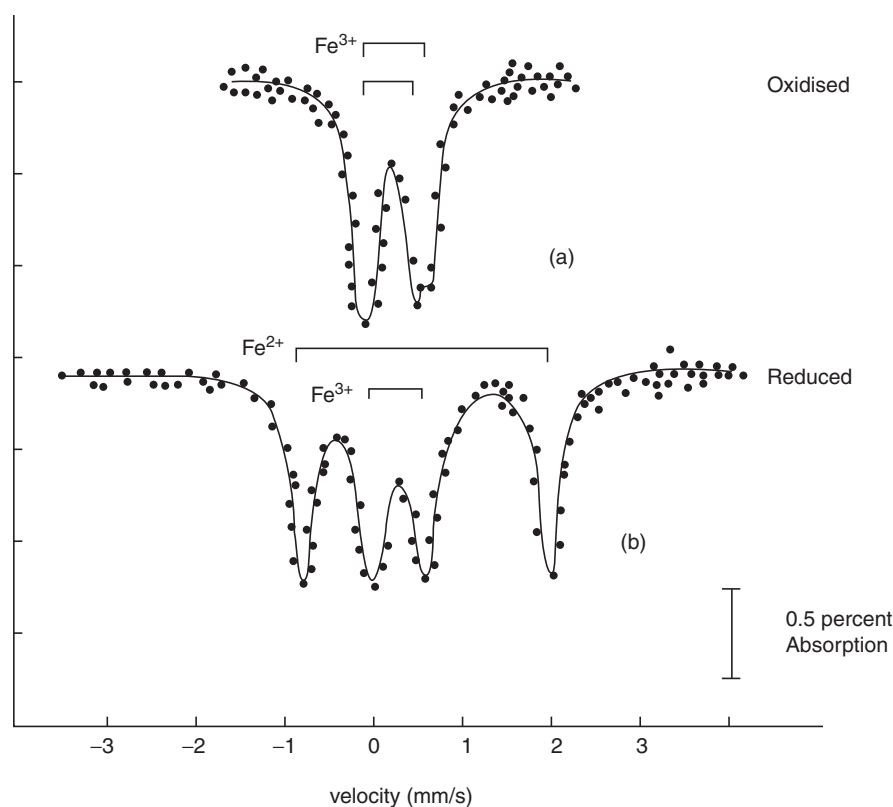


Fig. 10.64 Mössbauer spectra of (a) oxidised, and (b) reduced form of ferredoxin at 195 K.

forms of ferredoxin at 195 K (Pd ^{57}Co source) are shown in Fig. 10.64. Broadly speaking, the spectrum of the oxidised form [Fig. 10.64 (a)] appears to consist of two resonances of nearly equal intensity, while on reduction, clearly two doublets are observed, one due to Fe^{2+} and one due to Fe^{3+} [Fig. 10.64 (b)]. In both forms of the protein, the iron atoms are believed to be coupled together antiferromagnetically. When oxidised, there are two

Fe^{3+} atoms and their total spin is zero which agrees with their observed temperature independent susceptibility. However, the widths of the resonances are slightly more than that for a standard absorber. The analysis showed that the spectrum is made up of two quadrupole doublets having almost equal quadrupole interaction but slightly different isomer shifts, suggesting that the compound contains iron atoms in two inequivalent sites.

At low temperatures (4 K and below) no magnetic hyperfine interaction is noticed in the oxidized protein even under the influence of external magnetic field, suggesting the nonmagnetic nature of the molecule in the oxidised state. This leads to conclude that in the oxidised form of protein, the two iron atoms are coupled together antiferromagnetically to give zero spin which is consistent with the observed temperature independent magnetic susceptibility as stated earlier.

Based on the MB data, a model of active centre of ferredoxin has been proposed by Moshkovskii. According to this model, seven iron atoms are distributed linearly and are bound to each other by seven atoms of sulphur that are part of cysteine molecule and by six atoms of inorganic sulphur. Such a model has two related but non-equivalent environments, viz., two iron atoms at the ends of the chain and the remaining iron atoms within the chain.

The spectrum of the reduced form consists of two clear doublets [Fig. 10.64(b)], i.e. $\Delta E_Q = 0.56$ and 2.66 mm/s. The isomer shifts and quadrupole splittings corresponding to these doublets are different, suggesting that the compound in the reduced form has iron atoms in two non-equivalent sites.

The MB data, viz., δ_{IS} and ΔE_Q corresponds to high-spin $S = 2$, $\text{Fe}^{2+}(\text{II})$ and high spin $S = 5/2$, $\text{Fe}^{3+}(\text{III})$ configurations. The coupling between Fe^{3+} atom ($S_1 = 5/2$) and the Fe^{2+} atom ($S_2 = 2$) gives rise to a ground state with total spin $S = S_1 + S_2 = 1/2$. This model accounts for the unusual g -values centred around 1.94 found from ESR spectra of these molecules.

The spectrum of the reduced form of the protein shows magnetic hyperfine splitting at low temperatures, i.e. 4.2 K since at these temperatures the electron spin relaxation time becomes long compared to $\left(\frac{h}{2\pi A}\right)$ where A is the hyperfine coupling. The spins S_1 and S_2 precess about their resultant S , and the observed spectrum is asym-

metrical and has broad and partly resolved lines. When a small magnetic field $H_{\text{ext}} > AS/g\beta$ is applied, a more symmetrical spectrum with sharper lines results. The effect of the field is to cause S_1 and S_2 to precess about it and results in two separate effective magnetic fields at the nuclei. The resulting spectrum is the superposition of two contributions, one from Fe^{3+} and one from Fe^{2+} and the lines from each are strongly overlapping. Under high magnetic field (30 kOe, at 4.2 K), the spectrum splits into two components, each having different effective magnetic fields with opposite signs also, i.e. -180 kOe (Fe^{3+}) and $+120$ kOe (Fe^{2+}). This observation suggests that the two iron atoms are coupled antiferromagnetically in reduced ferridoxin also. Thus MB spectra provide direct evidence for antiferromagnetic coupling between the Fe^{2+} and Fe^{3+} iron atoms in plant type ferredoxins. Atoms with spins pointing up (i.e. parallel to resultant spin, S) have effective magnetic field at the nucleus reduced by the external field (since the hyperfine field is negative) so that their spectrum is compressed by the field. On the other hand, atoms with spins down, have their effective field increased, i.e. spectrum appears to expand in the external field.

(b) 4- and 8-iron Proteins These proteins include the bacterial ferredoxins which may contain four iron atoms per molecule, e.g. (Bacillus ferredoxin) or light iron atoms, e.g. from chromatium or clostridium as well as the high-potential iron proteins (HIPIP's) four iron atoms per molecule and the conjugated iron-sulphur proteins, e.g. flavoproteins, iron-molybdenum proteins containing eight or more iron atoms per molecule. The MB spectrum data for ^{57}Fe in oxidised and reduced iron-sulphur proteins at 195 K is given below.

State/Protein	Oxidised		Reduced	
	δ_{IS}	ΔE_Q	δ_{IS}	ΔE_Q
Ferredoxin (plant)	0.22	0.59	0.56 ^(a)	2.75 ^(a)
HIPIP	0.28 ^(b)	0.77 ^(b)	0.38 ^(b)	1.01 ^(b)
Ferredoxin (bacterial)	0.39 ^(b)	0.75 ^(b)	0.52 ^(b)	1.07 ^(b)

(a) Value for ferrous atom (b) Average value

Many features of the bacterial ferredoxins resemble with the simpler plant-type ferredoxins, i.e. their oxidised form is nonmagnetic and have negative redox potentials, while their reduced form is magnetic with an average g -value less than two ($g < 2$). Their MB spectra are more complex than 2-iron proteins. In eight iron

proteins, the high-temperature MB spectra do not show distinct quadrupole doublets corresponding to Fe^{3+} and Fe^{2+} states. At high temperatures (77 K and above), the spectra of both the oxidised and reduced form of proteins consist of the superposition of two or more closely similar doublets. The average isomer shift for the oxidised protein suggests that each of the two four-iron active centres consists of two Fe^{3+} and two Fe^{2+} atoms. Molecular structure of Peptococcus aerogenes shows that the iron in this 8-iron protein is in units containing four atoms close together (Jensen, Sieker, Watenpaugh, Adman and Herriott; Biochem. Soc. Trans. 1 (1973) 27). Both the average isomer shift and the quadrupole splitting increase in going from oxidised to reduced form. This conforms to one Fe^{3+} and three Fe^{2+} atoms per sub-unit in the reduced molecule. This change in isomer shift and quadrupole splitting on reduction shows that all the iron atoms are affected when one electron is added to each four-iron centre. The non-observance of spectra for Fe^{3+} and Fe^{2+} (as they are in reduced two iron plant ferredoxin) suggests that d -electrons are not localised on particular atoms but are shared equally by all four atoms in the four-iron centres.

The low-temperature (4 K and below) spectra of oxidised form do not show hyperfine splitting even when external magnetic field is applied confirming, thereby, the nonmagnetic nature of the molecule in the oxidised state. This suggests that the four-iron atoms in each sub-unit are antiferromagnetically coupled together to give zero spin in the oxidised state. On the other hand, magnetic hyperfine splitting has been observed in case of reduced form at low temperatures. This shows that all the iron atoms are magnetic. This demonstrates that one electron goes to each centre on reduction. Further, both positive and negative hyperfine fields have been observed when large external magnetic field is applied to the reduced form at low temperatures. Thus MB spectra provide direct evidence for antiferromagnetic coupling between iron atoms in bacterial as well as plant type ferredoxins.

The HIPIPs have four iron atoms per molecule all close together in a cluster. They have positive redox potentials and are nonmagnetic in the reduced form but they lose one electron per molecule when oxides and become magnetic with an average g value greater than two ($g > 2$). MB data on the reduced state confirm that it is nonmagnetic. MB spectra of oxidised form in the presence of applied magnetic fields show both positive (+90 kOe) and negative (−120 kOe) hyperfine fields. This shows antiferromagnetic coupling between iron atoms in the oxidised form of HIPIPs. The isomer shifts and quadrupole splitting suggests that there are two Fe^{3+} and two Fe^{2+} atoms in the nonmagnetic reduced state and three Fe^{3+} atoms and one Fe^{2+} atom in the oxidised state. Since no separate spectrum is observed for Fe^{3+} and Fe^{2+} shows that the d -electrons are mobile and not localised on particular iron atoms. The distribution of Fe^{2+} and Fe^{3+} atoms in the four iron centres of the oxidised and reduced forms of 4- and 8-iron proteins is summarised in the tabular form as below.

State/Protein	Reduced	Oxidised
HIPIP	$2\text{Fe}^{2+} + 2\text{Fe}^{3+}$	$1\text{Fe}^{2+} + 3\text{Fe}^{3+}$
Clostridium	$3\text{Fe}^{2+} + 1\text{Fe}^{3+}$	$2\text{Fe}^{2+} + 2\text{Fe}^{3+}$

10.16.4 Studies of Cytochrome-C

The enzyme cytochrome-C also contains a haeme unit attached to a protein and is associated with the oxidation of nutrients in the cell, i.e. the biological activity of cytochrome-C is associated with the reduction and subsequent oxidation of the haeme which occurs during the electron transfer down the enzyme chain. The MB spectra as well as the valence electron population on the basis of molecular orbital calculations of both the oxidised and reduced cytochrome-C are shown in Figs 10.65 and 10.66 respectively. The MB spectra of both the oxidised and reduced cytochrome-C (frozen solutions) consist of a symmetrical quadrupole doublet at high temperature (225 K). The quadrupole splitting of 2.3 mm/s in case of oxidised cytochrome-C is attributed to electron hole in the d_{xz} orbital. Dry cytochrome shows splitting of ~1.9 mm/s. The difference between the solid and solution state spectra may be attributed to the hydration of various protein chains in the vicinity of the haeme. However, the observed quadrupole splitting of 1.2 mm/s in case of reduced cytochrome-C could not be because of electron population in the t_{2g} orbital as in the case of oxidised cytochrome-C since all the electrons in the t_{2g} orbital exist in pairs. The splitting could be due to lattice EFG or because of selective delocalisation of $3d$ electrons. The observed isomer shift of 0.38 mm/s and quadrupole splitting of 1.2 mm/s show that iron exists as low spin $S = 0$ ferrous (II) in reduced cytochrome-C.

The MB spectrum of oxidised cytochrome-C becomes broaden and asymmetrical at lower temperatures between 150 and 100 K (broad magnetic spectrum at 4.2 K). The broadening followed by decrease in intensity of the wing of the doublet on the high velocity side is more as compared to its counterpart on the low-velocity side of the

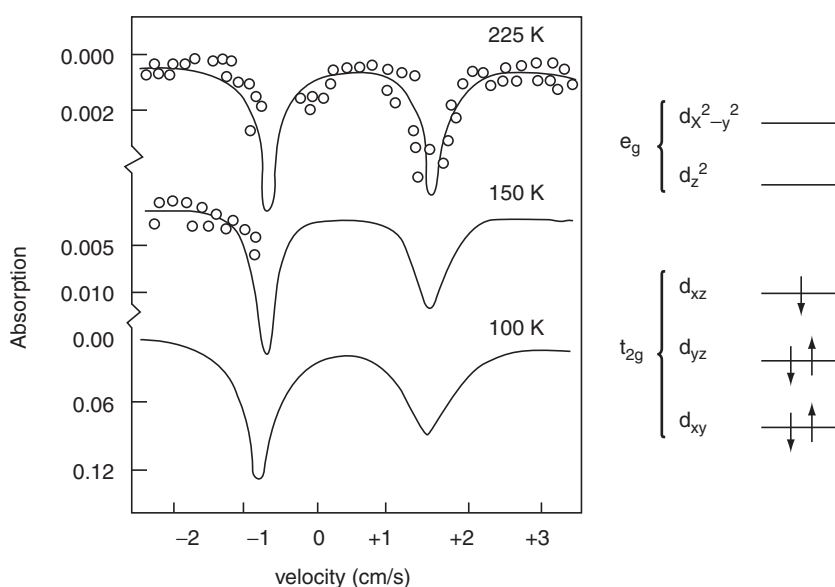


Fig. 10.65 Mössbauer spectrum of oxidised cytochrome-C in frozen solution.

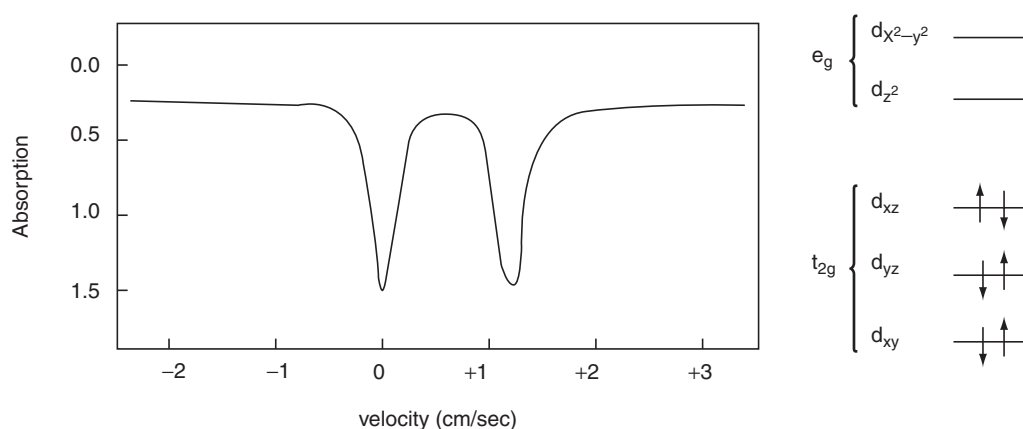


Fig. 10.66 Mössbauer spectrum of reduced cytochrome-C in frozen solution.

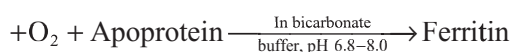
spectrum. The broadening is attributed to the magnetic hyperfine interaction which results because of slow-spin relaxation rates at low temperatures. The chemical isomer shift (relative to Fe) of 0.18 mm/s at 100 K, and magnetic broadening are compatible with low spin $S = 1/2$ iron (III) configuration with an electron hole in the d_{xz} orbital.

10.16.5 Ferritin

Ferritin is widely distributed throughout the various organs of mammals, with particularly high concentrations being found in liver, spleen and bone marrow. Physiologically, it represents a depot in which surplus iron can be stored within the cell in a nontoxic form and from which it can be mobilised as and when required either within that particular cell itself or in other cells of the organism. In cells of erythroid series (i.e. cells which are precursors of erythrocytes and which synthesise haemoglobin), transferrin molecules carrying Fe^{3+} bind to specific receptor sites on the cell membrane and transfer iron to the cells. This iron, probably, after reduction to Fe^{2+} is then incorporated into ferritin; the process involves oxidation to the ferric state. Ferritin iron then serves as a source of iron for haeme synthesis and its mobilisation requires reduction to Fe^{2+} .

Ferritin consists of a shell of protein sub-units surrounding a core of ferric hydroxy phosphate. Apoferritin is the term used for the protein part of ferritin. Native apoferritin is the term used to describe the nearly iron-free protein which can be isolated from ferritin by centrifugal techniques. Thus simple equation can be written to describe ferritin formation.

Fe^{2+} (Ferrous ammonium sulphate or ferrous sulphate)



The MB spectrum at liquid nitrogen temperature and above (Fig. 10.67) has an isomer shift and quadrupole splitting of 0.47–0.50 and 0.6–0.74 mm/s respectively. At low temperatures ($T = 11$ K) a six-finger hyperfine

spectrum is observed, characteristic of magnetic ordering. As the temperature is raised, the hyperfine spectrum is replaced by the paramagnetic quadrupole-split doublet spectrum. This super magnetism is because of antiferromagnetism of fine particles (super-antiferromagnetism) analogous to that seen in certain metal oxides reduced to fine powders.

The ESR and MB spectra of iron in ferritin over the range 4.2–295 K confirms that the temperature dependence of the spectra can be explained by the supermagnetic properties of the micelles. A weak ESR signal is also observed near $g = 4$ at 77 K and above and this is attributed to a small number of Fe^{3+} which are not bound to the micelle.

The MB parameters of ferritin and a synthetic polymer derived from hydrolysed ferric nitrate has a similar room temperature MB spectrum with isomer shift and quadrupole splitting of 0.48 and 0.67 mm/s respectively. At very low temperatures the spectrum of the polymer is also closely similar to ferritin.

The magnetic susceptibility of ferritin is markedly affected by magnetic field. At very high field $\mu_{\text{eff}} = 5.08$ B.M. The Curie point situated at -200 K proves the existence of a strong negative coupling between the atoms. MB studies show the progressive establishment of a magnetic order below 30 K. $\mu_{\text{eff}}(275\text{--}301\text{ K}) = 3.81$ B.M. μ_{eff} in the temperature range 4.2 – 300 K shows that ferritin is antiferromagnetic with a Neel temperature of 20 ± 3 K.

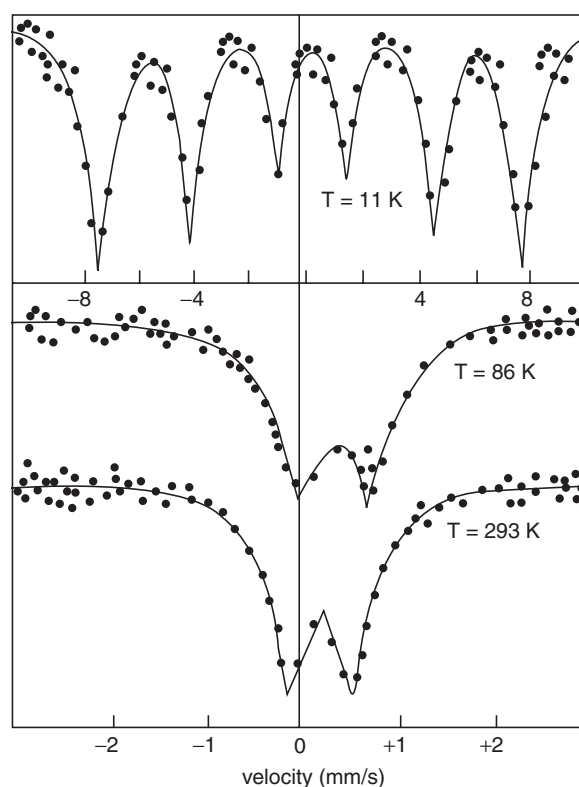


Fig. 10.67 Mössbauer absorption spectrum obtained using a ^{57}Co in Pd source at room temperature and ferritin as absorber at 11.86 and 293 K.

PROBLEMS

1. Using the data in Table 10.5 on p.i.s., predict the isomer shifts for

- (a) *cis*-Fe(SnCl₃)₂(ArNC)₄
 (b) [FeCl(ArNC)₅] ClO₄
 (c) *trans*-FeHCl(depe)₂
 (d) *trans*-Fe(CN)₂(MeNC)₄
 (e) *trans*-Fe(CN)₂(EtNC)₄

[Ans. Calc(obs) in mm/s: (a) + 0.24 (+ 0.27)
 (b) + 0.26 (+ 0.23) (c) + 0.42 (+ 0.39)
 (d) + 0.18 (+ 0.16) (e) + 0.18 (+ 0.21).]

2. Calculate the critical γ -ray energy for

- (a) ⁵⁷Fe ($\theta_D = 400\text{K}$, $f(T=0) = 5.4 \times 10^{-4}$)
 (b) ¹⁹²Os ($\theta_D = 315\text{K}$, $f(T=0) = 1.6 \times 10^{-3}$) and
 (c) ¹³⁹La ($\theta_D = 270\text{K}$, $f(T=0) = 1.5 \times 10^{-3}$)

[Ans. (a) 136.5 keV (b) 206 keV (c) 163 keV]

3. Calculate the recoil energy for the

- (a) 14.4 keV transition of ⁵⁷Fe
 (b) 23.87 keV transition of ¹¹⁹Sn
 (c) 57.60 keV transition of ¹²⁷I

[Ans. (a) 1.928×10^{-3} eV (b) 2.537×10^{-3} eV
 (c) 13.845×10^{-3} eV.]

4. Draw the energy-level diagram and the stick spectrum

for the MB $\frac{7}{2} \rightarrow \frac{5}{2}$ transition of ¹²⁷I in

- (a) polycrystalline state
 (b) $\theta = 0^\circ$
 (c) $\theta = 90^\circ$ indicating intensity and polarisation of the lines in the spectrum

5. (a) For ¹¹⁹Sn, $\mu_e = +0.67$ nm; $\mu_g = -1.047$ nm, $I_e = \frac{3}{2}$ and $I_g = \frac{1}{2}$. Prove that the separation between any

two consecutive magnetic hyperfine levels in the excited state is small as compared to their counterparts in the ground state.

- (b) Show that for ⁵⁷Fe (14.4 keV),

$$\frac{g_e}{g_g} = + \frac{\mu_e}{3\mu_g}$$

- (c) For ¹²⁷I, $I_g = 5/2$, $\mu_g = +2.809$ nm, $I_e = 7/2$ and $\mu_e = +0.202$. Prove that the separation between any two consecutive Zeeman levels in the excited state is approximately one half as compared to their counterparts in the ground state, i.e. $\beta > \alpha$.

6. From the data given below, calculate the bandwidth (in mm/s) of the respective nuclei. Also, determine the half life of the excited state.

Nucleus	$v(\text{cm/s})$	$E_\gamma(\text{keV})$
⁵⁷ Fe	9.6×10^{-3}	14.4125
⁶⁷ Zn	1.5×10^{-5}	93.31
¹⁹⁷ Au	9.4×10^{-2}	77.35

[Ans. Γ (in keV): ⁵⁷Fe: 4.612×10^{-12} ; ⁶⁷Zn: 4.665×10^{-14} ; ¹⁹⁷Au: 2.423×10^{-10}]

7. Using the data on p.q.s. from Table 10.12, calculate the quadrupole splitting for

- (a) FeCl(ArNC)₅ClO₄
 (b) *cis*-Fe(SnCl₃)₂(ArNC)₄
 (c) Fe(SnCl₃)₂(ArNC)₅ClO₄
 (d) *cis*-Fe(CN)₂(EtNC)₄

- (e) Fe(CN)(EtNC)₅ClO₄

[Ans. Calc. (obs) in mm/s: (a) -0.78 (0.73) (b) 0.52 (0.50)
 (c) -0.52 (0.32) (d) 0.30 (0.29) (e) -0.30 (0.17).]

8. The MB technique is only applicable for the range of lifetime 10^{-7} – 10^{-10} second. From the following data on line width of the ¹⁹⁷Au transmission at different thickness of metallic gold, calculate the half life of the ¹⁹⁷Au isotope.

$T_a(\text{mg/cm}^2)$	20	50	75	134	180
$\Gamma_{\text{exp}}(\text{mm/s})$	2.03	2.19	2.33	2.64	2.89

[Ans. $t_{1/2} = 9.8$ ns]

9. Assign the data given below to the *cis* and *trans*-forms of FeCl₂(ArNC)₄ where ArNC is *p*-methoxyphenyl isocyanate.

$\Delta E_Q(\text{mm/s})$	$\delta_{\text{IS}}(\text{SS})/\delta_{\text{IS}}(\text{Fe}) \text{ mm/s}$
-0.83	0.12/0.03
+1.59	0.20/0.11

10. From the data on tetrahedral high spin, (Et₄N)₂FeCl₄, calculate the value of quadrupole splitting at zero K and the energy difference between two d_γ levels.

Temperature K	$\delta_{\text{IS}}(\text{mm/s})$	$\Delta E_Q(\text{mm/s})$	$\Gamma(\text{mm/s})$
80	1.00	2.49	0.79
190	0.93	1.63	0.75

[Ans. 2.70 mm/s, 180 cm⁻¹]

11. For tin-119, calculate the line width and Doppler velocity to achieve resonance absorption. The transition energy of the 3/2 level is 23.8 keV, the half life is 19 ns.

12. The MB spectrum of ⁵⁷Fe ferrocene, Fe(C₅H₅)₂ at 20 K consists of two lines at -0.50 and +1.88 mm/s relative to a stainless steel source. Calculate the isomer shift and eqQ for the excited nucleus. Assume cylindrical symmetry.

[Ans. Shift = 7.9 MHz; $|eqQ| = 55$ MHz]

13. Predict the positions of quadrupole hyperfine lines in the MB spectrum of ¹²⁹I in KIO₃ from the data reported in Example 10.5(a).

14. The MB technique is only applicable for the range of lifetime of 10^{-7} – 10^{-10} second. Calculate the range of line width of the Mössbauer line.

15. The MB parameters as deduced from the MB spectra of ¹²⁹I in I₂ and in triethylamine (TEA)–I₂ complex (at 16K in CS₂ and with respect to ZnTe source) are

System	e^2qQ (MHz)	$\delta(\text{mm/s})$	$\eta(\text{per cent})$
I ₂	-2242	0.93	11
TEA–I ₂ (A)	-2604	1.56	...
(B)	-1261	0.40	9

The MB lines corresponding to (A) are more intense than (B) and the quadrupole coupling constant (e^2qQ) has been converted to ¹²⁷I. (a) Calculate the charge densities on the terminal and bridged iodine atoms from the quadrupole coupling constant as well as from the isomer shift data. (b) Determine the π bond character in the complex and (c). Comment on the nature of chemical bond in the charge transfer TEA–I₂ complex. $e^2Qq_{\text{atom}} = 2293$ MHz (for iodine atom)

[Ans. (b) 8 per cent]

CHAPTER 11

MASS SPECTROMETRY

To keep a lamp burning we have to keep putting oil in it.

—Mother Teresa

Never give up! If the end of the world were imminent, I still would plant a tree today.

—Unknown

11.1 INTRODUCTION

Broadly speaking, Mass Spectrometry (MS) deals with the sorting out the mass to charge (m/e) ratios of the positively charged fragments produced by bombarding the analyte (a few milligrams to submicrogram or even nanogram quantities in case of liquids and solids provided they are in the gaseous state and 0.1 mL to 10^{-8} mL in case of gases) with medium energy electrons (25–70 eV), under conditions of high vacuum (10^{-7} – 10^{-9} mm of Hg) as a function of their kinetic energies/intensities by applying an electric field and a magnetic field. MS has a dynamic history dotted with Nobel laureates and a continually advancing technology that has made significant inroads into drug discovery, protein characterisation, and even disease diagnosis. The history of science reveals that MS had its roots in physics, branched into chemistry and in the past two decades or so, has budded into biology.

The theoretical basis of MS lies in the Lorentz rule, according to which the force exerted by a magnetic field of strength H on an electron travelling at the velocity v at right angles to the lines of force is

$$F = \frac{q}{c} \vec{v} \bullet \vec{H} \quad (11.1)$$

which reduces to $F = evH$ for electrons assuming $c = 1$ (11.2)

where, e is the charge of the particle (the law is valid not only for electrons, but for any charged particles). When however a charged particle travels along the line of force in a magnetic field, the field has no effect on the particle. The above equation (11.1) is called the *Lorentz equation* after H A Lorentz, the Dutch physicist who proposed it in 1895. For his theoretical explanation of the Zeeman effect, he shared the Nobel prize in physics with P Zeeman in 1902. W Wien who got the Nobel prize in 1911 for laws governing radiation of heat was the first to show in 1898 that positively charged electrical entities produced in electric discharge anode tube were also deflected in a magnetic field. This paved the way for mass spectrometry. But the first mass spectrometer (then called the parabola spectrograph) was constructed by J J Thomson in 1912 in which positively charged fragments of polyatomics (e.g. those corresponding to COCl_2^+ , CO^+ , C^+ , O^+ , etc., from COCl_2), produced in an electric discharge anode tube, were separated by their different parabolic trajectories in electromagnetic fields and detection occurred by the ions striking a fluorescent screen or photographic plate. Note that he was the first to obtain a plot of the ion current as a function of mass to charge (m/e) ratios. However, it was not until 1920 that F W Aston first introduced the term ‘mass spectrum’ for such plots. The clear demonstration of mass spectrometry came at the end of World War I by F W Aston (Thomson’s protegee) who, in 1919, designed a mass spectrometer in which he used both electrostatic and magnetic fields to focus ions produced in electric discharge tubes on a photographic plate. In case of neon, he obtained two mass lines on the photographic plate at 20 and 22 with the intensity ratio of 10 : 1 consistent with the average mass of 20.20, the known atomic mass of neon. Note that Thomson was not able to assign these lines to the isotopes of Ne. Aston was presented with the Nobel prize in chemistry in 1922 for isotopic studies; he demonstrated the existence of isotopes in some thirty other gaseous elements. The first electron impact ion source and magnetic deflection mass spectrometer was introduced by A J Dempster in 1918. A beam of electrons from a hot-wire filament was used for the ionisation of volatilised molecules. Dempster’s magnetic deflection MS could not be used for precise mass measurements, but it was better suited than Aston’s instrument

for measuring relative abundances of the ionic species and was suitable for studying electron impact processes in gases. Electron impact ion sources are still widely used in modern mass spectrometers.

Thus, by 1920, the early instruments were capable of handing three types of measurements, viz., (i) precise mass determination, (ii) measurement of relative abundances of ions, and (iii) electron impact studies. However, the full potentialities of the methods of mass spectrometry were realised when in February, 1942, the first commercial mass spectrometer was built and this was considered the birth of the present-day mass spectrometry. The chronology regarding the historical developments in present-day mass spectrometry is summarised below.

<i>Year</i>	<i>Contribution</i>
1946	Time of flight mass analysis
1949	Ion cyclotron resonance
1953	Double focussing instruments
1953	Quadrupole analysers
1956	High resolution mass spectrometry
1966	Peptide sequencing
1966	Chemical ionisation
1968	Electron spray ionisation
1969	Field desorption mass spectrometry of organic molecules
1974	Plasma desorption mass spectrometry
1974	Fourier-transform spectrometry
1978	Triple quadrupole mass spectrometry
1981	Fast atom bombardment
1983	Matrix assisted laser desorption/ionisation
1984	Electron Spray Ionisation (ESI) on biomolecules
1990	Protein conformational changes with ESI mass spectrometry
1991	Micro ESI
1991	Non covalent complexes with ESI mass spectrometry
1993	Oligonucleotide ladder sequencing
1993	Protein mass mapping
1996–2001	Intact viral analysis
2002	J B Fenn and K Tanaka shared the 2002 Nobel prize in chemistry of their works on developing soft ionisation techniques for large biomolecule analysis

11.2 COMPARISON OF MASS SPECTROMETRY WITH OTHER SPECTROSCOPIC TECHNIQUES

The techniques of mass spectrometry and photoelectron spectroscopy resemble in that they are based on the principle of ionisation of gases under high vacuum, but in the former, positively charged fragments formed when the sample is bombarded with medium energy electrons (25–70 eV) are sorted out as a function of their kinetic energies while in the latter, the sample is irradiated with UV (10–45 eV)/x-ray (200–2000 eV) radiations. Milligrams of a sample are required for PES while for mass spectrometry subnanogram quantities of a sample are sufficient.

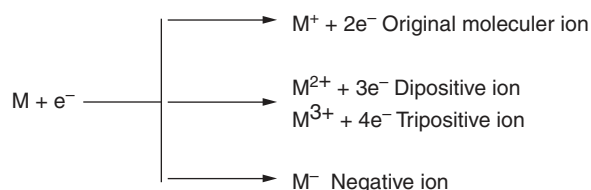
Mass spectrometry differs from electromagnetic spectroscopy in that the ions are separated according to their masses in the former while in the latter, electromagnetic waves are separated according to wavelengths. Mass spectrometry permits us to determine the molecular mass and molecular formula of a compound as well as certain structural features. Infrared spectroscopy gives us information about the types of functional groups present in the molecule. Ultraviolet/visible spectroscopy imparts information about the conjugation contained in a molecule. NMR spectroscopy imparts information about the arrangement of functional groups present in the molecule while electron-spin resonance spectroscopy tells us about the presence of free radicals in the molecule.

Furthermore, mass spectrometry is not a pure spectroscopic technique since chemical reactivity is involved in the fragmentation, i.e. decomposition process. But it is still considered an analogue of the spectroscopic methods since it complements the information provided by spectroscopic techniques, namely, infrared, ultraviolet/visible, nuclear magnetic resonance, etc.

11.3 VARIOUS TYPES OF IONS ENCOUNTERED IN MASS SPECTROMETRY

When a molecule of mass M , which is in the gaseous state, under conditions of high vacuum (10^{-7} – 10^{-9} mmHg) is bombarded with medium energy electrons (25–70 eV), the initial processes which can occur are the following:

(a) Parent or Original Molecular Ion As a rule, electron bombardment ejects one of the valence electrons, i.e. one of the free (unshared) electron pair of a hetero atom or one of the π -electrons of an aromatic system or a multiple bond to produce a highly excited positively charged ion (in time of the order of 10^{-15} second) known as the parent molecular ion or simply molecular ion. The molecular ion is formed when the energy of the bonding electrons is equal to the ionisation energy of the molecule and the lifespan of the molecular ions is of the order of 10^{-10} – 10^{-3} second.



For molecules containing multi-isotope elements, a number of different isotopologue molecular ions will be formed. The one containing the most abundant naturally occurring isotopes of all atoms that make up the molecule is termed the *mono-isotopic molecular ion*, whereas the others are termed isotopic molecular ions. The most abundant of these isotopologue molecular ions is sometimes termed the *top molecular ion*. The mass of the molecular ion is by definition, calculated for the mono-isotopic molecular ion using therefore the masses of the most abundant isotopes with a correction for the mass of the electron(s) that has been removed. For instance, electron ionisation of BF_3 gives two isotopologue ions, $^{10}\text{B}^{19}\text{F}_3^+$ of m/e : 67 and $^{11}\text{B}^{19}\text{F}_3^+$ of m/e : 68, the heavier one being the (top) mono-isotopic molecular ion with a nominal mass of 68 Da since ^{11}B is more abundant than ^{10}B . The lighter ion of m/e : 67 $^{10}\text{B}^{19}\text{F}_3^+$ is an isotopic molecular ion. The mass of molecular ion of ethylbromide $\text{C}_2\text{H}_5^{79}\text{Br}$ will be equal to $[29.039 + 79.918 - \text{mass of the electron } (m_e)]$. This is equal to $107.957 - m_e$, Da, based on the standard that the mass of the isotope $^{12}\text{C} = 12$ Da exactly.

Formation of some typical molecular ions are shown here.

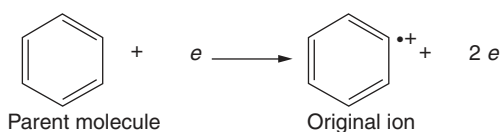
Removal of an electron from hetero atom.



Removal of π -electron from a multiple bond:



Removal of π -electron from an aromatic system:



(b) Fragment Ions A molecular ion is labile due to high degree of excitation, undergoes a number of successive fissions with the formation of positively charged ions called fragment ions and neutral molecules or radicals.

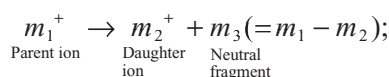
The decomposition or fragmentation of the molecular ion usually involves the fission of the bonds near the site of localisation of the positive charge. Bond fissions that occur without migration of individual atoms or groups are known as ordinary fissions and the resulting ions are termed as ordinary fragment ions. Such ions are a part of the original molecule.

In particular cases, fissions can also occur with migration of individual atoms or groups. Such fissions are termed *rearrangement fissions* and the fragment ions which result because of such fissions are known as *rearrangement ions*. Hydrogen-transfer rearrangements are most common, though migration of an alkyl group can also occur. For example, in the mass spectrum of *n*-butyraldehyde (C_4H_8O), the parent molecular ion is $C_4H_8O^{+\bullet}$ ($m/e : 72$). The ordinary fragment ions are $C_4H_7O^{+\bullet}$ ($m/e : 71$), $HCO^{+\bullet}$ ($m/e : 29$), $C_2H_3O^{+\bullet}$ ($m/e : 43$) and $C_3H_5O^{+\bullet}$ ($m/e : 57$). The ion $C_2H_4O^{+\bullet}$ ($m/e : 44$) is formed via rearrangement process.

The internal energy E_{int} of the precursor ion may affect the rate constant, k , for a particular ion decomposition. Molecular ions containing internal energy $< E_a$, the activation energy, cannot decompose, irrespective of the amount of time allowed for decomposition. If $E_{int} > E_a$, the probability of decomposition of $M^{+\bullet}$ in the source depends on the rate constant, k , $\ln [M^+]_0/[M^+] = kt$. For conventional mass spectrometers, ions whose half-life corresponds to the ion source residence time, decompose with rate constants of $\approx 10^6/\text{second}$.

(c) Multicharged Ions Dipositive or tripositive ions are also encountered in a mass spectrum. The peak corresponding to the doubly charged ion appears at m/e which is one half of that fragment while that of the triply charged ion appear at m/e which is one third of that fragment, e.g. in the mass spectrum of CH_4 there are observed lines corresponding to the following values of $m/e : 16, 15, 14, 13$ and 8 . The values at $m/e : 16$ and 8 correspond to the singly charged ion CH_4^+ and doubly charged ion CH_4^{++} ($m/e : \frac{1}{2}(CH_4^{++}) = \frac{1}{2} \times 16 = 8$) respectively. The peaks at $m/e : 15, 14$ and 13 are due to the fragment ions CH_3^+ , CH_2^+ and CH^+ respectively. Mass spectrum of chrysene (molecular mass = 228) shows molecular ion peak M^+ at $m/e : 228$ (45 mm) and a doubly charged peak at M^{2+} at $m/e : 114$ (8 mm).

(d) Metastable Ions Neutral fragments produced in process of fragmentation, e.g. $M^+(g) \rightarrow m_1^+ + m_2$ or $m_1 + m_2^+$ cannot be detected in the mass spectrum since they can never qualify the condition kinetic energy = eV ($e = 0$ for neutral particles). However if an ion of mass m_1 , called the parent or original ion having a lifetime of the order 10^{-5} – 10^{-6} second decomposes while traversing the field-free region before the magnetic field to another charged fragment of mass m_2 called the product or daughter ion and to a neutral fragment of mass $m_3 = m_1 - m_2$, i.e.



the resultant peak neither appears at m_1 , nor at m_2 , since the daughter ion m_2^+ does not qualify the condition of kinetic energy = eV obeyed by the parent or daughter ion formed in the ion source; and the parent ion m_1^+ imparts some of its kinetic energy to the daughter ion m_2^+ and to the neutral fragment m_3 in the ratio of their masses. Accordingly, the kinetic energy of m_2^+ ion formed in the field-free region equals $\frac{m_2}{m_1} \text{eV}$ which is less than that of the normal m_2^+ ion by a factor of $\frac{m_2}{m_1}$. Hence the peak due to m_2^+ ion formed in the field-free region neither appears at m_1 , nor at m_2 (i.e. the normal positions for m_1^+ and m_2^+ ions on the mass scale in the spectrum) but appears as a metastable peak (m^*), the position of which is given by the relationship

$$m^* = \frac{m_2}{m_1} \times m_2 = \frac{(m_2)^2}{m_1} \quad (11.3)$$

The peaks due to metastable ions are weaker and broader compared to the normal peaks due to parent and daughter ions. The relative abundance of metastable peaks is of the order of 10^{-2} or less compared to normal peaks because the metastable peaks are given by reactions with rate constants in the region of 10^4 – 10^6 s^{-1} (contributions from ion lifespan of about 10^{-6} s). The rate constant grows from 10^4 – 10^6 s^{-1} in a very narrow range of energies given by the expression

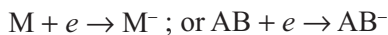
$$k = v \left(\frac{\Delta E}{E_a} \right)^{S-1 = 3n-6 \text{ or } 3n-5} \quad (11.4)$$

Here, $\Delta E = E_{\text{int}} - E_a$; E_{int} is the internal energy of the reacting ion and E_a is the activation energy for decomposition, and ν is the frequency factor and so very few ions have these energies, i.e. ΔE . The broadening of metastable peaks occurs since some of the exciting energy leading to bond fission may be converted into additional kinetic energy. Further in a spectrum which is linear with respect to m/e values, metastable peaks lie on the lower side of m_2 normal peak on the mass scale and the magnitude of distance of m^* from the daughter ion m_2 is similar to that of the daughter ion below the parent ion. Mass spectrometers in which the mass scan has an exponential function, m_2 will be equidistant between m_1 and m^* . The metastable peaks usually occur at non-integral values of m/e . Note that the absence of a metastable peak from the spectrum does not prevent a particular decomposition.

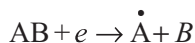
The study of metastable ions is helpful in detecting the mode of fragmentation of a particular compound and the presence of such peaks suggests that the reaction $m_1^+ \rightarrow m_2^+ + m_3$ takes place in one step, e.g. mass spectrum of toluene (C_7H_8) shows strong peaks at m/e : 91, 65 and a weak metastable peak at 46.4. The metastable peak at 46.4 reveals that the reaction m/e : 91 $\rightarrow$ 65 is occurring. Mass spectrum of tolylphenylether ($\text{C}_{13}\text{H}_{12}\text{O}$) exhibits a parent peak at m/e : 184 (10 percent), the base peak at m/e : 91 and small peaks at m/e : 77, 65. Metastable peaks are located at m/e : 46.5 and 45.0. The presence of two metastable peaks at 46.5 and 45.0 indicates that the reactions m/e : 91 $\rightarrow$ 65 and 184 $\rightarrow$ 91 are occurring. Isopropylphenylthioether ($\text{C}_9\text{H}_{12}\text{S}$) exhibits a parent peak at m/e : 152 (45 per cent) and fragment ion peaks at m/e : 137 (7 per cent), 110 (100 per cent), 77 (7 per cent), 66 (11 per cent), 65 (8 per cent) and 43 (12 per cent). Metastable peaks are observed at m/e : 123, 79.6 and 54.1. The presence of three metastable peaks at 123, 79.6 and 54.1 indicates the reactions respectively at m/e : 152 $\rightarrow$ 137, 152 $\rightarrow$ 110 and 110 $\rightarrow$ 77.

(e) Negative Ions Occasionally negatively charged ions or anions are also encountered in a mass spectrum. They originate from the impact of electron on the molecule by the following processes:

- (i) Resonance capture or electron attachment



- (ii) Dissociative resonance capture (dissociative electron attachment)



- (iii) Ion-pair production



The threshold energy of electrons for this process is above 10–15 eV. This process can also be initiated by ionising radiations such as α -particles or photons. Negative ions are not commonly formed in this process.

All the three processes can occur under normal conditions (70 eV) but each process being pressure dependent, the relative abundance of ions will vary with the sample pressure. The formation of negative ions can be enhanced using low-energy electrons (2 to 4 eV) from an argon source. Since high source pressure (about 10^{-3} torr) is necessary for the production of anions by such processes, ion–molecule reactions are also common under these conditions. The most common ions produced in such processes correspond to M^- (resonance capture), $\text{M} - 1$ (loss of hydrogen), $\text{M} + 16$ and $(\text{M} - 1) + 16$; the latter two ions result due to the presence of oxygen in the ion source.

Negative ions also result in various types of reactions observed during negative-ion chemical ionisation.

(f) Franck–Condon Principle and Stability of Negative Molecular Ions The potential energy diagrams for the formation of negative ion by the impact of electrons are shown in Figs 11.1 (a)–(d).

The phenomenon of resonance capture may take place in two ways depending on whether the electron affinity of AB is (i) positive [Fig. 11.1(a)] or (ii) negative [Fig. 11.1(b)]. When the electron affinity is negative, a Franck–Condon transition results in an unstable anion $[\text{AB}^-]^*$ which may have energy either below or above the dissociation limit. When the energy of the excited anion is below the dissociation limit, it may disappear by the autodetachment process, i.e. $[\text{AB}^-]^* \rightarrow \text{AB} + e^-$ and if the energy of the excited anion is above the dissociation limit it may dissociate to give a radical and an ion, i.e. $[\text{AB}^-]^* \rightarrow \text{A}^\bullet + \text{B}^-$.

The molecular anions formed by resonance capture being less stable relative to autodetachment, are stabilised by radiation emission or by collisional deactivation. For significant collisional stabilisation at pressures of about 1 torr (CI pressure), the lifespan of the $[\text{AB}^-]$ species formed by resonance capture should be $>1 \mu\text{s}$.

In dissociative electron attachment, the vertical Franck–Condon transition (due to electron capture) produces a repulsive state of AB^- [Fig. 11.1(c)], the dissociation of which gives rise to an atom and ion, with excess internal and kinetic energies



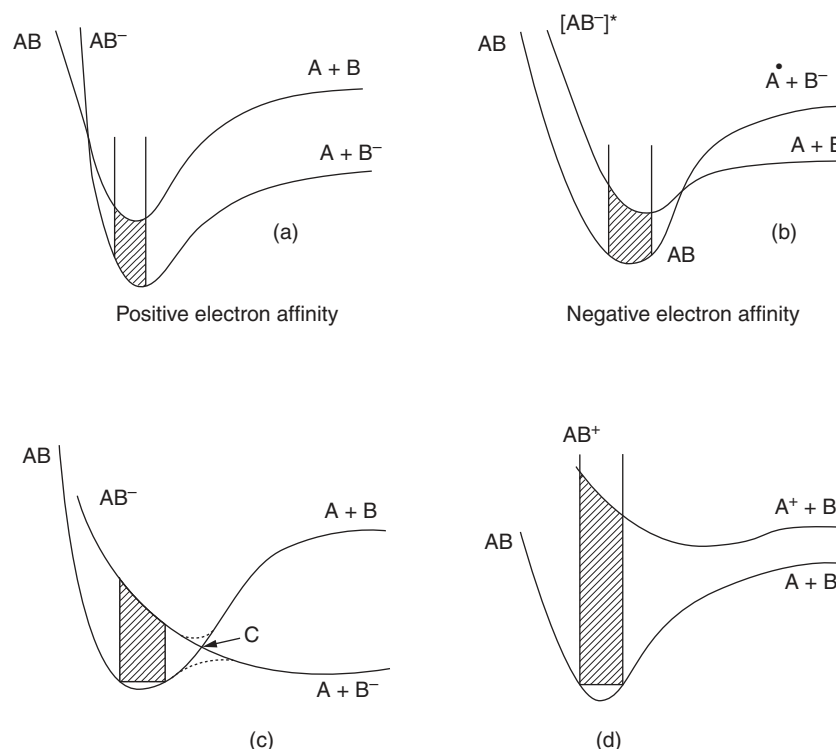
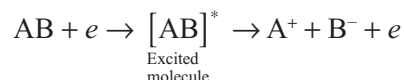


Fig. 11.1 Potential-energy diagrams for the formation of negative ion by electron bombardment.

The repulsive state of AB^- is also possible below point C by the tunnel process.

In ion-pair production, the vertical Franck–Condon transition results in an excited molecule which dissociates into a positive and a negative ion [Fig. 11.1(d)].



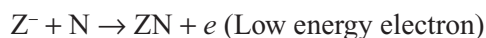
As already stated, the threshold electron energy for ion-pair production usually lies above 10 to 15 eV.

The specific electron energy required to generate a stable carbanion is determined from the ionisation energy curve of the system. For *p*-nitrobenzyl-*N*-acetylalaine, the specific electron energy curve shows a maximum at 2.9 eV and decreases to zero at about 7 eV. This energy (i.e. 2.9 eV) of electrons for the production of carboxylate anions from amino acid derivatives is very specific, a variation of 1 eV from 2.9 eV maximum, causes a substantial decrease in ion current, i.e. intensity.

Negative ions are not only produced by the interaction of an electron with a molecule but can also be generated by negative ion chemical ionisation. The various types of ion-molecular reactions observed during negative-ion chemical ionisation are:

(i) Electron–molecule Interactions The phenomena involved for the production of negative ions by this process has already been discussed (see negative ion in this section).

(ii) Associative Detachment Reactions Such reactions take place between an anion (Z^-) and a neutral molecule (N) to give an electron.



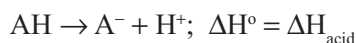
Such low-energy electrons are used to produce stable anions.

(iii) Displacement Reactions Such reactions in the gas phase $Z^- + RY \rightarrow ZR + Y^-$ are equivalent of the S_N2 reactions in solutions; for example the reaction of Cl^- with *cis*- and *trans*-4-bromocyclohexanol in the gas phase takes place with inversion of configuration as expected for S_N2 displacement reactions.

Displacement reactions occur provided they are exothermic and there is no facile proton transfer process from RY to Z^- , e.g. the reaction between OH^- ion and CH_3CN takes place by proton abstraction but not by displacement of CN^- , i.e.

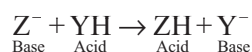


(iv) Proton Transfer/Deprotonation Reactions The gas phase acidity scale is defined in terms of ΔH° for the reaction



Here, ΔH° represents the proton affinity of A^- . Since ΔH° is positive, the acidity is greater, the smaller the $\Delta H_{\text{Acid}^\circ}$.

Accordingly, the deprotonation reaction

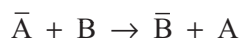


will occur or will be exothermic provided acidity of YH is greater than that of ZH in the gas phase or the proton affinity of Z^- is greater than that of Y^- in the gas phase.

Some proton-transfer reactions are of importance in negative-ion chemical ionisation mass spectrometry not only because of their efficiency, but also because of the formation of $[\text{M}-\text{H}]^-$ ions which provide information about the molecular anion.

(v) Association Reactions Third-order association reactions for anions are as common as for positive ions. Just like cations, anions in the presence of polar solvents such as water also form solvated species commonly via third-order mechanism. The magnitude of third-order rate constants for such anionic reactions is similar to that of similar positive ion reactions including those for solvation reactions.

(vi) Charge-Exchange Reactions Such reactions can take place exothermically as well as endothermically also. The charge exchange reaction



will be exothermic, if the electron affinity of B is greater than that of A and endothermic provided electron affinity of B is smaller than the electron affinity of A. In addition to exothermic charge-exchange reactions, the study of endothermic reactions as function of ionic translational energy reveals that the energy threshold for endothermic reactions can be used to establish the difference in electron affinities of the reactions.

11.4 BASIC PRINCIPLES OF MASS SPECTROMETRY

The technique of mass spectrometry is based on the principle of ionisation of gaseous molecules under vacuum and segregating the positively charged fragments according to their mass/charge ratio, i.e. m/e groups as a function of their relative abundance (intensity) using electrostatic field and uniform magnetic field.

11.4.1 Theory

The basic theory which laid the foundation for manufacturing the various types of magnetic deflection instruments to measure the m/e ratio of each of the positively charged fragments as a function of their numbers or kinetic energy is described here.

When ions of mass m and charge e are made to pass through a static electrostatic field of voltage V they gain energy equal to the work done by the electrical forces, i.e. eV . The kinetic energy of an individual ion when it leaves the electrostatic accelerating field is thus given by

$$\frac{1}{2}mv^2 = eV \quad (11.5)$$

where, v is the velocity of an ion leaving the accelerating electrostatic field. Algebraic rearrangement of Eq. (11.5) yields

$$v = \sqrt{\frac{2eV}{m}} \quad (11.6)$$

When the accelerated ions with velocity v are subjected to a perpendicularly directed uniform magnetic field of strength H , they experience a magnetic centripetal force given by Lorentz law

$$F = evH \quad (11.7)$$

The magnetic field deflects the ions from their initial direction differently according to their mass to charge ratio and thus are separated into m/e groups, each of which moves in a path with different radius of curvature r . Since the force exerted by the magnetic field on the ion is a centripetal force, it must be equal to the centrifugal force on the ions coming out of the accelerating field and we can readily calculate the radius of the circular path equating mv^2/r and evH , i.e.

$$mv^2/r = evH \quad (11.8)$$

Thus, the radius of the path is

$$r = \frac{mv}{eH} \quad (11.9)$$

Substituting the value of v from Eq. (11.6) into Eq. (11.9), we get

$$r = \frac{m}{eH} \sqrt{\frac{2eV}{m}} \quad (11.10)$$

Algebraic rearrangement yields

$$\frac{m}{e} = \frac{H^2 r^2}{2V} \quad (11.11)$$

For a particular value of V and H ; $r^2 \propto m$ and thus at the point of focus only the mass m^+ collects and those of higher mass will be above and below it. If we now have a tube of definite radius and a slit at the other end of it only the masses satisfying the equation (11.10) will enter. However, by varying either the electric field or magnetic field or both, other masses can be made to come to focus at the same point. In practice, one of them is kept constant and the other is continuously varied such that masses come to focus one after the other like 1, 2, 3, ... n . The results are recorded suitably. When electric field is kept constant and magnetic field is varied, it is called magnetic scanning and vice versa. The electrostatic scanning is easier to design but because

$$m \propto \frac{1}{V},$$

a wide range of masses cannot be scanned with one setting of the magnetic field. On the other hand, since $m \propto H^2$, it is possible to cover masses from 12–500 or 1000 Da in one spectrum.

11.4.2 Basic Principle of a Simple Mass Spectrometer

The schematic diagram of a simple single focussing low-resolution mass spectrometer for recording the mass spectrum of charged particles is shown in Fig. 11.2. The five major component parts of the mass instrument are vacuum system, inlet sample system, ionisation chamber/reservoir, analyser tube and magnet; and detector and recorder.

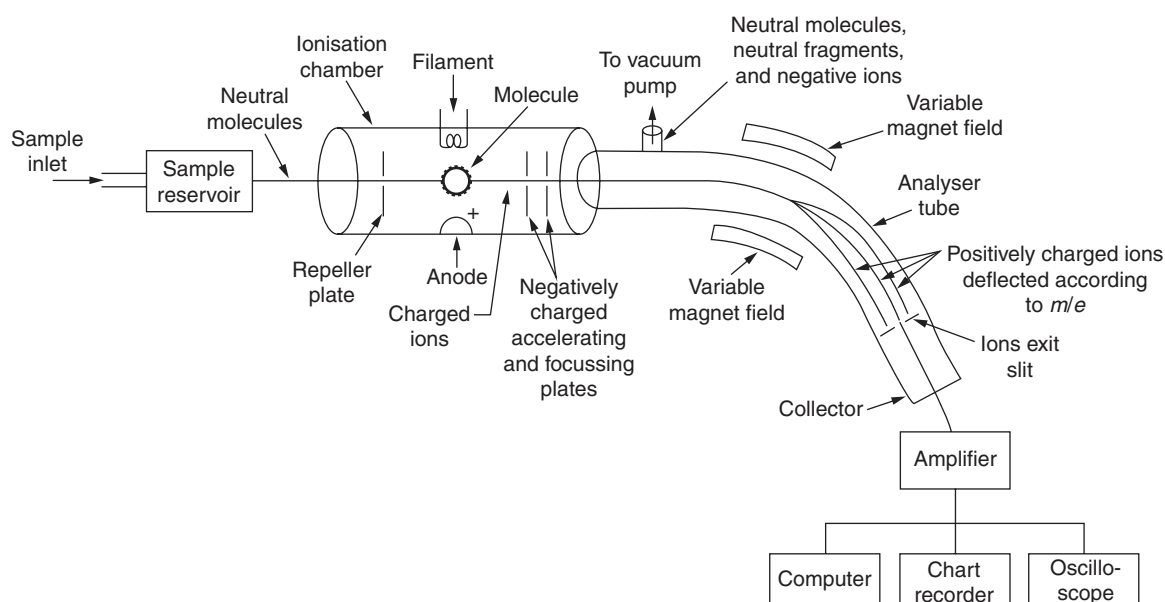


Fig. 11.2 Schematic diagram of a mass spectrometer.

(a) Vacuum System It is an essential part of the mass spectrometer and it operates at a very low pressure (10^{-6} – 10^{-7} mmHg). The low pressure is maintained in order to avoid collisions, between the charged ions and the air molecules otherwise the ions will get scattered and will not reach the collector and also secondary reactions will occur. The high vacuum is achieved by using mercury diffusion pump in addition to a mechanical pump or an oil diffusion pump in addition to a mechanical pump. In the former, traces of mercury may appear and are sometimes useful for indexing the mass numbers. While in the latter a few peaks due to hydrocarbons are obtained in the blank which does not affect the performance of the spectrometer but can be eliminated by the use of mass molecular sieve trap for hydrocarbons in the source and ionising regions of the spectrometer.

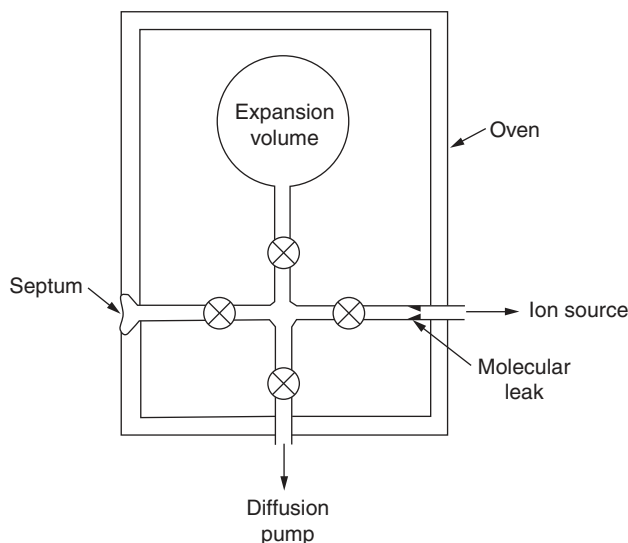


Fig. 11.3 Standard diagram of a sample inlet system.

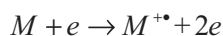
(b) Inlet Sample System The mode of introduction of the sample into the ionisation chamber depends upon the method of the production of charged ions. When the ions are to be generated by electron bombardment, the sample should flow as a gas. For gaseous samples, the inlet sample system usually consists of an evacuated chamber of 1–2 litres capacity at a pressure of about 100–200 μ Hg (Fig. 11.3). The sample is allowed to diffuse into the ionisation chamber through a sinter, i.e. tiny orifices; the rate of diffusion must remain constant throughout so that the relative abundance of masses in the mass spectrum may become of some sense in qualitative analysis and is discussed in Section 11.4.2.1.

The pressure in the sample chamber is measured and it bears a constant relationship to the pressure in the ion chamber. The sample chamber can be heated up to 400°C in order to vapourise the volatile liquids and solids. A few micrograms of high boiling liquids or solids can directly be introduced into the ionisation chamber on the end of a probe. In such cases, sample vapour pressure of about 10^{-6} mmHg at the operating temperature of the ion source would suffice. Many substances in the molecular mass range of 300 to 1200 fall into the latter class. Moreover, in favourable cases, useful information can be obtained from samples in the ng to pg (10^{-9} – 10^{-12} g) range. The high sensitivity of the method is one of its greatest advantages.

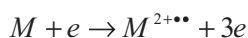
Note that these methods are not suitable for highly nonvolatile substances such as metals, oxides and refractory materials since sufficient vapour cannot be developed to flow the vapour into the ion source. In such a case other methods of ionisation like surface ionisation, spark discharge, field ionisation, etc., are used and are discussed in detail in Section 11.6.

(c) Ionisation Chamber Ionisation chamber contains an electron impact ion source and positive ion repelling and an ion-accelerating systems. The ion-repelling system acts as negative ion and electron trap also. The chamber is maintained at a pressure of 0.005 torr and at a temperature of 200°C. The stream of neutral molecules entering the ion chamber is ionised by the electron bombardment. Electrons are produced by heated rhenium or thoriated indium or carbonised tungsten filament and collimated towards an anode by a small magnetic field (of the order of 100 G) which is confined to the ionisation region only. At the time of collimation, the electrons are subjected to a controllable electric field varying from 5–75 V.

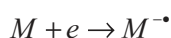
These energetic electrons intercept the neutral molecular stream at right angles to their flow. A range from 5–14 V is used for molecular mass determination and to study isotopically labelled compounds. The impact electrons eject one (or occasionally two) electrons from the outermost shells. Therefore for a molecule M, we have



or occasionally



The electron may also be captured by the neutral molecule to produce a negative radical ion; the formation probability of which is 10^{-2} – 10^{-3} as compared to that of $M^{+\bullet}$ radical cations



When the electrons are highly energetic (50–75 eV), the fragmentation of the molecular ion (M^+) results in fragment ions of varying masses. The positively charged ions (parent or fragment or both) so produced are repelled by the repelling electrode (positive) placed just behind the ionisation region towards the accelerating region where they are subjected to electrostatic field of several kilovolts (400–8000 V) of energy. The entire assembly consisting of ion source, ion-repelling electrode and ion accelerating system is known as ion gun. The ions of masses $m_1, m_2, m_3, \dots$, etc., are accelerated in the accelerating region to their final velocities. The ions leaving the accelerating region will have velocities and kinetic energies given by

$$eV = \frac{1}{2}mv_1^2 = \frac{1}{2}mv_2^2 = \frac{1}{2}mv_3^2 = \dots \quad (11.12)$$

(d) Mass Analyser The heart of any mass spectrometer is its analyser. The analyser tube is a semicircular tube of 1–2 cm (internal diameter) and made of nonmagnetic material like copper or inconel and highly polished inside. The ion beam from the ionisation chamber passes from the ion source to the collector. The ion path diameter is about 15–20 cm. The entire ionisation chamber, analyser tube and collector are housed between the two poles of a powerful magnet (4000–6000 G). The uniform and variable magnetic field is applied perpendicular to the direction of the ion path. An ion takes about 1–5 μs to leave an electron impact source after its formation and about 1 μs to traverse the field free region in front of the magnetic analyser. For fixed values of accelerating electric field and the magnetic field, only ions of a particular mass reach the ion detector of the instrument, other ions collide with the walls of the tube and collapse. If a fragment's path matches the curvature of the analyser tube, the fragment will pass through the tube and out the ion exit slit.

(e) Ion Detector and Recorder The ions passing through the slit at the other end of the analyser tube are often collected either on a collector or on a photographic plate. The ion collector is linked through amplifying circuits to a recorder. This is, in turn, coupled with a variable magnetic field, and as the strength of this field is gradually increased, ions of increasing mass enter the collector. A collector records the relative number of fragments with a particular m/e passing through the slit. The more stable the fragment, the more likely it will make to the collector. By slowly increasing the strength of the magnetic field, fragments with progressively larger values of m/e can be guided through the tube and come out through the exit slit. Usually, for high-resolution works, the ions are collected on an electrode called the *electron multiplier* or *dynode*. The ion beam strikes the surface of a dynode of a multistage Be–Cu electron amplifier (12–20 dynodes) as shown in Fig. 11.4. The collision releases a number of electrons from this surface. The electrons are accelerated to a second such surface. The latter surface generates several electrons each time a single electron impinges on the surface. The process is continued until a cascade of electrons arrives at the collector. In this way, a single fragment ion can produce hundreds of electrons. Since the charge on one ion is 1.6×10^{-19} coulomb, the gain of the multiplier can be calculated. A typical single spike might be 10^{-10} ampere in height and 10^{-3} second in width, so that charge equals $10^{-10} \times 10^{-3} = 10^{-13}$ coulomb. The multiplier gain is thus $\frac{10^{-13}}{1.6 \times 10^{-19}} = 6.3 \times 10^5$. The ion beam currents which are of the order of $10^{-15} - 10^{-5}$. After amplification by the above technique are fed into a recorder and the results are displayed as peaks. The heights of the peaks (which are proportional to peak areas) are proportional to the number of ions (i.e. relative abundances) of each mass. For a doubly charged ion of mass M , the peak will appear at a mass value of $M/2$. Thus the mass spectrum is a plot of number of ions of each mass against their mass to charge ratios.

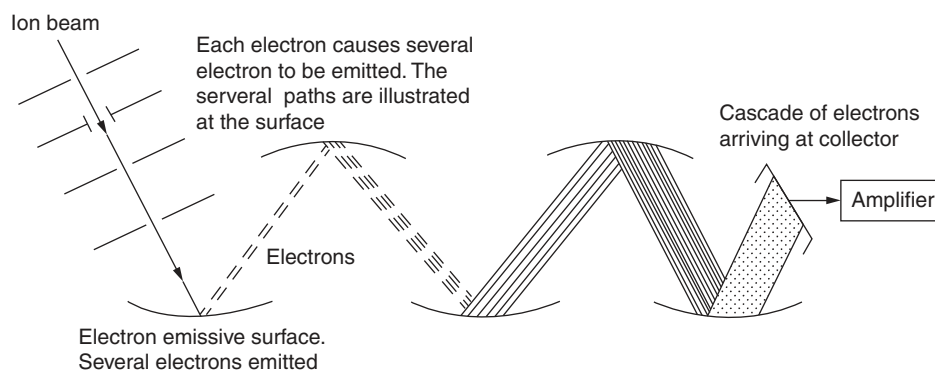


Fig. 11.4 Schematic diagram of dynode amplifier.

The mass spectrum in the bar graph form or in the peak form is displayed on an oscilloscope or recorded on a paper chart as shown in Fig. 11.5. The peak of highest intensity is called the *base peak* and is assigned a value of 100 per cent. The intensities (height $\times$ sensitivity factor) of other peaks, including molecular ion peak, are expressed as percentages of the base peak.

Modern mass spectrometers are coupled with computers for storing and analysing data. When the peaks at the higher end of the spectrum are weak and the background trace is indistinct, a calibrant which gives a large number of peaks is used. Perfluorokerosene is often used for indexing the mass numbers.

The utility of the mass spectrometer depends upon one of its most important parameters, called the *resolving power*. The greater the resolving power of the mass spectrometer, the better is its utility as an analytical tool. Sensitivity is the other most important parameter that is used in the evaluation of mass spectral performance.

(i) Rate of Sample Flow to the Mass Spectrometer Since the molecular flow rate is inversely proportional to the square root of molecular mass, the molecular conductance will be lower for higher molecular compounds. The leak conductance for normal operation should be in the range 0.1–0.4 cc/s.

Suppose the molecular conductance (C) of a peak is specified as 0.4 cc/min for N_2 at 25°C . For molecular mass of 200, the conductance will be $0.4 \text{ cc/min} \times \sqrt{28/200} = 0.15 \text{ cc/min at } 25^\circ\text{C}$. Since the effusion rate is proportional to the square root of the absolute temperature ($C_{or} = A \sqrt{RT/2\pi M}$ lit/s if T is in K and R is in ergs/K/mole, C_{or} is the orifice conductance), then at 150°C (423 K), the conductance for a molecular mass of 200 will be $0.15 \text{ cc/min} \times \sqrt{423/298} = 0.21 \text{ cc/min}$. This value can be used to determine the rate of sample flow to the mass spectrometer. If $2 \times 10^{-4} \text{ g}$ of ethyl decanoate is injected into a 1-litre inlet at 150°C , the inlet pressure, as calculated from $PV = nRT$ comes out to be $2.6 \times 10^{-2} \text{ torr}$ (1 Torrecelli = 1 mmHg pressure).

The rate of sample flow or effusion to the mass spectrometer can be calculated from a variation of gas formula in which the static volume V is replaced by the volume flow rate C . Thus

$$n(\text{moles/s}) = \frac{PC}{RT} \quad (11.13)$$

where, P = pressure in torr, C = conductance, lit/s, R = gas constant, 62.3 lit torr/mole K, T = absolute temperature.

For $P = 2.6 \times 10^{-2} \text{ torr}$, $C = 0.21 \text{ cc/min}$, and $T = 423 \text{ K}$, the number of moles of ethyl decanoate (molecular mass = 200) effusing to the mass spectrometer per second will be $2.4 \times 10^{-10} \text{ mole/s}$ or $4.8 \times 10^{-8} \text{ g/s}$. This amount of sample will give an intense mass spectral pattern in most mass spectrometers operating at a resolution of 500–1000. For vacuum calculations, the unit of litre torr/s is often preferred.

Accordingly, Eq. (11.13) then reduces to

$$Q = PC. \quad (11.14)$$

at constant temperature. Thus, for the above example $Q = 5.5 \times 10^{-6} \text{ lit torr/s}$.

If the conductance of the peak is not known, it can be determined by measuring the decrease in the intensity of the spectral patterns as a function of time. As sample effuses to the mass spectrometer, the sample pressure in the inlet system decreases exponentially according to the equation

$$P = P_0 e^{-\frac{ct}{V}} \quad (11.15)$$

where, P_0 = initial pressure, $t = 0$; C = conductance, cc/s; V = volume, cc; t = time.

By algebraic rearrangement,

$$C = \frac{V}{t} \ln(P_0/P) \quad (11.16)$$

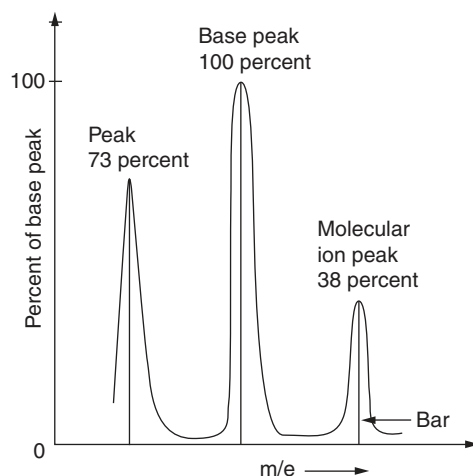


Fig. 11.5 Hypothetical mass spectrum of a molecule. Here in mass spectrometry 'e' is not the electronic charge, i.e. $0.16 \times 10^{-18} \text{ C}$, but 'e' represents the charge on the ion. To avoid this confusion, after 1980, m/z is being used in place of m/e , where z is the charge on an ion.

The volume V includes both the 1-litre expansion volume and the manifold volume of about 100 cc.

If in the above example, the mass 88 peak is observed to change from an initial peak height of 8200 mm deflection to 5810 mm after 30 minutes, the conductance for a molecular mass of 200 at 150°C will be

$$C = \frac{1100(\text{cc})}{30 \times 60(\text{s})} \ln \frac{8200}{5810} = 0.21 \text{cc/s}$$

When the many fold volume is known with sufficient accuracy (5–10 per cent), the expansion volume can be closed off to decrease the time required to attain the same reduction in mass peak intensity or pressure. This method of measuring and calculating sample consumption is the most convenient method of obtaining the mass spectrometer sensitivity.

(ii) Resolving Power or Resolution of a Mass Spectrometer The resolving power, R_p , of a mass spectrometer is arbitrarily defined as the ratio $\frac{M_1}{M_2 - M_1}$

$$R_p = \frac{M_1}{M_2 - M_1} \quad (11.17)$$

When two peaks at masses of M_1 and M_2 of equal intensities are just separated in the mass spectrum and the difference in mass numbers gives a valley of 10 per cent between peaks of masses M_1 and M_2 (Fig. 11.6) it is considered to be satisfactory if $\Delta M = M_2 - M_1$ is not greater than unity. Thus a resolution of four hundred distinguishes between two peaks with m/e of 401 and 400. To resolve a mass 238 doublet from the parent peaks of 1-methoxy-anthraquinone (A) and 1,4-diaminoanthraquinone (B) taken on double focus mass spectrometer, the resolving power of the instrument should be

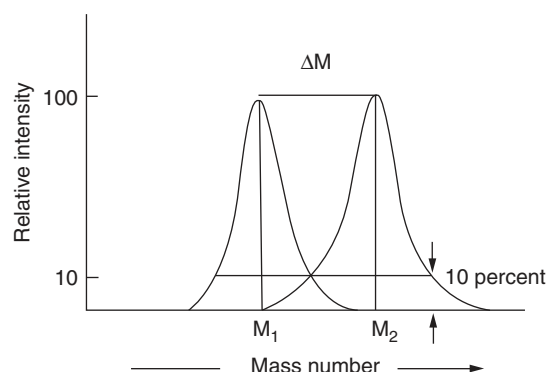
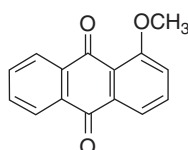
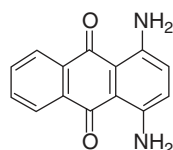


Fig. 11.6 Schematic representation of 10 per cent valley resolution in mass spectrometry.

$$\frac{238.1387}{238.1499 - 238.1387} = \frac{238.1387}{0.0112} \geq 21262$$



(A) m/e : 238.1387



(B) m/e : 238.1499

The resolution of a mass spectrometer depends upon width of the ion beam as determined by slits, distribution of kinetic energies in the beam, space change of ion beam, variations in magnetic field, variations in accelerating voltage, poorly collimated ion beam.

The $\text{CH}_2\text{—N}$ doublet (m/e : 14.0156, 14.0031) at mass 14 will be adequately resolved if the resolving power of instrument is $\geq \frac{14.0031}{0.0125} \geq 1120$.

(iii) Mass Spectrometer Sensitivity It is the most important parameter used in the evaluation of mass spectral performance. It should describe the output ion current received at the collector for a specified rate of sample consumption. The definition should state (i) the chemical substance, (ii) the mass peak that is measured, (iii) the mass spectrometer resolution, (iv) the quantity of the sample used per second, (v) the electron beam intensity, and (vi) the ion current arriving at the conversion dynode of the electron amplifier. Practical units would be amps of ion beam/nanogram/second/ampere of electron current at the resolution R_p . The compound used to establish the basic sensitivity should qualify certain criteria, namely (i) it should be highly stable, (ii) it should be easily available, (iii) preferably it should be a liquid to facilitate handling and have sufficient volatility to permit introduction via a 150°C inlet, (iv) a fairly high molecular mass in the 200–400 Da range is preferred, and (v) the mass spectrum should show a significant

molecular ion (5–30 per cent of base peak).

The compound chosen for sensitivity determination should be such that it may thermally decompose prior to electron bombardment. Cholesterol is a common example. Some manufacturers specified result with methyl

stearate ($\text{CH}_3 - (\text{CH}_2)_{16} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{CH}_3$). Measurement of the base peak (e.g. mass 74 in methyl ester spectrum) gives the most uniform sensitivity comparison between different instruments. Ideally, the base peak should be used to specify the basic instrument sensitivity and the ratio, $\frac{\text{base peak}}{\text{parent peak}}$, should be given to indicate instrument

variations. The term amp/torr is particularly useful for residual gas analysis. In essence, there are two aspects of mass spectrometry, that must be considered in defining sensitivity. One is the basic instrument sensitivity that gives the amount of current arriving at the collector for a specified sample consumption rate. The second is the method of handling the sample which thus determines the efficiency of sample utilisation, this aspect is a chemical problem dealing with the mass transfer of small quantities of chemicals.

11.5 VARIOUS FORMS OF MASS SPECTROMETRY ON THE BASIS OF METHODS OF SEPARATION OF IONS

Depending on the method of separation of charged ions produced by electron bombardment, according to their mass-to-charge ratios in the mass spectrometer, spectrometry has broadly been divided into the following classes:

11.5.1 Magnetic Field Deflection Mass Spectrometry

(a) Single Focussing Magnetic Field Deflection Mass Spectrometry (SFMDS) In a single focussing magnetic deflection mass spectrometry, the positive ions are separated by uniform and variable magnetic field according to their mass to charge ratios. The first electron impact ionisation and single focussing magnetic deflection mass spectrometer was developed by A J Dempster in 1918. Such type of electron impact sources (i.e. electron from a hot-wire filament) are still very widely used in modern spectrometers. The schematic diagram of a 180° single focussing Dempster mass spectrometer is shown in Fig. 11.7; the theory and working of which has already been explained in sections 11.4.1 and 11.4.2 respectively.

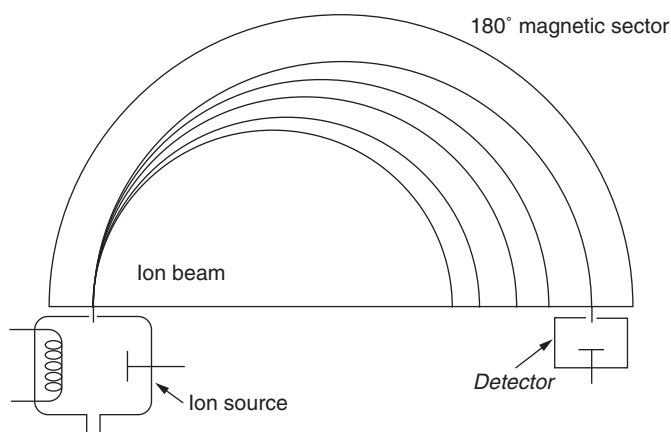


Fig. 11.7 Schematic diagram of a single focussing mass spectrometer.

(b) Double Focussing (Electrostatic and Magnetic Fields) Mass Spectrometry (DFMS) The basis of DFMS is that the ions are first sorted out according to their energies by applying radial electric field perpendicular to the path of the ions and subsequently according to their mass-to-charge ratios by applying magnetic field again perpendicular to the path of the ions.

The ions at the time of generation have different energies (because of Boltzmann kinetic energy distribution) which would affect resolution. However, in a magnetic single focussing spectrometry, it is assumed that all the ions have same kinetic energy and the ions are separated according to their mass to charge ratios. Due to this assumption, the magnetic single focussing spectrometers have low resolution generally between 200–1000. This can be overcome by employing a very high accelerating potential so that $\frac{\Delta V}{V}$ becomes very small. But a better way would be to apply a radial electrostatic field, i.e. the voltage is applied across the plates of a cylindrical condenser. When the ions pass through such a radial field, the centripetal force of the electric field is balanced by the centrifugal force of the ion, i.e.

$$\frac{mv^2}{r} = eV \text{ or } r = \frac{mv^2}{eV} \quad (11.18)$$

Thus, for a fixed value of V , the ions of same energy will follow the circular path of radius r . The radius of curvature of ions deflected in an electrostatic field is given by

$$r = \frac{2V}{\bar{V}} \quad (11.19)$$

where, $\bar{V}$ is in volts/cm. Thus ions with energy $V + \Delta V$ and $V - \Delta V$ will be separated.

Subsequently, magnetic field is applied on such ions to achieve double focussing. In a magnetic field analyser, ions are separated by differences in their m/e ratios as they move in a circular path towards a collector in order of increasing mass to charge ratio, i.e.

$$\frac{m}{e} = \frac{H^2 r^2}{2V} \quad (\text{Eq. 11.11})$$

where the terms and symbols have their usual meanings.

High mass resolution double-focussing spectrometers were developed for the purpose of determining the exact atomic masses of the elements. One type of double focussing instrument was developed in 1930s by Josef Mattuch and Richard F F Herzog and another was developed by E G Johnson and A O Nier in 1953. Both the mass spectrometers are based on the same principle but differ in their magnetic and electric field geometries. The block diagram for the former is shown in Fig. 11.8 and that of the latter in Fig. 11.9.

(c) Cycloidal Focussing Mass Spectrometry In this type of mass spectrometry, the ions are passed through a homogeneous electric field at right angles to and superimposed on a magnetic field. The ions passing

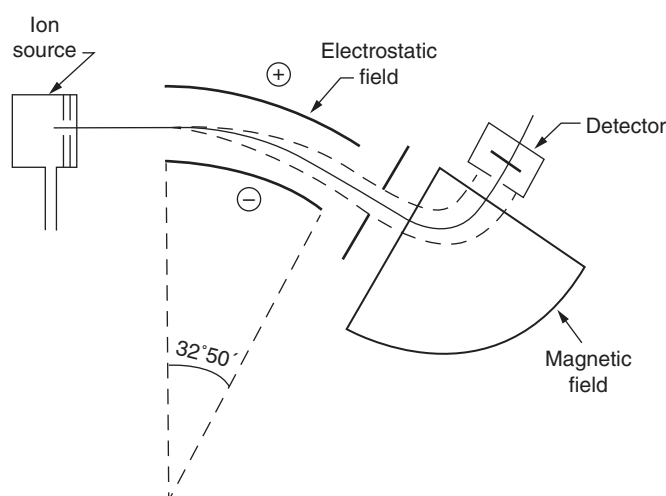


Fig. 11.8 Mattauch-Herzog geometry for double-focussing mass spectrometer.

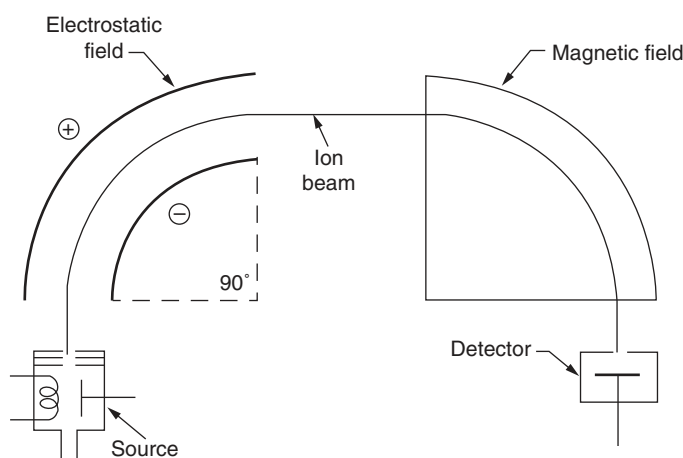


Fig. 11.9 Nier-Johnson geometry for double focussing mass spectrometer.

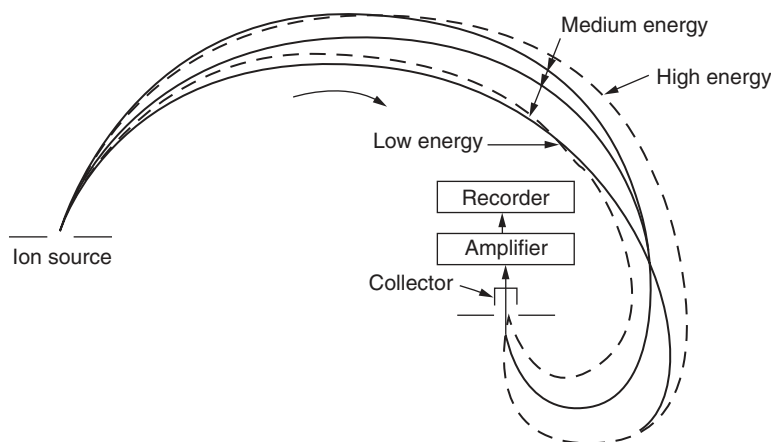


Fig. 11.10 Schematic diagram of a cyclotidal mass spectrometer.

through such crossed magnetic and electric fields generate a cyclotidal path as shown in Fig. 11.10. As either of the two crossed fields is varied, ions of identical m/e ratio focus on the fixed collector slit even though not of equivalent energy. For ions focussed in the cyclotidal analyser,

$$m/e = \frac{kH^2}{2\pi V} \quad (11.20)$$

where k is a constant. Here, the small radius of curvature allows the use of a smaller magnet without sacrificing resolution. The resolution is at least 1000 in the mass range extending from 10 to 2000.

11.5.2 Ion, Resonant/Cyclotron Resonance, Mass Spectrometry (IRMS/ICRMS)

ICRMS was developed by J A Hipple, H Sommer and H A Thomas in 1949 and it made inroads into chemistry in the middle to late 60s'. The basic principle of ICRMS is that when ions are subjected to simultaneous mutually perpendicular magnetic and radio frequency fields, they follow spiral paths. The ions are collected sequentially either by scanning the radio frequency of the electric field or by magnetic field. This technique is particularly useful for the characterization of ion-molecule reactions. In 1974, Melvin B Comisarow and Alan G Marshall revolutionised ICR by developing Fourier transform ICR mass spectrometry (FTICRMS). The major advantage of FTICRMS is that it allows many different ions to be determined at once rather than one at a time. This technique has also the higher mass resolution than that of any other type of mass spectrometric technique.

The block diagram of a typical ICR mass spectrometer often called the *Omegatron* is shown in Fig. 11.11.

When only magnetic field is operative, the centripetal force of the magnetic field is balanced by the centrifugal force acting on the ion, i.e.

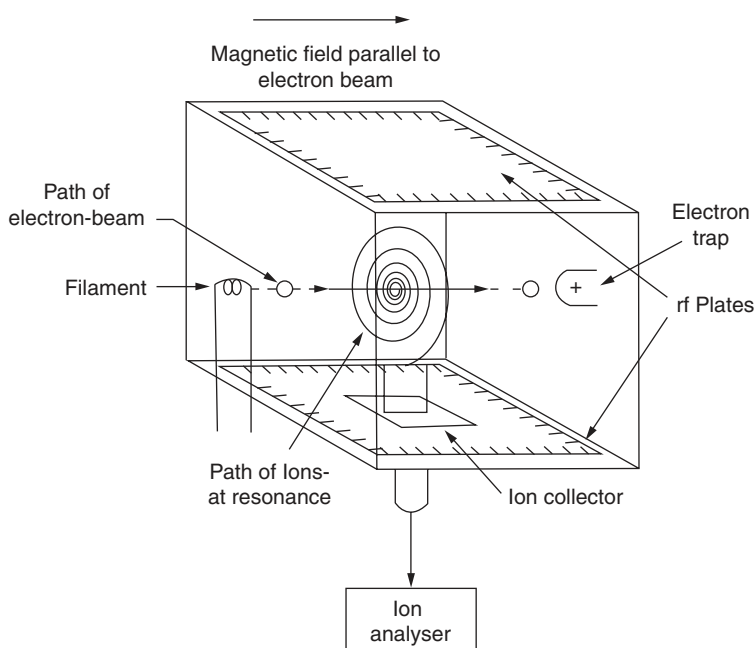


Fig. 11.11 A schematic diagram of an omegatron.

$$\frac{mv^2}{r} = Hev \quad (\text{Eq. 11.8})$$

$$\text{or} \quad \frac{v}{r} = H(e/m) = \omega = 2\pi\nu \quad (11.21)$$

where, $\omega = \frac{v}{r}$ is the angular velocity of the ion and $\nu = \frac{\omega}{2\pi}$ is the frequency of revolution in Hz.

Rearrangement of Eq. (11.21) yields

$$m/e = \frac{H}{2\pi\nu} \quad (11.22)$$

Thus, the magnetic field causes the ion to move in a circular path with angular velocity ω and frequency ν .

When both the mutually perpendicular fields simultaneously operate on the ions, they follow the spiral path at right angles to both the fields. The frequency ν is now called the cyclotron frequency of the ion and is expressed as the number of complete spirals/cycloids per second and is given by

$$\nu_c = \left(\frac{e}{m} \right) \frac{H}{2\pi}, \quad (11.23)$$

$$\text{or} \quad \nu_c = 19.16 \times 10^3 (e/m) \frac{H}{2\pi},$$

when m is in amu, and H is in gauss, the cyclotron frequency will be in Hz which is independent of radius r and speed v . When the radio frequency of the rapidly applied oscillating electric field matches with that of the cyclotron frequency of ions, the ions will gain energy, consequently only ions of an m/e ratio in resonance with the oscillating radio frequency field will be successively accelerated and follow the spiral path of ever increasing radius until they strike the ion collector. The maximum kinetic energy of the ions when they leave the cyclotron is given by

$$\text{Kinetic energy} = \frac{1}{2} m v_{\max}^2 = \frac{1}{2} \left(\frac{e}{m} \right)^2 H^2 r_{\max}^2 \quad (11.24)$$

Ions with other m/e ratios, i.e. nonresonant ions adopt smaller circular paths near the axis of the electron impact beam. The resonant frequencies for ions over a mass range of 1–200 amu with magnetic field of 15000 G range from 50 kHz to about 25 MHz. The energy that is absorbed by the ions is measured by an oscillator detector rather than collecting the ions in an ion collector. A mass spectrum is thus obtained by plotting the energy absorbed by the ions against either the rate of scan of the magnetic field at constant radio frequency of the electric field or the rate of change of the electric field frequency at constant magnetic field.

The mass resolution of an Omegatron is 700 over a mass range of 1–280 amu and is 50 over a mass range of 2–50 amu.

When a positive voltage is applied to the side plates of an IRMS, the positive ions motion down to the centre of the analyser and are said to be trapped while the negative ions and scattered electrons are expelled from the chamber. For trapping of negative ions, the trapping potential is simply reversed. Since the drift velocities of ions are of the order of 500 cm/s, the residing time of ions is over a range of 0.5–25 ms, and path lengths for thermal velocity ions are over a range of 1–50 m. This is 1000 times longer than in a sector mass spectrometer. This very feature of the IRMS makes it useful for the study of ion–molecule reactions at low pressures. It is also used to measure the density of molecular nitrogen in the upper atmosphere via rocket flights.

Problem 11.1: The ion resonant mass spectrum of molecular ion of O_2 shows a peak at m/e : 32. Calculate the cyclotron frequency of the molecular ion if the strength of the applied magnetic field is 15000 G.

Solution Substituting the data given in the problem into Eq. (11.23), we get

$$\begin{aligned} \nu_c &= 19.16 \times 10^3 \left(\frac{1}{32} \right) \times \frac{15000}{2 \times 3.14} \text{ Hz} \\ &= 1.43 \times 10^6 \text{ Hz} = 1.43 \text{ MHz} \end{aligned}$$

11.5.3 Time of Flight Mass Spectrometry (TOFMS)

The concepts of TOFMS were proposed in 1946 by William E Stephens. This technique does not use the magnetic field at all. In this technique, the original ions are separated into 'wafers' of ions by the difference in their velocities as they move in a straight path in a field-free region towards a collector according to their masses.

The block diagram of a TOFMS for recording the mass spectrum of a sample is shown in the self-explanatory Fig. 11.12. Ions are produced in the ionisation region by one μs pulse of the bombarding electrons having preselected energy in the 0–100 eV range, typically 70 eV. The ions so produced are accelerated by an electric potential. The ion focus grid is subjected to an accelerating potential of 100 V in the form of a voltage pulse of negative charge having repeating frequency of few thousands/second; the lifespan of voltage pulse is 1 μs or less. This positive pulse accelerates the ions through the grid where they are picked up by the field of the ion energy grid which is positioned at a distance of less than 2 cm from the ion pulse grid. After successive accelerations, all the ions acquire a drift energy of 2700 eV (or 2800 eV) in a distance of less than 2 cm and hence at the ion energy grid. These ions then move in a straight path of length 100 cm (= 1 m) in a field-free region towards a magnetic electron multiplier detector which collects and amplifies the ion signals. Although the energy of all the ions is the same, they drift through the field-free region at different velocities $[v = \sqrt{2 \text{ eV/m}}]$ and thus arrive at the detector end one after another according to their masses. The arrival time between two successive ions can be $\leq 10^{-7}$ s. The mass spectrum is displayed on an oscilloscope or recorded on a paper chart. Modern TOFMSs are coupled with computers for storing and analysing data.

The TOF, t (in microseconds) of ions through a distance L (in cm) is given by the expression

$$t = L \sqrt{\left(\frac{m}{e}\right) \left(\frac{1}{2V}\right)} \quad (11.25)$$

Here, V is in volts. A typical flight time for a one-metre drift tube is in the range of 1–30 μs .

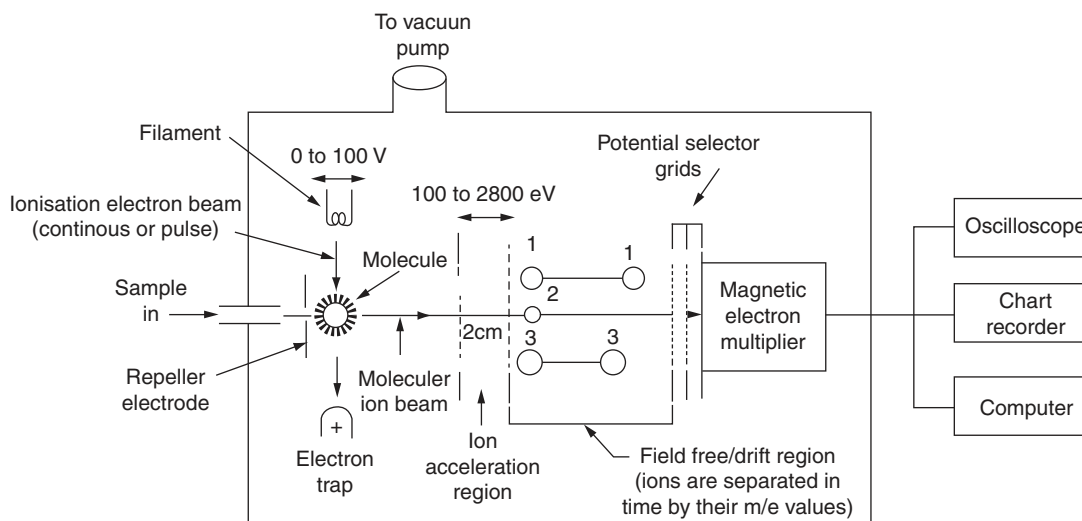


Fig. 11.12 A schematic diagram of a time of flight spectrometer.

The difference in the flight time for ions of different masses can be calculated using Eq. (11.25) in the form

$$\Delta t = (t_2 - t_1) = \sqrt{L^2 / 2eV} (\sqrt{m_2} - \sqrt{m_1}) \quad (11.26)$$

In this method, ions cannot be continuously produced; otherwise there will be mix up of masses. Hence, ion bunches are pulsed. The analysis is very rapid and an entire mass over a range of 0–1000 can be scanned in 50 μs ; the frequency of repetition of spectrum may be 10,000–50,000 times/second; but 20,000 is commonly used. The resolution is about 1 part in 400.

This technique is very useful for isotope ratio studies, kinetic studies of fast reactions, direct analysis of effluent peaks from a gas chromatography, and analysis of samples volatilised by a single pulse from a laser. Time of flight devices are now largely used with sophisticated ionising methods such as FAB, etc., for high mass measurements including large biomolecules.

Problem 11.2: In a TOFMS of a mixture of CO_2 and CH_4 there are observed lines corresponding to the following values of m/e : 8, 13, 14, 15, 16, 28 and 44. What transit times might these lines correspond to if the drift path length is 100 cm and the accelerating voltage is 2800 V?

Solution In order to determine the TOFs' for the ions given in the problem, we proceed as follows:

The TOF of an ion is given by

$$t = L \sqrt{\left(\frac{m}{e}\right) \left(\frac{1}{2V}\right)} \quad (11.25)$$

$$\text{or} \quad = k \sqrt{m/e} \text{ where } k = L \sqrt{(1/2V)}; \quad (11.26)$$

Since the quantities L and V are constants in the problem, the value of parameter k needs be determined first.

$$\text{Thus,} \quad k = 100 \sqrt{\frac{1}{2 \times 2800}} = 100 \sqrt{1.7857 \times 10^{-4}} = 100 \times 1.336 \times 10^{-2} = 1.336$$

and Eq. (11.25) reduces to

$$t = 1.336 \sqrt{m/e}$$

Substituting the respective values of m/e into the above equation, we obtain

$$t(m/e : 8) = 1.336 \sqrt{8} \mu s = 1.336 \times 2.828 \mu s = 3.78 \mu s$$

Proceeding as above, we obtain

$$t(m/e : 13) = 4.81 \mu s; t(m/e : 14) = 4.99 \mu s, t(m/e : 15) = 5.17 \mu s;$$

$$t(m/e : 16) = 5.34 \mu s, t(m/e : 28) = 7.06 \mu s \text{ and } t(m/e : 44) = 8.86 \mu s,$$

11.5.4 Radio Frequency Mass Spectrometry (RMS)

In radio frequency mass spectrometry, the ions can be resolved according to their m/e ratio without the need of a heavy magnet. When electrostatically accelerated ions with uniform energy are subjected to simultaneous radio frequency field and electrostatic field of potential, V , they are sorted out according to their velocities provided

$$v = sv \quad (11.27)$$

where v is the velocity of ions, ν is the frequency of the radio frequency field (in the order of 10–100 MHz) and s is the spacing between the adjacent grids.

Also we know that

$$eV = \frac{1}{2} m v_1^2 = \frac{1}{2} m v_2^2 = \frac{1}{2} m v_3^2 \quad (\text{Eq. 11.12})$$

Combining Eqs (11.12) and (11.27), we obtain

$$\frac{m}{e} = \frac{2V}{s^2 \nu^2} \quad (11.28)$$

or in cgs units

$$\frac{m}{e} = \frac{0.266 V}{s^2 \nu^2} \quad (11.29)$$

Thus, the mass spectrum can be scanned by varying the radio frequency (ν) while keeping the potential V of the electrostatic field constant.

Based on this principle, one type of radio frequency mass spectrometer was developed by W H Bennet in 1950, the block diagram of which has been shown in Fig. 11.13.

Problem 11.3: What is the radio frequency range of a radio frequency mass spectrometer analyser for a singly charged nitrogen molecule if the accelerating voltage varies from 400–4000 volts and the spacing between the adjacent grids in the analyser is 1 cm?

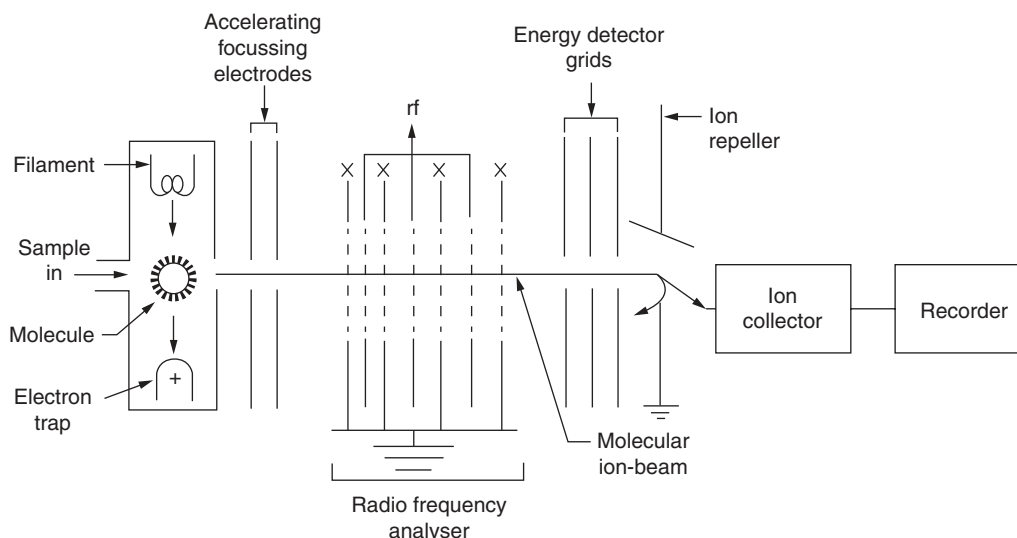


Fig. 11.13 A schematic diagram of a radio frequency mass spectrometer. All grids marked x are at the same potential.

Solution Algebraic rearrangement of Eq. (11.29) yields

$$v = \frac{1}{s} \sqrt{0.266V(e/m)} \text{ MHz}$$

Substituting the given data into this expression we get

$$v(400) = \sqrt{\frac{0.266 \times 400}{28}} \text{ MHz} = 4.45 \text{ MHz}$$

and

$$v(4000) = \sqrt{\frac{0.266 \times 4000}{28}} \text{ MHz} = 6.16 \text{ MHz}$$

Thus, the radio frequency range for the accelerating voltage over the range of 400–4000 volts is from 4.45–6.16 MHz.

Problem 11.4: The radio frequency mass spectrum of CO_2 shows a peak at m/e : 44. Calculate the accelerating voltage of the analyser if its radio frequency is 5 MHz and the spacing between the adjacent grids in the analyser is 1 cm.

Solution Algebraic rearrangement of Eq. (11.28) gives

$$V = \frac{1}{2} (m/e)(sv)^2 \text{ volts}$$

Substituting the given data into the rearranged expression, we obtain

$$V = \frac{1}{2} (44)(1 \times 5)^2 \text{ volts} = 50 \text{ volts}$$

11.5.5 Quadrupole Mass Spectrometry (QPMS)

QPMS was first developed in the mid 1950s' by the group of Professor Wolfgang Paul of the University of Bonn (where once Kekule and Hertz also made great discoveries) in Germany and is of two types, namely quadrupole mass filter-mass spectrometry (QPMF-MS) and quadrupole ion trap-mass spectrometry (QPIT-MS). In the former, a two dimensional quadrupolar fields generated by both a direct current (dc) voltage (V_{dc}) and a radio frequency (rf) voltage (V_{rf}) are used to filter and mass analyse the ions while in the latter a three dimensional quadrupolar radio frequency field is used to trap and mass analyse the ions in the same place. Just like time of flight, and radio frequency mass spectrometric techniques and unlike single

and double-focussing mass spectrometry there is no need of heavy magnet to sort out ions according to their mass to charge ratios.

(a) Quadrupole Mass Filter Spectrometry (QPMF-MS) In this technique, a two-dimensional quadrupole electric field comprising both radio frequency and direct current components are used to filter out ions according to their m/e ratios. Mass selection is achieved by varying each of the radio frequency and direct current frequency while keeping their ratios accurately constant. Although the techniques are not as accurate as double-focussing mass spectrometric techniques, but they being faster are widely used as GC and LC-detectors these days.

The heart of 2-D quadrupole mass filter mass spectrometer is the quadrupole mass filter, the block diagram of which is shown in Fig. 11.14(a) and that of quadrupole mass spectrometer in Fig. 11.14(b). It consists of four metallic rods. Typical dimensions of the quartz rods coated with platinum in the mass quadrupole are about 12 mm diameter and 25 cm long, operating with 3 MHz *rf* and 10 V *dc*. The diagonally opposite rods are joined together electrically, the two poles to opposite poles of a dc source and simultaneously to a radio frequency oscillator. These voltages create a hyperbolic field between the rods for any specified combination of radio frequency and dc voltages.

In such a geometry of the quadrupole, the interaction between both a direct current voltage and a radio frequency voltage causes complex oscillations in the *X*- and *Y*-directions but a stable oscillation in the direction which is perpendicular to the plane of the paper. The stable oscillations sort out the ions according to their mass to charge ratios as they shoot down with constant velocities from one end of the quadrupole to the other end (i.e. along *Z*-axis) without striking the poles. All the other ions experiencing complex oscillations along the *X*- and *Y*-directions will strike the poles and collapse. Mass spectrum is obtained by varying each of the radio frequency and direct frequency while keeping their ratios constant. The scanning time varies from 500 μ s to 30 minutes. The filtered out ions are amplified and the spectrum is displayed either on an oscilloscope or paper chart. The mass spectral data can also be stored in a digital computer for analysis. The mass resolution is 500 over a mass range of 1–500 and 100 over a mass range of 1–120 amu.

Smaller quadrupole mass spectrometers are used as residual gas analysers and simpler monopole mass spectrometers employ only a single rod.

(b) Quadrupole Ion Trap-Mass Spectrometry (QPIT-MS) In this technique, a three dimensional rotationally symmetric quadrupole radio frequency field is used to trap and mass analyse the ions in the same place. The original

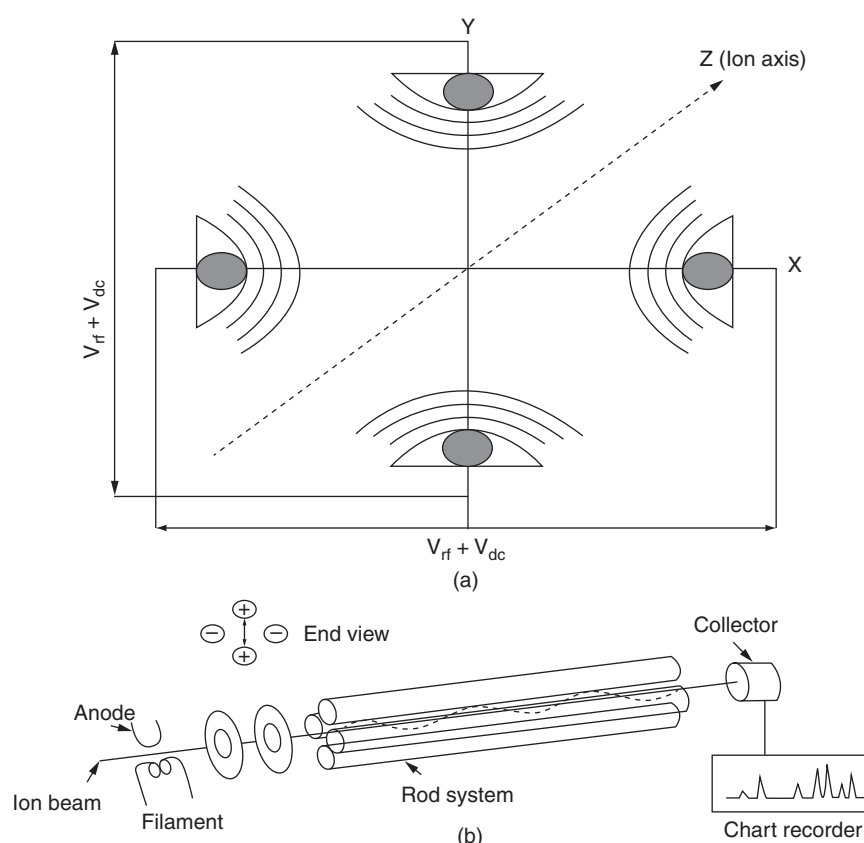


Fig. 11.14 A schematic diagram of the (a) geometry of the rods/quadrupole mass filter in a quadrupole mass spectrometer, and (b) quadrupole mass spectrometer. The *Z*-axis is perpendicular to the plane of the paper.

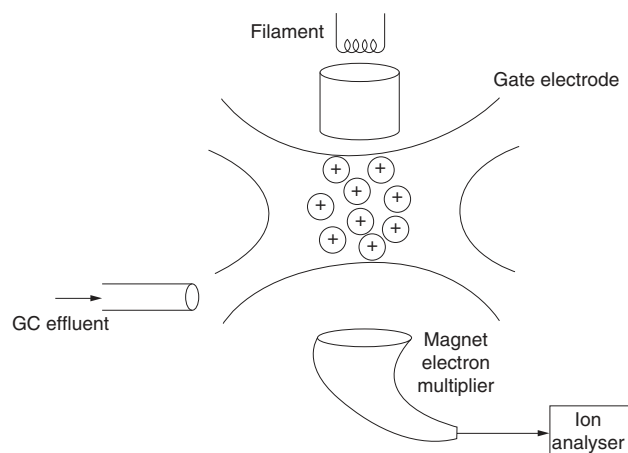


Fig. 11.15 A schematic diagram of an ion trap mass spectrometer.

tor of QP-MS, Professor Wolfgang Paul, shared one half of the 1989 Nobel Prize in physics with Hans G Dehmelt for the development of ion trap technique and the other half was awarded to Norman F Ramsey for the invention of the separated oscillatory fields method and its use in the hydrogen maser and other atomic clocks.

The commercial version of quadrupole ion trap mass spectrometer based on the design of George C Stafford and co-workers was introduced in 1983 as a GC detector, the block diagram of which is shown in Fig. 11.15. The heart of this spectrometer is the quadrupole ion trap that consists of three electrodes connected together to a radio frequency circuit. One electrode, known as the gate electrode, is a doughnut-shaped piece of metal that horizontally encircles the chamber while the other two are hemispherical caps on the top and the bottom of the chamber. These electrodes generate a three-dimensional rotationally symmetric field to trap and analyse the ions according to their masses in the same place. Mass scanning is carried out by varying the radio frequency voltage, ions of increasing mass-to-charge ratios successively become unstable as the radio frequency voltage is increased. Such a type of mass scanning is called the 'Stafford's' mass-selective instability scanning. The separated ions according to their m/e ratios are fed to electron multiplier, i.e. an ion signal collector and amplifier. The spectrum is displayed either on an oscilloscope or a paper chart. The mass spectral data can also be stored in a digital computer for analysis. The scanning times of mass spectra of ions over a mass range of 20–650 amu varies from one tenth of a second to few second. Although QIT-MS at the embryonic stage were introduced as GC-detectors, but these days, they are not only used as GC-detectors but also as LC-MS detectors and stand alone as mass spectrometers.

11.6 VARIOUS FORMS OF MASS SPECTROMETRY ON THE BASIS OF IONISATION PROCESSES OTHER THAN EIMS

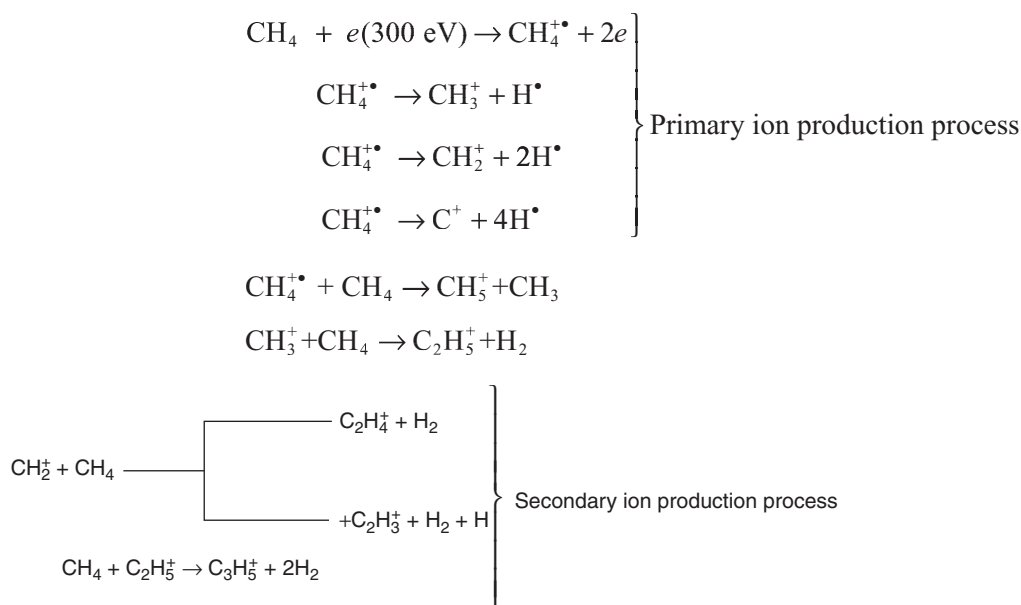
Many times the molecules do not show molecular ions in electron impact mass spectrometry because of which it becomes impossible to determine the exact molecular masses of such systems by this technique. Also many nonvolatile compounds such as amino acids, peptides, proteins, sugars, etc., cannot be introduced as such into the mass spectrometer. They have to be converted into some reasonably volatile derivatives. The other major drawback of EIMS is that the electron bombardment destroys the small bio-molecules. Such problems encountered in EIMS have been solved to a large extent with the emergence of new processes of ionisations such as chemical ionisation, desorption ionisation, i.e. fast atom bombardment ionisation; electrospray ionisation, etc. Thus, just like EIMS, other forms of mass spectrometry have also been named after the ionisation processes.

11.6.1 Chemical Ionisation Mass Spectrometry (CIMS)

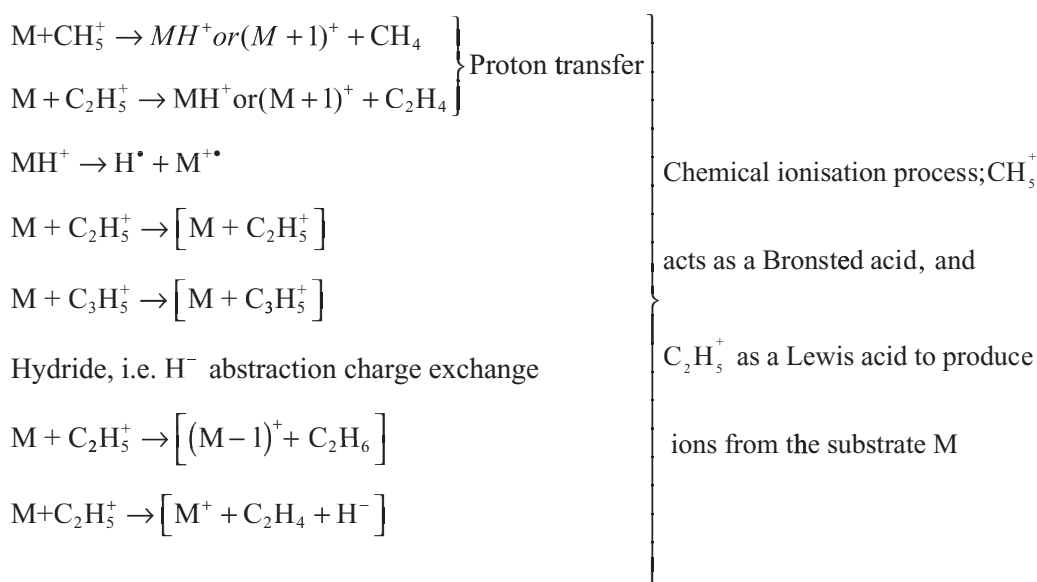
Chemical ionisation is a bimolecular process in which ionisation occurs as a result of ion-molecule reactions. It was first observed in 1913 by J J Thomson in hydrogen gas but he did not characterise the process at that time. CIMS was first characterised in the mid 1960s by Frank H Field and M S Burnby Munson. CIMS is a soft ionisation technique in which volatilised analyte molecules are ionised by reaction with the secondary ions of the reagent gas such as methane, isobutane, ammonia, etc., which is ionised by the impact of electrons. The sample is introduced at about one torr pressure with a carrier gas. The molecular ions produced by the CI process appear at $m/e : M + 1$ and MH^+ ions and are known as quasi-molecular ions and often appear as prominent or base peak in the mass spectrum. They possess less internal energy compared to the molecular ions produced by EI and hence

undergo less fragmentation, i.e. generate fewer fragment ions compared to EIMS. Moreover, the nature of the CI process is such that the product ions formed contain even number of electrons.

Proton-releasing tendency of the secondary ions of the carrier gases follows the order: $\text{CH}_5^+ < \text{C}_4\text{H}_9^+ < \text{NH}_4^+$. Thus by the choice of the carrier gas, we can control the tendency of CI produced MH^+ ion to yield fragment ions. NH_4^+ does not protonate same molecules and if it protonates, the resultant MH^+ ion produced will have insufficient amount of internal energy for fragmentation. Consequently, MH^+ ion will appear as a base or prominent peak in the resultant mass spectrum. Thus, ammonia CI is an excellent technique for the determination of molecular masses of volatile compounds. The mechanism of production of MH^+ ions when methane is used as a carrier gas is given here.

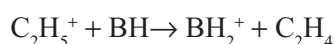
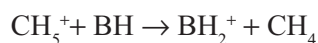


Small relative concentrations of C_3H_7^+ , C_2H_2^+ , C_3H_3^+ , C_3H_4^+ , and C_4H_9^+ are formed, but they do not make significant contribution to the total ionisation.

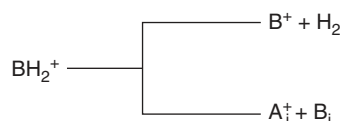


However, proton transfer may still occur from C_2H_5^+ to stronger bases (i.e. $\text{C}_2\text{H}_5^+ + \text{BH} \rightarrow \text{BH}_2^+ + \text{C}_2\text{H}_4$) and this behaviour has been observed for water and ammonia. Hydride transfer reactions, i.e. $(\text{B}^+ + \text{C}_2\text{H}_6 \text{ formations})$ in which C_2H_5^+ acts as a Lewis acids are also observed.

In the presence of a good proton acceptor, the ions CH_5^+ and C_2H_5^+ act as Bronsted acids and protonate the sample molecule:



Here, B represents any organic (possibly inorganic group). Since CH_4 is a weak Bronsted base, CH_5^+ is a strong Bronsted acid and proton-transfer reactions to stronger bases than CH_4 will occur. These reactions being exothermic, BH_2^+ ions produced above will dissociate to form other ions.

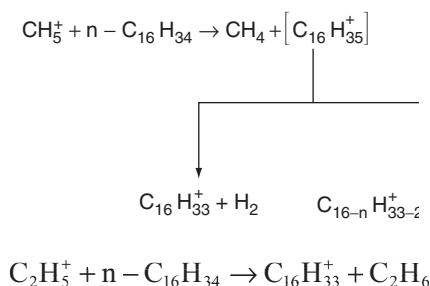


where A_i^+ is one of the possible fragmentations. C_2H_4 is a stronger Bronsted base than CH_4 , and hence C_2H_5^+ is a weaker Bronsted base than CH_5^+ .

These reactions are typical of those observed for alcohols, aldehydes, esters, etc., and also for many biochemical compounds typically encountered in recent chemical ionisation applications.

If the sample material is not a good proton acceptor, the chemical ionisation process will occur as a hydride ion abstraction or as a dissociative proton transfer.

e.g. the CI spectra of *n* – hexadecane (Methane reactant, $P_{\text{CH}_4} = 1.0$ torr) are consistent with our previous discussion.



The most striking difference between the CI and EI mass spectra of *n* – hexadecane is much larger relative intensity of the chemical ionisation $\text{C}_{16}\text{H}_{33}^+$ ($m/e : 225$) ion (relative intensity 36 percent) than any electron impact C_{16} ion.

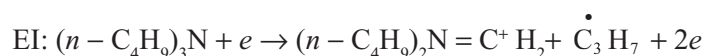
Additional fragmentation occurs to give a mass spectral pattern that is similar in appearance to the electron impact spectrum of a hydrocarbon, but the abundance of the quasi-parent ion is greatly increased relative to the fragment ions. The increased relative abundance of the quasi-molecular ion has proven to be of great value in many studies, particularly with relatively complex bioorganic molecules. CIMS can be used to obtain the mass spectra of low molecular mass (200 daltons) molecules having a large number of polar functionalities or high molecular mass compounds (800–10,000 Da).

Typical peaks in the CI (reactant gas: CH_4 , $P_{\text{CH}_4} = 1$ torr) and EI mass spectra of some molecular systems are compared in Table 11.1.

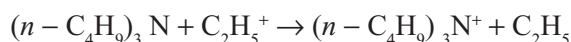
Table 11.1 A comparison of CI and EI mass spectra of some amines.

<i>m/e</i>	CI Intensity	EI Intensity	Remarks
142	19.9	29.6	$(n\text{-C}_4\text{H}_9)_2\text{NCH}_2^+$
156	2.5	0.3	$(n\text{-C}_4\text{H}_9)_2\text{NCH}_2\text{CH}_2^+$
170	3.5	0.0	$(n\text{-C}_4\text{H}_9)_2\text{NCH}_2\text{CH}_2\text{CH}_2^+$
184	23.1	0.0	$(n\text{-C}_4\text{H}_9)_2\text{NC}^+\text{HC}_3\text{H}_7$, $(M-1)^+$, hydride abstraction
185	10.8	1.6	$(n\text{-C}_4\text{H}_9)_3\text{N}^+$, M^+ , charge transfer
186	21.1	0.0	$(n\text{-C}_4\text{H}_9)_3\text{NH}^+$, $(M+1)^+$ proton transfer
214	1.7	0.0	$(n\text{-C}_4\text{H}_9)_3\text{NC}_2\text{H}_5^+$, addition

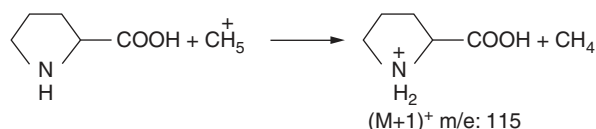
The $(M+1)^+$ and $(M-1)^+$ ions are caused by proton transfer and hydride-transfer reactions. The ions at m/e : 214 and m/e : 186 indicate that the electrophilic attack takes place on the nitrogen atom of the molecule while the ion at m/e : 184 shows that attack occurs on the alkyl radicals resulting in the abstraction of H^- . The peaks at m/e : 142, 156 and 170 result due to the following types of reactions.



Since the ionisation energy of C_2H_5^+ (8.3–8.8 eV) is large compared to that of tri-*n*-butylamine (7–8 eV), the large relative abundance of parent ion, i.e. = 7.7 per cent of the total ionisation in CI, is due to the transfer of charge from ethyl ion to the amine molecule.



The meaningful difference between ionisation potentials of primary (8.5 eV) and tertiary (7–8 eV) aliphatic amines enables to distinguish between isomers by the CI technique.

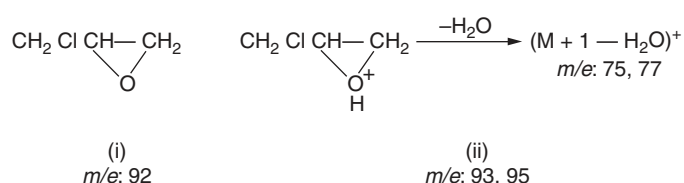


A comparison of CI and EI mass spectra of 3-chloro-1, 2-epoxypropane (Table 11.2), $\text{ClCH}_2\text{CH}_2\text{CH}_2$ shows that virtually no parent ion is formed by the EI technique but an appreciable amount of $(M + 1)^+$ ion is formed in the CI system.

Table 11.2 A comparison of CI and EI mass spectra of 3-chloro-1, 2-epoxypropane.

<i>m/e</i>	<i>CI</i>	<i>EI</i>	<i>Assignment</i>
57	38.7	17.6	C ₃ H ₅ O ⁺ (M + 1–HC1) ⁺
75	0.8		³⁵ ClCH ₂ –CH=CH ⁺ , (M + 1–H ₂ O) ⁺
77	0.3		³⁷ ClCH ₂ –CH=CH ⁺ , (M + 1–H ₂ O) ⁺
91	0.5	0.03	(M – 1) ⁺ , Hydride, i.e H [–] abstraction
92	0.0	0.06	M ⁺
93	31.3		(M + 1) ⁺
95	10.0		(M + 1) ⁺

The fact that the oxygen is held by two bonds in a cyclic structure (i) results in stability of the protonated molecule, and (ii) *m/e*: 93 and 95; contrasted with loss of water molecule resulting from protonation of the OH group in higher molecular mass alcohols.



The attack at Cl also involves proton transfer but with immediate loss of HCl to form $\text{C}_3\text{H}_5\text{O}^+$ (m/e : 57).

Let us now examine the CI and EI mass spectra of *n*-heptyl-propionate ($\text{C}_2\text{H}_5\text{COOC}_7\text{H}_{15}$) listed below in Table 11.3.

The addition of ethyl and allyl ions to the ester produces four different ions in the spectrum as follows:

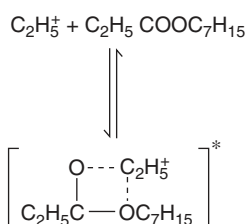
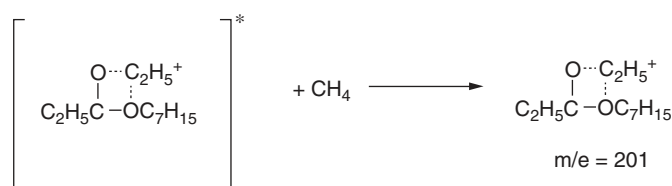


Table 11.3 A comparison of CI and EI mass spectra of *n*-heptyl propionate.

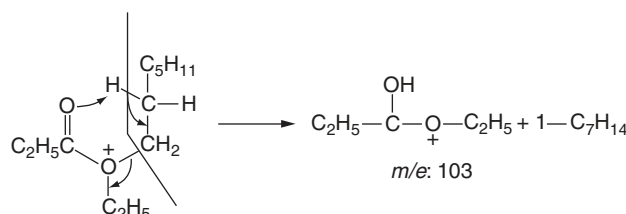
<i>m/e</i>	CI	EI	Assignment
57	15.3	20.5	C ₃ H ₅ O ⁺
75	38.0	7.2	C ₂ H ₅ COOH ₂ ⁺
97	6.3	0.5	C ₇ H ₁₃ ⁺
103	7.7	0.0	C ₂ H ₅ ^H COOC ₂ H ₅ ⁺ , alkyl exchange
115	0.9	0.2	C ₂ H ₅ ^H COOC ₃ H ₅ ⁺ , alkyl exchange
171	0.9	0.00	(M - 1) ⁺ , hydride (H ⁻) abstraction
172	0.0	0.00	M ⁺
173	12.6		(M + 1) ⁺ , proton transfer
201	0.8		C ₂ H ₅ C(OC ₂ H ₅)(OC ₇ H ₁₅) ⁺ , ethyl addition
213	1.0		C ₂ H ₅ C(OC ₃ H ₅)(OC ₇ H ₁₅) ⁺ , allyl addition

The dotted lines in the structural formula indicate that the ionic attack may be on either oxygen atom. This transient intermediate can react forward in two ways:

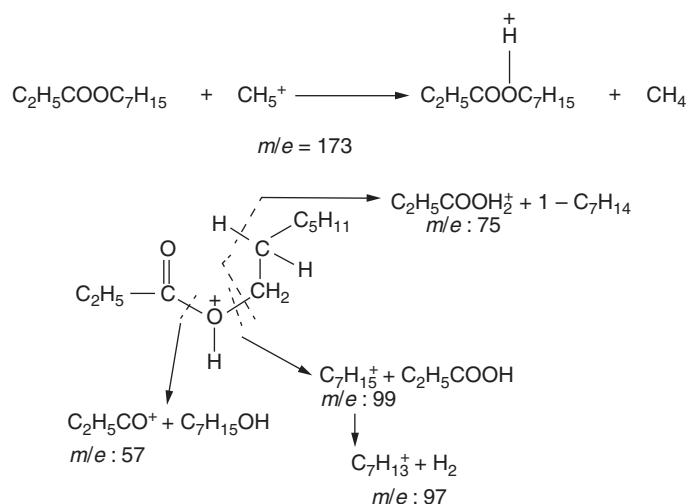
(i) Stabilisation by collision with methane, i.e.



(ii) Elimination of C₇H₁₄ to form a protonated ethylpropionate ion (alkyl exchange reaction), i.e.



The allyl ion also reacts in an analogous manner, i.e.



Quantitative analysis of a mixture of known compounds can also be carried out by CIMS from the relative sensitivities of the compounds under analysis. The relative sensitivities of the compounds in question are

estimated from the mixture of known composition. These values are then used for the analysis of unknown mixtures of these compounds. Analysis of mixtures of *n*-dodecane, *n*-tetradecane, and *n*-hexadecane have been carried out by this technique and satisfactory results have been obtained, $n\text{-C}_{12}\text{H}_{26}$: 24.3 (25.0), $n\text{-C}_{14}\text{H}_{30}$: 50.4 (50.0), $n\text{-C}_{16}\text{H}_{34}$: 25.2 (25.0). The quantities within parenthesis are the expected values.

In conclusion, the spectra produced by CIS are very different from conventional EIS and are sometimes much more useful for both qualitative and quantitative analysis, particularly of high molecular mass and polyfunctional compounds.

11.6.2 Desorption Ionisation Mass Spectrometry (DIMS)

Analysis of high melting inorganic solids such as metals, oxides, refractory materials, etc., and of large polar nonvolatile organic molecules of interest in biology and medicine, i.e. protein and antibiotics, is not possible by classical mass spectrometry that is based on the ionisation of the volatile substances in the gaseous phase by electrons as in electron impact mass spectrometry, photons as in photon impact mass spectrometry and chemical reactions as in chemical ionisation mass spectrometry. The nonvolatile high molecular mass organic biological molecules can't be vapourised without extensive, even catastrophic decomposition. However, such analytes can be mass analysed by desorption mass spectrometry, also known as soft ionisation mass spectrometry, that is based on the extraction of ions from a substrate surface either by the use of strong electrostatic fields or by particles such as atoms or ions or by the use of radiations, i.e. lasers.

The electrostatic desorption ionisation techniques, viz., Field Ionisation Mass Spectrometry (FIMS), Surface Ionisation Mass Spectrometry (SUIMS), Electrohydrodynamic Ionisation Mass Spectrometry (EHIMS), Spark Source Ionisation Mass Spectrometry; (SSIMS) except Electrospray Ionisation Mass Spectrometry (ESIMS) is usually preferred for the analysis of high melting inorganic substances, while the particle or radiation desorption ionisation spectrometry (as well as ESIMS) are usually used for the analysis of high molecular mass nonvolatile large biological molecules. The particle or radiation desorption ionisation mass spectrometry is also known as violent ionisation or energy sudden ionisation mass spectrometry. The energy sudden ionisation techniques, viz., Plasma Desorption Mass Spectrometry (PDMS), Fast Atom Bombardment Mass Spectrometry (FABMS), secondary ion/fast ion bombardment mass spectrometry (SIMS–FIBMS) and Laser Ionisation Mass Spectrometry (LIMS) have been able to produce intact ions from remarkably large molecules. In these methods, particles or radiations with high translational energies are used for ionisation of molecules from the surface of the analyte. The ionisation occurs via the translational modes of the sample molecule rather than the vibrational modes of the sample, consequently less thermal destruction of the ionised molecules occurs since the analyte molecule leaves its solid or liquid environment within a time of the order of 10^{-12} s. Efficient ionisation has been observed when the analyte is dispersed in a layer of suitable matrix of high boiling polar liquid rather than on a bare solid surface of the analyte. The sample should be more hydrophobic than the matrix so that it will occupy the matrix/vacuum interface. The polar solvent promotes ionisation and allows diffusion of fresh sample to the surface. The lifespan of the ions thus produced is about 20–30 minutes compared to a few seconds for ions produced from solid samples. The product ion currents are usually very small and except in the case of laser desorption, decrease rapidly with increasing molecular mass of the sample. When the ions are very large, their detection with multipliers (dynodes) requires post acceleration that are sometimes awkwardly high. Furthermore, the ions often have high levels of internal excitation that can cause significant peak broadening due to pre-dissociation.

The mass spectra usually exhibit prominent peaks corresponding to the adduct ions such as $(M + H)^+$ compared to M^+ ions which are sometimes not observed at all. The adduct ions such as $(M + Na)^+$ or $(M + K)^+$ or $(M + NH_4)^+$ also appear in the spectrum either due to the presence of salt impurities such as NaCl or KCl or NH_4Cl in the sample or upon addition of such salts to the analyte. Adduct ions due to the solvent such as $[(\text{solvent})_nH]^+$ are also prominent but do not complicate the spectrum and may be used for indexing the mass numbers.

The combination of DI, such as SIMS, LD and MS/MS, allows surface analysis of heterogeneous materials with both sensitivity (of a surface) and selectivity (of a compound). In addition, it improves the analysis of bulk samples and allows species generated directly by desorption or by ion/molecule reactions in the ion source to be characterised.

The selectivity of DI to both precharged moieties as well as surface has been used for derivatisation of samples chemically so as to produce ionic species at the surface. This can be done in situ and has been found effective in enhancing sensitivity and specificity of detection.

(a) Spark Source/Spark Source Ionisation-Mass Spectrometry (SS/SSI-MS) The potential value of SSMS was first demonstrated by Dempster around 1920s, but the technique came of age in 1950s when N B Hannay used the SSM spectrometer for the analysis of semiconductors. A schematic diagram of a spark source mass instrument

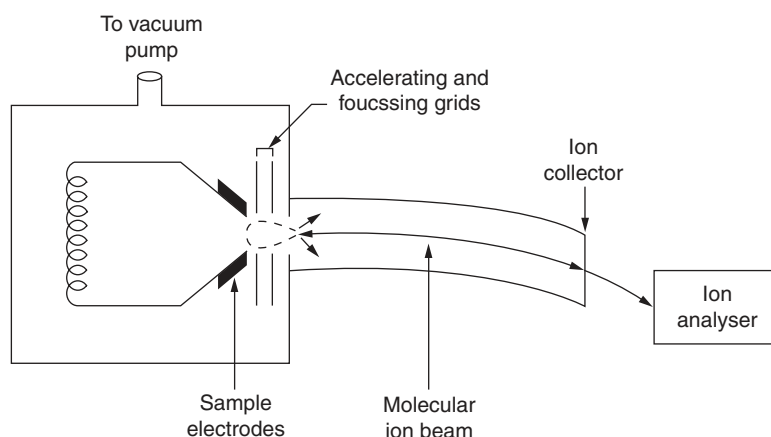


Fig. 11.16 A schematic diagram of a spark source mass spectrometer.

is shown in Fig. 11.16. In SSMS, the radio frequency (800 kHz) spark of high intensity using potential field of greater than 100 kV is produced between the two sample electrodes provided the sample is an ionic compound. Nonconducting samples can be mixed with some conducting material and converted into an electrode. The amount of sample required is less than 10 mg. Pulse length and repetition rate are controlled for selective volatilisation and to avoid overheating of the sample. The spark vapourises and ionises the sample. This method often leads to multiple ionisation like M^{++} and ions of high kinetic energy. The ions produced in the ionisation chamber are accelerated and fed to the mass analyser. For better resolution, double focussing instrument (especially with Mattuch–Herzog geometry) is used in SSMS.

The most important advantages of SSMS as an analytical tool are its high detection sensitivity and nonselectivity for all elements (including impurities as well) in the sample.

The technique is used for trace analysis of wide range of sample types, for example, high melting solids such as metals, oxides, refractory materials, etc.

(b) Surface Ionisation (SUI)/Filament Coating Mass Spectrometry (SUI/FC-MS) Just like SSMS, FCMS is also used for the analysis of inorganic materials. In FCMS, a very small amount of the material, i.e. a few micrograms is coated on a ribbon (tungsten) filament which also generates electrons. At a very high temperature (2000°C), of the filament, the sample vaporises and also ionises. For better efficiency, different numbers of filaments and configurations are used for which a triple filament is the most popular one. The filament is placed in the ionisation chamber and the ions are fed to the mass analyser after acceleration.

The probability of volatilisation of sample from a surface as a positive ion is a function of the ionisation potential (IP) of the sample and the work function (ϕ) of the filament and is expressed as

$$\frac{m^{\circ}}{m^{+}} \propto \exp\left(\frac{IP - \phi}{kT}\right) \quad (11.30)$$

where, m° is the number of neutral molecules and m^{+} is the number of positive ions.

This technique is very useful for analysis of inorganic compounds that have low ionisation potentials (3–6 eV) but is hard for organic compounds with ionisation potentials over the range of 7–13 eV. The method is especially useful for determining the isotopic abundance in inorganic compounds for geochemical applications such as age of rocks and minerals.

(c) Field Desorption/Field Ionisation Mass Spectrometry (FDMS/FIMS) This technique provides sample ionisation at relatively low energy with resultant reduced fragmentation and increased relative abundance of the parent ion. Desorption of adsorbed species under the action of very high electrostatic fields (of the order of 10^8 V/cm) was first observed by E W Muller in 1956 and by M G Inghram and R Gomer in 1955. But field ionisation mass spectrometry of organic molecules was first introduced, i.e. put into practice by H D Beckey in 1969. In this technique, a few micrograms of a sample is applied to a fine wire of a few micrometers diameter on whose surface is disposed an array of sharp needles or ‘whiskers’. The wire is placed in a vacuum and is maintained at + 8 kV (for positive ions) or –8 kV (for negative ions) and can be heated (Fig. 11.17). The field at the tips of the needles can be as high as 10^8 V/cm. The

analyte molecules desorb as M^+ ions from the tips of the needles by Coulombic repulsion where the field strength is very high. The energy available for field ionisation and subsequent excitation of a molecule is generally about 12–13 eV. Since organic molecular ionisation potentials range from 7–13 eV, many molecules will have very little excess energy in the parent ion to cause fragmentation. Frequently, a quasi-molecular ion MH^+ is observed due to a surface reaction of the sample with adsorbed water on the blade or emitter. A significant ion peak is observed in the heptanal $[CH_3(CH_2)_5CHO]$ spectrum at a mass of 115 ($C_7H_{14}OH^+$).

Although highly nonvolatile substances can be converted into ions but sample preparation is very tedious. It is very difficult to find and maintain the combination of temperature and voltage suitable for a particular species. Further, since the desorbed ions have very high energy, relatively high-resolution expansive magnetic sector analysers are used for their analysis.

This technique proved to be valuable for studying surface phenomena such as adsorbed species and the results of chemical reactions on surfaces. Since only a very small amount of internal energy is excited in the molecule by this process, few or no fragment ions are formed. This enables to determine the molecular mass and with a high-resolution spectrometer, the empirical formula for labile compounds; the amount of component parts of a mixture of compounds.

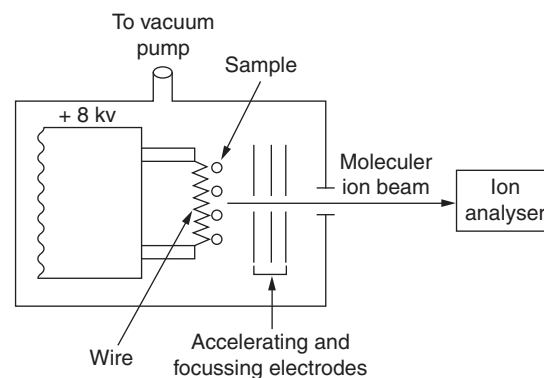


Fig. 11.17 A schematic diagram of a field desorption mass spectrometer.

(d) Electrohydrodynamic Ionisation Mass Spectrometry (EHMS) EHMS was first introduced by D S Simons, B N Colby and C A Evans, Jr. in 1974. In EHMS, the sample is dissolved in a low vapour pressure nonvolatile liquid such as glycerol and injected into an evacuated chamber through a small capillary which is maintained at high voltage. The low vapour pressure nonvolatile liquid is preferred, otherwise it will freeze dry from rapid evaporation into vacuum. Solute ions along with molecules and clusters of solvent are desorbed from the emerging liquid by the high field at its surface and are mass analysed. The drawback of this technique is that the desorbed ions are usually solvated with one or the other molecule of the solvent. As in FDMS, the high ion energies in EHMS require expansive magnetic sector analysers. Moreover, few liquids that have low vapour pressure are good solvents.

(e) Electrospray Ionisation Mass Spectrometry (ESI-MS) Electrospray ionisation has emerged as a powerful tool for producing intact ions from large and complex species in solution. In ESI-MS, highly charged droplets of an analyte in a suitable solvent are dispersed from a capillary or needle in an electric field and evaporated in flowing gas such as N_2 or CO_2 called the bath gas at atmospheric pressure, and the resulting ions are drawn into a mass spectrometer inlet. Electric field at the tip of the liquid orifice (i.e. capillary or needle) should be of the order of 40,000 V/cm magnitude and the liquid should have an electrical conductivity in the range 10^{-9} – 10^{-8} $\text{ohm}^{-1} \text{cm}^{-1}$. The number of unit charges per drop may run as high as 6×10^6 for a drop 34 μ in radius. ESI-MS differs from FD- and EH-MS in that desorption is from small charged droplets of solution into an ambient bath gas instead of into vacuum.

The initial experiments on electrospray ionisation were carried out in 1917 by John Zeleny, but the idea of using electrospray dispersion of an analyte solution in a bath gas (N_2) to produce solute ions for mass analysis including charge residue model (CRM) was originally developed in 1968 by Malcolm Dole and co-workers (L L Mack, R L Hines, R C Mobley, L D Ferguson and M B Alice). A well-defined breakthrough of the ESI-MS in its applications to identify large biomolecules, i.e. polypeptides and proteins of molecular mass 40 kDa was made in 1988 by M Mann, C K Meng and J B Fenn.

Charge Residue Model According to CRM, the charge on each droplet of an analyte solution is given by

$$q^2 = \alpha(3V\gamma\epsilon) \text{ (or } q = [\alpha(3V\gamma\epsilon)]^{1/2} \text{)} \quad (11.31)$$

where q is the charge on the droplet, V its volume, γ its surface tension and ϵ its dielectric constant. Evaporation of solvent from each droplet causes a decrease in their diameters. Consequently, the charge density on the surface of each droplet increases until the so called Rayleigh limit is reached at which the Coulomb repulsion becomes of the order as the surface tension. The resulting instability, sometimes, called a 'Coulomb explosion' tears the droplet apart, producing charged daughter droplets that also evaporate. It has been shown that the most stable state is obtained if the droplet having $\alpha = 4$ breaks down into four equal daughter droplets provided the charges remain on the parent droplet as the droplet evaporates. This sequence of events repeats until the radius of

curvature of the daughter droplet becomes small enough that the field due to the surface charge density is strong enough to desorb ions from the droplet into the ambient gas. The desorbing ions include cations (or anions) to which are attached neutral solvent or solute species; thus generating so called quasi-molecular ions for mass analysis. The schematic diagram for formation of quasi-molecular ions from the parent charged droplets has been shown in Fig. 11.18.

It is to be borne in mind that the electrospray of the dilute solution of an analyte is to be carried out in vacuum otherwise the drops would not evaporate within the required fraction of a second because of the strong evaporation cooling of the drop. The fall in temperature of the drop due to evaporation in vacuum, provided no heat is transferred to the drop, is given by the expression

$$\Delta T = T - T_o = (\Delta H_v / C_p) \ln x \quad (11.32)$$

where, T is the temperature to which the residue drop falls from the initial temperature T_o , ΔH_v is the heat of vaporisation of the liquid and C_p is the heat capacity of the liquid, x is the fraction of the drop remaining at temperature T . When half of the drop has evaporated, $x = 0.5$, the drop in temperature of the analyte droplet for benzene as solvent would be 160°C . Thus in order to maintain a high rate of evaporation, heat must be transferred to the drop. This is done by evaporating the drop in flowing nitrogen gas at atmospheric pressure.

A block diagram of an ESI apparatus has been shown in Fig. 11.19. The dilute solution of an analyte to be ionised is introduced into the evaporation chamber of plastic film through a hypodermic needle which is maintained at a few kilovolts relative to the walls of the chamber. The high voltage of the needle varies between 0 and 30 kV. The operating voltage needle is usually 10 kV negative with -3 kV on the first collimating plate and -1.4 kV on the second plate. The distance between collimating plates and the needle and supersonic nozzle can easily be changed. The resulting field at the needle tip charges the surface of the emerging liquid, dispersing it by Coulomb forces into a fine spray of charged droplets. A concurrent flow of bath gas (N_2) at one atmospheric pressure (pressure, temperature, rate of flow and direction of flow of the gas depend on the purpose of studies and the design of a particular ESI apparatus) enhances the evaporation of the charged droplets. The solvent vapours from the evaporating droplets along with any other uncharged material are swept away by the flow of the bath gas. The stream of quasi-molecular ions are collimated by electrostatic plates to the supersonic nozzle-skimmer system. Some of these ions emerge at the exit end of the nozzle as a supersonic free jet in the first of the two vacuum chambers, i.e. nozzle and skimmer chambers. The nozzle chamber is pumped by a mechanical pump (I) while the skimmer chamber is pumped by a cold trapped diffusion pump backed by a mechanical pump (II). When the pressure in the evaporation chamber is atmospheric, the pressure in the nozzle chamber is 0.13 torr and in the skimmer chamber is 1×10^{-4} torr. The beam of skimmed ions are directed by electrostatic lenses to the MS for mass analyses.

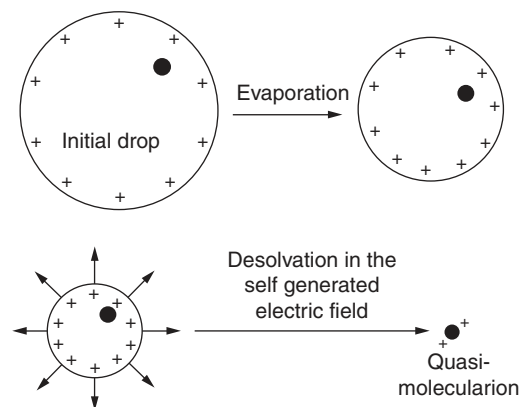


Fig. 11.18 Schematic diagram for the formation of quasi-molecular ions from the parent charged droplets.

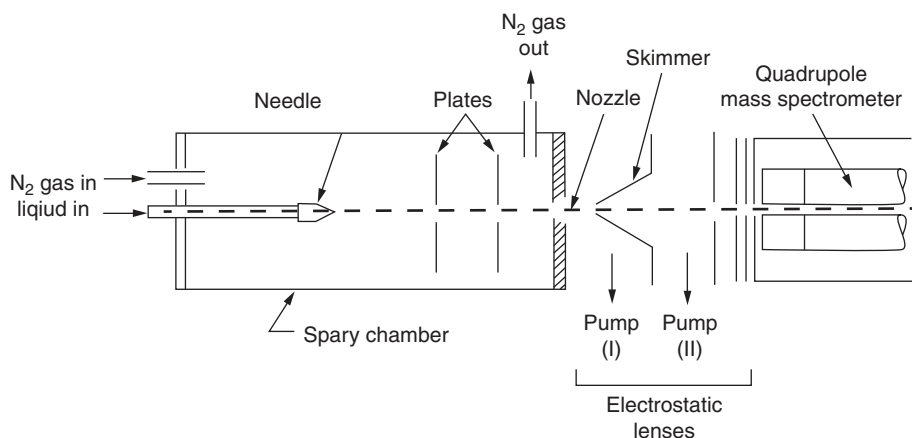


Fig. 11.19 Schematic diagram of apparatus for the production and detection of macroions.

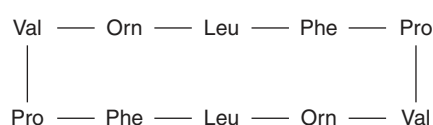
The supersonic nozzle and skimmer system has the following advantages: (i) Studies can be carried out at much higher pressures in the evaporation chamber since a two-stage reduction of pressure is operative in the system (ii) the intensity of the final beam of ions is much higher (eleven times or more) compared to that of conventional oven beam, (iii) in case of beam of mixed gases, i.e. seeded beams, the heavier molecules are more concentrated in the beam, and (iv) considerable velocity monochromisation takes place.

The ESI-quadrupole mass spectrum of a mixture of seven quaternary ammonium salts which cannot be vapourised without decomposition in a mixture of methanol–water (50:50) shows no evidence of either fragmentation or interference between species. The spectrum of the mixture gives peaks at

Components of the mixture	m/e ($\approx$ Peak height in mm)
$(\text{CH}_3)_4\text{N}^+$	74 (3)
$(\text{CH}_3)_3\text{C}_{10}\text{H}_{21}\text{N}^+$	200 (3)
$(\text{CH}_3)_3\text{C}_{12}\text{H}_{25}\text{N}^+$	228 (22)
$(\text{C}_4\text{H}_9)_4\text{N}^+$	242 (4)
$(\text{C}_4\text{H}_9)_4\text{P}^+$	259 (13)
$(\text{CH}_3)_3\text{C}_{16}\text{H}_{33}\text{N}^+$	284 (4)
$(\text{CH}_3)_3\text{C}_{18}\text{H}_{37}\text{N}^+$	312 (7)

The ESI-quadrupole mass spectrum of the antibiotic cyclic decapeptide gramicidin *S(A)*: in a methanol–water mixture (50 : 50) shows peak corresponding to the singly and doubly charged parent ions respectively at m/e : 1141 (2 mm) and 571:(41 mm). The average value of molecular mass of the compound based on the natural abundance of isotopes has been found to be 1141.5. The relative intensities of these peaks depend not only upon the composition of the solution but also on the concentration of the analyte. The intensity of the doubly charged ion grows enormously while that of the singly charged ion disappears at very low concentration. The relative magnitudes of intensities of the singly and doubly charged ions also depend on the structure. At concentrations for which the peptide cyclosporin (made up of eleven amino acids; one of which is not a normal acid but has been found to be a β -hydroxy, singly unsaturated amino acid and is derivative of threonine) whose size is similar to that of gramicidin *S(A)* shows peak corresponding to singly charged ion while gramicidin *S* produces doubly charged ions. The smaller peptide bradykinin (*B*) exhibits a strong peak corresponding to triply charged ion as expected since gramicidin *S* has two basic amino acids in its ring while the slightly smaller sized bradykinin has basic residues at both ends of the sequence.

Amino-acid sequence data in proteins can be obtained by mass spectrometry, i.e. ESI-tandem MS using even nanogram material of the sample. The mass analysis of proteins with molecular masses up to at least 130,000 can be carried out by ESI-mass spectrometry. The marriage of ES with FT ICRR to provide high resolution proved to be very useful in the analysis of very large macro ions, i.e. macromolecular ions with molecular mass greater than 130,000.



(A) : Gramicidin. S

Arg—Pro—Pro—Gly—Phe—Ser—Pro—Phe—Arg

(B) : Bradykinin

(f) Plasma Desorption Mass Spectrometry (PDMS) In PDMS, very high energy ions are used to desorb and ionise molecules in a solid-film sample. It was developed in 1976 by R D Macfarlane and D F Torgerson and was the first method to demonstrate feasibility for studying high molecular mass proteins and complex antibiotics.

Desorption and ionisation of a solid film of analyte on nickel foil (10^{-3} mm thickness) is carried out by the impact of a fission product of a radioactive isotope, usually californium-252 (Fig. 11.20). Each fission event of ^{252}Cf gives rise to two fragments $^{142}\text{Ba}^{18+}$ and $^{106}\text{Tc}^{22+}$ with kinetic energies of 79 and 104 MeV respectively. These fission fragments when pass through the sample, raise its temperature to about 10^4 K. Consequently, at such high temperature, desorption and ionisation of the molecules of the sample takes place, i.e. the analyte exists in

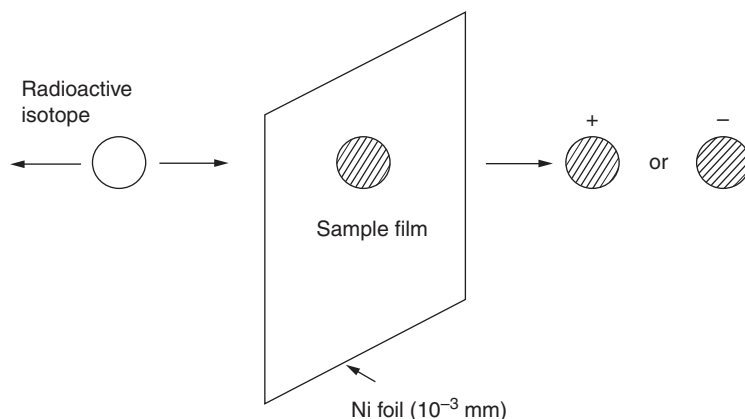


Fig. 11.20 A schematic diagram showing the impact of a fission product of a radioactive isotope on a solid sample film on nickel foil (10^{-3} mm).

the plasma state (gaseous state with equal number of positive and negative ions). The ions are accelerated and fed to the mass analyser. PD produces better molecular ion signals than FAB and FIB over the molecular mass range of 10,000–20,000 Da. The high molecular mass of ions that have been produced by this technique in 1989 by G Jonsson et al. is 45,000. The liquid matrix used in PD spectrometry is nitrocellulose.

(g) Secondary Ion/Fast Ion Bombardment Mass Spectrometry (SIMS/FIBMS) In SIMS, a beam of secondary ions is used to desorb and ionise the molecules from the solid or liquid surface of an analyte. The former technique was first developed as an analytical method in 1950s by Richard E Honig while liquid SIMS was developed in 1981 by M Barber and co-workers.

An incident beam of high-energy ions, such as 40 keV Cs^+ is used to bombard the sample layer obtained by dispersing the analyte in thioglycerol, glycerol, thioglycerol/diglycerol (1:1). More hydrophobic matrices used are tetragol [$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_4\text{H}$] and tetracol [$\text{HO}((\text{CH}_2)(\text{CH}_2)(\text{CH}_2)(\text{CH}_2\text{O})_n\text{H})$]. The desorbed ions after acceleration are fed to the mass analyser. Just like PDMS, MH^+ is usually the most abundant ion in the spectra of large molecules. The high molecular mass obtained using this technique was 24,000 Da by M Barber and B N Green in 1987.

(h) Fast Atom Bombardment Mass Spectrometry (FAB-MS) A block diagram of fast atom bombardment mass spectrometer is shown in Fig. 11.21. In FAB-MS, beams of neutral atoms of Xe or Ar having high translational energy are used to desorb and ionize compounds gently from the surface of a solid or liquid matrix, making it possible to obtain spectra of large, involatile polar organic molecules such as peptides, amino acids, etc. Fast atom bombardment of solids as a new ion source for mass spectrometry was first introduced in 1981 by M Barber, R S Bordoli, R D Sedgwick and A N Tyler. In matrix assisted FAB-MS, the liquid matrix used are the same as those used in fast ion bombardment mass spectrometry. The fast atoms of Xe (or Ar) are produced first by ionising Xe atoms with electrons to give xenon ‘radical cations, i.e. $\text{Xe} + e \rightarrow \text{Xe}^{+\bullet} + 2e$. The radical cations are then accelerated to 6–10 keV to obtain radical cations $\text{Xe}^{+\bullet}$ of high translational energy. The accelerated radical cations so produced when passed through xenon give rise to Xe atoms with high translational energy.

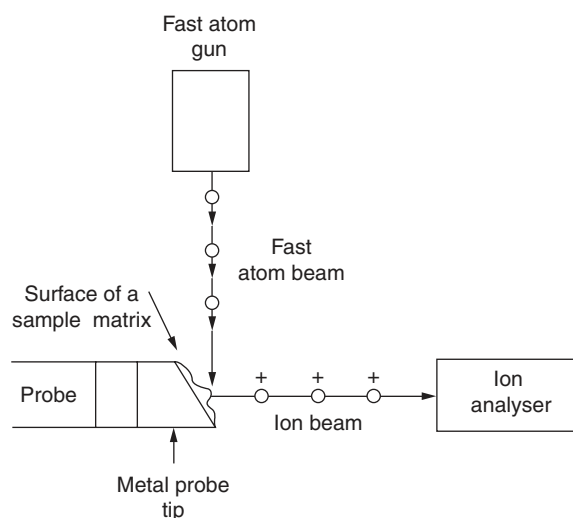
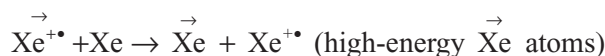
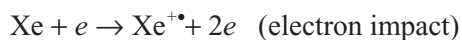
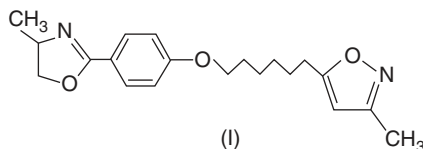


Fig. 11.21 A block diagram of a fast atom bombardment mass spectrometer.



The highest molecular mass of ions of polar analytes that have been analysed with FAB-MS is 24000 by M Barber and B N Green in 1989.

(i) Laser/Soft Laser Desorption Ionisation Mass Spectrometry (LIMS/SLIMS) A soft laser beam is used to desorb and ionise molecules from the surface of the analyte. It was developed in the late 1970s by Matten A Post Thumus, Peiet. Kistemaker and Henk L C Meuzelaar while matrix-assisted laser desorption deionisation mass spectrometry (MALDIMS) was developed in 1985 by Franz Hillenkamp and Michael Karas and independently by Koichi Tanaka and co-workers. In MALDI, different solid or liquid matrices containing a highly ultraviolet substance with absorption maximum matched to the wavelength of the laser pulse are used. For example, a nitrogen laser beam which has a wavelength of 337 nm, which is not absorbed by the aromatic amino acids in proteins and peptides, is used to avoid fragmentation. YAG laser at 266 nm is also used. The organic acids such as nicotinic acid, α -cyano-4-hydroxycinnamic acid, etc., are used as matrices. In matrix-free desorption, porous silicon surface is used to trap the analyte molecule because of its high absorptivity in the ultraviolet, acts as an energy receptacle for the laser radiation. Laser desorption ionisation on silicon (LDIOS)-TOFMS can handle a broad range of compounds including carbohydrates, peptides, glycolipids, natural products and small drug molecules in the mass range of 150–12000 Da with little or no fragmentation, e.g. 337 nm N_2 laser mass spectra of des-arg-bradykinin show peaks at m/e : 905 (MH^+) in absence of any salt; 905 (MH^+), 927 (MNa^+) in presence of NaCl and 905 (MH^+), 943 (MK^+) in presence of K_3PO_4 buffer solution; of antiviral win drug (I) exhibit peaks at m/e : 357 (MH^+), fragment peaks; 299, 180, 177, 121, of N-octyl- β -D-glucopyranoside exhibit peaks at m/e : 293 (MH^+), 315 (MNa^+) and 23 (Na^+); and of mixture of caffeine ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$), win drug and reserpine ($\text{C}_{33}\text{H}_{40}\text{N}_2\text{O}_9$) exhibit peaks at 196 (MH_2^{++}), 357 (MH^+) and 609 (MH^+) respectively.



The highest molecular mass of ions that have been produced with LD is 2,10,000 by Karas and Hillenkamp in 1988.

To summarise, some of the typical desorption ionisation mass spectral techniques and the energisation of a surface by various types of sources for the ejection of charged particles are shown in Fig. 11.22.

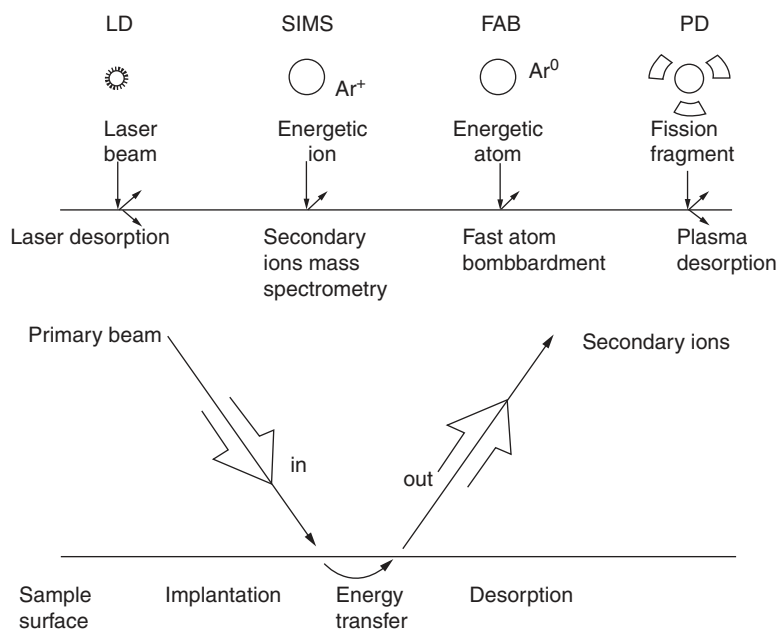


Fig. 11.22 Energisation of a surface by a variety of means results in ejection of charged species which give a mass spectrum of the solid.

11.7 ISOTOPE RATIO MASS SPECTROMETRY

Isotope ratio mass spectrometry deals with the direct measurement of ratio of isotopes, e.g. $^{12}\text{CO}_2$, $^{13}\text{CO}_2$; ^1HOH , ^3HOH , etc. A trace material can be detected even after great dilution. In an isotope ratio mass spectrometer, the ion currents corresponding to the two isotopic ion beams are measured simultaneously. The ratio of the two currents will give the ratio of the isotopic species. Isotopically labelled tracers are used to study the functions of the body. The age dating of minerals and rocks is based on the rate of decay of radioactive nuclides. Thus if the decay rate of ^{238}U to ^{206}Pb , ^{40}K to ^{40}Ar and ^{87}Rb to ^{87}Sr is known, and the ratio of the isotopes of one of these pairs is measured then the age of minerals and geological deposits can be estimated.

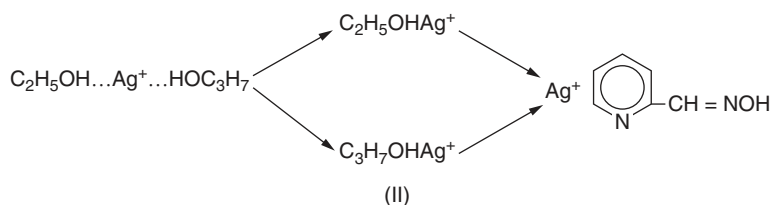
11.8 TANDEM MASS SPECTROMETRY (TANDEM MS)

With tandem-MS technique, it is possible to zero in on molecules of a particular compound or on groups of molecules which share a chemical trait. In tandem MS, i.e. MS-MS, a precursor ion usually M^+ or MH^+ is mass selected and fragmented by 'collision-induced dissociation (CID), also known as 'collisionally activated dissociation (CAD)', followed by mass analysis of the resulting product ions. Heavier collision gas such as Ar or Xe is used for low-energy collisions whereas He is used for high-energy collisions.

The collision-induced dissociation method was introduced in 1968 by Keith R Jennings. The technique requires two mass analysers in series (or a single mass analyser that can be used sequentially) to analyse the precursor and product ions and a schematic diagram of tandem-MS technique is presented in Fig. 11.23. This technique provides structural information by establishing relationships between precursor ions and their fragment products.

The combination of soft ionisation methods with collision induced provides power to tandem-MS in the analysis of mixture. One of the most popular types of MS instrument is the triple quadrupole mass spectrometer which was invented by Richard A Yost and Christie G Enke in 1978.

Tandem-MS technique provides evidence for the formation of metal–ligand bonds in the solvated metal ions and new metal–metal bonds in metal complexes in laser desorption process. For example, LD-MS/MS spectrum of pure silver foil in the presence of vapours of ethanol and isopropanol shows peaks at m/e : 107, 153 and 167 and are attributed to $^{107}\text{Ag}^+$, $\text{Ag} \dots \overset{+}{\text{O}}\text{Et}$ and $\text{Ag} \dots \overset{+}{\text{O}}\text{Pr}$ respectively. The kinetics of desolvation reaction provides direct information on the relative solvating power of the various organic molecules attached to the metal centre.



LD-MS/MS spectrum of Co_2L_3 ($M = 377$) where L represents the acetylacetonate ligand ($\text{CH}_3\text{COCH}_2\text{COCH}_3$, molecular mass = 100) shows peaks corresponding to the Co_2L_3^+ (377^+), CoL_3^+ (359^+), $\text{Co}_2\text{L}_2\text{O}^+$ (334^+), Co_2L_2^+ (318^+), Co_2LO^+ (234^+), Co_2L^+ (218^+) and CoL^+ (159^+) ions. The data show a strong tendency for both metal atoms to remain associated in the daughter ions formed from a mass selected parent ion of Co_2L_3^+ .

LD-MS/MS spectrum of zwitter ion $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_5\text{CO}_2^-$ in varying amounts of HCl indicates that the intensity of the MH^+ peak (m/e : 174) grows while that of peak at m/e : 128 decreases as the concentration of acid increases. This suggests that the intensity of the molecular ion peak of zwitter ion can be enhanced by converting the zwitter ion to molecule with a net charge.

The formation and characterisation of derivatives of amines by quaternisation in the gas phase can be carried out by LD/SI—MS/MS technique. For example, pyridine aldoxime (II) and ethyliodide adsorbed on a silver surface when sputtered into the gasphase by secondary ionisation and analysed by MS/MS technique shows peaks at m/e : 179^+ , 119^+ and 109^+ , 107^+ . They are attributed to the formation of diethyl analog of pyridine aldoxime and its decomposition products. The peaks at m/e : 109^+ and 107^+ are attributed to silver ions.

The last two examples prove the selectivity of DI to both precharged moieties, as well as surfaces.

Positive ion ESI-CID-MS/MS or CID-MS/MS or ESI-MS/MS and other soft ionisation MS/MS techniques proved to be very useful for identification and sequencing of polysaccharides and their derivatives. The nature of precursor ion depends upon the type of derivatisation. Thus the molecular mass related ions such as $(\text{M} + \text{Na})^+$, $[\text{M} + \text{H}]^+$, $[\text{M}' + \text{Na}]^+$, etc. (where M represents the free acid form and M' represents the full sodium salt) act as precursor ions. As an example, the basic structures of trisaccharides and their fragmentation patterns based on ESI-CID-MS/MS are given in schemes (1) and (2) respectively.

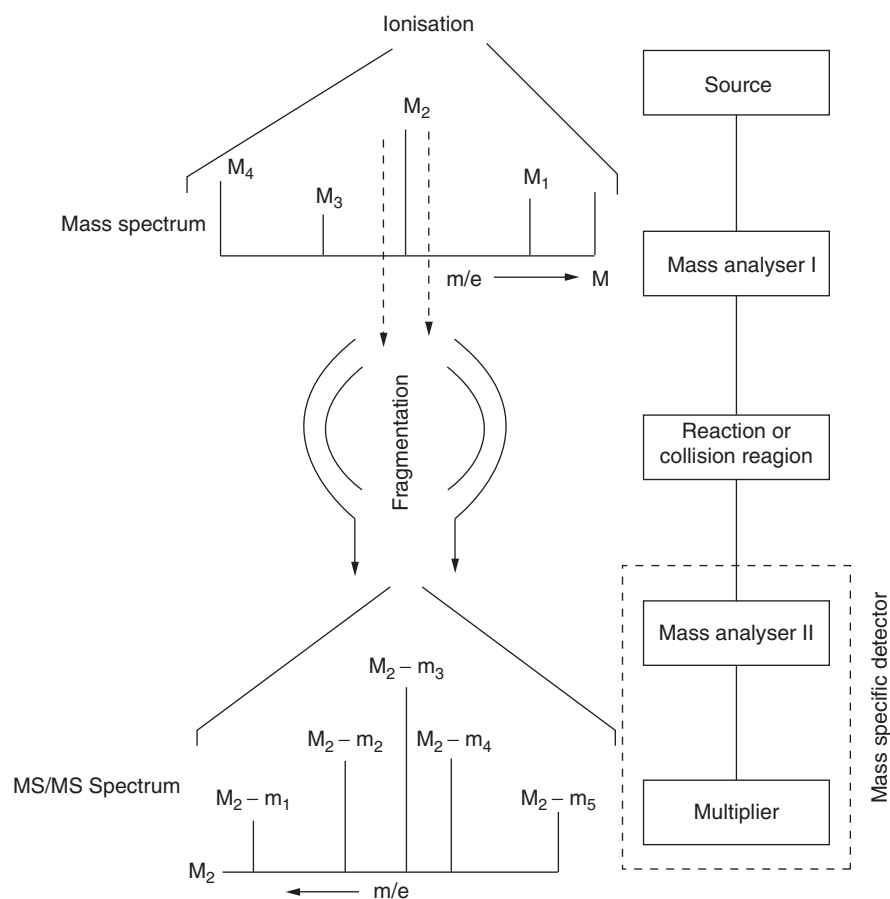
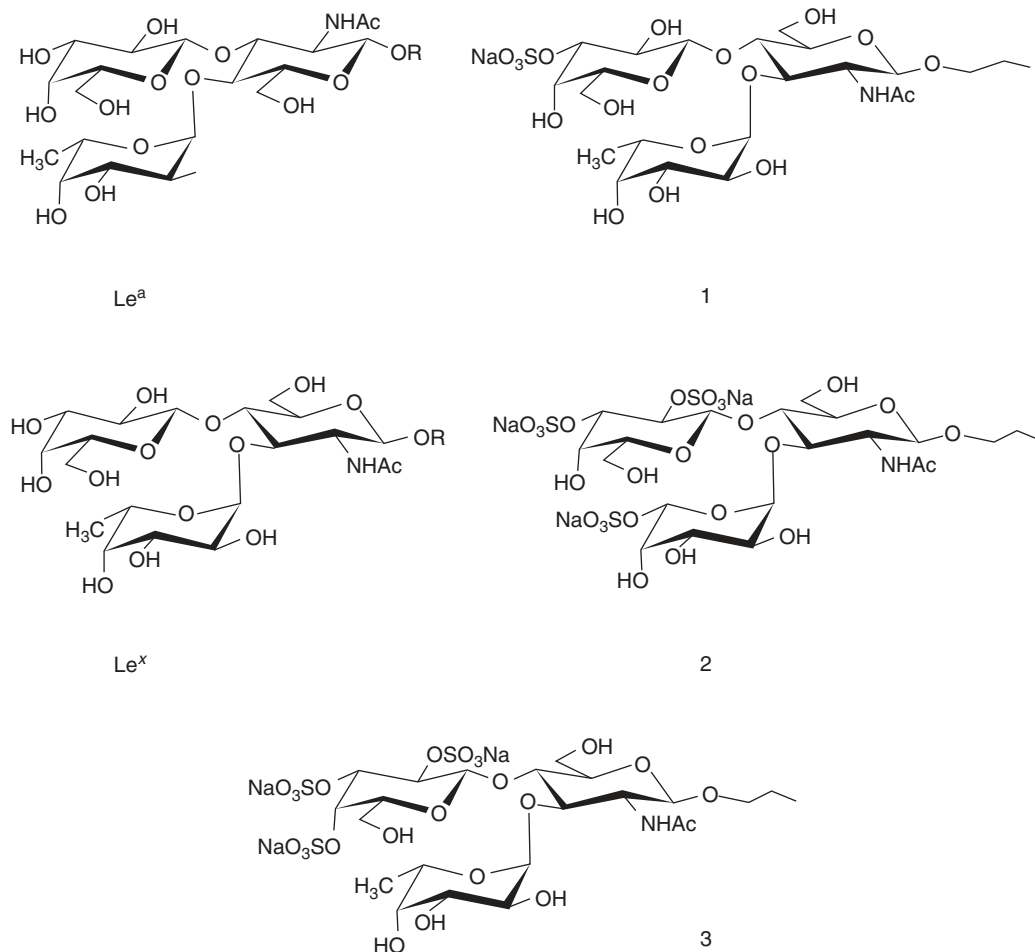
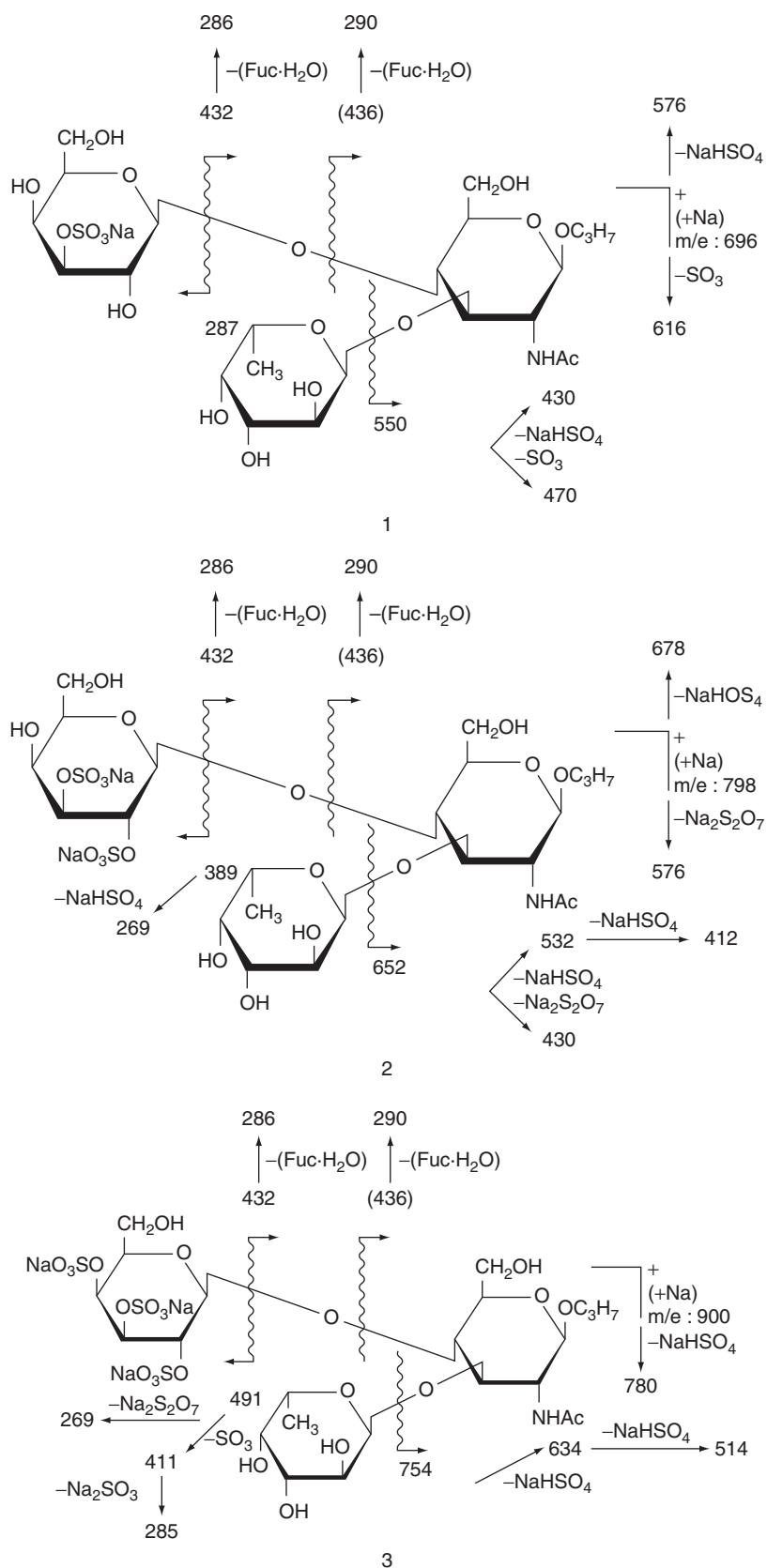


Fig. 11.23 A schematic representation of Tandem-MS technique.



Scheme 1. Basic structures of Le^a- and Le^x-type trisaccharides (left) and mono-, di-, and trisulphated Le^x-trisaccharide propyl glycosides (1-3) (right).



Scheme 2. Fragmentation patterns of the positive ion ESI C1D-MS/MS of sulphated Le^x -trisaccharides having the respective $(M' + \text{Na})^+$ as precursor ion.

11.9 GLC MASS SPECTROMETRY

GLC separates a mixture either of original volatile components or their volatile derivatives but does not characterise the components. One can infer indirectly by comparing the retention times with the possible known compounds. It can play a valuable role in combination with any other instrumental technique which can accept gaseous or volatile liquid samples and which is compatible in speed. The most important are infrared spectrometry, mass spectrometry,

etc. But such a marriage of GLC with MS proved to be very fruitful. GLC chromatograph is directly coupled to a mass spectrometer and the mass spectrum of each separated component is obtained as it emerges from the GLC. The effluent from a gas chromatograph is usually a pure substance in small quantity (10^{-12} – 10^{-3} g) in the gas phase and the identification of such a pure substance in very small quantity (10^{-9} – 10^{-12} g) is thus possible from its mass spectrum. Such different types of gas liquid chromatograph-mass spectrometers are widely used these days for the separation and characterisation of the components of a mixture of volatile substances. To summarise, GLC-mass spectrometry deals respectively with the separation and characterisation of the components of mixture of volatile substances with GLC chromatograph and mass spectrometer combination. The gas chromatograph separates the components of a mixture, while the mass spectrometer then imparts structural information about each one.

The direct coupling of GC and TOFMs was achieved in the mid 1950s by Roland S Gohlke and F W McLafferty in collaboration with W C Wiley, Maclaren and Dan Harrington. At about the same time, GC was coupled to a magnetic sector spectrometer by Joseph C Holmes and Frank A Morrell. But the great utility of modern GC-MS was made possible by the advent in 1960's of carrier gas separators also known as sample enriching devices that removed the GC carrier gas (i.e. He) prior to introduction of a sample into the high vacuum mass spectrometer. Schematic diagram of a typical computerised gas chromatograph/mass spectrometer is shown in a self-explanatory, Fig. 11.24 (a) and (b). Separators were developed independently by Einar Stenhagen; Kagnar Ryhage and by Watson and K Biemann. Separators designed for the enrichment of concentration of sample in the carrier gas are based on (i) the faster diffusion of carrier gas through the membrane, and (ii) preferential passage of sample molecules through a membrane called the semipermeable membrane.

Ryhage introduced the effluent of the GLC as a jet striking against a metal surface which had two, very closely spaced tiny holes. The sample passed through the holes but the bulk of the lighter carrier gas was pumped out. This led to enrichment and the same process was repeated again when a sample sufficiently enriched to give a good mass spectrum was obtained. A schematic diagram of a two-stage membrane separator based on the model of Watson and Biemann separator is shown in Fig. 11.25.

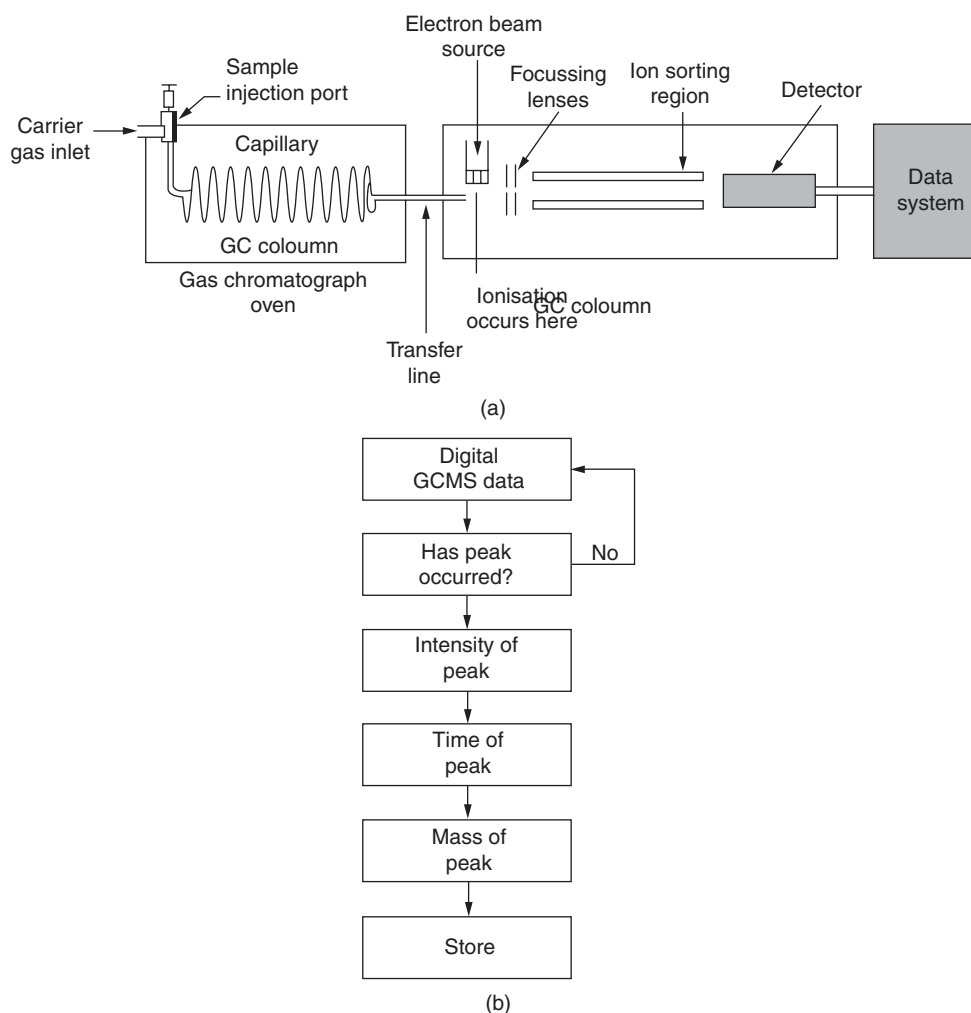


Fig. 11.24 (a) Schematic diagram of a typical capillary gas chromatograph/mass spectrometer, and (b) a conceptual representation of computer processing of digitised GCMS data.

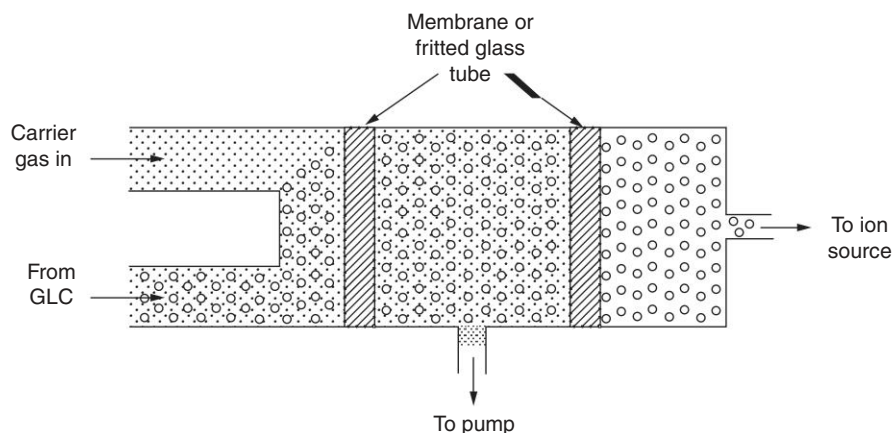


Fig. 11.25 Schematic diagram of a two-stage membrane separator based on Watson and Biemann model.

As the sample carrier gas mixture passes through the glass fritted disc, the lighter gas diffuses out faster and the sample gets enriched. The whole system can be heated up to 400°C. The quantity of any gas going through the porous glass is given by

$$Q = k p \sqrt{1/M} \quad (11.33)$$

where, p is the partial pressure of the component, M is the molecular mass, and k is a constant that depends on the conductance of the porous tube. The pressure on the outside of the porous tube is assumed to be sufficiently reduced so that back effusion is negligible. The ratio of the sample Q_s to the quantity of helium carrier gas V_{He} that goes through the frit, is

$$\left(\frac{Q_s}{V_{He}} \right)_{\text{frit}} = \frac{p_s}{p_{He}} \sqrt{\frac{M_{He}}{M_s}} \quad (11.34)$$

V_{He} is expressed in units of $\text{cm}^3 \text{ atm/min}$.

For molecular flow to occur through the porous tube, the mean free path of the gas must be large in comparison with the diameter of the pores. The average pore size in ultrafine sintered glass is about 10^{-4} cm .

Thus, the allowed pressure, corresponding to $L = 10^{-4} \text{ cm}$; ($L = \frac{5 \times 10^{-3}}{p} \text{ cm}$, where p is the pressure in torr;

1 torr = 1 mm of Hg) is 50 torr. In practice, 1–10 torr is preferred to avoid adverse effects from the pore-size distribution. Silver membranes instead of glass-fritted disc, have also been used. However, if a Teflon membrane (up to 300°C) is used instead of the fritted disc then only the organic substrate diffuses into the mass spectrometer. Silicon rubber membranes, which act as semipermeable membranes for organic vapours and reject the carrier gas, are also used. By such techniques, good mass spectra have been obtained for compounds as large $\text{C}_{20}\text{--C}_{24}$ fatty acid esters. It is to be noted that one separator should perform over the entire range of GCMS analysis. The effectiveness of every separator depends on the chromatograph (flow conditions), the chemical sample (temperature), and the mass spectrometer (pumping speed). Time of flight, or quadrupole mass filter or quadrupole ion trap spectrometers are ideal for coupling with gas liquid chromatographs as they are fast compared to double focussing mass spectrometers. Scan times being faster (i.e. fraction of second is required to record each spectrum), and so several mass spectra can be obtained during the elution of a single peak from the GLC unit. Such mass scans at different points of a GLC peak enable to check its homogeneity. Thus, partially overlapping chromatographic peaks can be resolved.

High-pressure or performance liquid chromatography-mass spectrometry (HPLC-MS) is used for compounds which are not amenable to GLC-MS analysis such as nonvolatile, thermally labile and high-molecular-mass polar compounds. Pumping pressures of several hundred atmospheres are required to achieve reasonable flow rates with modern packings which are made up of particles with diameters of $10 \mu\text{m}$ or less.

Applications of modern GLC-MS include identification of optical isomers, environmental analysis, drug testing, e.g. the identification of steroids and drug metabolites in urine and blood, pharmacological studies, etc.

In conclusion we can say that chromatographic methods normally mated to mass spectrometry are liquid chromatography, however, particularly for desorption ionisation, it is possible to interface thin layer, and paper chromatography and electrophoresis directly impinging the ionisation beam on the surface of the chromatogram, i.e. direct examination of chromatograms to characterise individual spots can be carried out. The primary ion, atom or laser beam is simply directed on the spot and a mass spectrum is recorded.

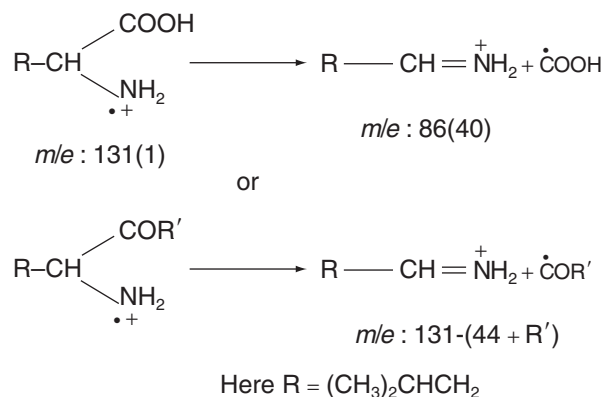
11.10 MERITS AND DEMERITS OF VARIOUS TYPES OF IONISATION—MASS SPECTROMETRY

The advantages and disadvantages of various types of ionisation techniques are related to the volatility and non-observance of the molecular ion peaks of the compounds. The volatility problem is mainly encountered in case of natural products (*in vivo* and *vitro*), i.e. amino acids, peptides, proteins, steroids, triglycerides, sugars, etc., because of their higher melting and boiling points, i.e. low vapour pressures. The merits and demerits of these techniques are elaborated here by taking examples of amino acids and steroids. The major peaks in the mass spectrum of leucine (molecular mass = 131) obtained by EI-MS, CI (isobutane, 200°C) and FD techniques are compared in Table 11.4.

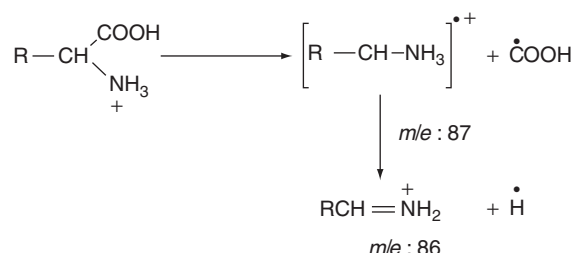
Table 11.4 A comparison of EI, CI and FD mass spectra of leucine.

Technique	<i>m/e</i> (peak highest in mm × 10)
EI	131(1), 86(40), 74(13), 44(26), 30(23)
CI	132(39)
FD	132(25), 87(39), 86(29), 60(11), 45(31), 31(22)

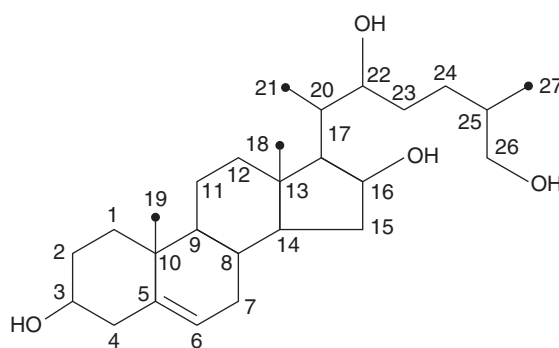
The data reveal that EI spectra of amino acids or their derivatives, i.e. ester give weak or nonsignificant molecular ion peaks, but non-EI spectra give either molecular or quasi-molecular ion peaks. The weak molecular ions in the EI spectra arise because amino acids easily lose their carboxyl group and the esters easily lose their carbo-alkoxyl group upon electron impact.



The FD spectrum exhibits an MH^+ ($m/e : 132$) peak that fragments as follows to give peak at $m/e : 86$.



The important peaks in the spectrum of cholesten-5-ene-3, 16, 22, 26-tetrol (molecular mass = 434) a polyhydroxy steroid (A) obtained by different M-S are EI (m/e (peak height in mm × 10)) : 434 (non-existent), 318 (2), 300 (5), 285 (4.8), 267 (6), 145 (7), 99 (39), CI (isobutane, 200°C) : 417 (16), 399 (32), 381 (13), 373 (non-existent), 283 (25), 271 (23), 255 (12), 99 (39) and FD : 434 (38).



(A): Cholesten-5-ene-3, 16, 22, 26-tetrol

EI spectrum exhibits a weak or non-existent molecular ion peak. This shows that dehydration is partly caused by heating. In CI-MS, the absence of protonated molecular ion peak reveals that the dehydration of the protonated ion occurs readily (i.e. m/e : $435 \xrightarrow{-H_2O} 417$). Facile dehydration is not observed at all in the FD spectrum that shows only a molecular ion peak at m/e : 434.

To summarise, it is concluded that the merits and demerits of a particular type of ionisation mass spectrometry are not only governed by the volatility and non-observance of molecular ions of the compounds but also upon the sensitivity and specificity of the ion-mass spectrometry.

11.11 INTENSITIES OF THE SIGNALS IN THE MASS SPECTRUM

Intensity of the signal is a measure of the relative abundance of ions which is given as the per cent intensity of a given peak relative to the most intense peak in the mass spectrum. The most intense peak in the spectrum is also called the base peak and is not necessarily the peak due to the molecular ion. Intensity of a given peak is also expressed in per cent of total ionisation (Σ) given by peak height and is obtained by dividing the intensity of a given peak by the sum of the intensities of all peaks, i.e.

$$\Sigma = \text{Peak height} = \frac{\text{Intensity of the given peak} \times 100}{\text{Sum of the intensities of all peaks}} \quad (11.35)$$

The relative peak heights of the peaks give a measure of the relative numbers of different ions produced from the sample.

Problem 11.5: Determine the peak heights corresponding to the mass spectral data on methanol given below:-

m/e	15	19	29	31	32	33
Per cent of base peak	35.48	0.29	58.80	100	68.03	0.98

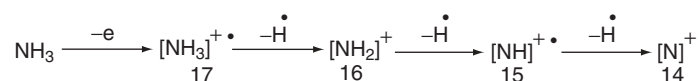
Solution Sum of the intensities of all peaks = 263.58

Substituting the needed data into Eq. (11.35) we get

m/e	15	19	29	31	32	33
Peak height (or Σ)	13.46	0.11	22.30	37.94	25.81	0.37

11.12 INTENSITY OF THE PARENT PEAK AND FACTORS AFFECTING IT

One finds a number of peaks in the mass spectrum. The parent peak is usually the last distinct peak in the spectrum and after that one usually observes small peaks due to isotopes at m/e : $M + 1$, $M + 2$, etc. For example, the mass spectrum of NH_3 shows peaks at m/e : 14, 15, 16 and 17 and a small peak at 18. These correspond to the molecular ion and to the fragments.



The $M^{++} + 1$ peak appears in the m/e = spectrum because most elements (e.g. nitrogen and hydrogen) have more than one naturally occurring isotope. Although most of the NH_3 molecules in a sample are present as $^{14}\text{N}^1\text{H}_3$, a small but detectable fraction of molecules is also present as $^{15}\text{N}^1\text{H}_3$ and $^{14}\text{N}^1\text{H}_2^2\text{H}$. These molecules, i.e. $^{15}\text{N}^1\text{H}_3$ or $^{14}\text{N}^1\text{H}_2^2\text{H}$, produce molecular ions at m/e : 18, i.e. at $M^{++} + 1$. This is true if the compound is pure and has no impurities. Thus if the compound contains only C, H, N, O, F and I only, the intensities of the $(M + 1)$ and $(M + 2)$ peaks can be calculated from the following formulae:

$$\text{per cent } (M + 1) = 100 \left[\frac{(M + 1)}{(M)} \right]$$

$$= 1.1 \times \text{number of carbon atoms} + 0.36 \times \text{number of nitrogen atoms} \quad (11.36)$$

$$\text{per cent } (M + 2) = 100 \left[\frac{(M + 2)}{(M)} \right] = \left[\frac{1.1 \times (\text{number of carbon atoms})^2}{200} \right] + 0.20 \times \text{number of oxygen atoms} \quad (11.37)$$

These formulae are useful provided we have a prior idea of the molecular formula of the compound under consideration. These equations aid in determining the molecular formulae of the compounds.

The parent peak is not equally prominent in all organic compounds. It is big in some cases, small in others and negligible in some others or totally absent (due to very fast rate of decomposition) in some others. Since delocalisation of positive charge over a large volume, i.e. polarisability, increases the stability of the compound the intensity of the molecular ions in such systems will be large. This is possible where ever π -electrons are present and as such aromatic compounds show the highest intensity for parent ions, i.e. double bonds, cyclic structures, and especially aromatic (or heteroaromatic ring) stabilise the molecular ion and thus increase the probability of its appearance. Biemann has classified molecular ions according to their stability (or intensity) as follows:

Aromatic compounds > Conjugated olefins > Alicyclic compounds > Sulphides > Unbranched hydrocarbons > Ketones > Amines > Esters > Ethers > Acids > Branched chain hydrocarbons > Alcohols.

The modified version of Biemann series has been expressed as follows:

(a) High Intensity Group Molecular ions of this group follow the order of intensity indicated below:

Aromatic compounds > Conjugated alkenes > Cyclic compounds > Organic sulphides > Short, normal alkanes > Mercaptans.

(b) Medium Intensity Group The order of intensity of molecular ions in this group are: Ketones > Amines > Esters > Ethers > Carboxylic acids~Aldehydes~Amides~Halides.

(c) Lowest Intensity Group The molecular ions are not frequently detectable in aliphatic alcohols, nitrites, nitrates, nitro compounds, nitriles, and highly branched chain compounds.

The nature of the functional groups also affects the stability or intensity of the parent ion like the following which assist in fragmentation:

- (i) side chain of the aromatic system
- (ii) allylic systems; $R-CH_2-CH=CH_2$
- (iii) hetero atoms like O, S, N, etc., which can stabilise charge.
- (iv) branching

Stabilisation of charge is also governed by resonance and inductive effects.

Ionisation voltage, i.e. energy of the bombarding electrons and temperature of the ionising source, also influence the parent-ion intensity and the fragment pattern. The relative intensity of the molecular ion increases as the ionisation voltage is decreased from 70–15 V but it decreases for all fragment ions. Thus one can obtain the molecular mass of the compound. The parent-ion intensity decreases as the temperature of the ion source, i.e. sample, increases and vice versa. The increase in temperature increases the initial thermal energy and thus the internal energy of the molecular ion and hence its instability. For instance, the average internal energy of 1,2-diphenylethane decreases by 0.4 eV on lowering the temperature from 200° to 75°C.

The effect of temperature on internal energy increases as the molecular size increases but the reduction of sample temperature for larger molecules is limited by sample vapour-pressure requirements. If the pressure in the ion source is increased, ion molecular reactions (i.e. collision reactions) take place and ions higher than the molecular mass may be observed with the reduction in the parent ion intensity.

11.13 RULES FOR THE MODE OF FRAGMENTATION OF MOLECULAR IONS

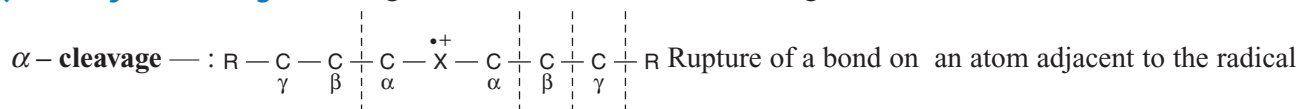
Before describing the rules for the mode of fragmentation of molecular ions, the most common terms and symbols used in the discussion need be defined:

- M^+ – designates an even electron ion (or an ion with paired electrons)
- $M^{\bullet+}$ designates an ion with unpaired or odd electrons or cation radical
- M^- designates a negative ion (i.e. an electron is added to the ion)
- $M^{\bullet-}$ represents a negative ion radical or anion radical.
-  – Full arrow represents the transfer of pair of electrons.

(a) Heterolytic Pair Cleavage A pair of electrons move together towards the charged site.

 – fish hook or a single barbed-arrow-represents the transfer of a single electron.

(b) Homolytic Cleavage A single electron moves towards the charged site.



(c) Precursor The decomposing ion in any reaction. For example, the parent ion is a precursor to the daughter ion.

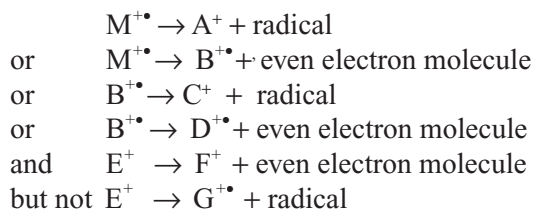
(d) Elimination Reaction Reaction in which cyclisation occurs to form a new bond between two parts of an ion with the loss of the actual group connecting these parts.

(e) Displacement Reaction Reaction in which cyclisation occurs to form a new bond at a carbon atom with the loss of another group attached to that carbon atom.

(f) Rearrangements Reaction in which the molecular arrangement of the atoms in either the ion or neutral product is not the same as in the precursor ion. Rearrangements occur via cyclisation, displacement, elimination, and hydrogen transfer.

Collision induced transformation.

(g) The Even Electron Rule The nitrogen rule is the basis of the even electron rule. According to the former rule, the molecular masses of compounds containing C, H, N, (O) are odd when the number of nitrogen atoms is odd. Thus when C, H, O compounds lose neutral molecules, i.e. even electron molecules such as H_2O , HCN , olefins, CH_3COOH , etc., even mass fragment ions are formed whereas odd mass fragment ions are formed when C, H, O molecules lose radicals such as CH_3 , OCH_3 , etc. According to the even electron rule, an odd-electron ion decomposes to an even electron ion or an odd electron ion respectively with the loss of a radical or an even electron molecule. Whereas an even electron ion always decomposes to an even electron ion with the loss of an even electron molecule but not to an odd electron ion with the loss of a radical. To summarise, the rule can be written as



Especially the rule is most common to decompositions which give metastable ions. Exceptions to the rule are some di-iodides which successively lose iodine radicals from the molecular ion.

(h) Mode of Fragmentation of Positively Charged Molecular Ion The mass spectrum of any compound shows dozen peaks, some big, some small and some negligible, e.g. hydrocarbons exhibit series of ions represented by $\text{C}_n\text{H}_{2n+1}^+$, $\text{C}_n\text{H}_{2n}^+$ and $\text{C}_n\text{H}_{2n-1}^+$. The mass interval between two consecutive ions in each series is always CH_2 (= 14 mass units) units. The largest peak in each ions series represents a $\text{C}_n\text{H}_{2n+1}^+$ fragment and this occurs at $m/e : 14n + 1$, this accompanied by $\text{C}_n\text{H}_{2n}^+$ by $\text{C}_n\text{H}_{2n-1}^+$ fragments.

Ion series	m/e
$[\text{C}_n\text{H}_{2n+1}]^+$	15, 29, 43, 57, ...
$[\text{C}_n\text{H}_{2n}]^{++}$	14, 28, 42, 56, ...
$[\text{C}_n\text{H}_{2n-1}]^+$	13, 27, 41, 55, ...

A substance having a strong parent peak often contains a ring, and the more stable the ring, the stronger the parent peak. Ring compounds usually contain peaks at mass numbers characteristic of the ring. Usually the most intense ion, called the base ion, is taken as 100 per cent and the intensities (height $\times$ sensitivity) of the other ions are expressed in percentage. Peaks with at least 5–10 per cent of the most intense ion are the only ones of interest. Secondly one does not usually gather much information from the low mass region of the spectrum as they arise from any number of routes from the major fragmentation processes. With these restrictions, let us consider the mode of fragmentation, i.e. the fragmentation pattern of the molecular ions. As has already been explained earlier, 'the more stable the ion the higher is its intensity and if a daughter ion is more stable than the parent ion, its intensity will be greater. The relative height of the molecular ion peak is greatest for the straight-chain compounds and decreases

as the degree of branching increases and usually decreases with increasing molecular mass in a homologous series except that of fatty acid esters. Accordingly, the branched chain hydrocarbons do not exhibit molecular ion peak while, straight chain hydrocarbons show a very weak peak. It follows from this that energetically more favourable tertiary carbonium ions, (carbocations) are usually produced by fragmentation in preference to primary and secondary ions, (i.e. the stability of carbocations follows the order: tertiary > secondary > primary); hence when one is considering a branched chain aliphatic system, fission takes place at the branching and the charge goes with the more substituted carbon atom and also stable allyl and benzyl groupings, ions and radicals; dehydration (water loss in alcohols) and decarboxylation reactions occur readily, etc. In alkanes, the stability of carbon ion has the order.



The stability of free radical lost depends upon (a) nature of the free radical, whether primary, secondary or tertiary and (b) length of the straight chain since it permits greater dispersal of odd electrons. Greater the dispersal of odd electrons, greater the stability of the free radical, e.g. $n\text{C}_4\text{H}_9^\bullet$ is more stable than $\text{C}_3\text{H}_7^\bullet$, i.e. generally the largest substituent at a branch is eliminated most readily as a radical. As stated earlier, the cleavage of the molecular ion usually involves the rupture of the bonds near the site of localised positive charge. Accordingly, the modes of fragmentation have been classified as follows. The bond fission at the carbon atom linked to a hetero atom (i.e. a noncarbon atom) or to a group on which the positive charge resides is called α -. The cleavages of the successive C—C bonds are respectively termed the α -, β -, γ -, etc., fissions; α -ruptures are most common. Bond fissions occurring without the migration of individual atoms or groups are known as ordinary fissions and those occurring with by such migration are called rearrangement fissions. Products of fission in the former are a part of the parent molecule while that of the latter are not.

(i) Ordinary Fissions These are primary single-bond cleavage processes associated with saturated and unsaturated aliphatic and aromatic compounds and with some common functional groups such as amine, ketal, ether (X = O), thioether (X = S), ketone, aldehyde, alcohol (X = O), thiol (X = S), ester, halides (X = F, Cl, Br, or I), etc.

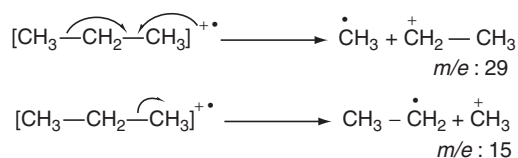
(i) Single-bond fissions in alkanes give rise to fragments which are even electron cations:



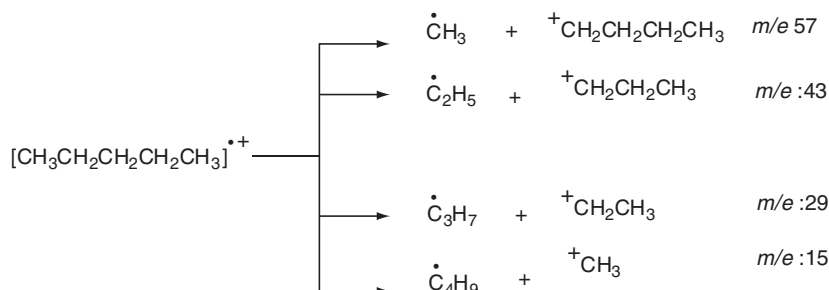
where R represents the alkyl group.

The loss of the largest alkyl group is favoured and the charge resides on it.

The mass spectrum of propane shows two peaks at m/e : 15, 29 and $\text{I}_{29+} > \text{I}_{15+}$. The ions are formed as



Dispersion of electrons is more in C_2^+H_5 as compared to C^+H_3 . Accordingly, C_2^+H_5 is more stable than C^+H_3 . In case of n -pentane, the mode of fragmentation is

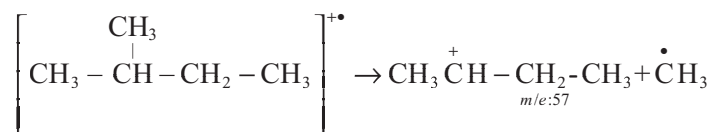


Further fragmentation of the carbocations causes the loss of one or two hydrogen atoms. This gives rise to additional peaks in the spectrum of the parent compound.



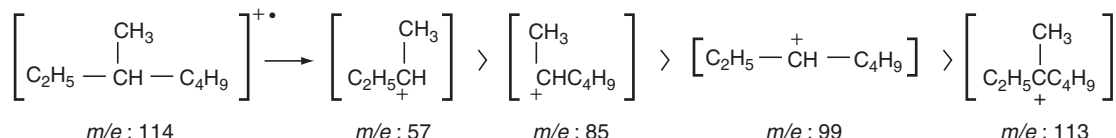
The base peak corresponds to 43^+ .

The mass spectrum of 2-methyl butane is similar to that of *n*-pentane except that the base peak is observed at m/e : 57.



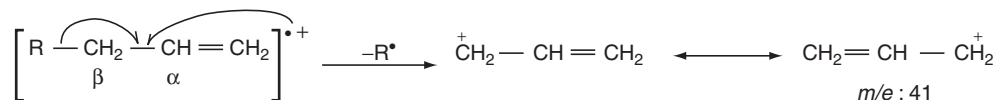
57⁺ being secondary carbocation is more stable than 72⁺, 43⁺ and 29⁺ ions.

Let us now consider the mode of fragmentation of 3-methyl heptane. The formation of carbocations follows the order:

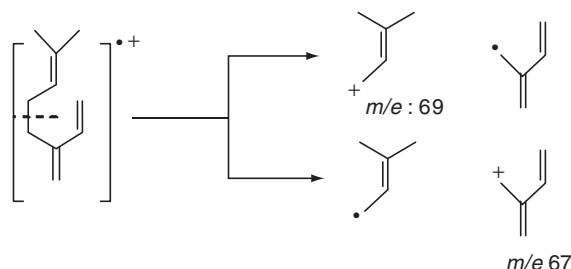


113⁺ is the most stable ion as compared to 114⁺, 99⁺, 85⁺ and 57⁺ ions. Thus loss of the largest alkyl radical at the reactive site, i.e. at the branch is preferred.

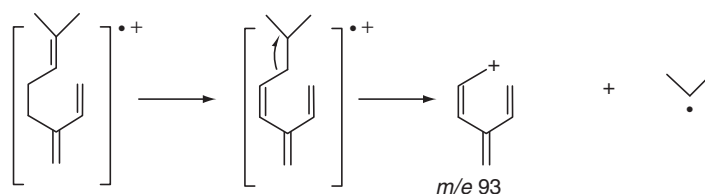
- (ii) Fragmentation often occurs at the allylic position (i.e. cleavage β to the double bond is favoured and results in the resonance stabilised allylic carbocation). The rule does not apply to simple alkenes because of ready migration of the double bond but applies to cyclo-alkenes.



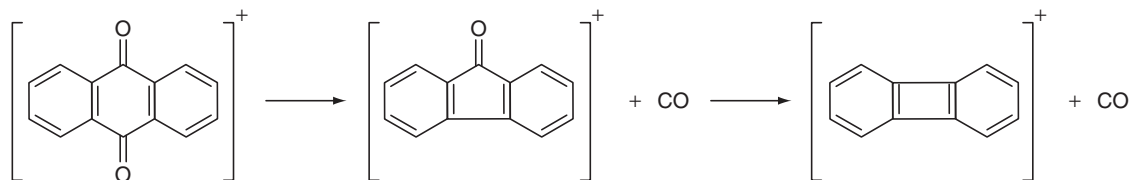
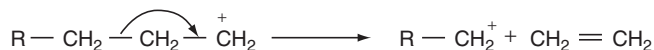
For example, the cleavage in myrcene occurs at the allylic position.



The peak at m/e : 93 is due to increased conjugation followed by allylic cleavage:

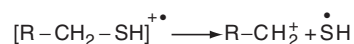
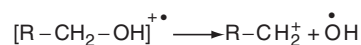
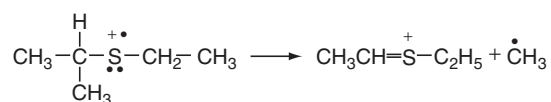
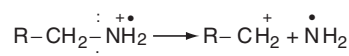
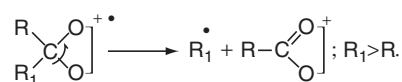
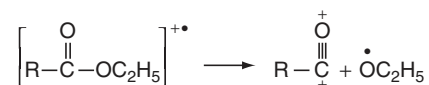
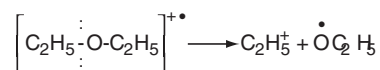


- (iii) The charge is often stabilised by the elimination of a neutral fragment like CO, HCN, olefins, H₂O, NH₃, H₂S, ketene or alcohols.

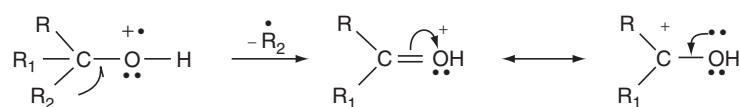
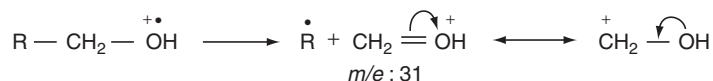
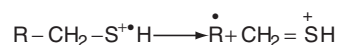
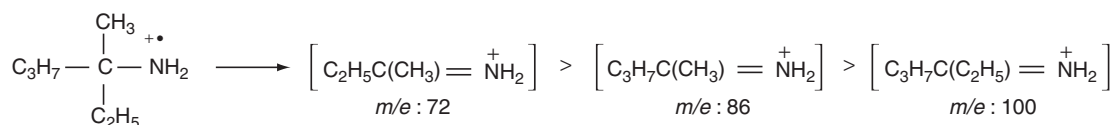
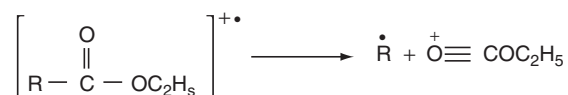
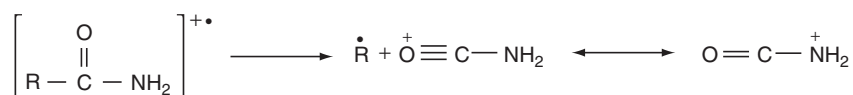
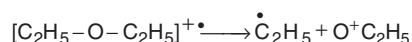


- (iv) When an electron negative atom is present, the rupture occurs adjacent to the hetero atom with the charge residing on the alkyl fragment. This applies to ethers, esters, halogens, alcohols, amines, etc. For example;



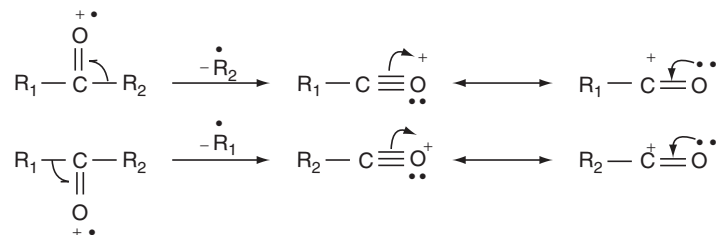


Hetero atoms stabilise the charge, i.e. the charge is retained by the hetero atom and the alkyl group appears as a radical.



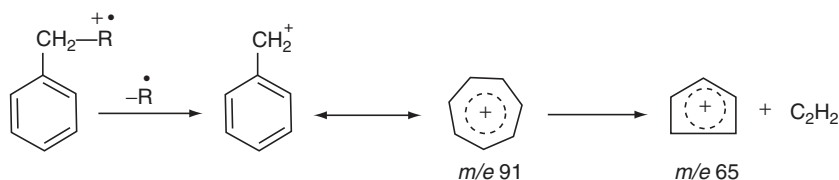
$R_2 > R_1$ or $R = \text{alkyl}$, when R_2 and/or $R_1 = \text{H}$ and $M - 1$ peak can usually be observed. Thus primary alcohols will give peaks of mass 31, secondary alcohols of mass $30 + R$ and tertiary alcohols of mass $29 + R$, i.e. at m/e : 31, 45 and 59 when $R = \text{CH}_3$.

- (v) If the hetero atom is connected by a multiple bond (e.g. $\text{C}=\text{O}$), the rupture occurs at the carbon-atom attached to it and the charge is retained by the carbonyl group, i.e. resonance stabilised acylium ion.



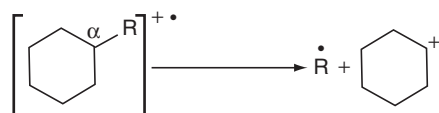
The base peak very often results from the loss of a larger alkyl group. Here, $R_2 > R_1$.

- (vi) In alkyl substituted aromatic compounds, the cleavage occurs at the benzyl position, i.e. at the bond β to the ring as benzyl ion will be in resonance with the tropylium ion:

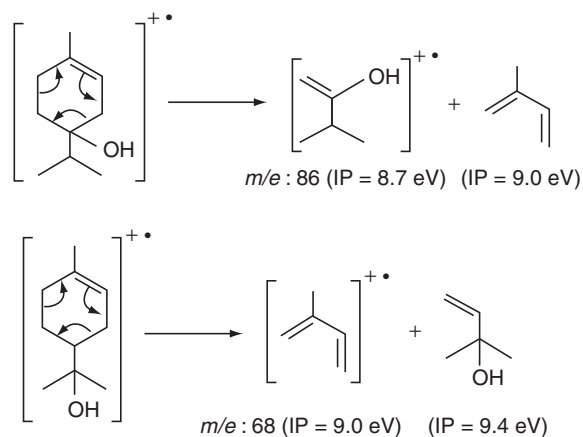


Phenyl alanine ester, benzyl acetate, etc., show a strong peak at $m/e : 91$.

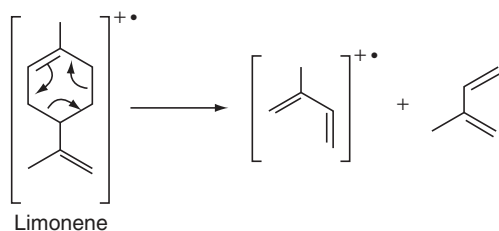
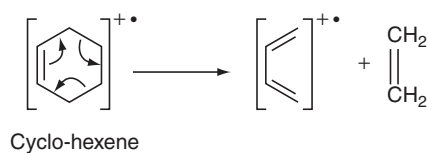
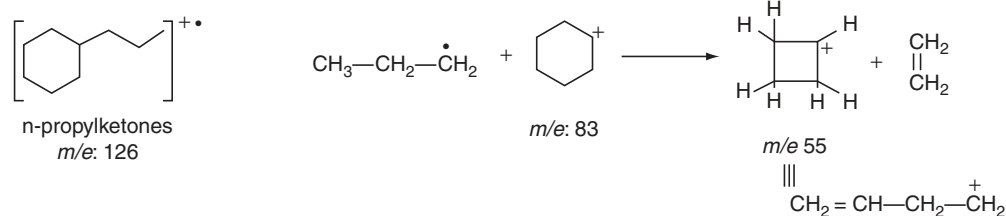
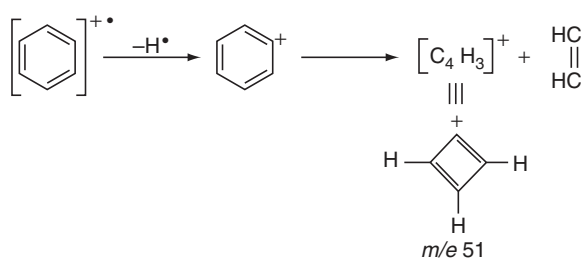
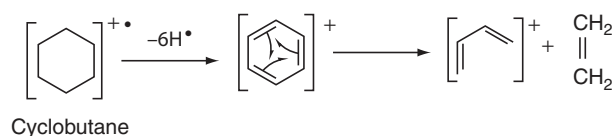
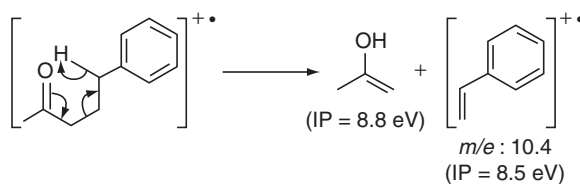
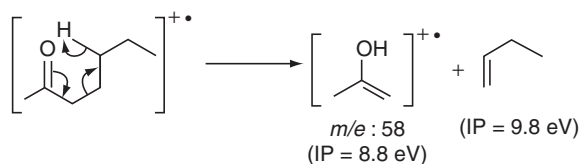
- (vii) Alkyl-substituted saturated rings lose side chains at the α -carbon and the positive charge tends to reside at the ring fragment. The peak corresponding to the loss of two ring atoms is much larger than for the loss of one ring atom.



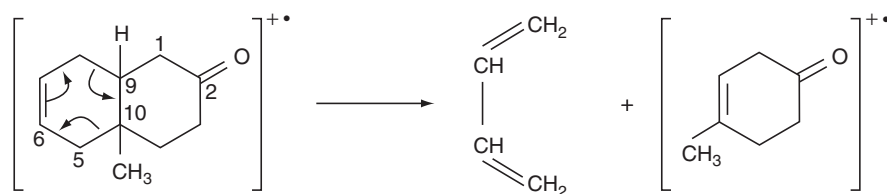
- (viii) Compounds which have a cyclic double bond (i.e. unsaturated rings) undergo fission giving rise to an olefin and the residual ion following a retro-Diels Alder reaction (i.e. double α -cleavage). The positive charge tends to stay with fragment with low ionisation potential (Stephenson's rule).



The following relative IP's and their consequences are also noteworthy.

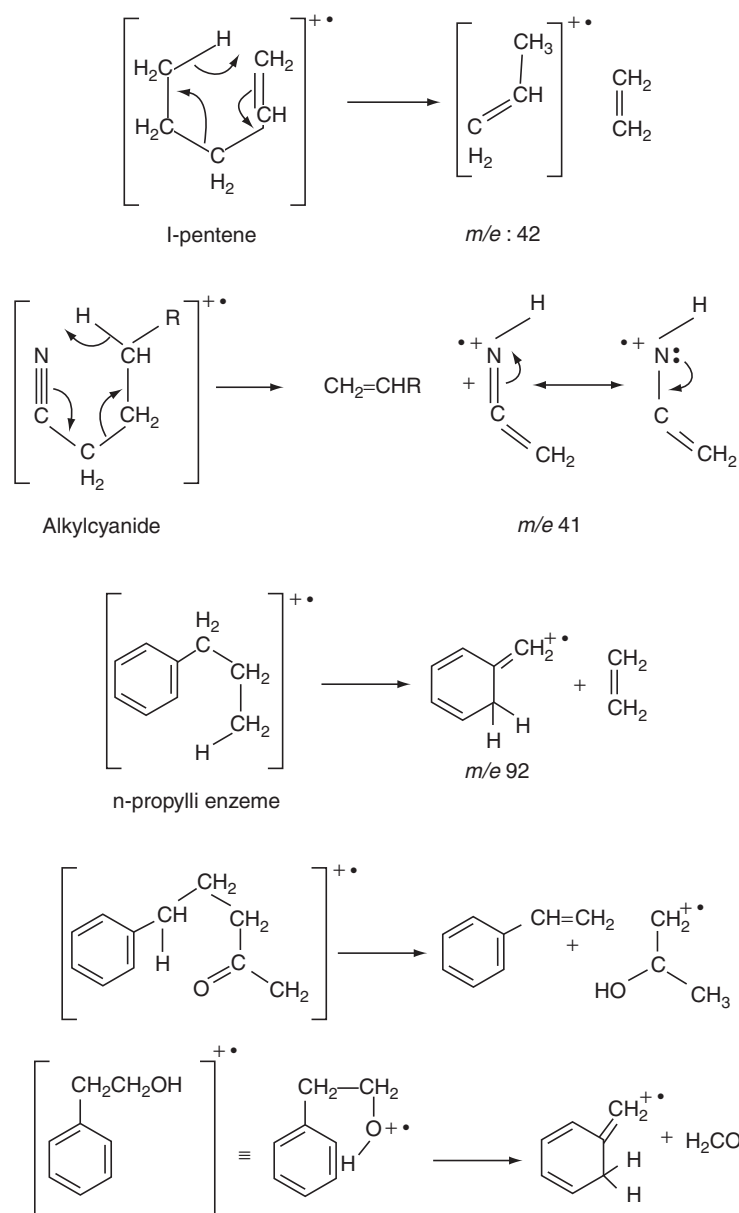


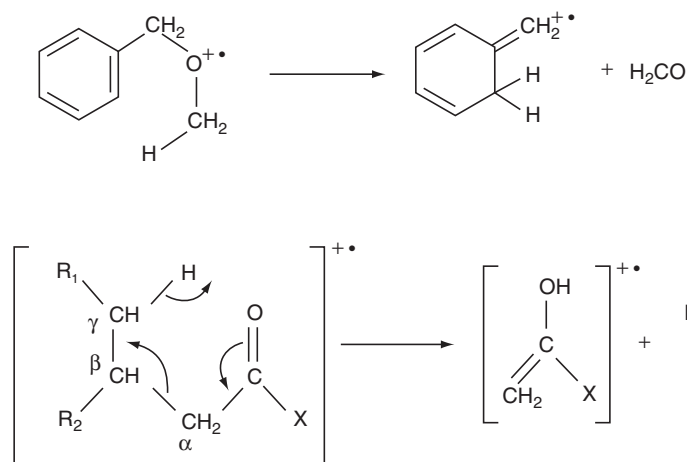
The mass spectra of polycyclic compounds often involve the peaks of fragments that are formed by a fragmentation which is the converse of diene synthesis (retrodiene-fragmentation). An example is the fragmentation observed in the spectrum of trans-10 methyl - Δ^6 -octan-2-one.



(j) Rearrangement Fissions Uptil now we have discussed the salient features of ordinary fissions in which the products of fission are a part of the parent molecular ion. Let us now examine the mode of bond fissions that occur with the migration of individual atoms or groups within the molecule, i.e. in rearrangement fissions, fragments are formed as a result of intramolecular atomic rearrangement. Rearrangements involving the migration of the groups heavier than hydrogen are termed skeletal rearrangements; but H-atom migrations are most common especially in molecules that contain hetero atoms. Hydrogen migration occurs not only in a molecular ion but also in the fragment ion. In hydrogen migration, generally a six-membered transition state is formed although other transition states are also common. Rearrangement fissions, i.e. molecular rearrangements are often associated with elimination of small stable neutral molecules such as CO, olefins, water, NH_3 , ketene, HCN, H_2S , or alcohols, etc., and sometimes radicals also. Some of the typical cases of hydrogen migrations giving rise to transition states before fragmentation are given here.

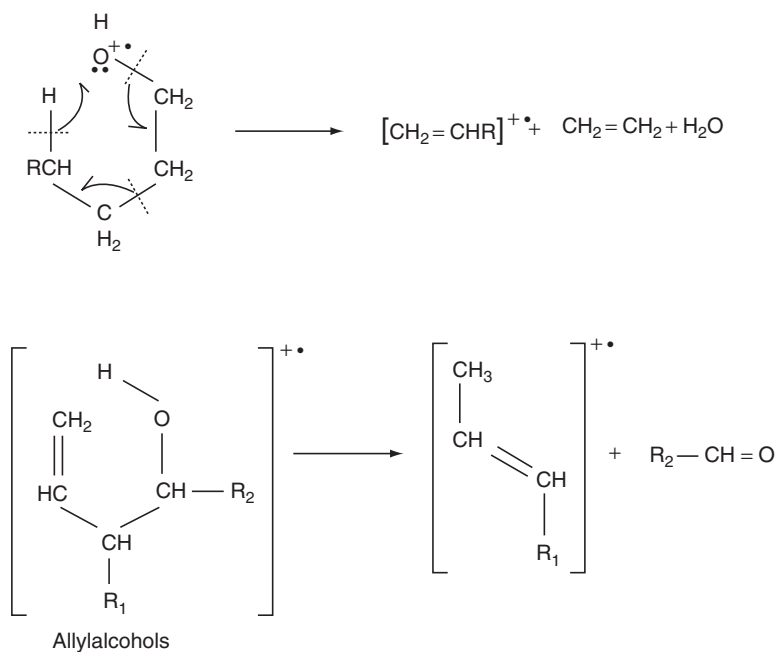
Hydrogen Migration via six-member Transition The fragment ions are also formed with the elimination of a neutral molecule as a result of the rearrangement β fission with the migration of a γ -hydrogen atom. The fission occurs in the six-membered transition state known as the McLafferty transition state. Such a state is formed when a molecule contains an heteroatom (e.g. O), a π system (usually a double bond and an abstractable hydrogen atom γ to the $\text{C}=\text{O}$ system). Fragmentation via McLafferty transition state occurs in aldehydes, ketones, esters and amino acid esters, alcohols, carboxylic acids, amides, unsaturated compounds, substituted aromatics. For example,



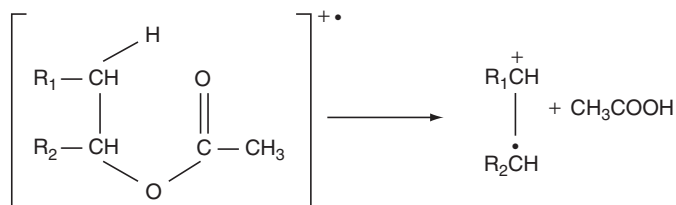


where, R_1 or R_2 = alkyl or H; X = H (aldehyde), CH_3 or C_2H_5 (ketone); OH (acid), OCH_3 or OC_2H_5 (ester), NH_2 (amide).

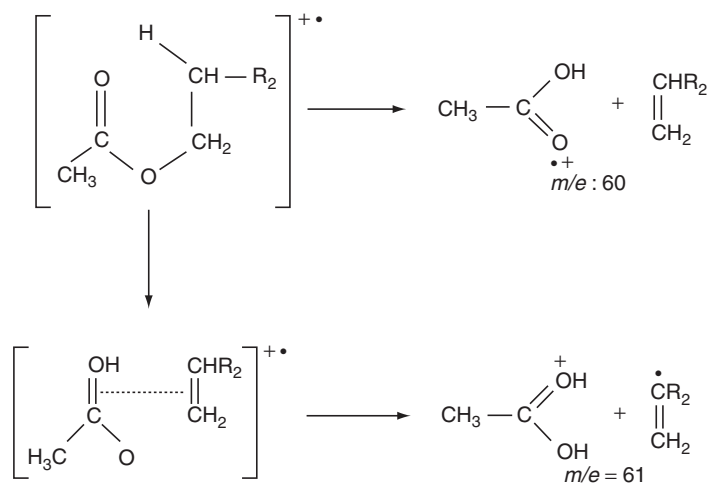
McLafferty rearrangement in alcohols occurs with the elimination of water molecule and alkene.



Many acetates show a peak corresponding to $(\text{M}^+ - \text{CH}_3\text{COOH})$ because of hydride transfer to carboxyl oxygen via McLafferty transition.

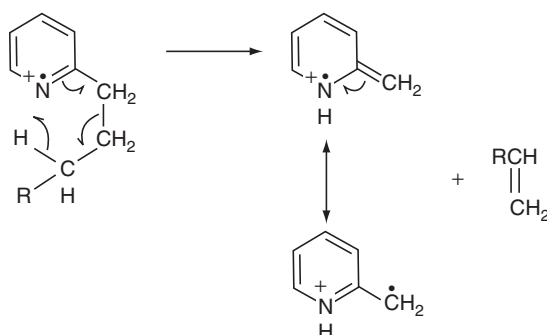


Higher esters $\text{R}_1\text{C}(=\text{O})\text{OR}_2$ where R_2 = ethyl, or propyl or butyl, etc., in addition to losing alkoxy group, also undergo single- and double-hydrogen rearrangements to give ionised carboxylic acid and protonated carboxylic acid species, respectively. The proportion of double-bond hydrogen arrangement grows with increasing size of R_2 .



An alkyl group of more than three carbon atoms in ortho position to the nitrogen atom of pyridines can undergo migration of hydrogen atom to the ring nitrogen.

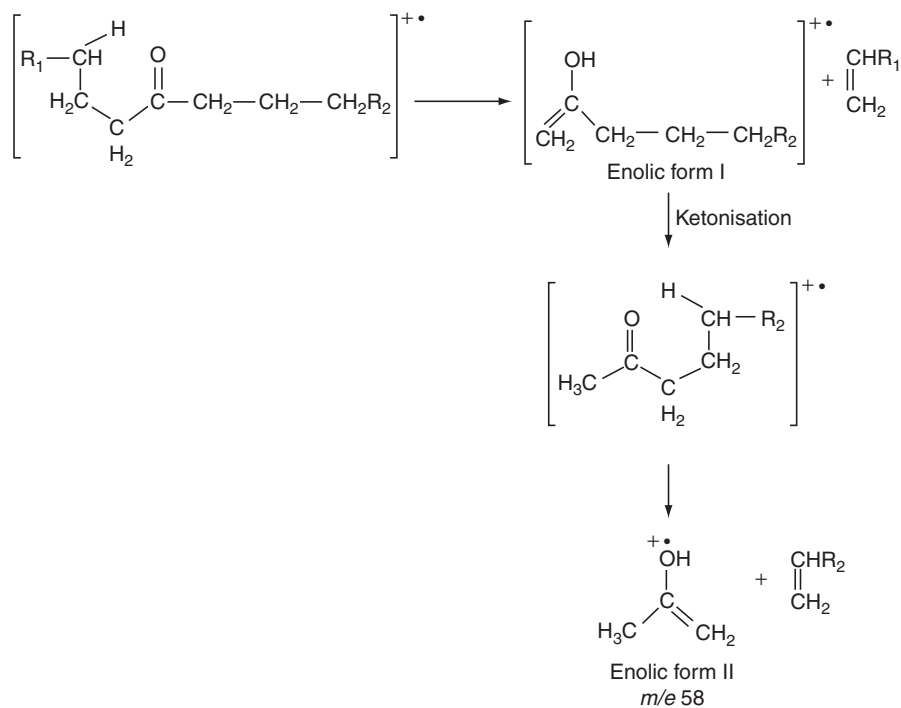
Here β -C—C bond fission occurs.



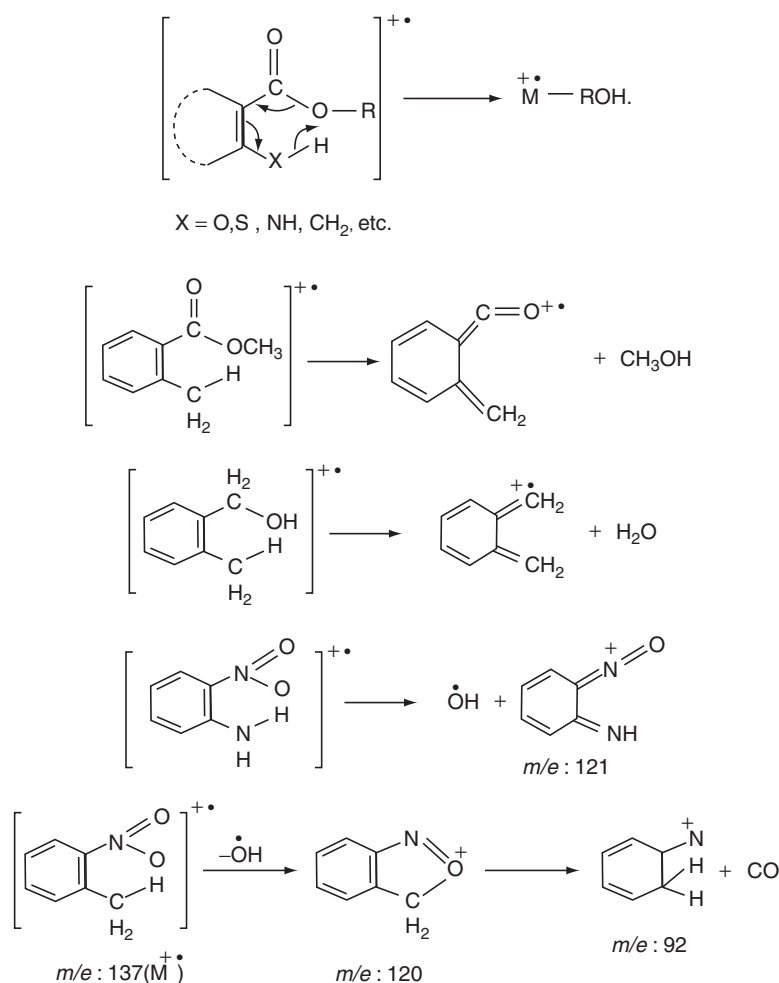
Such a fission also occurs in pyrazines since all ring substituents are ortho to one of the nitrogen atoms.

(k) Double McLafferty Rearrangement Ketones in which the groups R_1 and R_2 contain three or more carbon atoms exhibit double McLafferty rearrangement. A secondary hydrogen is preferred to a primary hydrogen atom in this process. The mechanism involves

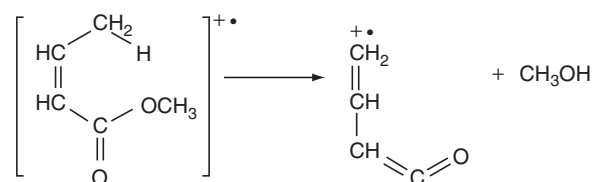
(i) Ketonisation of the intermediate enol by the hydrogen transfer, and (ii) Transfer of hydrogen to enolic oxygen.



Orthoeffect Hydrogen migration via six-member transition state occurs in ortho-substituted aromatic compounds or *cis*-olefins with the elimination of a neutral molecule or radical. For examples



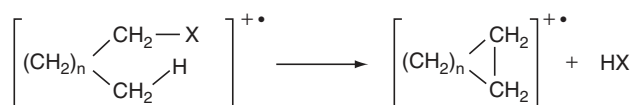
In amines, a hydrogen radical is lost from the parent ion to M⁺-1 peak.



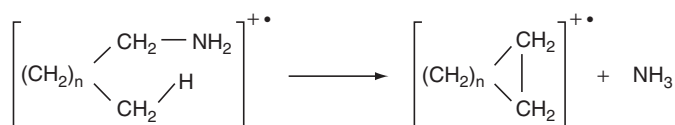
Such an elimination of neutral molecule enables to distinguish (a) between *cis* and *trans* isomers, and (b) ortho-substituted compound from *m*- and *p*-substituted isomers.

(I) Hydrogen Migration via Five-Member Transition

In hydrogen migration rearrangements, generally a six membered transition state is formed although other transition states are also common. Hydrogen migration via five-member transition occurs as follows in the following cases.

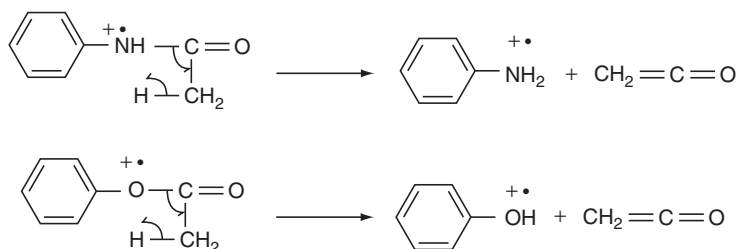


where, X can be OH, OCOR, NH₂, CN, etc.

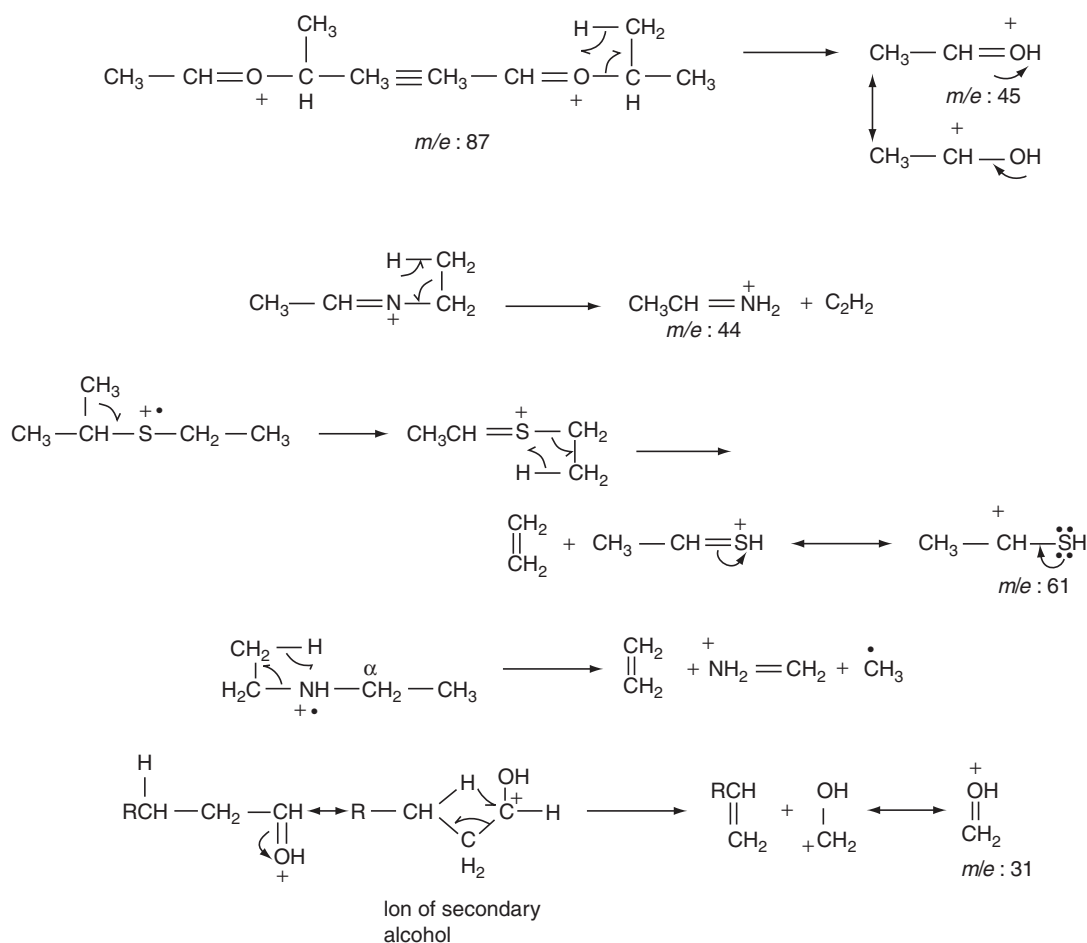


(m) Hydrogen Migration via Four-Member Transition

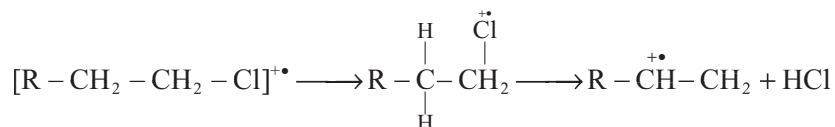
In case of *n*-alkylamides and *o*-acetates of phenols, hydrogen arrangements occur via four-member transition state and ketene ($\text{CH}_2=\text{C}=\text{O}$) is eliminated



Hydrogen migration in molecular and fragment ions of ethers or alcohols or amines also occur via four-member transition. For example,



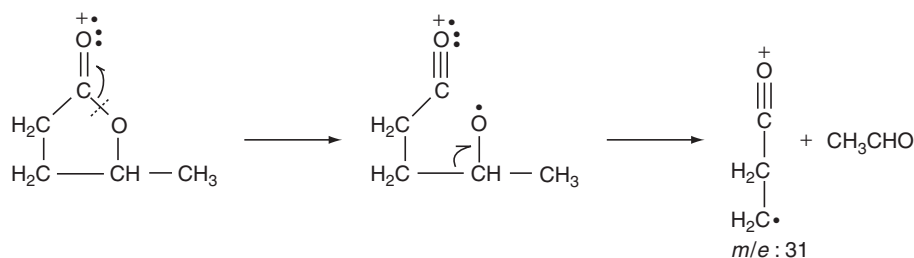
α -hydrogen abstraction by 1,3-mechanism occurs in long-chain chlorides, e.g. *n*-pentyl and *n*-butyl chlorides with the elimination of HCl. This is also the case of hydrogen migration via four-member transition.



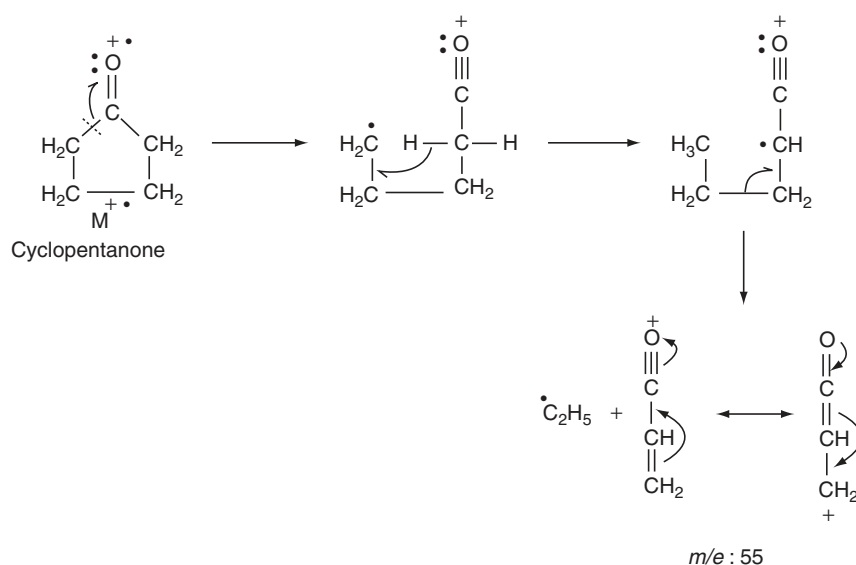
For $\text{R} = \text{C}_2\text{H}_5$; $m/e: 56$.

(i) Fission in Ring Compounds via C—C or C—X (where X = O, S, NH) Bond Followed by Rearrangement Five-membered ring lactones, cyclic ketones ($\geq \text{C}_4$) and five-membered ring hetero aromatics, namely furan, thiophene, and pyrrole, undergo fission via C—O, C—C and C—X (X = O, S, NH) bond cleavage followed

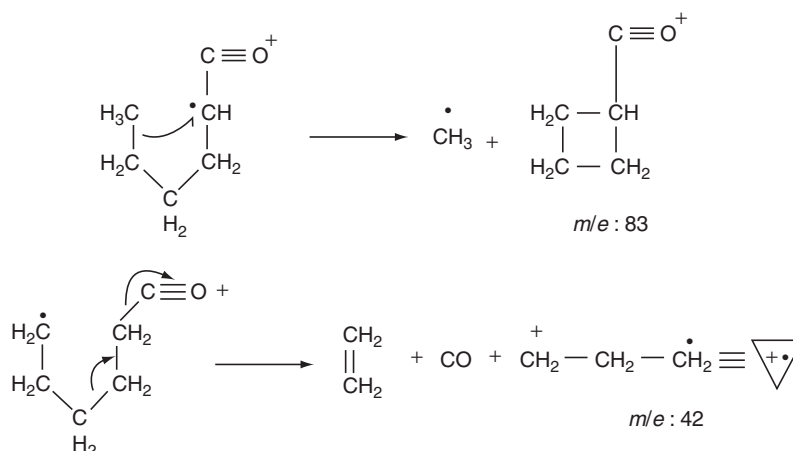
by rearrangement respectively with the elimination of neutral molecule or radical. For example, the base peak (m/e : 56) of γ -valerolactone and the same peak of butyrolactone originates as follows:



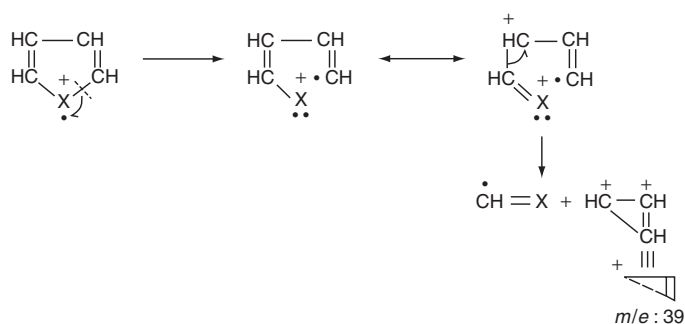
Cyclobutane, cyclopentanone and cyclohexanone undergo fission via C—C bond cleavage followed by rearrangement to give a peak at m/e : 55 as follows:

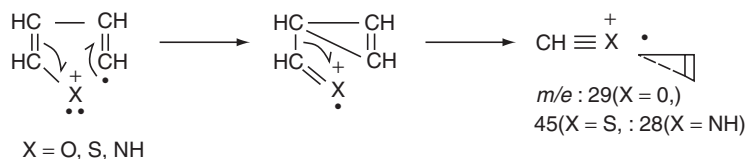


Cyclohexanone also gives characteristic peaks at m/e : 83 and 42 as follows:

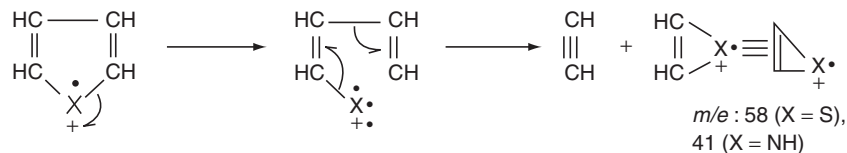


(ii) Fission in Five-Membered Ring Hetero Aromatics Fission proceeds via C—X where, X = O, S, NH, cleavage and rearrangement to give fragment ions with the elimination of neutral molecule or radical as follows:





For $X = S, NH$, we write as follows:

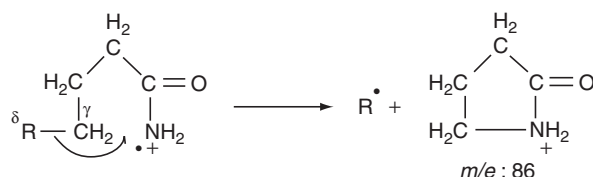


The principal peaks of five-membered hetero aromatics are summarised below:

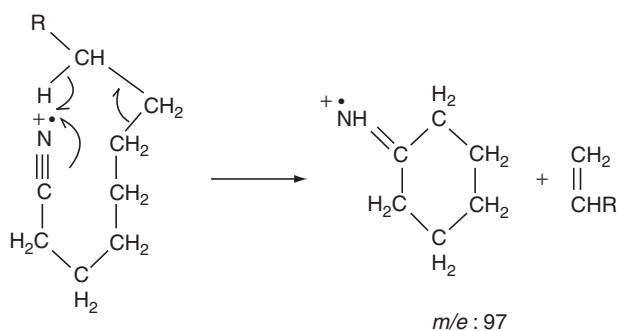
Heteroaromatic five-membered hetero aromatics m/e peaks

<i>Furan</i>	<i>Thiophene</i>	<i>Pyrrole</i>
	$39(C_3H_3^+)$	$39(C_3H_3^+)$
$39(C_3H_3^+)$	$45(H-C \equiv S^+)$	$28(HC \equiv NH^+)$
$29(HC \equiv O^+)$	$58(C_2H_2S^+)$	$41(C_2H_2NH^+)$

(iii) **Fissions Followed by Cyclisation** $\gamma\delta$ C—C fission possibly followed by cyclisation gives rise to peak in the spectrum of amides, e.g. isobutyramide.



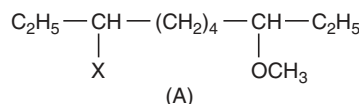
C_8 and higher nitriles undergo fission via hydrogen migration followed by cyclisation to give a six-membered molecular ion



These general rules for the fragmentation of molecular ions apply to electron impact mass spectrometry. This would change depending upon the relative importance of several processes occurring simultaneously. Molecular ions with much lower energy or quasi-molecular ions with very different fragmentation pattern are generated by

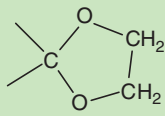
other ionising techniques, i.e. chemical ionisation, desorption ionisation, etc., and the fragmentation caused by such ionisation follows different rules.

(iv) Fragmentation of Polyfunctional Molecules The presence of more than one functional group in the molecule makes the interpretation of the mass spectrum complicated. The complexity results due to the competition between two functionalities to control the fragmentation in the molecule. Based on the relative fractions of ions, currents i_{OCH_3} and i_X arising from decompositions initiated by OCH_3 , and X-groups in bifunctional decanes (A) at 70 eV, a parameter that measures, the ability of some functional groups relative to OCH_3 (which is assumed to be unity) to control fragmentation in the mass spectra of polyfunctional molecules, has been defined.



The values of parameter for some functional groups (X) relative to OCH_3 are listed in Table 11.5.

Table 11.5 A comparison of the ability of functional groups to control fragmentation in polyfunctional molecules of general formula (A) with reference to OCH_3 taken as unity.

X	$i_{X(a)}$	X	$i_{X(a)}$
—COOH	0.02	—SCH ₃	0.90
—CH ₂ OH	0.06	—OCH ₃	1.00
—Cl	0.08	—NHCOCH ₃	1.21
—COOCH ₃	0.17	—I	1.31
			
—Br	0.23		5.14 (b)
—OH	0.25		
—SH	0.36	—NH ₂	6.16
	0.41 (b)	—N(CH ₃) ₂	12.00

(a) Relative to OCH_3 taken as unity, (b) data refer to the 3-methoxy-8-ketodecane and 3-methoxy-8-keto-decane ethylene ketal derived from (A).

As an example, the characteristic peaks at m/e (mm) : 218(11), 189(7), 186(10), 171(13), 157(3), 141(1), 139(5.2), 138(10), 109(17.5), 89(38.3) and 73(40) in the mass spectrum of 8-methyl mercapto-3-methoxy decane are translated by the following scheme of fragmentation.

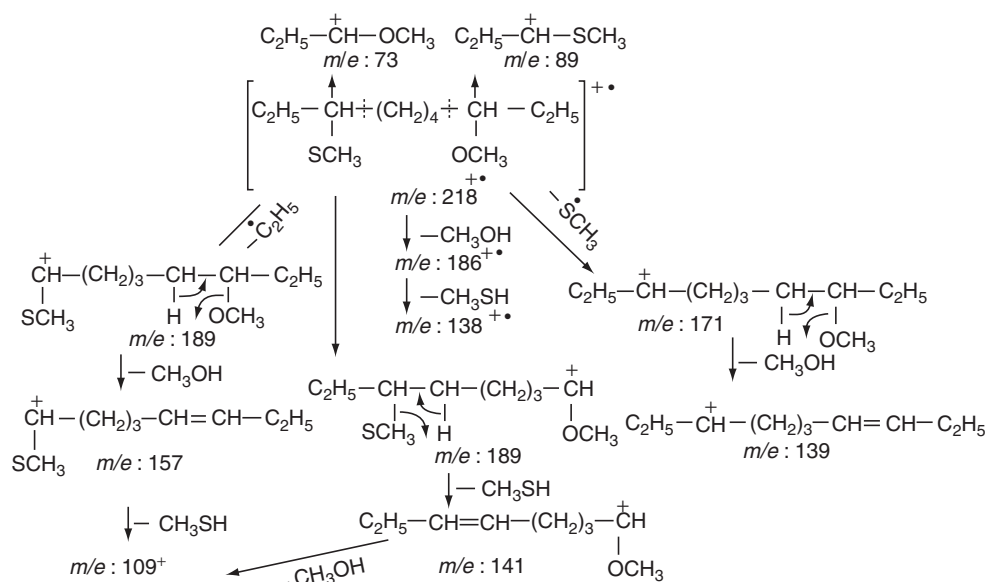


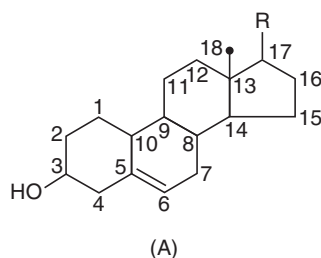
Fig. 11.24 Scheme of fragmentation of 8-methylmercapto-3-methoxydecane.

11.14 INTERPRETATION OF MASS SPECTRA OF UNKNOWN COMPOUNDS

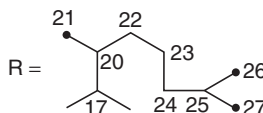
The validity of structures assigned to the fragments generated by the electron impact and their origin from this or that part of the molecule under examination is confirmed by comparison with the mass spectra of reference, i.e. related compounds; particularly, if the structure of one of these is known and by examination of the mass spectra of deuterated analogues. The derivation of the structure from the fragments requires great skill. When a molecule contains both aromatic and non-aromatic parts in the structure, the aromatic part shows up a stable entity and the fragmentation occurs in the non-aromatic part. Fission is often accompanied with elimination of small stable neutral molecules such as carbon monoxide, water, ammonia, olefins, hydrogen sulphide, hydrogen cyanide, mercaptans, ketene or alcohols, often with rearrangements. Thus starting from the M^+ ion, one should follow progressively lower mass numbers; however in many cases it is convenient to start from the lower mass numbers, i.e. from the peaks at $m/e : 28(N_2^+)$ and $m/e : 32(O_2^+)$. M-18 indicates water elimination, M-15 reveals methyl group in the molecule and if in addition there is M-29, it may be an ethyl group. M-28 indicates the loss of either CO or C_2H_4 . In a group of compounds from the same origin, the difference may be small like OH being OCH_3 , vinyl being ethyl, etc., and they can easily be recognised. In some cases, compounds are labelled with either stable isotopes (^{18}O , ^{15}O) or chemical labelling is resorted to (e.g. incorporation of CH_3 or OCH_3 groups). The latter procedure, however, should be adopted only in those cases where there is no risk of a given chemical label causing the change of the fragmentation routes. Some common losses from molecular ions and the possible inferences drawn from the respective losses are tabulated in Table 11.6. The other useful data for interpreting the mass spectra of organic compounds have been summarised in Tables 11.7–11.10.

The mass spectra of samples collected from thin layer plates, columns and greased apparatus contain impurity peaks at $m/e : 149, 167, 279$ (phthalic acid derivatives plasticisers); $129, 185, 259, 329$ (due to tri-*n*-butyl acetyl citrate plasticisers); $133, 207, 281, 355, 429$ (silicon grease); $99, 155, 211$ (due to tributyl phosphate plasticisers). So in such cases care must be taken while interpreting the mass spectra of the molecules.

Reproducible breakdown patterns have not only been obtained in small organic molecules with different functionalities but also in high-molecular mass natural products, namely terpenoids, steroids, polysaccharides, peptides and alkaloids. For instance in a steroid (A), the parent peak is strong. After ascertaining the formula from the molecular mass, one should look for a peak corresponding to $(M^+ - 18)$, i.e. $(M^+ - H_2O)$. The peak at $(M^+ - 18)$ indicates the presence of OH group in the molecule with ~ 10 per cent certainty. But for acetates, one finds a peak corresponding to $(M^+ - CH_3COOH)$. Side chain at C(17) can be found out by locating a peak at $205-245$. Then $M\text{-peak} = 42 + R + 18n$ where, n is the number of hydroxyls, and R is the mass number of the side chain. If there is no side chain on C(17), or a $C = O$ then one will not get this peak. Then there will be fragmentation due to the cyclic double bond and by postulating the double bond at the likely sites, one can derive some of the fragments in the mass spectrum.



For cholesterol (deposition of cholesterol in the blood vessels causes atherosclerosis) with molecular formula $C_{27}H_{46}O$ (molecular mass—386.67), there is a methyl group on C—10 also in (A) and



This alcohol is synthesised in the body.

Table 11.6 Some common losses from molecular ions.

<i>Mass loss from the ion (groups associated with the mass lost)</i>	<i>Possible molecular candidate</i>
1(H)	—
2(H ₂)	—
14	—
15(CH ₃)	—
16(O)	Ar-NO ₂ , ≥ N ⁺ —O ⁻ , sulfoxide
16(NH ₂)	ArSO ₂ NH ₂ , —CONH ₂
17(OH)	—
17(NH ₃)	—
18(H ₂ O)	Alcohol, aldehyde, ketone, etc.
19(F) } 20(HF) }	Fluorides
26(C ₂ H ₂)	Aromatic hydrocarbon
27(HCN)	Aromatic nitriles, nitrogen heterocycles
28(CO)	Quinones
28(C ₂ H ₄)	Aromatic ethyl ethers, ethyl esters, n-propylketones
29(CHO)	—
30(C ₂ H ₆)	—
30(CH ₂ O)	Aromatic methyl ether
30(NO)	Ar—NO ₂
31(OCH ₃)	Methyl ester
32(CH ₃ OH)	Methyl ester
32(S)	—
33 (H ₂ O + CH ₃)	—
33(HS) } 34(H ₂ S) }	Thiols
41 (C ₃ H ₅)	Propyl ester
42 (CH ₂ CO)	Methylketone, Aromatic acetate, ArNHCONH ₂
42 (C ₃ H ₆)	n-or isobutyl ketone, aromatic propylether, Ar—n—C ₄ H ₉
43 (C ₃ H ₇)	Propyl ketone, Ar—n—C ₄ H ₉
43 (CH ₃ CO)	Methyl ketone
44 (C ₃ H ₈)	—
45 (COOH); 17(OH)	Carboxylic acid
45 (OC ₂ H ₅)	Ethyl ester
46 (C ₂ H ₅ OH)	Ethyl ester
46 (NO ₂)	Ar—NO ₂
48 (SO)	Aromatic sulfoxide
55 (C ₄ H ₇)	Butyl ester
56 (C ₄ H ₈)	Ar- <i>n</i> -C ₅ H ₁₁ , ArO- <i>n</i> -C ₄ H ₉ ; Ar-iso-C ₅ H ₁₁ , ArO-iso-C ₄ H ₉ ; Pentyl ketone
57 (C ₄ H ₉)	Butyl ketone
58 (C ₄ H ₁₀)	—
60 (CH ₃ COOH)	Acetate

Table 11.7 Characteristic decomposition pathways of some saturated carbonium ions.

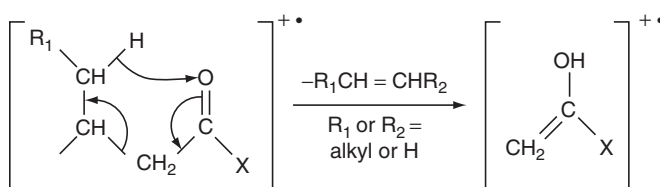
Precursor ion	Decomposition products	Transition (m/e)	m*
$C_2H_5^+$	$C_2H_3^+ + H_2$	$29 \rightarrow 27$	25.14
$C_3H_7^+$	$C_3H_5^+ + H_2$	$43 - 41$	39.09
$C_4H_9^+$	$C_4H_7^+ + H_2$	$57 - 55$	53.07
$C_4H_9^+$	$C_3H_5^+ + CH_4$	$57 - 41$	29.49
$C_5H_{11}^+$	$C_3H_7^+ + C_2H_4$	$71 - 43$	26.04
$C_6H_{13}^+$	$C_4H_9^+ + C_2H_4$ and $C_3H_7^+ + C_3H_6$	$85 - 57$ $85 - 43$	38.22 21.75
$C_7H_{15}^+$	$C_4H_9^+ + C_3H_6$	$99 \rightarrow 57$	32.82

Alkyl moiety M^+ , produces the characteristic $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$ ion series while $M^{+\bullet}$ produces series $C_nH_{2n}^{+\bullet}$

Table 11.8 m/e values associated with some members of ion types produced by some of the fragmentations.

Functional groups	Ion type	Ion series m/e
*Amine	$CH_2 = \overset{+}{N}H_2$ (m/e:30)	30,44, 58,72...
*Ether } Alcohol }	$CH_2 = \overset{+}{O}H$ (m/e:31)	31,45,59,73
Ketone	$CH_3C \equiv \overset{+}{O}$ (m/e:43)	43, 57, 71,85
Hydrocarbon	$C_2H_5^+$ (m/e:29)	29, 43, 57, 71

*Molecular mass of saturated monoamine is an odd number. # Peak due to H_2O loss suggests alcohol but not ether.

Table 11.9 m/e values of some rearrangement ions formed from various carbonyl compounds.

Compound	X	m/e
Aldehyde	H	44
Ketone (methyl)	CH ₃	58
Ketone (ethyl)	C ₂ H ₅	72
Acid	OH	60
Ester (methyl)	OCH ₃	74
Ester (ethyl)	OC ₂ H ₅	88
Amide	NH ₂	59

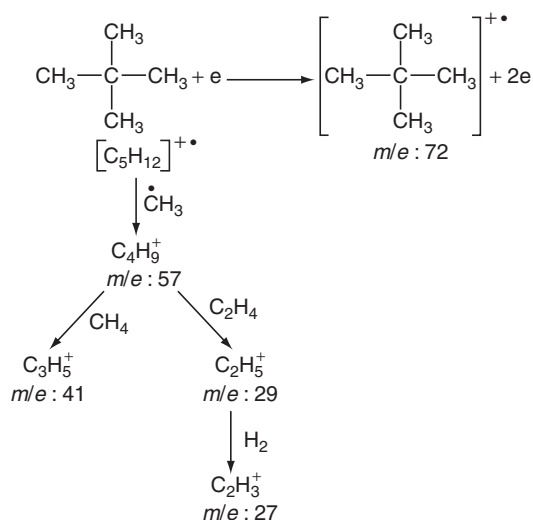
Table 11.10 Order of ease of cleavage of some C_6H_5X compounds, $\text{C}_6\text{H}_5\text{X}$. The bond strength of X increases as we move downwards, e.g. $\text{CH}_3 > \text{OCH}_3 > \text{COCH}_3$.

X	Radicals or neutral fragments lost from $M^{+\bullet}$
COCH_3	CH_3
$\text{C}(\text{CH}_3)_3$	CH_3
$\text{CH}(\text{CH}_3)_2$	CH_3
COOCH_3	OCH_3
$\text{N}(\text{CH}_3)_2$	H
CHO	H
C_2H_5	CH_3
OCH_3	$\text{CH}_2\text{O}, \text{CH}_3$
I	I
OH	CO
CH_3	H
Br	Br
NO_2	NO_2, NO
NH_2	HCN
Cl	Cl
CN	HCN
F	$\text{C}_2\text{H}_2, \text{F}$
H	C_2H_2

The energy required for the decomposition of the functionalities X grows as we move downwards in the table.

Problem 11.6: In the mass spectrum of neopentane there are observed lines corresponding to the following values of m/e : 57, 41, 29 and 27. What positive ions might these lines correspond to?

Solution The molecular ion $[\text{C}_5\text{H}_{12}]^{+\bullet}$ for neopentane should appear at the m/e value of 72. The fragmentation of $[\text{C}_5\text{H}_{12}]^{+\bullet}$ ion occurs as follows to yield the positive ions corresponding to the m/e values in questions.



Problem 11.7: Predict the structural formula of the compound ($\text{C}_9\text{H}_2\text{O}$) having a molecular mass of 128 from the mass spectral data indicated below:

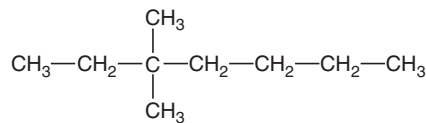
m/e	113	99	71	57	55	43	41	29	27
Intensity (in mm)	1.5	8	45	50	10	50	21	20	15

Metastable peaks : 25.14, 39.09, 53.07.

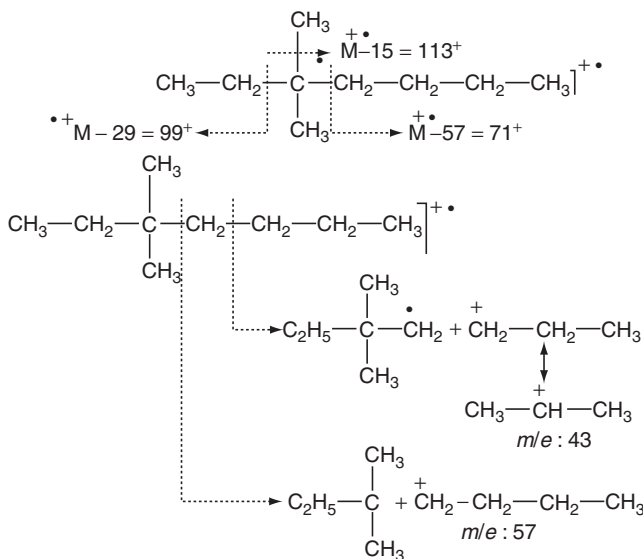
Solution The metastable peaks are due to the following transitions:

	<i>Transition</i>	<i>Metastable peak</i>
$29^+ \rightarrow 27^+$	$\text{C}_2\text{H}_5^+ \rightarrow \text{C}_2\text{H}_3^+ + \text{H}_2$	25.14
$43^+ \rightarrow 41^+$	$\text{C}_3\text{H}_7^+ \rightarrow \text{C}_3\text{H}_5^+ + \text{H}_2$	39.09
$57^+ \rightarrow 55^+$	$\text{C}_4\text{H}_9^+ \rightarrow \text{C}_4\text{H}_7^+ + \text{H}_2$	53.07

Thus, the peaks at m/e : 29, 43, 57 spaced at an interval of 14 mass units are attributed to the hydrocarbon ion series of the type $C_nH_{2n+1}^+$ i.e., $C_2H_5^+$, $C_3H_7^+$, $C_4H_9^+$ while the peaks at m/e : 27, 41, 55 are attributed to hydrocarbon ion series of the type $C_nH_{2n-1}^+$ formed from the ion series $C_nH_{2n+1}^+$ with the loss of H_2 molecule. The absence of molecular ion peak in the spectrum rules out the possibility of straight-chain hydrocarbon. The peaks at 113, 99 and 71 arise due to mass loss of $15(CH_3)$, $29(C_2H_5)$ and $57(C_4H_9)$ from the molecular ion peak respectively and indicates the formation of tertiary carbon atoms. Accordingly, the structural formula of the compound is

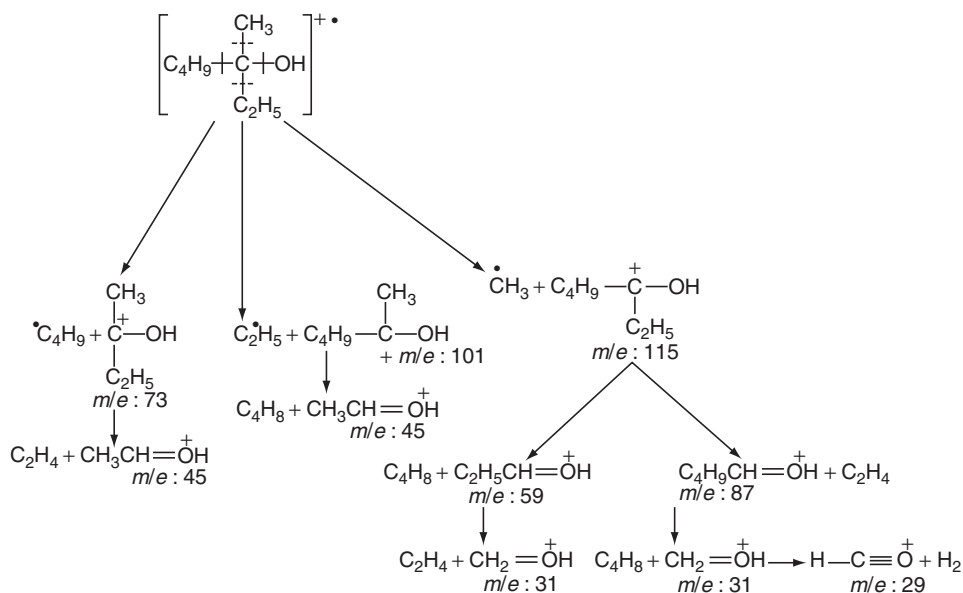


The decomposition routes for the formation of expected ions have been summarised below:

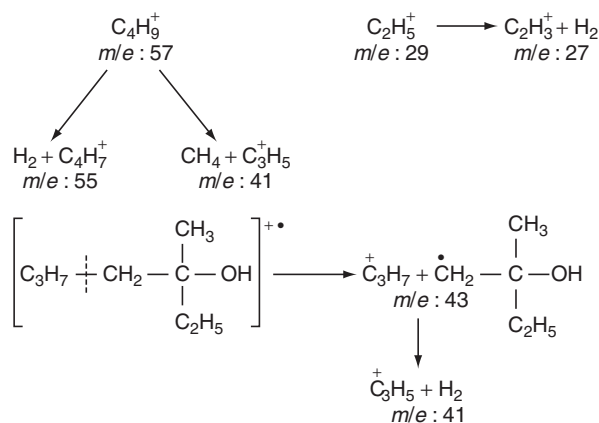


Problem 11.8: The mass spectrum of 3-methyl-3-heptanol, $\text{C}_4\text{H}_9-\text{C}(\text{OH})(\text{C}_2\text{H}_5)_2$, includes lines corresponding to the following mass numbers, m/e : 115, 101, 87, 73, 59, 55, 45, 43, 41, 31, 29, 27. What ions might these lines correspond to?

Solution The m/e values in question results due to the fragmentation modes of molecular ion of 3-methyl-3-heptanol indicated below:

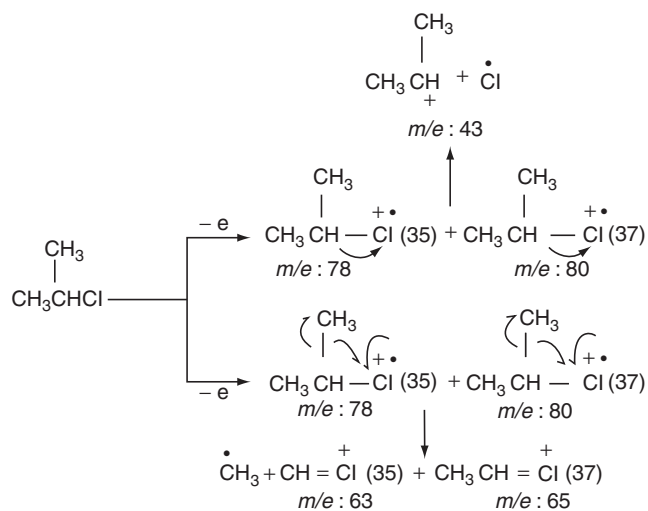


The peaks at 57, 43 and 29 are due to the formation of C_4H_9^+ , C_3H_7^+ , and C_3H_5^+ fragment ions respectively.



Problem 11.9: In the mass spectrum of 2-chloropropane ($\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{Cl}$) there are observed two doublets and a base peak corresponding to the following values of m/e (intensity ratio): 80, 78 (1:3); 65, 63 (1:3) and 43 (Base peak). What ions might the doublets correspond to?

Solution The intensity ratio and a mass difference of two units between the lines corresponding to each of the doublets suggest that the doublets in the spectrum are due to the two isotopes of chlorine. Accordingly, the m/e values in question are due to the following modes of fragmentation of the molecular ion:



For 1-bromopropane, the mass spectrum is 122, 124 (1:1) and 43 (base peak).

Problem 11.10: (a) Deduce the structural formula of the compound (molecular formula = $C_5H_{12}O$) from the mass spectral data indicated below and justify the structures so obtained from the mode of fragmentation of the compound.

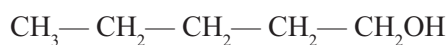
	m/e	$87(M^{++}-1)$	70	57	55	43	42	31	29
A:	Peak height (in mm)	0.5	17	10	28	13	47 (Base peak)	33	31
	m/e :	$88(M^{++})$	87	73	70	55	45	43	42
B:	Peak height (in mm)	0.5	0.6	3	0.6	7.5	47 (Base peak)	8	1.5
	m/e :	73	70	59	55	42	29		
C:	Peak height (in mm)	25	0.5	47 (Base peak)	16	2.3	14		

(b) What inference can be drawn regarding the characterization of alcohols?

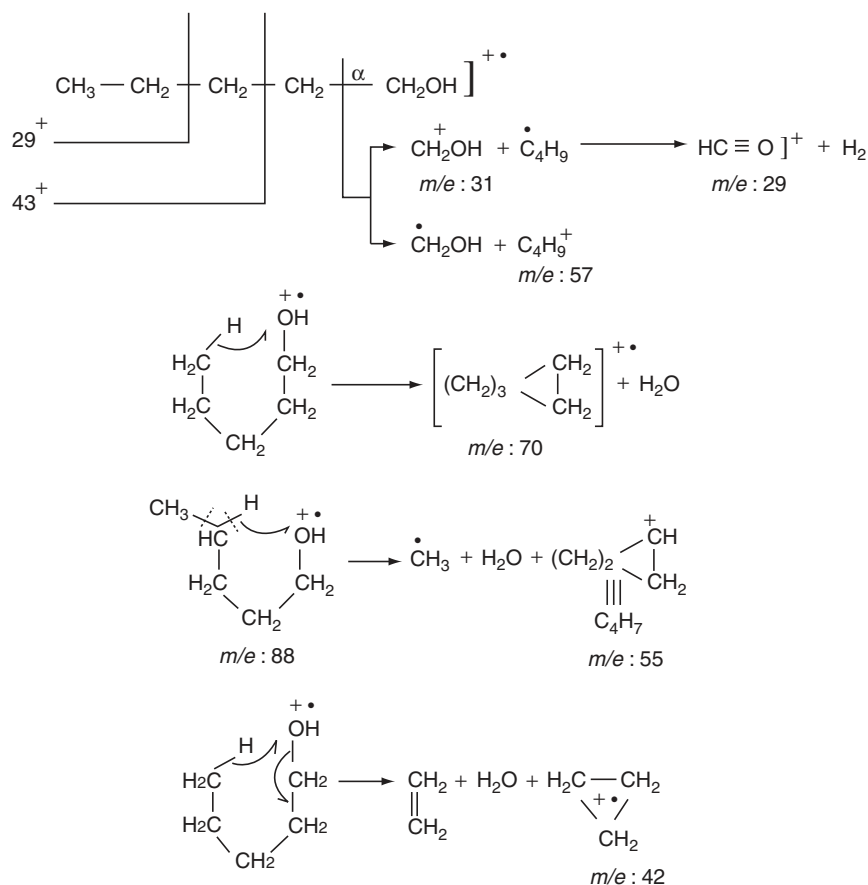
Solution (a) A: A $M^{++}-1$ peak is characteristic of an alcohol. The $(M^{++}-1)$ peak at $m/e : 87$ suggests that the molecular ion is expected at $m/e : 88$. The peak at $m/e : 70$ corresponding to $(M^{++} - H_2O)$ and the mass loss of 57 giving rise to a peak corresponding to CH_2OH at $m/e : 31$ suggests that the compound in question is a primary alcohol with formula $R-CH_2OH$, where $R \equiv 57$. This suggests that the $R \equiv 57 \equiv C_4H_9 \equiv CH_3-CH_2-CH_2-CH_2-$

CH_2^+ or $\frac{57}{12} = 4Cs + 9Hs$ or $\frac{57}{14} = 4CH_2s + 1H$, i.e. $R = CH_3-CH_2-CH_2-CH_2-$

Accordingly, the compound in question is 1-pentanol with the structural formula

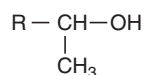


The peaks in the spectrum can be translated by the following mechanisms.



This lends support to the structure of the compound as 1-pentanol.

(B) The peak at $m/e : 87$ corresponding to $(M^{+\bullet} - 1)$ and at $m/e : 70$ corresponding to $(M^{+\bullet} - H_2O)$ suggest that the compound in question is an alcohol. The base peak at $m/e : 45$ and a peak at 73 corresponding to $(M^{+\bullet} - CH_3)$ suggest that the compound is a secondary alcohol with the formula

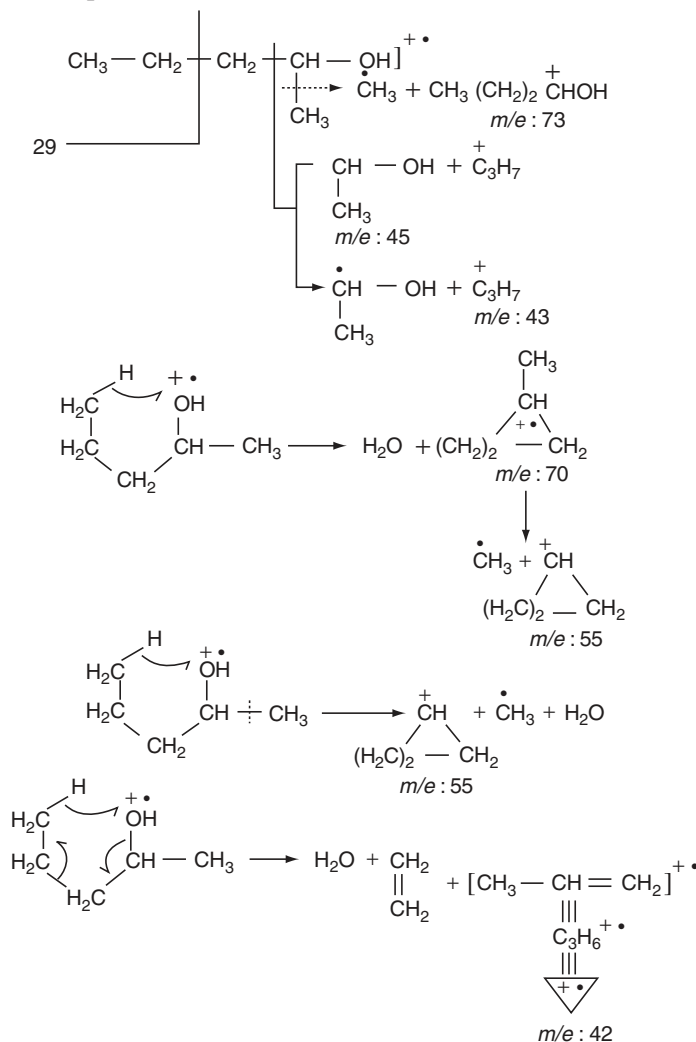


Since $M^{+\bullet} = 88$, $R = (88 - 45) = 43 = 3Cs + 7H$ or $3CH_2$'s + $1H$.

The peaks at $m/e : 43$ and 29 with mass interval of 14 mass units suggest the presence of the C_3H_7 group in the molecule. Thus, the structural formula of the compound is $CH_3 - CH_2 - CH_2 - CH - OH$

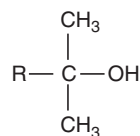


Accordingly, the peaks in the spectrum can be translated as

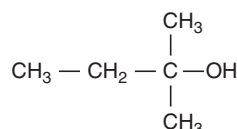


This lends support to the structure of the compound as 2-pentanol, a secondary alcohol.

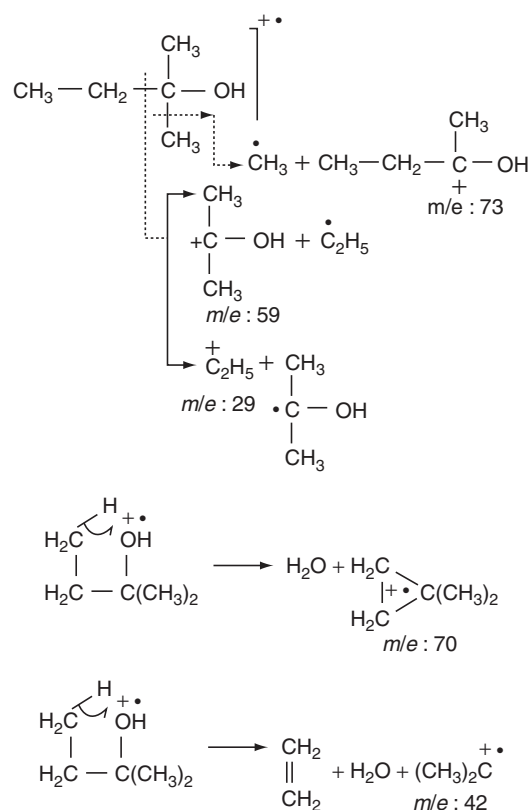
(C) According to the molecular formula of the compound, i.e., $C_5H_{12}O$, the molecular ion peak should appear at $m/e : 88$. The absence of a molecular ion peak and the peaks at $m/e : 73$ corresponding to the $M - CH_3$, and at $m/e : 59$ corresponding to $M^{+\bullet} - 29$, indicate that the compound in question is a tertiary alcohol with the structural formula



where $R = 29 \equiv 2Cs + 5Hs$ or $2CH_2$'s + $1H$, i.e. $R = CH_3 - CH_2$. The peak at $m/e : 29$ thus corresponds to the C_2H_5 group. Accordingly, the structural formula of the compound is



According to this formula, the peaks in the spectrum can be translated as



This lends support to the structure of the compound as 2-methyl-2-butanol, a tertiary alcohol.

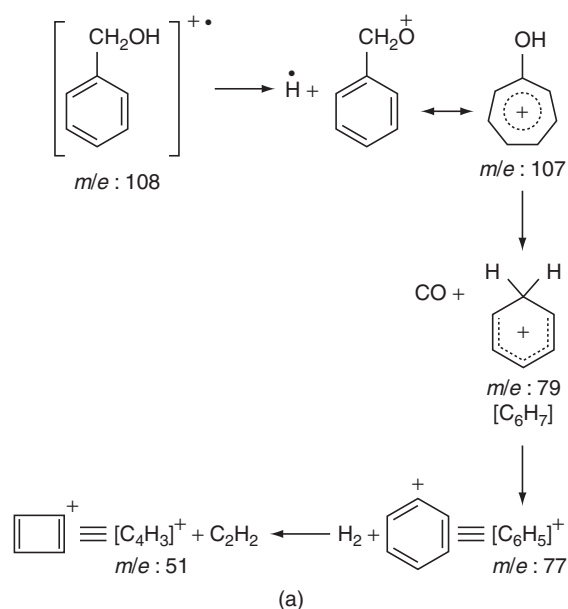
(b) This is left an exercise for the readers. (See section 11.13)

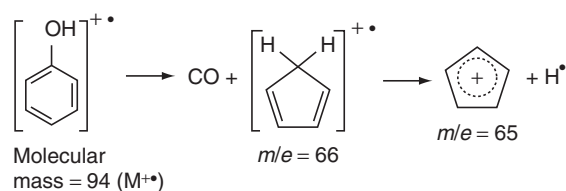
Problem 11.11: Given below are the characteristic peaks from the mass spectra of (a) benzylalcohol, (b) phenol, (c) *p*-methylcresol, and (d) o-ethylphenol.

(a)	m/e	108	107	79	77	51		
(b)	m/e	66	65					
(c)	m/e	108	107	79	77	51		
(d)	m/e	122	121	107	104	79	77	51

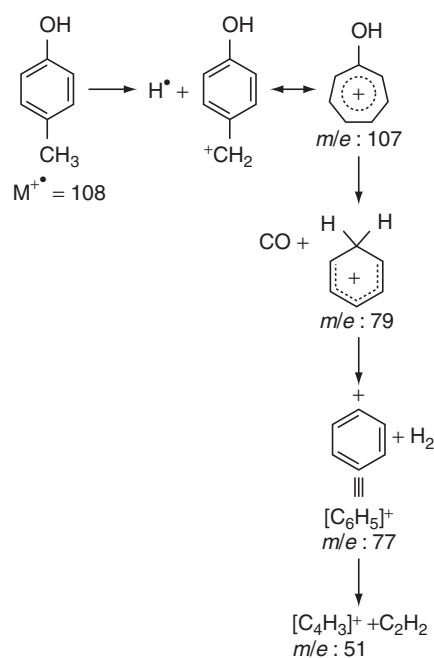
What ions might these peaks correspond to?

Solution The peaks in the respective spectrum are translated as

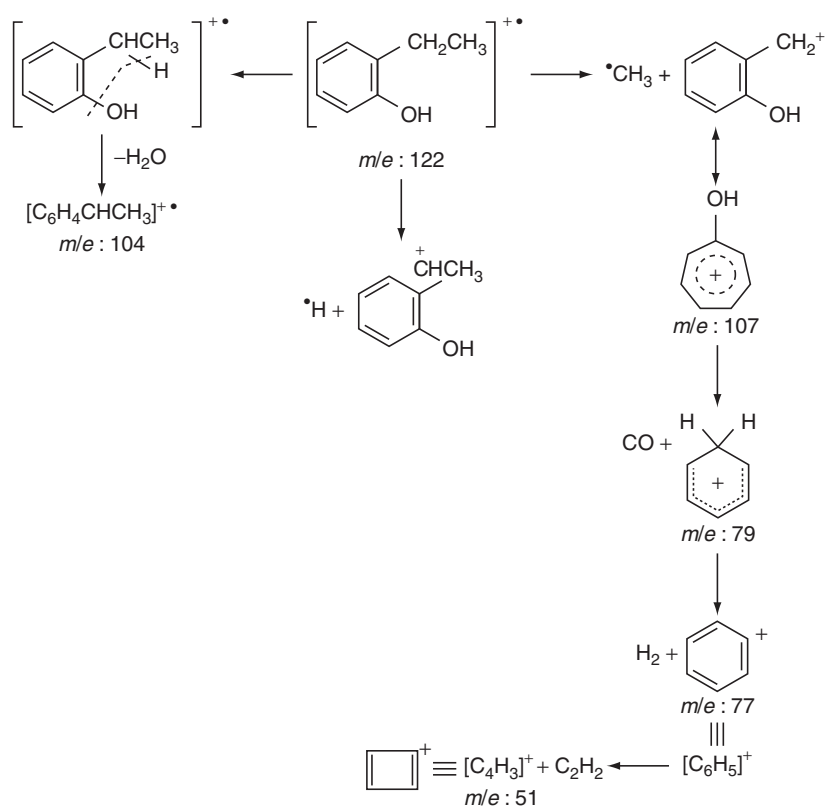




(b)



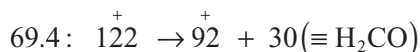
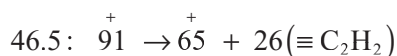
(c)



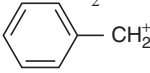
(d)

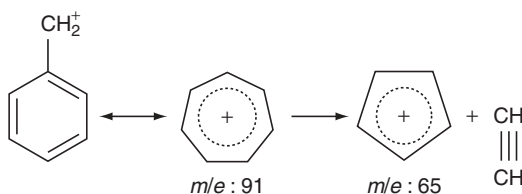
Problem 11.12: The mass spectrum of a compound exhibits a strong molecular ion peak at $m/e : 122$ (35 per cent), the base peak at $m/e : 91$ and other two peaks at $m/e : 92$ (65 per cent) and 65 (15 per cent). Metastable peaks appear at $m/e : 46.5$ and 69.4 mass units. Deduce the structure of the compound.

Solution The two metastable peaks correspond to the transitions:

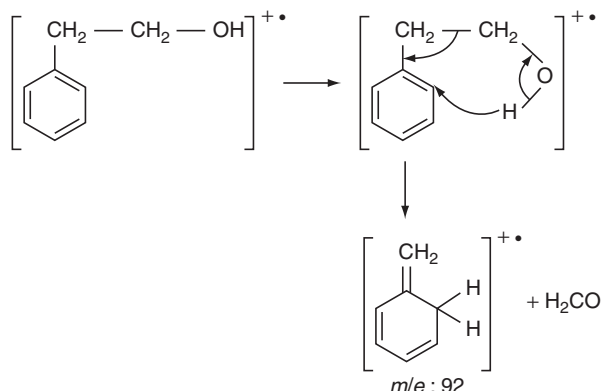


The mass loss of 31 from the strong molecular ion peak at $m/e : 122$ giving rise to a peak at $m/e : 91$ indicates that the compound is methyl ether but the strong molecular ion peak suggests that the compound is an aromatic alcohol and thus the mass loss of 31 is due to $-\text{CH}_2\text{OH}$ but not to because of $-\text{OCH}_3$ group. Thus the peak at

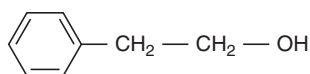
$m/e : 91$ is attributed to the benzyl group, i.e.  which fragments to yield a peak at $m/e : 65$ as follows:



Ion peak at even mass arising from an even mass molecular ion indicates McLafferty rearrangement reaction. Thus the peak at 92 arises as



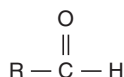
Thus, keeping in view the mass spectral data in question, the compound is 2-phenyl ethanol with the structural formula



Problem 11.13: Deduce the structural formula of a compound from the mass spectral data indicated below:

m/e	72(M^+)	71	57	44	43	29
Peak height (in mm)	25	3	9	34	27	19
Relative abundance (as percent of base peak)	73.5	8.8	26.5	100	79.4	55.9

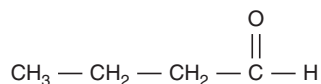
Solution Since even molecular mass ion results in even mass base peak, a molecular rearrangement occurs in the molecule. The strong peak at $m/e : 44$ is attributed to the aldehyde group (i.e. CHO) in the molecule. This peak in the aldehyde appears due to an internal molecular rearrangement involving a six-membered cyclic transition state, i.e. 'McLafferty transition state'. Thus, there are at least three carbon atoms in the side chain of the aldehydic group. The peak at $m/e : 71$ is because of loss of hydrogen from the aldehydic group by α -fission. Accordingly, the possible structure of the compound in question is



The side chain group must contain at least three carbon atoms, otherwise McLafferty rearrangement will not be possible.

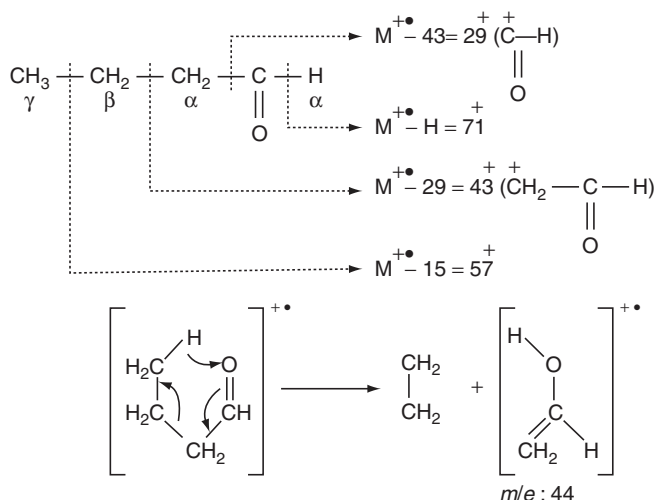
The mass of side chain group $R = 72 - 29 = 43 \equiv 3\text{CH}_2 \text{ s} + 1\text{H}$ or $3\text{Cs} + 7\text{Hs}$.

Thus, the side chain group $R = \text{C}_3\text{H}_7$ or the length of the side chain group R can also be deduced from the peaks at $m/e : 15, 29$ and 43 . These three peaks with a mass interval of 14 units belong to an ion series of the type $\text{C}_n\text{H}_{2n+1}^+$. Thus the side group R corresponds to $\text{C}_3\text{H}_7 = 43$ mass units. In view of it, the structural formula of the compound is



The mass loss of 15 from the parent molecular ion, i.e. $(\text{M}^{+\bullet} - \text{CH}_3)$ giving rise to a peak at $m/e : 57$ corresponding to $\overset{\text{O}}{\parallel} \text{CH}_2 - \text{CH}_2 - \text{C} - \text{H}$ lends support to the structure of the compound as butraldehyde.

The modes of fragmentation of the aldehyde in question is summarised below.



Problem 11.14: (a) The characteristic peaks in the mass spectrum of an unknown compound are indicated below:

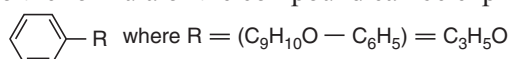
m/e	136	135	134	105	91	78	65	51	39	29
			($\text{M}^{+\bullet}$)							
Relative abundance	0.41	5.80	57.4	41	100	50	18	29	23	18
					(Base peak)					

What is the likely structural formula of the compound? (b) Based on the following values of $m/e : 139, 111, 105$ and 77 , write the fragmentation pattern of *p*-chloro benzophenone.

Solution (a) The number of carbon atoms in the molecule $= \frac{5.80}{0.011 \times 57.4} = 9$. So the number of hydrogen atoms $= (134 - 12 \times 9) = 26$.

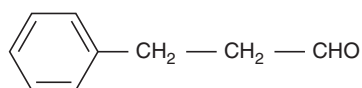
Accordingly, the molecular formula of the compound if it contains C and hydrogen only should be C_9H_{26} ; but this is impossible. For a compound containing C, H and O, the molecular formula is $\text{C}_9\text{H}_{10}\text{O}$. The percent abundance of $\text{M} + 2$ peak, i.e. 0.41 reveals that the compound does not contain a sulphur atom.

The strong molecular ion peak at $m/e : 134$ and a base peak at $m/e : 91$ show that the compound is aromatic in nature and has a phenyl ring also. So the formula of the compound can be expressed as

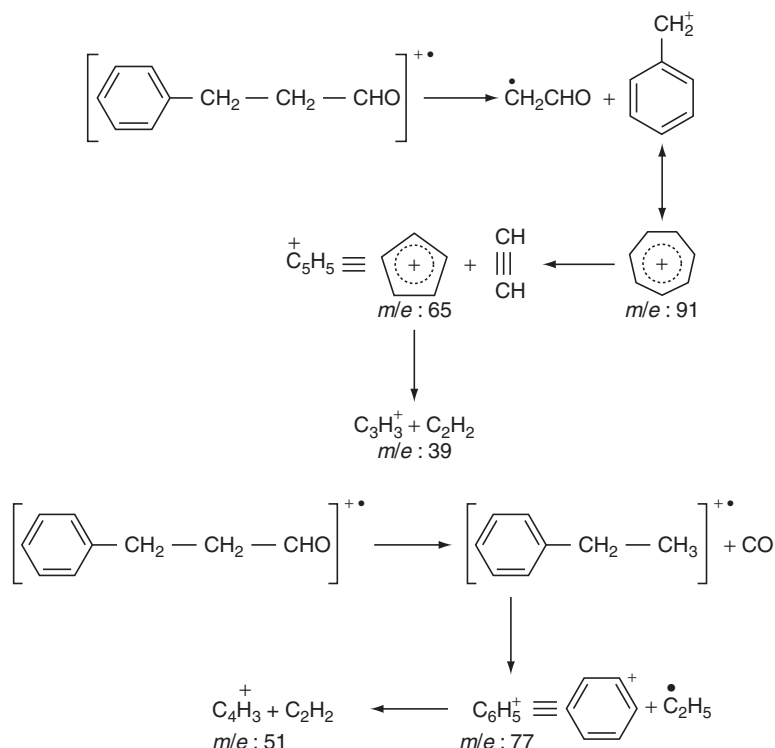


The mass loss of 29 giving rise to a peak at $m/e : 105$ and a peak at $m/e : 29$ (due to α -cleavage) suggest that the compound possesses an aldehydic group, i.e. $-\text{CHO}$ and the peak at $m/e : 78$ corresponds to $(\text{M}^{+\bullet} - \text{CH}_2\text{CHO})$.

Accordingly, the structural formula of the compound is

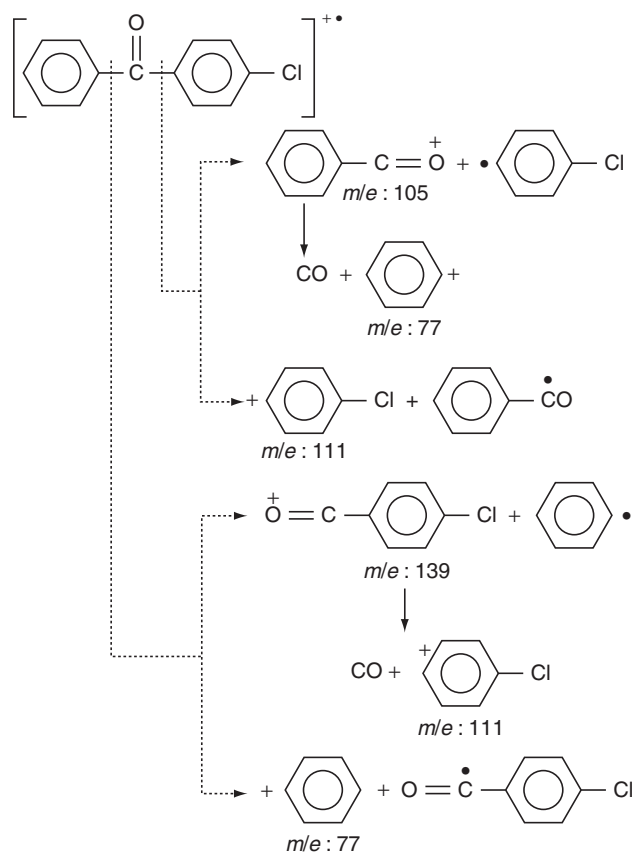


The peaks at m/e : 65, 39 and 51 appears as

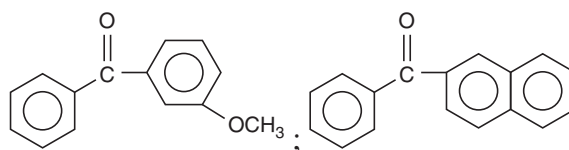


This lends support to the structure of the compound in question.

(b) The peaks characteristic of *p*-chlorobenzoquinone are translated by the following mechanism.



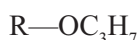
Similarly, we can write the characteristic peaks of other aromatic ketones such as



Problem 11.15 Deduce the structure of a compound ($C_6H_{14}O$) from the mass spectral data indicated below:

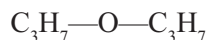
m/e	102 (M^+)	87	59	45	43	27
Peak height (in mm)	< 0.5	9	5	50	25	8

Solution: The peaks at m/e : 45, 59 and 87 suggest that the compound in question is either an ether or an alcohol. Since there is no peak corresponding to loss of a water molecule from the molecular ion, i.e. $(M^+ - H_2O) = 84$, the possibility of alcohol is ruled out. The peaks at m/e : 43 and 59 indicate that the compound contains propyl ester group (i.e. OC_3H_7). Accordingly, the formula of the compound is written as

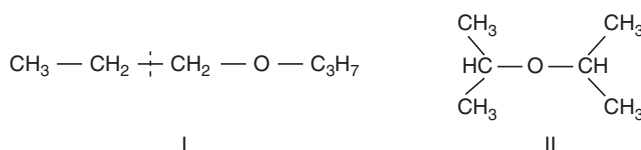


$$R = (102 - 59) = 43 \equiv 3Cs + 7Hs \text{ or } \equiv 3CH_2s + 1H$$

So, $R = C_3H_7$ and the general structural formula of the compound can be written as

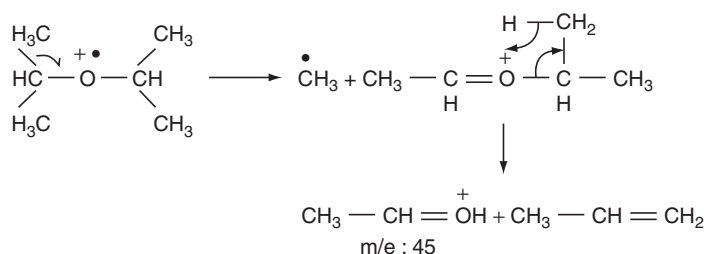


The two possible structural formula corresponding to $C_3H_7-O-C_3H_7$ are

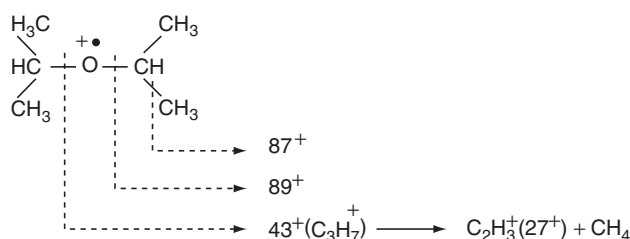


The absence of peak at m/e : 71 corresponding to $M^+ - C_2H_5$ rules out the possibility of structure I.

The structural formula II seems to be correct since according to this structure, the peak at m/e : 45 can be translated by fragmentation followed by the molecular rearrangement indicated below:



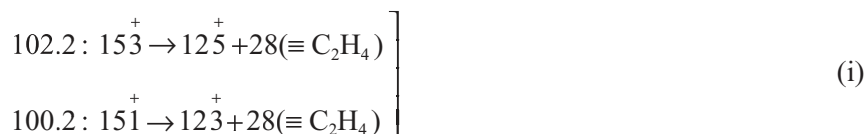
The fragmentation pattern of the ether in question is summarised below:



Problem 11.16: Deduce the structural formula of the compound from the following mass spectral data.

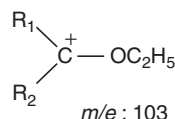
<i>m/e</i>	196/198 (<i>M</i> ⁺)	167/169	151/153	123/125	103	75	47
Peak height (in mm)	1/1.1	1/1.2	19/18	28.5/26.5	5.0	13	27
Metastable peaks	102.2	100.2	54.7				

Solution The metastable peaks in question are attributed to the following transitions:



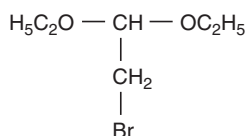
The *M* and *M* + 2 peaks at 196 and 198 respectively with intensity ratio of 1:1 suggest that the compound contains one bromine atom. The mass loss of 45 giving rise to a 151/153 doublet with an intensity ratio of 1:1 indicates that the compound contains either a carboxylic group (—COOH) or an ethyl ester group (—OC₂H₅). However, the 167/169 doublet, still with an intensity ratio of 1 : 1 that arises because of mass loss of 29 from the molecular ion, rules out the possibility of the presence of —COOH group in the molecule.

The peak at *m/e* : 103 in the form of a singlet corresponds to (*M*⁺ — CH₂Br) ≡ (*M*⁺ — 93). This indicates that the compound contains a CH₂Br group. Thus, the structure of the particle corresponding to the peak at *m/e* : 103 can be written as

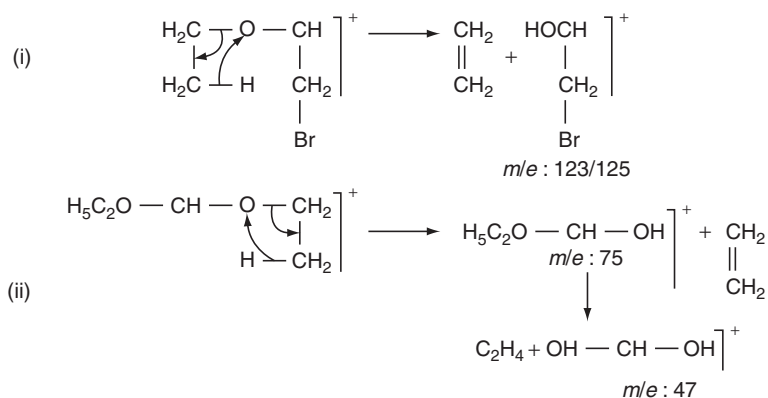


Let us now find the nature of R₁ and R₂ groups. The mass due to both the groups should be (103 — 57) ≡ 46

mass unites. So $\frac{46}{14} \equiv 3\text{CH}_2\text{s} + 4\text{Hs}$ or $\frac{46}{12} \equiv 3\text{Cs} + 10\text{Hs}$, i.e. R₁ + R₂ ≡ C₃H₁₀, but this is not possible. If either of the groups contains an oxygen atom then R₁ + R₂ ≡ C₂H₆O (since CH₄ ≡ O). Since the compound contains an ester group so most probably R₂ = OC₂H₅ and R₁ = H. Thus the compound in question is most likely a double ether with the structural formula

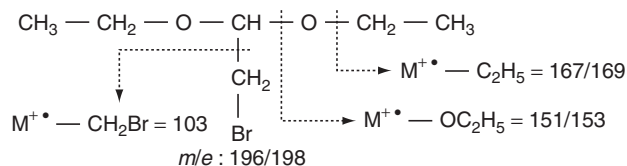


The 123/125 doublet with intensity ratio of 1:1 and a singlet at 75 arise due to transition of (i) and (ii) respectively, i.e.



This lends support to the structure of the compound as a double ester.

The major routes of fragmentation of the compound have been summarised below.



Problem 11.17: In the mass spectrum of a compound with molecular formula $C_4H_8O_2$ there are observed peaks corresponding to the values of m/e indicated below:

<i>m/e</i>	27	29	39	41	42	43	45	60	73	88(<i>M</i> ⁺)
Relative content, as per cent of base peak	39.3	19.8	14.8	23.7	24.7	22.3	19.1	100 (Base peak)	27.1	1.6

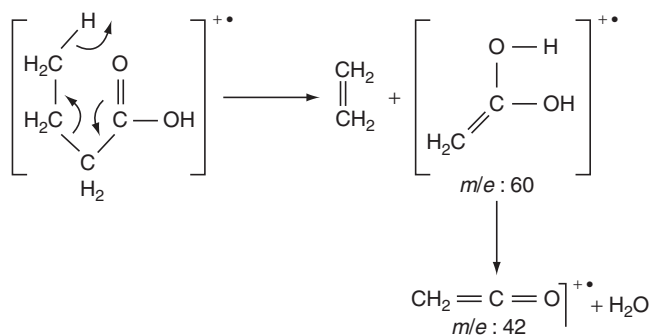
Solution The mass loss of 45 from the molecular ion peak, i.e. M^+ —45 giving rise to peak at 43^+ and a peak at $m/e : 45$ indicates that the compound in question is carboxylic acid.

The empirical formula of the acid will be $R-COOH$, where $R = C_4H_8O_2-RCO_2H=C_3H_7$ or the mass of the alkyl part of the acid $= 88 - 45 = 43 \equiv 3CH_2s + 1H$ or $\equiv 3Cs + 7Hs$. Thus the empirical formula of the compound is C_3H_7COOH and the peak at 45 corresponding to $(M^+ - C_3H_7)$, i.e. ^+COOH . The ion at 73 corresponds

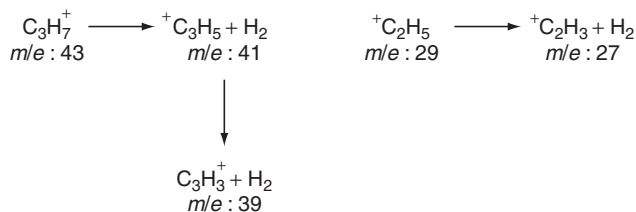
to $M^+ - CH_3$ i.e. $C_3H_7COOH \rightarrow \dot{C}H_3 + C_2H_4^+ - COOH$. Thus a residual mass due to $M^+ - 15 - 45 = 28 \equiv 2Cs + 4Hs \equiv 2CH_2s$.

Accordingly, the structural formula of the compound is $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{COOH}$.

Since an even molecular ion gives rise to an even mass base peak, a molecular rearrangement occurs in the molecule. The McLafferty rearrangement in this compound yields a peak at m/e : 60. This substantiates the structure of the compound as butyric acid.



The other peaks result due to the decomposition of the ion series of the types $C_nH_{2n+1}^+$ to $C_nH_{2n-1}^+$



The peak at $m/e : 39$ being intense cannot be the metastable peak for the transition $43^+ \rightarrow 41^+$ which is expected

$$\text{at } m/e : \frac{41 \times 41}{43} = 39.09.$$

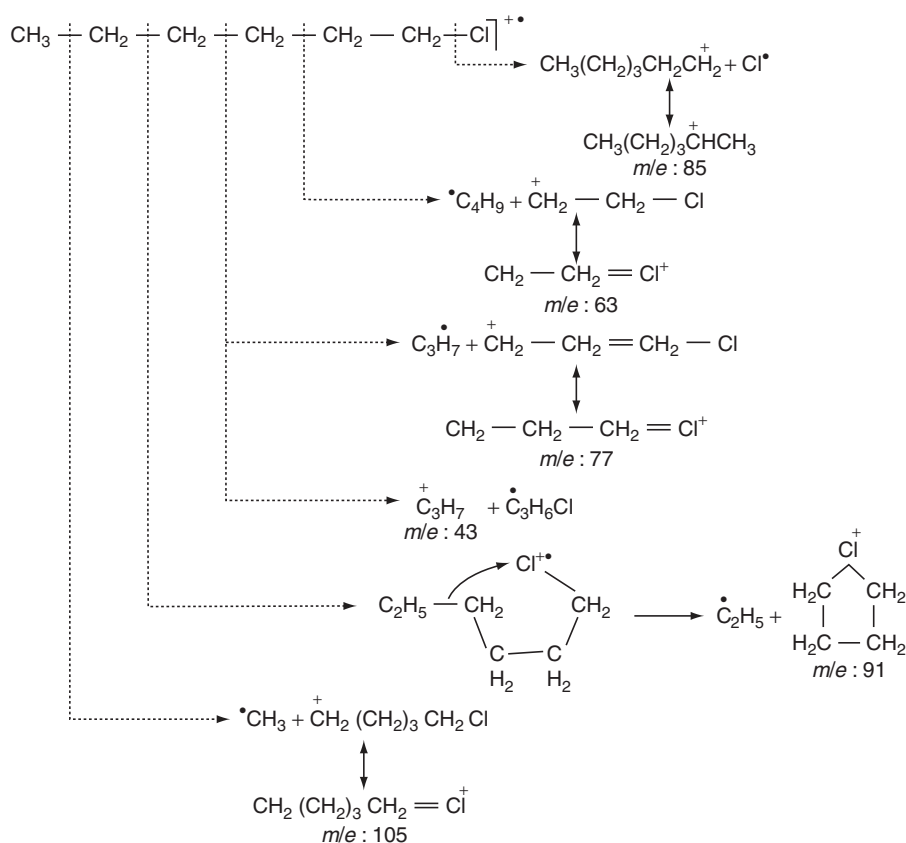
Problem 11.18: The characteristic peaks in the mass spectrum of 1-chlorohexane are indicated below:

<i>m/e</i>	122/120	107/105	93/91	85	79/77	65/63	43
Intensity ratio of peaks in the doublet	1:3	1:3	1:3	—	1:3	1:3	—

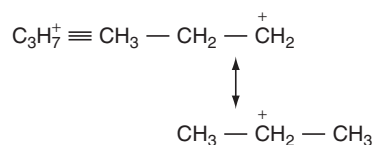
What might be the ions corresponding to these peaks?

Solution The peaks in each of the doublets in the spectrum are two units apart and the intensity ratio of peaks in each doublet is 1 : 3. This suggests that the doublets in the spectrum results because of the two isotopes, i.e. ^{35}Cl and ^{37}Cl of chlorine. The 122/120 doublet corresponds to the molecular ion of the compound in question.

The following modes of fragmentation give rise to ions corresponding to the other peaks in question:

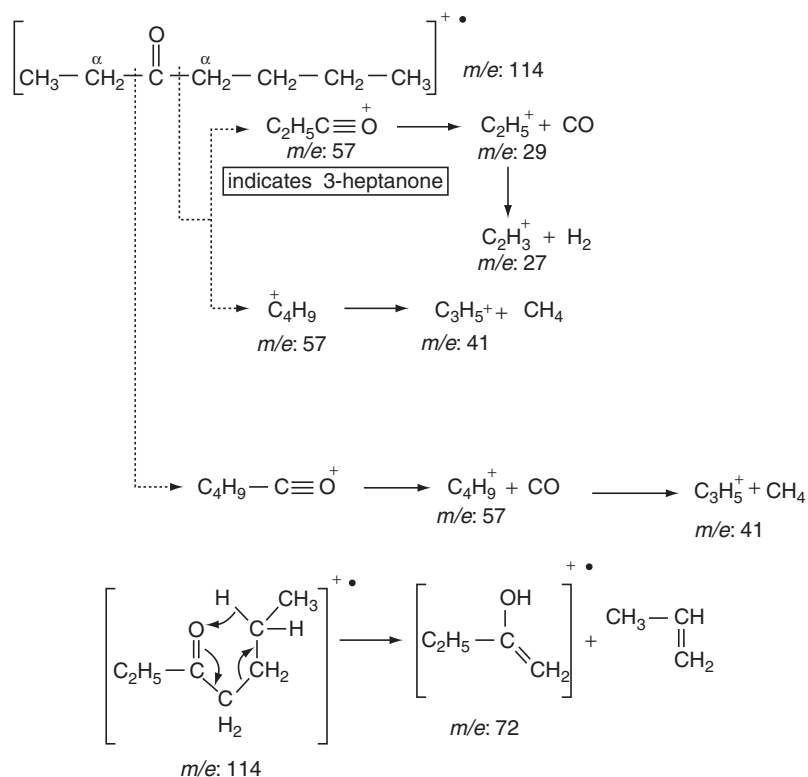


Note that the stability of $\text{C}_4\text{H}_8\text{Cl}^+$ ion (m/e : 91) is because of a five-membered cyclic structure.

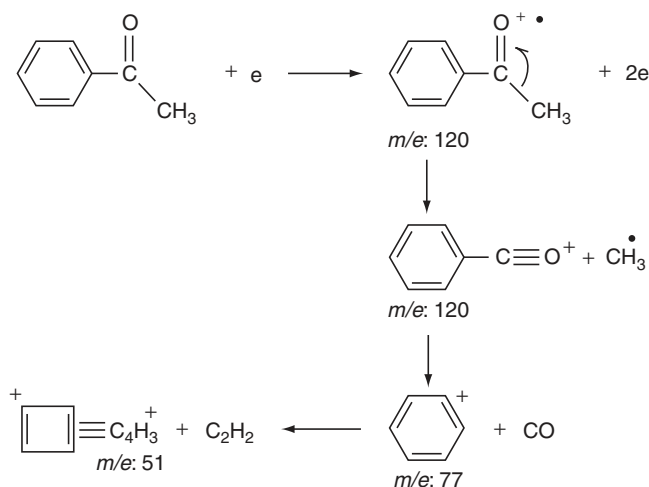


Problem 11.19: The mass spectra of 3-heptanone (a) and methyl phenyl ketone (b) show peaks at m/e : (peak height): 114 (M^+ ; 4 mm), 85 (8 mm), 72 (7 mm), 57 (44 mm) (base peak), 41 (9 mm), 29 (31 mm), 27 (12 mm), and at m/e : 120 (M^+) 105, 77, 51 respectively. What ions might these peaks correspond to?

Solution (a) The peaks in the mass spectrum of 3-heptanone originate from the following modes of fragmentations:



(b) By Table 11.10, we write:



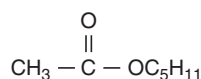
Problem 11.20: The mass spectrum of a compound contains a molecular ion peak at $m/e : 130(\text{M}^+)$ plus peaks at 71, 70, 59, 57.5, 44, 42, 28 and 14. Deduce the structure of the compound.

Solution The ion at $m/e : 59$ and another ion corresponding to $(\text{M}^+ - 59)$, i.e. $m/e : 71$ suggest that the compound in question is an ester and contains an acetate group. The ions at $m/e : 70, 42, 28, 14$, belong to the ion series of the type $\text{C}_n\text{H}_{2n}^+$. This suggests that the hydrocarbon component of the compound contains at least $\frac{70}{12} = 5$ carbon atoms or $\frac{70}{14} = 5 \text{ CH}_2$ s. Accordingly, the formula of the compound can be written as $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{OR}$ where, R contains at least five carbon atoms.

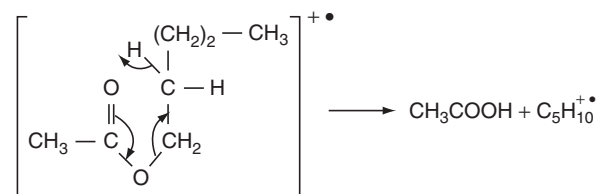
Now $\text{R} = 130 - 59 = 71 = 5\text{Cs} + 11\text{Hs}$ or $\equiv 5\text{CH}_2\text{s} + 1\text{H}$, i.e. $\text{R} = \text{C}_5\text{H}_{11}$.

Since, there is no ion corresponding to $(\text{M}^+ - \text{CH}_3)$, i.e. $m/e : 115$, the presence of methyl group in the side chain of the hydrocarbon part of the molecule is ruled out.

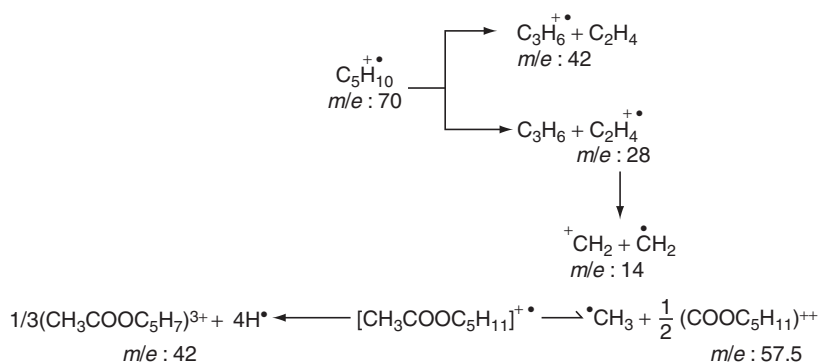
Thus, the compound in question is amyl acetate with structural formula



Ion peak at $m/e : 70$, an even mass arising from an even mass molecular ion suggests a McLafferty rearrangement, i.e.

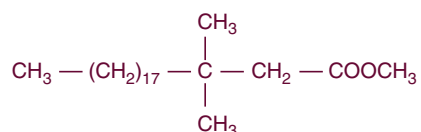


This further lends support to the structure of the compound in question. The other ions are formed by the following routes of fragmentations:



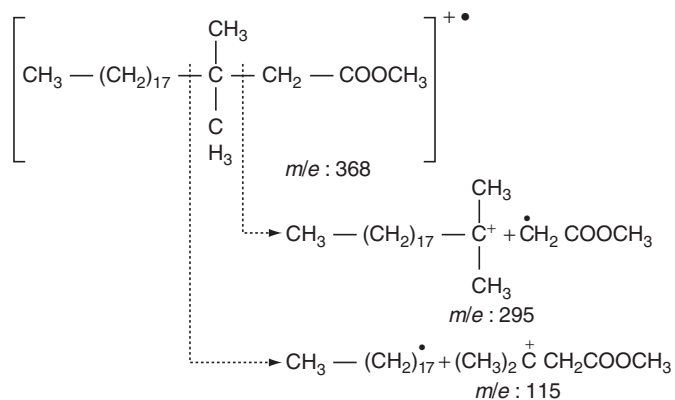
The peak at $m/e : 44$ is attributed to $^+\bullet\text{CO}_2$ and CO^+ ion also contributes to peak at $m/e : 28$

Problem 11.21: The mass spectrum of the compound with structural formula

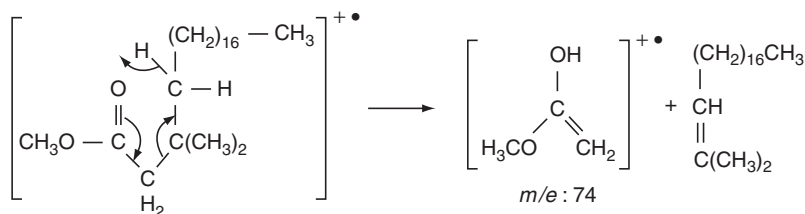


exhibits peaks at $m/e : 74, 115, 295$ and 368 . What ions might these peaks correspond to?

Solution The molecular ion corresponding to the compound in question will appear at $m/e : 368$ while the peaks at $m/e : 295$ and 115 are due to cleavage at the quaternary carbon atom on either side.



The peak at $m/e : 74$ is attributed to $\left[\text{CH}_2 = \text{C} \begin{matrix} \text{OH} \\ \text{OCH}_3 \end{matrix} \right]^{\bullet+}$ which is translated by McLafferty rearrangement as follows:



Problem 11.22: The mass spectral data of a compound with molecular formula $\text{C}_9\text{H}_{12}\text{S}$ is indicated below:

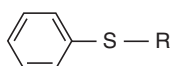
m/e	152 (M^+)	137	110 (Base peak)	77	66	65	43
Abundance, as per cent	45	7	100	7	11	8	12

Metastable peaks are observed at $m/e : 123, 79.6$ and 54.1 . Deduce the structure of the compound.

Solution The metastable peaks are due to the following transitions.

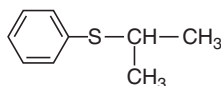
123	$152^+ \rightarrow 137^+ + 15 (\text{CH}_3)$	
79.6	152^+	$\rightarrow 110^+ + 42 (\text{CH}_3-\text{CH}=\text{CH}_2)$
54.1	110^+	$\rightarrow 77^+ + 33 (\text{HS})$

The strong molecular ion peak suggests the presence of an aromatic group. The transition states suggest that the mass loss is due to elimination of CH_3 , $\text{CH}_3-\text{CH}=\text{CH}_2$ and HS groups respectively. The loss of HS from base peak indicates that $-\text{SH}$ is bounded to phenyl ring. In view of it, the structural formula of the compound may be written as

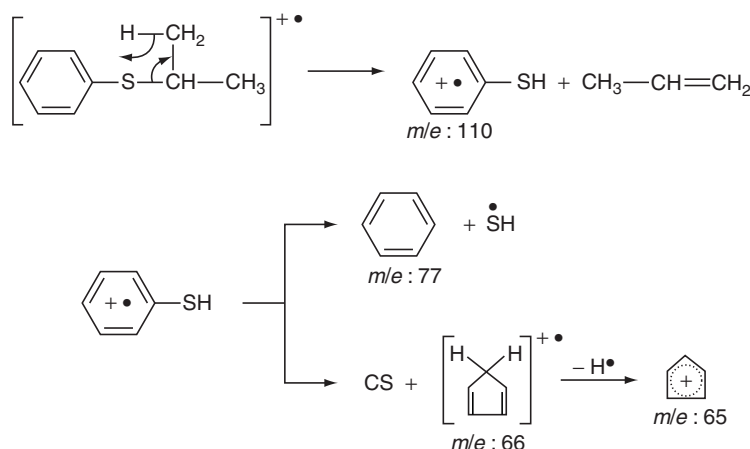


where, $\text{R} = \text{C}_9\text{H}_{12}\text{S} - \text{C}_6\text{H}_5\text{S} = \text{C}_3\text{H}_7 \equiv \text{CH}_3-\text{CH}-\text{CH}_3$.

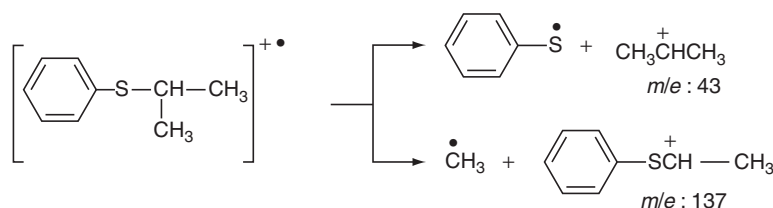
The initial loss of CH_3 group indicates R to be isopropyl group. Accordingly, the structure of the compound is



Even mass molecular ion resulting in even mass base ion suggests molecular rearrangement in the molecular ion. Thus, the base peak at $m/e : 110$ appears due to such a process as follows:

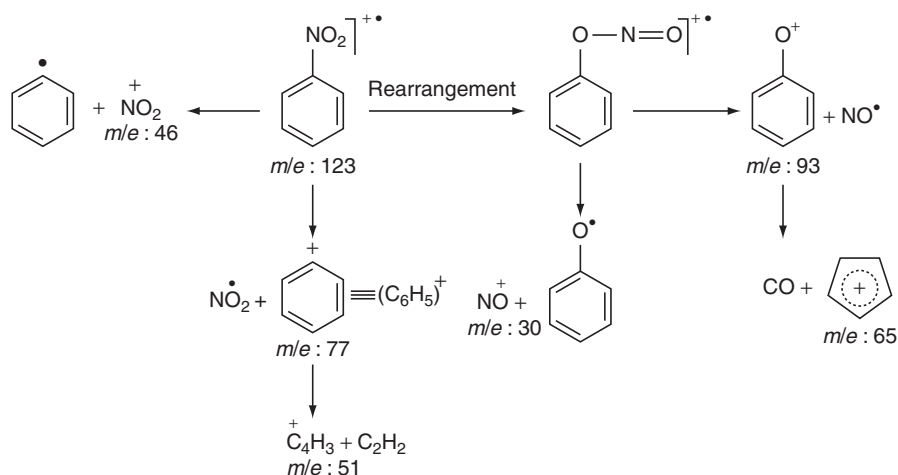


This further lends support to the structure of the compound in question which is isopropyl phenyl thioether. The peaks in the mass spectrum appear as follows:



Problem 11.23: The mass spectrum of nitrobenzene shows the presence of particles with the following mass numbers: 123 ($M^{+\bullet}$, prominent), 93, 77, 65, 51, 46 and 30. Based on this data, what would be the modes of fragmentation of nitrobenzene? (Use Table 11.10.)

Solution The modes of fragmentation of $C_6H_5NO_2$ giving rise to the peaks in question are



Problem 11.24: The mass spectrum of a compound exhibits peaks at m/e : 129, 114, 86, 58 and 44. Deduce the structure of the compound if it shows metastable peaks at m/e : (a) 29.5 and 16.9 and (b) 16.9 mass units.

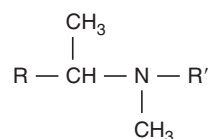
Solution (a) The metastable ions at 29.5 and 16.9 are translated by the following transitions:

29.5	: $114^+ \rightarrow 58^+ + 56 (\equiv C_4H_8)$
16.9	: $114^+ \rightarrow 44^+ + 70 (\equiv C_5H_{10})$

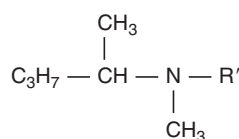
The transition states suggest that the mass loss is due to elimination of C_4H_8 and C_5H_{10} groups respectively.

The odd mass molecular ion peak at m/e : 129 and peaks at m/e : 58 and 44 suggest that the compound in question

is an aliphatic mono-amine. The peaks 44^+ and 58 correspond to $CH_2 = \overset{+}{N}(CH_3)H$ and $CH = \overset{+}{N}H(CH_3)$ respectively. Consequently, the general structure of the compound may be written as

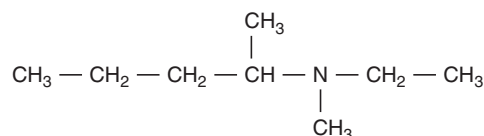


A mass loss of 43 from the molecular ion, i.e. ($M^{+\bullet} - C_3H_7$) suggests that the side chain group R is C_3H_7 . Accordingly, the structure of the compound is written as



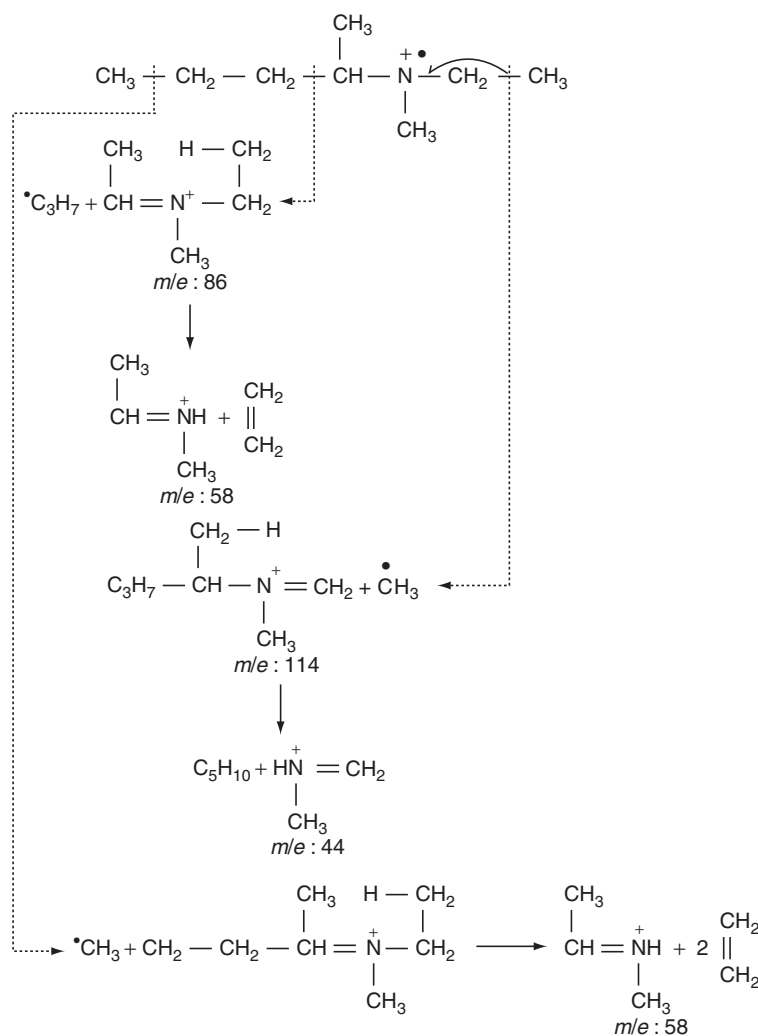
So, $R' = 129 - 100 \equiv 29 = 2Cs + 5Hs$ or $\equiv 2CH_2S + 1H$, i.e. $R' = C_2H_5$.

Thus, the structural formula of the compound is

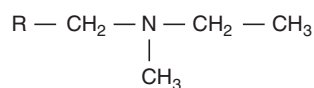


A mass loss of 15 from the molecular ion, i.e. ($\text{M}^{+\bullet} - \text{CH}_3$) giving rise to a peak at $m/e : 114$ lends support to the structure of the compound.

The fragmentation of the molecular ion followed by molecular rearrangement of the products of fragmentation results in ions at $m/e : 58$ and 44 , i.e.



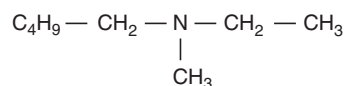
(b) In this case, the transition $29.5: 114^+ \rightarrow 58^+ + 56$ is not allowed, so the peaks at $m/e : 58$ and 86 will not appear in the spectrum. Since the transition $16.9: 114^+ \rightarrow 44^+ + 70$ is allowed, the peaks at $m/e : 44$ and 114 will appear in the spectrum. Accordingly, the structural formula of the compound should be



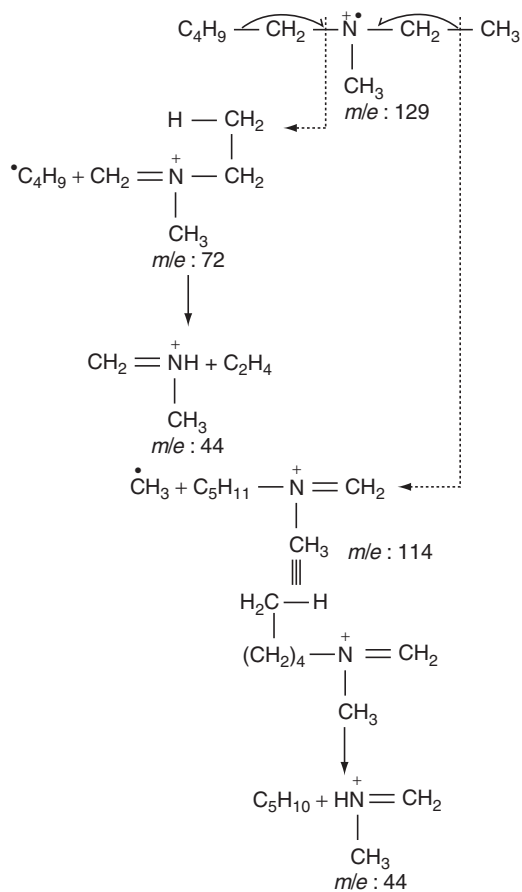
Thus

$$\text{R} = 129 - 72 = 57 \equiv 4\text{CH}_2\text{s} + 1\text{H} \text{ or } \equiv 4\text{Cs} + 9\text{Hs} = \text{C}_4\text{H}_9.$$

So the structural formula of the compound is

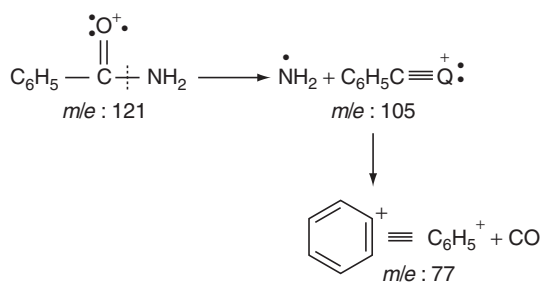


According to this formula, the peak at $m/e : 44$, will be translated by the following routes of fragmentations followed by molecular rearrangement.

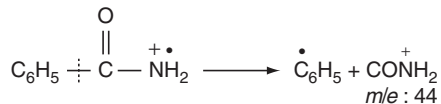


Problem 11.25: (a) In the mass spectrum of benzamide $\text{C}_6\text{H}_5\text{CONH}_2$, there are observed peaks corresponding to the following values of m/e : 121, 105, 77, 44. What ions might these peaks correspond to? (b) The mass spectrum of an amide with molecular formula $\text{R}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CONH}_2$ includes lines corresponding to the following mass numbers (m/e): 86, 59, 44. What particles might these peaks correspond to?

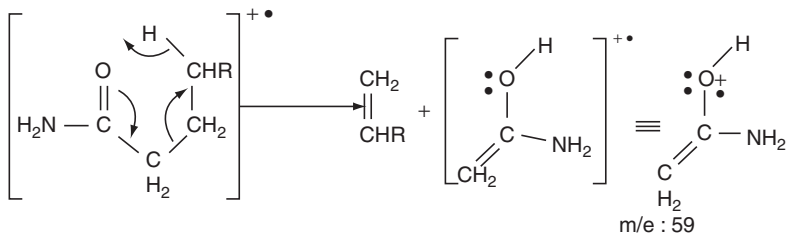
Solution (a) Loss of NH_2 from molecular ion gives rise to a resonance stabilised benzoyl cation that in turn fragments to a phenyl cation.



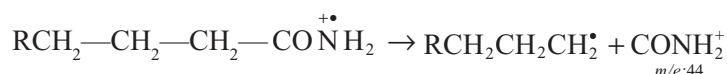
The loss of phenyl radical yields a peak at m/e : 44.



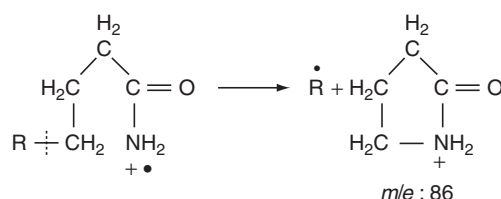
(b) The peak at 59 in primary amides is because of the molecular rearrangement.



The peak at $m/e : 44$ is due to the loss of alkyl part of the amide.



The peak at $m/e : 86$ arises from $\gamma\delta\text{C—C}$ cleavage accompanied by cyclisation.



Thus, the peaks at $m/e : 44, 59, 86$ are characteristic of the primary amides.

11.15 COMPUTERS IN MASS SPECTROMETRY

Modern spectrometers are fitted with computers and they play an important role in assisting the mass spectroscopists in interpreting the mass spectral data. The spectra of a large number of compounds are known to us and to match the unknown with the known would be a tedious problem. Computers can be used for this purpose. Even then if all the peaks are to be matched then it will consume a lot of computer time and the process becomes expensive. It is advisable to select five or six largest peaks and try to match them with the mass data of the compound stored in the memory of the computer. Very often the large peaks are to be found at the low mass region, which is not the ideal region to compare for identification. It is better to choose these peaks at different mass regions. These days softwares are available that can recognise patterns of structure like alcohol, ketone, ester, etc., by their mode of fragmentation. Softwares are also available to interpret the spectra of specific type of compounds like the sequence of amino acids in polypeptides and proteins as well as the sequence in oligonucleotides. A schematic diagram for structure determination of an unknown compound from its spectrum is shown in Fig. 11.26.

11.16 APPLICATIONS OF MASS SPECTROMETRY

MS is a versatile tool which has contributed to the development of many sciences and found applications in all branches of sciences and industries. It was originally used for accurate measurements of atomic masses and isotopes of elements and by the early 1960s the ever-increasing precision in measurement of isotopic masses and abundances gave rise to new international standards for atomic masses of elements. Since 1960, the applications of this technique blossomed like a mushroom cloud. The period of determination of purity, accurate molecular mass and molecular formula of compounds have been reduced from years to days. Sample size, as small as, sub-ngm, can be handled by this technique. The technique has played a significant role in material analysis and process monitoring in the petroleum, chemical and pharmaceutical industries and is being used in food processing and electronic industries, e.g. the petroleum chemists use this technique for grading a complex mixture of hydrocarbons. The technique is widely used by forensic scientists to know about the nature of poison given to the victim; in forensic science, the size of the sample under examination is usually small and here the sensitivity and specificity of mass spectrometry are very important. Spark source mass spectrometry has been utilised for the detection of trace elements in liver tissue (especially arsenic, mercury, lead, etc.), hair, glass, metal fragments and synthetic fibres. Organic mass spectrometry is used for the identification of drugs, e.g. strychnine, drug metabolites and other materials including pesticides, namely dichlorodiphenyltri-chloroethane (DDT), 1-naphthyl-methylcarbamate (Serin), etc., and the pyrolysis products of polymers, by sport scientists to know about the banned

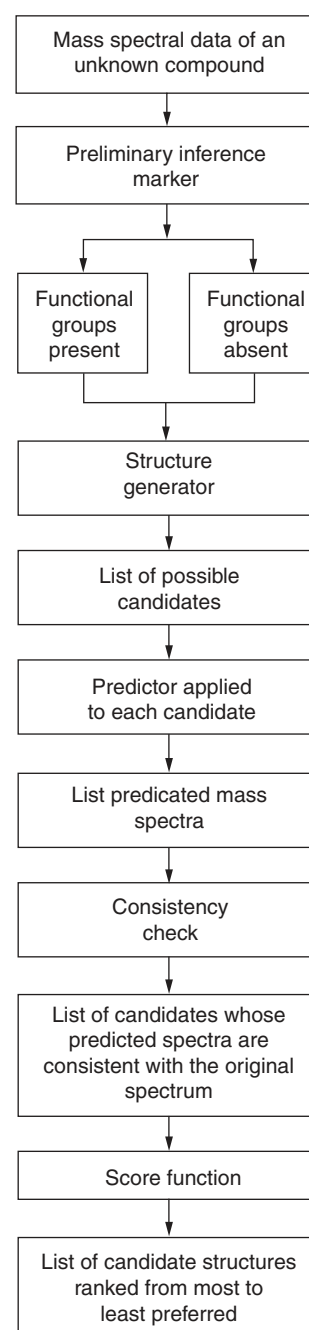


Fig. 11.26 Flowsheet diagram for structure determination of an unknown spectrum.

performance-enhancing drugs used by the athletes from their urine samples, by medical scientists for analysis of drugs like lysergsäure diethylamid (LSD, $C_{20}H_{25}N_3O$, 323) in illicit preparation and morphine ($C_{17}H_{19}NO_3$, 285.35) in the urine of heroin addicts, by environmental scientists to check organic and inorganic polluting agents, etc., in water and in the atmosphere. Mass spectrometry is also used in geology to have a better estimate of ages of rocks on earth and other planets. MS, being non-invasive (thus politically viable), is used for international monitoring of nuclear facilities. The technique has proved to be very useful in the identification and analysis of biological macromolecules including oligonucleotides and proteins; the main actors in the make-up of life.

The applications have been discussed here under two subtitles, namely nonbiological and biological applications. However, there may be some overlap between these two classes of applications.

11.16.1 Nonbiological Applications of Mass Spectrometry

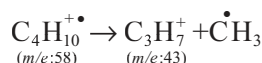
Some of the typical nonbiological applications of this technique are the following:

(a) Leak Detection Inexpensive and portable helium mass spectrometers have been widely used as leak detectors and as the most sensitive gauges for the most extreme vacuum we can produce. The sensitivity of the helium mass spectrometer is of the order of 10^{-11} atm ml/s of helium and the exact leak locations within 1.0 mm can be detected. The instrument is coupled to a vacuum system under examination and a fine jet of helium is sprayed around any joints or other locations suspected of leaking. Helium entering the system through the leaking location, if any, is drawn into the instrument for detection and the exact location of the leak is determined for repair. The major merit of this method is that the entire system is scanned first for locating the exact leaking points and the repair work is done after the scanning.

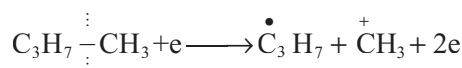
(b) Identification of Molecular Species from Fragmentation Pattern Each compound has a characteristic mass spectrum which can be used as a 'molecular fingerprint' alike infrared spectrum. In other words, we can say that like infrared spectrum, mass spectrum also enables to discern which peaks are of importance in identifying the different molecular systems. Even positional isomers can be distinguished from their mass spectra. This is demonstrated here on the basis of mass spectra of the two isomeric butanes, viz., *n*-butane and isobutane shown in Figs 11.27(a) and (b). Both the spectra have the same number and positions of peaks, except that they differ in their relative intensities. The molecular ion occurs at mass number of 58 for each isomer, but in each case it is not the most abundant ion. We know that molecular ions are odd electron species, and because of energetic considerations they have the general tendency to become even electron ions. The most abundant ion for the butanes occurs at a mass number of 43; and is attributed to $C_3H_7^+$ ion, i.e. (even number of electrons):



or alternatively, we can write



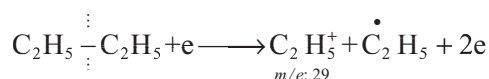
The low-intensity peak at a mass number of 15 in each spectrum corresponds to $^+CH_3$ which also has an even number (6) of outer shell electrons. This reveals that the fission of a methyl-carbon bond occurs less frequently.



or



The fairly strong peak at a mass number of 29 in the straight-chain isomer is due to the fission of an ethyl-ethyl bond:



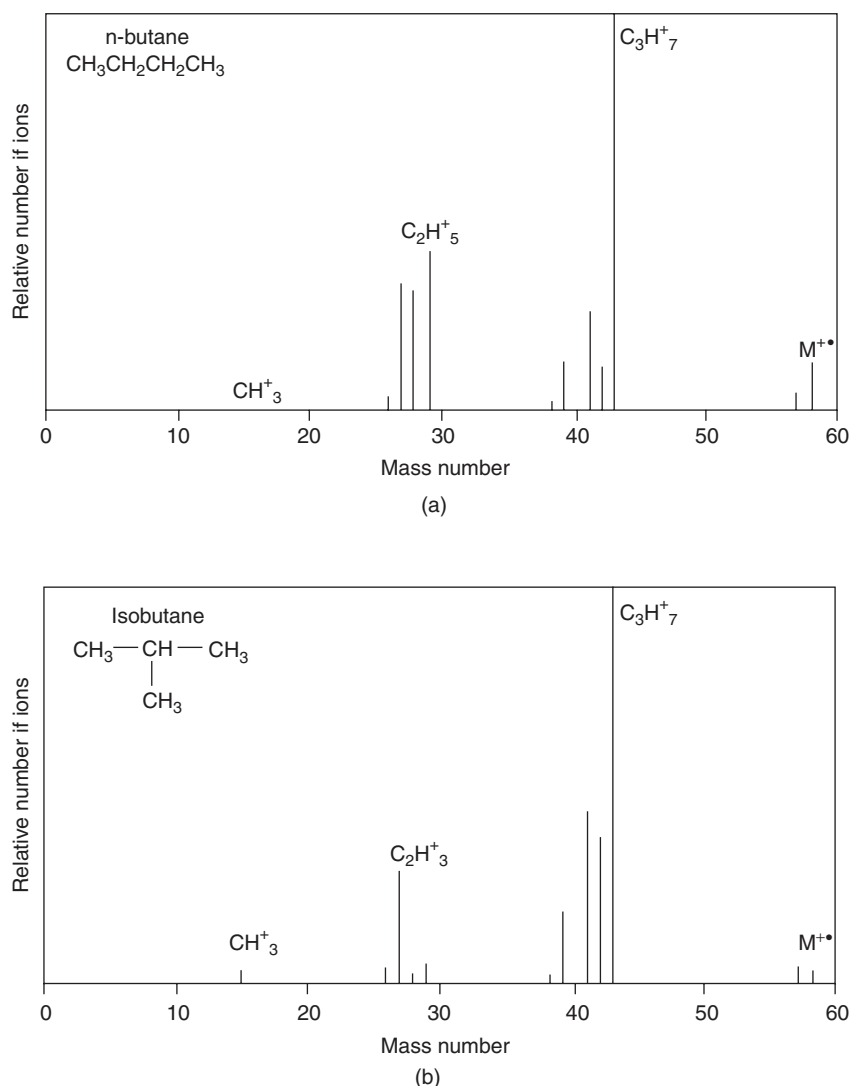
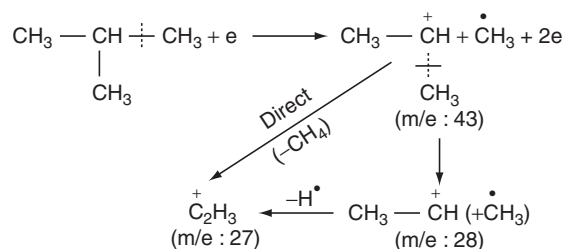


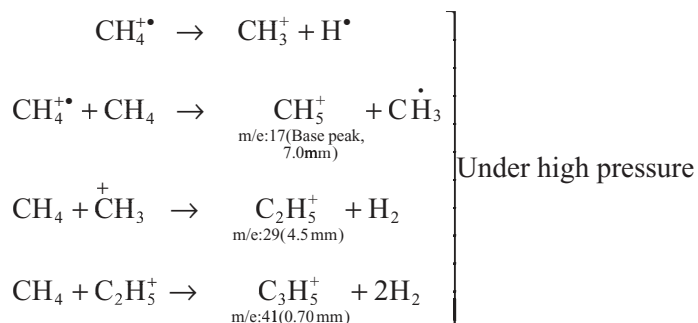
Fig. 11.27 Mass spectrum of (a) *n*-butane, and (b) isobutane.

A peak at a mass number of 29 is hardly evident in the spectrum of a branched-chain isomer. This shows the absence of an ethyl group in the branched chain isomer; only rearrangement of the structure of isobutane can yield a peak at a mass number of 29. The strong peak at a mass number of 27 in the mass spectrum of isobutane is attributed to $C_2H_3^+$ which is formed according to the following bond fissions:

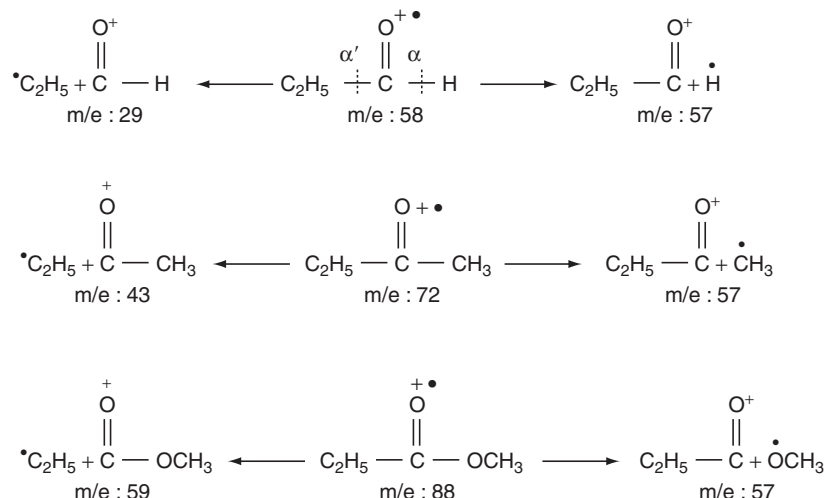


Thus, the comparison of mass spectra of *n*- and iso-butaness shows that the peaks at $m/e : 29$ ($C_2H_5^+$) and $m/e : 27$ ($C_2H_3^+$) respectively can be fixed a criterion to distinguish between *n*-butane and isobutane. Similarly, a comparison of the mass spectra of the four isomeric butyl alcohols indicate that the base peaks (except that of the iso-isomer) at $m/e : 31$ (CH_3O^+), 45 ($C_2H_5O^+$), 59 ($C_3H_7O^+$), and 74 ($C_4H_9O^+$, molecular ion) respectively can serve to identify the normal, i.e. primary, secondary, tertiary and isobutyl alcohols.

The characteristic peaks in the low-pressure mass spectrum of methane are observed at $m/e : 16, 15, 14, 13, 12$ and are respectively attributed to CH_4^+ , CH_3^+ , CH_2^+ , CH^+ and C^+ ions. While the peaks at $m/e : 17, 19, 41$ in the high-pressure mass spectrum of CH_4 are due to the following ion-molecule reactions occurring by collision of methane molecule with ions.



The mass spectra of aldehydes, ketones and esters have common features. A comparison of the intensity of the peak due to α -cleavage with that of the α' -cleavage reveals that the latter is preferred with the loss of larger alkyl radical than the former. Thus, the peaks due to α and α' fragmentations in simple aldehydes, ketones and esters can be fixed a criterion for their identification. For example, the peaks at m/e : 58, 57 and 29 are characteristics of propionaldehyde.



Identification of Optical Isomers Optical isomers can be identified by GC-MS. For example, the GC-QPMS of a sample of mixture of the two optical isomers of the N-acetyl derivatives of the amino-acid alanine with the L-form labelled with an atom of deuterium is shown in Fig. 11.28. The upper trace containing two peaks is the normal signal from the GC detector. From this trace alone it is not possible to make out which peak is due to which compound. The lower trace is the mass scan of the sample at a 10 second interval. The presence of two peaks in the spectrum at m/e : 159 (intense) followed by a satellite at 158 and 158 (intense) followed by a satellite at 159, clearly shows the presence of two optical isomers in the sample; the former is attributed to the L-form while the latter to the D-form of the acid. Based on this, one can assign the signals in the GLC trace to the two optical isomers. The first signal corresponds to L-form while the second to the D-form.

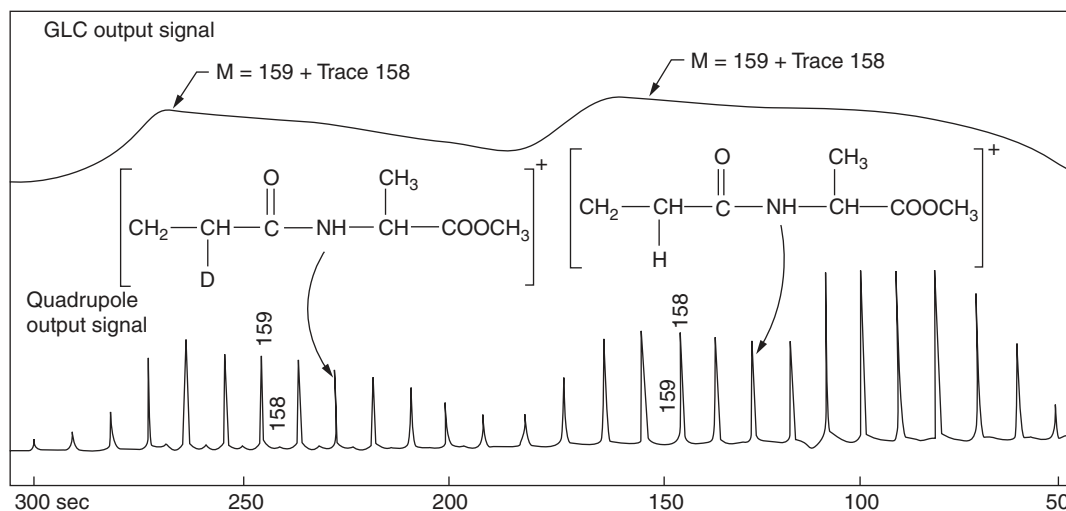


Fig. 11.28 GC-Quadrupole mass spectrum of N-acetylated derivatives of amino acid alanine with the L-form labelled with an atom of deuterium. No helium separator is used between GLC and quadrupole mass spectrometer. The satellite peaks being of very low intensity are not visible here in the spectrum.

(c) Determination of Atomic Masses of Elements Most samples of elements in nature are a mixture of isotopes. MS has proved to be an ideal method for separation of isotopes. The isotopes of many elements have been discovered by this means and their isotopic masses measured. The existence of isotopes of elements explains the markedly non-integral nature of some atomic masses.

The average atomic masses of polyisotopic elements are determined from the peak heights corresponding to the respective isotopic mass numbers in the mass spectrum. From the peak heights in the mass spectrum, the percentage of relative abundance of isotopes and the number of atoms in 100 atoms of the isotopic mixture are calculated. The relative isotopic mass contributions to a sample of 100 atoms of the isotope mixture are then calculated from the formula.

Mass unit of an isotope in 100 atoms of the isotopic mixture = Isotopic mass number $\times$ number of atoms of the isotope in 100 atoms of the isotopic mixture.

The addition of mass units of constituent isotopes in 100 atoms of isotopic mixture will yield the total mass units for 100 atoms which on division by 100 will give the average atomic mass of the element.

Atomic masses of some polyisotopic elements are listed here in Table 11.11 for ready reference.

Table 11.11 Exact atomic masses of principal polyisotopic elements.

Isotope	Mass	Isotope	Mass
^1H	1.00783	^{31}P	30.9738
^2H	2.01410	^{32}S	31.9721
^{12}C	12.00000 (std)	^{33}S	32.9715
^{13}C	13.00336	^{34}S	33.9679
^{14}N	14.0031	^{35}Cl	34.9689
^{15}N	15.0001	^{37}Cl	36.9659
^{16}O	15.9949	^{56}Fe	55.9349
^{17}O	16.9991	^{79}Br	78.9183
^{18}O	17.9992	^{81}Br	80.9163
^{19}F	18.9984	^{127}I	126.9045
^{28}Si	27.9769		

Problem 11.26: The mass spectrum of naturally occurring lead shown in Fig. 11.29 yields the following data.

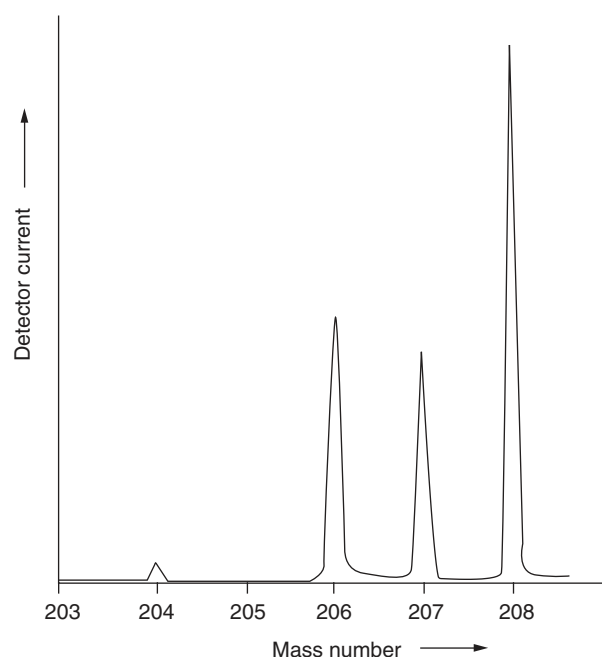


Fig. 11.29 Mass spectrum of naturally occurring lead.

Isotopic mass number	Peak height $\times 10$ (in mm)
204.0	2
206.0	24
207.0	22
208.0	52

Calculate the average atomic mass of lead.

Solution Following the general procedure for the determination of average isotopic atomic masses of polyisotopic elements, we write

Isotopic mass number	Per cent relative abundance	Number of atoms in 100 atoms of the mixture	Mass units of isotopes in 100 atoms of the mixture
204.0	2	2	408
206.0	24	24	4944
207.0	22	22	4554
208.0	52	52	10816

Thus, the total mass units of isotopes in 100 atoms of the isotopic mixture

$$= 408 + 4944 + 4554 + 10816 = 20722$$

Accordingly, the average isotopic atomic mass of lead = $\frac{20722}{100} = 207.22$

Problem 11.27: From the mass spectrum of nickel in Fig. 11.30, determine the atomic mass of nickel and compare it with the periodic table value (i.e. 58.933).

Solution From Eq. (11.35); we write

$$\text{Peak height} = \frac{\text{Relative intensity of an isotopic peak} \times 100}{\text{Sum of the isotopic relative intensities}}$$

The relative intensity data at various mass numbers shown in Fig. 11.30 is converted into peak-height data by making use of the formula (11.35). The resultant peak height data at different isotopic mass numbers so determined are

Isotopic mass number	Relative intensity	Peak height
58	11.2	67.87
60	4.4	26.66
61	0.2	1.21
62	0.6	3.63
64	0.1	0.6
Sum = 16.5		

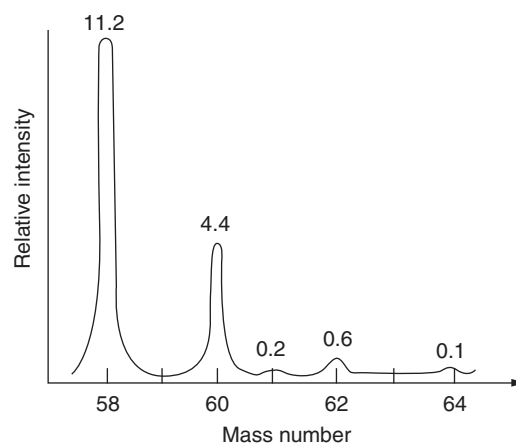


Fig. 11.30 Mass spectrum of naturally occurring nickel.

Proceeding as in Example (11.26), the average isotopic atomic mass of Ni comes out to be 58.733 amu.

The table value of atomic mass of Ni is 58.933 amu. Thus the difference between the present and the table value

$$= 0.2 \text{ amu} \quad \text{or} \quad = \frac{0.2 \times 100}{58.933} = 0.3 \text{ per cent}$$

(d) Determination of Percentage Content of X^{m*} in a Diatomic Gas (say X_2) Sample Containing Isotopic Binary Mixture of the type X^mX^m and X^mX^{m*}

Let relative abundance of X^mX^m in sample of air (X_2) = h_1

and relative abundance of X^mX^{m*} in the air sample = h_2

Thus, the relative abundance of X^{m*} in the air sample = $\frac{h_2}{2}$

Accordingly, the per cent content of X^{m*} in the binary mixture

$$x = \frac{\frac{h_2}{2} \times 100}{\frac{h_2}{2} + h_1} = \frac{100h_2}{2h_1 + h_2} = \frac{100}{2(h_1/h_2) + 1} = \frac{100}{2R + 1} \quad (11.38)$$

where, $R = \frac{h_1}{h_2}$ is the relative abundance of X^mX^m and X^mX^{m*} in the air sample.

Further, if a diatomic gas X_2 contains three isotopic species of the type X^mX^m , X^mX^{m*} and $X^{m*}X^{m*}$ and their abundances are respectively h_1 , h_2 and h_3 ; then it can easily be proved that the percentage content of the element X^{m*} is given by

$$\frac{(h_2 + 2h_3) \times 100}{2(h_1 + \frac{h_2}{2} + h_3)} \quad (11.39)$$

Problem 11.28: The mass spectrum of oxygen produced from heavy water is characterised by the presence of peaks of the isotopic forms of oxygen $^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}$ with wave heights of 101 and 25 mm, respectively. Determine the percentage content of ^{18}O in the mixture.

Solution The content of nitrogen ^{18}O is determined from the formula

$$x = \frac{100}{2R + 1} \quad (11.38)$$

where R is the ratio of the peak heights of the isotopes of the element being determined in the mass spectrum.

$$R = \frac{h_{^{16}\text{O}}}{h_{^{18}\text{O}}} = \frac{101}{25} = 4.04$$

Hence,
$$x = \frac{100}{2 \times 4.04 + 1} = \frac{100}{9.08} = 11.06 \text{ per cent}$$

Problem 11.29: The mass spectrum of nitrogen produced from the air is characterised by the presence of peaks at $m/e = 28, 29$ and 30 having peak heights (i.e. height $\times 10$) 980, 360 and 53 mm respectively. Identify the isotopic species and calculate the percentage content of the element ^{15}N in the gas.

Solution The mass numbers at $m/e = 28, 29$ and 30 correspond to the isotopic species $\text{N}^{14}\text{N}^{14}$, $\text{N}^{15}\text{N}^{14}$ and $\text{N}^{15}\text{N}^{15}$ respectively. Substituting the data given in the problem into the general formula (11.39), we obtain percentage content of element ^{15}N

$$\frac{(360 + 2 \times 53) \times 100}{2(980 + 180 + 53)} = \frac{466 \times 100}{2 \times 1213} = 19.21$$

(e) Determination of Molecular Mass Molecular mass is a useful quantity for the identification of compounds, and it can easily be determined by mass spectrometry by measuring the intensity of the molecular ion peak as a function of the energy of the impact electrons. Intensity of molecular ion peak goes on increasing as the energy of the bombardment electron beam is increased. It is assumed that no ions heavier than the molecular ion will be produced by the ionising voltages ranging from 9 to 14 V. Thus the mass of the heaviest ion except that of the isotopic molecular ion gives the molecular mass of the molecule under study. The technique is especially useful where conventional methods fail to give reliable results as in the case of $\text{C}_6\text{F}_8\text{Fe}(\text{CO})_3$ and $\text{Fe}(\text{CO})_4(\text{CF}_2)_4$. These compounds have been shown to be monomers from their mass spectral data. The molecular ion peak of the latter has been observed at m/e : 368. Furthermore, the molecular mass of a compound in a mixture can also be determined provided the components

of a mixture have different ionisation potentials, e.g. in a mixture of hydrocarbons, the proper selection of the ionisation voltage will provide the mass spectrum of the desired component. *n*-paraffins, olefins and aromatics have ionisation potentials respectively over a voltage range of 10.2–11.2 eV, 9.4–9.7 eV and ≥ 9.7 eV.

The isobaric compounds, i.e. compounds having the same mass numbers, can easily be identified from their exact molecular masses as determined from their high-resolution mass spectra. For example, the exact masses of some molecular species with mass number 28, viz., H_2CN , $\text{CH}_2=\text{CH}_2$, N_2 and CO respectively are 28.0187, 28.0313, 28.0061 and 27.9949.

(f) Determination of Molecular Formula The mass defect is the difference between the accurate mass and the mass number. The mass defect of a molecular ion can be determined accurately by high resolution (i.e. double focussing) spectrometers. This defect enables one to determine the molecular formula directly. Let us suppose that the measured molecular mass of the compound is 60.0324 and the molecule does not contain sulphur and halogens which can be detected by their isotope peaks. The following compounds have mass number 60.

CH_2NO_2	60.0085	$\text{C}_2\text{H}_6\text{NO}$ 60.0449
$\text{CH}_4\text{N}_2\text{O}$	60.0324	$\text{C}_2\text{H}_8\text{N}_2$ 60.0688
CH_6N_3	60.0563	$\text{C}_3\text{H}_8\text{O}$ 60.0575
$\text{C}_2\text{H}_4\text{O}_2$	60.0211	

A simple examination of the table shows that the assumed compound has a molecular formula $\text{CH}_4\text{N}_2\text{O}$. Tables due to Beynon are available for each mass number, the possible formula corresponding to the general formula and their mass defects. They can be referred or they can be computed. This type of analysis can be applied to the fragment ions and also their compositions can be determined.

Beynon Method for Computation of Abundance Parameters The number of possible formulas can be restricted on the basis of relative abundance of natural isotopes of different elements (Table 11.12) and at masses 1 and 2 or more units larger than the parent ion. The calculations are made for all possible combinations of naturally occurring heavy isotopes of the elements and the values so obtained are compared with the observed values in order to choose the molecular formula of the compound.

The per cent of heavy isotopic contributions from a peak at mass M to the peak at mass $M + 1$ is calculated from the formula

$$\frac{(M+1)100}{M} = 0.015x + 1.1w + 0.37y + 0.037z \quad (11.40)$$

and to the peak at mass $M + 2$ by

$$\frac{(M+2)100}{M} = 0.20x + 0.006w(w-1) + 0.004wy + 0.0002wx \quad (11.41)$$

Table 11.12 Natural abundance of principal polyisotopic elements.

Element	Natural abundance (as per cent)	Element	Natural abundance (as per cent)
^1H	99.985	^{28}Si	92.18
^2H	0.015	^{29}Si	4.71
^{12}C	98.892	^{30}Si	3.12
		^{32}S	95.02
^{13}C	1.108	^{33}S	0.76
^{14}N	99.63	^{34}S	4.22
^{15}N	0.37	^{35}Cl	75.53
^{16}O	99.76	^{37}Cl	24.47
^{17}O	0.037	^{79}Br	50.52
^{18}O	0.204	^{81}Br	49.48

Natural abundance based on 100 atoms of most common isotope can also be calculated and reported, e.g.

$$\text{for } ^{12}\text{C} = 100; ^{13}\text{C} = \frac{1.108 \times 100}{98.892} = 1.120; \text{for } ^{32}\text{S} = 100, ^{34}\text{S} = \frac{4.22 \times 100}{95.02} = 4.441$$

where w , x , z , and y are the numbers respectively of C, H, O and N in the compound $C_wH_xO_zN_y$. Based on these formulas, Beynon calculated the abundance parameters for all combinations of C, H, N and O up to mass 500. For ready reference, contributions of C, H, O and N to parent peaks of masses 72 and 73 are reported here in Table 11.13. Thus the most probable formula of such compounds can be obtained from the relative heights of isotopic peaks $M + 1$ and $M + 2$. For example, suppose we have 100 molecules of methane (CH_4). There will be 1.11 molecules that contain ^{13}C and 4×0.015 molecules that contain ^2H . These heavier isotopes should contribute an $M^{++} + 1$ peak whose intensity is about $1.11 + 4(0.015) = 1.17$ of the intensity of the molecular ion peak. This conforms to the observed intensity of the $M^{++} + 1$ peak in the observed spectrum of methane, i.e. $P(^{12}\text{C}^1\text{H}_4) : P(^{13}\text{C}^2\text{H}_4) :: 100 : 1.15$.

Table 11.13 Heavy isotope contributions to parent peaks of masses 72 and 73.

M^{++}	Empirical formula	Per cent of M^{++} intensity $\frac{M^{++} + 1(M^{++} + 2)}{M^{++} + 1(M^{++} + 2)}$	M^{++}	Empirical formula	Per cent of M^{++} intensity $\frac{M^{++} + 1(M^{++} + 2)}{M^{++} + 1(M^{++} + 2)}$
72	$\text{CH}_2\text{N}_3\text{O}$	2.30 (0.22)	73	CHN_2O_2	1.94 (0.41)
	CH_4N_4	2.67 (0.03)		$\text{CH}_3\text{N}_3\text{O}$	2.31 (0.22)
	$\text{C}_2\text{H}_2\text{NO}_2$	2.65 (0.42)		CH_5N_4	2.69 (0.03)
	$\text{C}_2\text{H}_4\text{N}_2\text{O}$	3.03 (0.23)		C_2HO_3	2.30 (0.62)
	$\text{C}_2\text{H}_6\text{N}_3$	3.40 (0.04)		$\text{C}_2\text{H}_3\text{NO}_2$	2.67 (0.42)
	$\text{C}_3\text{H}_4\text{O}_2$	3.38 (0.44)		$\text{C}_2\text{H}_5\text{N}_2\text{O}$	3.04 (0.23)
	$\text{C}_3\text{H}_6\text{NO}$	3.76 (0.25)		$\text{C}_2\text{H}_7\text{N}_3$	3.42 (0.04)
	$\text{C}_3\text{H}_8\text{N}_2$	4.13 (0.07)		$\text{C}_3\text{H}_5\text{O}_2$	3.40 (0.44)
	$\text{C}_4\text{H}_8\text{O}$	4.49 (0.28)		$\text{C}_3\text{H}_7\text{NO}$	3.77 (0.25)
	$\text{C}_4\text{H}_{10}\text{N}$	4.86 (0.09)		$\text{C}_3\text{H}_9\text{N}_2$	4.15 (0.07)
	C_5H_{12}	5.60 (0.13)		$\text{C}_4\text{H}_9\text{O}$	4.51 (0.28)
				$\text{C}_4\text{H}_{11}\text{N}$	4.88 (0.10)
				C_6H	6.50 (0.18)

This means that the number of carbon atoms in a compound can be calculated if the relative intensities of both the M and $M + 1$ peaks are known.

$$\text{Number of carbon atoms} = \frac{\text{Relative intensity of } M + 1 \text{ peak as per cent of base peak}}{0.011 \times \text{Relative intensity of } M \text{ peak as per cent of base peak}} \text{ or } = \frac{\text{Relative intensity of } M + 1 \text{ peak as per cent of } M}{1.1} \quad (11.42)$$

This formula works because ^{13}C is the most important contributor to $M^{++} + 1$ peak and the approximate natural abundance of ^{13}C is 1.1 per cent.

In general, the number of isotopic peaks is one more than the number of carbon atoms of the particular element spaced at an interval of one mass unit and the intensities of the peaks correspond to the coefficients of the binomial expansion $(a + b)^n$, i.e.

$$(a + b)^n = a^n + na^{n-1}b + \frac{n(n-1)a^{n-2}b^2}{2} + \frac{n(n-1)(n-2)a^{n-3}b^3}{6} + \dots + b^n \quad (11.43)$$

where, a is the relative abundance of light isotopes, b is the relative abundance of heavy isotopes and n is the number of atoms of the particular element present in the molecule.

The number of peaks expected = $n + 1$. In order to obtain the intensities of the peaks, the terms of the binomial expansion in which the sum of the superscripts is the same are collected and arranged in the ascending order of the masses. Accordingly, for $n = 1$, number of peaks will be 2 with intensity ratio : 98.89 : 1.11 or 100 : 1.12. For $n = 2$ carbon atoms.

Number of peaks expected = $2 + 1 = 3$

The intensities of the peaks can be worked out by applying the binomial expansion (11.43), i.e.

$$(98.89 \text{ } ^{12}\text{C} + 1.11 \text{ } ^{13}\text{C})^2 = 9.77 \times 10^3 (\text{C}^{12})^2 + 2.19 \times 10^2 ({}^{12}\text{C}^{13}\text{C}) + 12.32 (\text{C}^{13})^2 \\ = 9.77 \times 10^3 \text{ } ^{24}\text{C} + 2.19 \times 10^2 \text{ } ^{25}\text{C} + 12.32 \text{ } ^{26}\text{C}$$

If M is the mass of the molecular ion, i.e. $(\text{C}^{12})^2 = M$ then the above expression can be written as

$$(98.89 \text{ } ^{12}\text{C} + 1.11 \text{ } ^{13}\text{C})^2 = 9.77 \times 10^3 M + 2.19 \times 10^2 (M + 1) + 12.32 (M + 2)$$

The relative intensity of the peaks will be,

Peak at m/e :	M	$M + 1$	$M + 2$
Relative intensity	9.77×10^3	2.19×10^2	12.32
Relative intensity	100	2.24	0.126
as per cent of M			

According to formula (11.42), the number of carbon atoms = $\frac{2.24}{1.11} = 2$.

The presence of Cl, Br, S and Si can be deduced from the unusual isotopic abundance patterns of these molecules. These and other elements such as P, F and I are also detectable from the unusual mass differences that they produce between some fragment ions in the spectrum.

The presence or (absence) of chlorine (33 per cent), S (4.4 per cent), Br (98 per cent) or Si (3.35 per cent) is indicated by the sharp peaks at mass $M + 2$ and $M + 4$, etc. Just like carbon isotopes—the number of isotopic peaks is one more than the number of atoms of the particular element, i.e. Cl, Br, Si or S—but spaced at intervals of two mass units and the intensities of the peaks correspond to the coefficients of the binomial expansion. When two elements are present in the molecule, the binomial expansion used in $(a + b)^n (c + d)^m$. In such a case, the number of peaks = $n + m + 1$; and the intensities of the peaks can be worked out by the rules applied to the binomial expansion $(a + b)^n$, the peak of the highest mass may sometimes be too weak to be detected. Let us now calculate the intensity ratio of the molecular ion clusters owing to halogen isotopes.

For $n = 3$ chlorine atoms in the molecule, the number of peaks expected = 4, and the binomial expansion is

$$(3 \text{ } ^{35}\text{Cl} + ^{37}\text{Cl})^3 = (3 \text{ } ^{35}\text{Cl})^3 + 3(3 \text{ } ^{35}\text{Cl})^2 ({}^{37}\text{Cl}) + 3(3 \text{ } ^{35}\text{Cl}) ({}^{37}\text{Cl})^2 + ({}^{37}\text{Cl})^3$$

Now combining the terms in which the sum of the superscripts is the same and arranging the resultant terms in the ascending order of masses, we obtain

$$(3 \text{ } ^{35}\text{Cl} + ^{37}\text{Cl})^3 = 27(^{35}\text{Cl})^3 + 27(^{35}\text{Cl})^2 ({}^{37}\text{Cl}) + 9(^{35}\text{Cl}) ({}^{37}\text{Cl})^2 + ({}^{37}\text{Cl})^3$$

If M is mass of the molecular ion containing three ^{35}Cl , i.e. $(^{35}\text{Cl})^3$ then the above equation reduces to

$$(3 \text{ } ^{35}\text{Cl} + ^{37}\text{Cl})^3 = 27 M + 27 (M + 2) + 9(M + 4) + (M + 6)$$

Accordingly, the intensity ratio of the peaks at M , $M + 2$, $M + 4$ and $M + 6$ will be 27 : 27 : 9 : 1.

For $n = 3$ chlorine atoms and $m = 2$ bromine atoms. Number of peaks expected = $3 + 2 + 1 = 6$

In order to determine the intensity ratio of the peaks we apply the formula $(a + b)^n (c + d)^m$ as follows:

$$(3 \text{ } ^{35}\text{Cl} + ^{37}\text{Cl})^3 ({}^{79}\text{Br} + {}^{81}\text{Br})^2 = [(3 \text{ } ^{35}\text{Cl})^3 + 3(3 \text{ } ^{35}\text{Cl})^2 ({}^{37}\text{Cl}) + 3(3 \text{ } ^{35}\text{Cl}) ({}^{37}\text{Cl})^2 + ({}^{37}\text{Cl})^3][({}^{79}\text{Br})^2 + 2({}^{79}\text{Br}) ({}^{81}\text{Br}) + ({}^{81}\text{Br})^2] \\ = 27 ({}^{35}\text{Cl})^3 ({}^{79}\text{Br})^2 + 54 ({}^{35}\text{Cl})^3 ({}^{79}\text{Br}) ({}^{81}\text{Br}) + 27 ({}^{35}\text{Cl})^3 ({}^{81}\text{Br})^2 + 27 ({}^{35}\text{Cl})^2 ({}^{37}\text{Cl}) ({}^{79}\text{Br})^2 \\ + 54 ({}^{35}\text{Cl})^2 ({}^{37}\text{Cl}) ({}^{79}\text{Br}) ({}^{81}\text{Br}) + 27 ({}^{35}\text{Cl})^2 ({}^{37}\text{Cl}) ({}^{81}\text{Br})^2 + 9 ({}^{35}\text{Cl}) ({}^{37}\text{Cl})^2 ({}^{79}\text{Br})^2 \\ + 18 ({}^{35}\text{Cl}) ({}^{37}\text{Cl})^2 ({}^{79}\text{Br}) ({}^{81}\text{Br}) + 9 ({}^{35}\text{Cl}) ({}^{37}\text{Cl})^2 ({}^{81}\text{Br})^2 + ({}^{37}\text{Cl})^3 ({}^{79}\text{Br})^2 + 2 ({}^{37}\text{Cl})^3 ({}^{79}\text{Br}) ({}^{81}\text{Br}) + ({}^{37}\text{Cl})^3 ({}^{81}\text{Br})^2$$

Combining the terms having the same sum of the superscripts and arranging the resultant terms in the ascending order of the masses, we get:

$$\begin{aligned}(3\ ^{35}\text{Cl} + ^{37}\text{Cl})^3(^{79}\text{Br} + ^{81}\text{Br})^2 &= 27(^{35}\text{Cl})^3(^{79}\text{Br})^2 + [54(^{35}\text{Cl})^3(^{79}\text{Br})(^{81}\text{Br}) \\ &\quad + 27(^{35}\text{Cl})^2(^{37}\text{Cl})(^{79}\text{Br})^2] + [27(^{35}\text{Cl})^3(^{81}\text{Br})^2 + 54(^{35}\text{Cl})^2(^{37}\text{Cl})(^{79}\text{Br})(^{81}\text{Br}) \\ &\quad + 9(^{35}\text{Cl})(^{37}\text{Cl})^2(^{79}\text{Br})^2] + [27(^{35}\text{Cl})^2(^{37}\text{Cl})(^{81}\text{Br})^2 + 18(^{35}\text{Cl})(^{37}\text{Cl})^2(^{79}\text{Br})(^{81}\text{Br}) \\ &\quad + (^{37}\text{Cl})^3(^{79}\text{Br})^2] + [9(^{35}\text{Cl})(^{37}\text{Cl})^2(^{81}\text{Br})^2 + 2(^{37}\text{Cl})^3(^{79}\text{Br})(^{81}\text{Br})] + [(^{37}\text{Cl})^3(^{81}\text{Br})^2]\end{aligned}$$

If M is the mass of the molecular ion containing three (^{35}Cl) and two (^{79}Br) , i.e. $(^{35}\text{Cl})^3(^{79}\text{Br})^2$, then the above expression reduces to

$$\begin{aligned}(3\ ^{35}\text{Cl} + ^{37}\text{Cl})^3(^{79}\text{Br} + ^{81}\text{Br})^2 &= 27M + [54(M + 2) + 27(M + 2)] + [27(M + 4) + 54(M + 4) + 9(M + 4)] \\ &\quad + [27(M + 6) + 18(M + 6) + (M + 6)] + [9(M + 8) + 2(M + 8)] + (M + 10) \\ &= 27M + 81(M + 2) + 90(M + 4) + 46(M + 6) + 11(M + 8) + (M + 10)\end{aligned}$$

Accordingly, the intensity ratio of the peaks at M , $M + 2$, $M + 4$, $M + 6$, $M + 8$ and $M + 10$ will be 27 : 81 : 90 : 46 : 11 : 1.

Such type of data has been generated for different numbers of particular halogen atoms in the molecule as well as for various combinations of different halogen atoms and the resultant data are presented graphically in Fig. 11.31. Contributions due to C, H, N and O are usually small as compared to those of Br and Cl.

To summarise, the following tools may be applied for determining the molecular formula by mass spectrometry.

- Convert the intensity (as per cent of base peak) to intensity as per cent of $M^{+\bullet}$.
- According to nitrogen rule, if $M^{+\bullet}$ is even, the compound must contain even number including zero of nitrogen atoms.
- Number of carbon atoms = Relative abundance of $(M^{+\bullet} + 1)/1.1$
- The relative abundance of the $M^{+\bullet} + 2$ peak indicates the presence (or absence) of S(4.4 percent), Cl(33 per cent) or Br(98 per cent).
- The molecular formula of the compound can now be accomplished by determining the number of hydrogen atoms and adding the appropriate number of oxygen atoms, if necessary.

Let us now apply these rules to the mass spectral data in order to accomplish the molecular formula.

m/e	86($M^{+\bullet}$)	87	88
Intensity (Per cent of base peak)	10	0.56	0.04
Intensity as per cent of $M^{+\bullet}$	100	5.6	0.4

According to nitrogen rule, there is no nitrogen present in the molecule and the number of carbon atoms $= \frac{5.6}{1.1} = 5$. Since the per cent of $M + 2$ ions is 0.4, the presence of S, Cl or Br is ruled out. Thus, the number of hydrogen atoms $= 86 - 60 = 26$.

Accordingly, the molecular formula of the compound is C_5H_{26} . But C_5H_{26} is impossible. For a molecule containing C, H and one oxygen atom,

$$\text{H} = 86 - (5 \times 12) - 16 = 10$$

Accordingly, the molecular formula of the unknown compound is $\text{C}_5\text{H}_{10}\text{O}$.

The number of possible molecular formulas can be further reduced provided the spectrum is recorded on a high-resolution instrument. In such a case, the molecular formula of the ion for combinations of C, H, N and O can be obtained from the exact mass defect alone by using the expression 11.44.

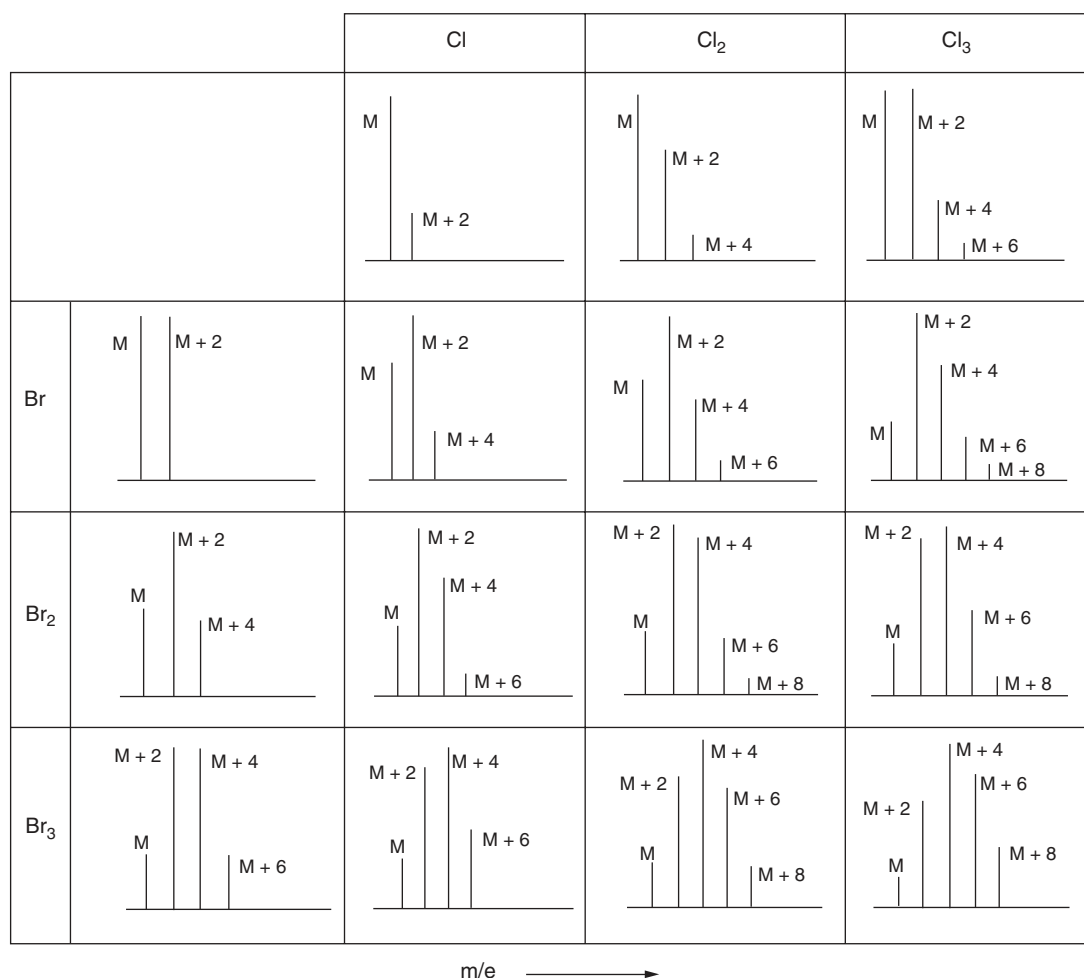


Fig. 11.31 Theoretically expected mass spectra of typical Cl and Br systems.

$$\text{Number of hydrogen atoms} = \frac{\text{Exact mass defect} + 0.0051x - 0.0031y}{0.0078} \quad (11.44)$$

where, x is for oxygen and y is for nitrogen.

In order to determine the number of hydrogen atoms, keep in mind the nitrogen rule and choose such integral values of x and y so that the denominator becomes an integral multiple of the numerator within 0.0002 units.

Computer programs are available or may be developed to determine the molecular formula of a compound from its exact molecular mass.

For example, if the exact molecular mass of a compound containing hydrogen, nitrogen and carbon is 28.0187,

$$\text{the number of hydrogen atoms} = \frac{0.0187 - 0.0031 \times 1}{0.0078} = \frac{0.0156}{0.0078} = 2.$$

Accordingly, the mass due to the carbon atoms present in the molecule $(28 - (14 + 2)) = 12$ ($\equiv 1$ C).

Thus the molecular formula of the compound is H_2CN .

Problem 11.30: Determine the molecular formula of a compound containing C, H, O or N whose exact molecular mass is 59.0370.

Solution Exact mass defect = 0.0370.

Substituting the value of mass defect into Eq. (11.44), we get

$$\text{Number of hydrogen atoms} = \frac{0.0370 + 0.0051x - 0.0031y}{0.0078}$$

For $x = 1$ and $y = 1$, we obtain

$$\text{Number of hydrogen atoms} = \frac{0.0370 + 0.0051 - 0.0031}{0.0078} = \frac{0.0390}{0.0078} = 5, \text{ i.e. an integral number.}$$

The mass due to carbon atoms in the molecule = $[59 - (5 + 14 + 16)] = 24 (= 2C)$
 Thus, the molecular formula of the compound is C_2H_5NO .

Problem 11.31: The characteristic peaks in the mass spectrum of an unknown compound are indicated below:

<i>m/e</i>	51	77	105	181	182	183	184
Relative abundance	19	62	100 (Base peak)	8.2	60.0 ($M^{+\bullet}$)	8.5	0.61

(a) Determine the number of carbon atoms in the compound, and (b) what is the likely molecular formula for the compound?

Solution (a) According to Eq. (11.42), the number of carbon atoms = $\frac{8.5}{60 \times 0.011} = 13$.

(b) Now number of carbon atoms = 13

Accordingly, the number of hydrogen atoms = $182 - 13 \times 12 = 26$

For a molecule composed of carbon and hydrogen, the molecular formula of the compound should be $C_{13}H_{26}$. But $C_{13}H_{26}$ is impossible since it does not correspond to either C_nH_{2n+2} or C_nH_{2n-2} . The possibility corresponding to C_2H_{2n} is also ruled out because the mass spectral data cannot be explained on the basis of this molecular formula.

For a molecule composed of C, H and one O,

Number of hydrogen atoms = $182 - (13 \times 12) - 16 = 10$

Thus, the possible molecular formula of the compound is $C_{13}H_{10}O$, i.e. $C_6H_5COC_6H_5$.

Problem 11.32: (a) Predict the Intensity ratio of the $M^{+\bullet}$, $M^{+\bullet} + 2$ and $M^{+\bullet} + 4$ peaks of CH_2Cl_2 , and (b) for the $M^{+\bullet}$, $M^{+\bullet} + 2$, $M^{+\bullet} + 4$ and $M^{+\bullet} + 6$ peaks of $CHBr_3$. (c) Determine the possible molecular formula of the unknown compound from the mass spectral data indicated below:

<i>m/e</i>	64	66
Intensity	3	1

Solution (a) Here $n = 2$, $a = 3$ and $b = 1$.

Substituting these values into Eq. (11.43), we obtain

$$(3\ ^{35}\text{Cl} + ^{37}\text{Cl})^2 = 9(\text{Cl}^{35})^2 + 6\ ^{35}\text{Cl}^{37}\text{Cl} + (\text{Cl}^{37})^2$$

Since $(\text{Cl}^{35})^2 = M^{+\bullet}$, the above equation can be expressed as

$$(3\ ^{35}\text{Cl} + ^{37}\text{Cl})^2 = 9M^{+\bullet} + 6(M^{+\bullet} + 2) + 1(M^{+\bullet} + 4)$$

Thus the intensity ratio of the peaks in question is 9 : 6 : 1.

(b) In this case, $n = 3$, $a = 1$, and $b = 1$.

Proceeding as in the preceding problem, we obtain

$$(\text{Br}^{79} + \text{Br}^{81})^3 = (\text{Br}^{79})^3 + 3(\text{Br}^{79})^2\text{Br}^{81} + 3\text{Br}^{79}(\text{Br}^{81})^2 + (\text{Br}^{81})^3$$

Since $(\text{Br}^{79})^3 = M^{+\bullet}$, the above equation in term of $M^{+\bullet}$ becomes

$$(\text{Br}^{79} + \text{Br}^{81})^3 = M^{+\bullet} + 3(M^{+\bullet} + 2) + 3(M^{+\bullet} + 4) + (M^{+\bullet} + 6)$$

Thus the intensity ratio of the peaks, i.e. $M^{+\bullet}$, $M^{+\bullet} + 2$, $M^{+\bullet} + 4$ and $M^{+\bullet} + 6$ is 1:3:3:1.

(c) The intensity ratio of the two peaks and the mass interval of two units between the peaks suggest that the compound contains one chlorine atom. For a compound containing C, H and Cl, the mass due to carbon and hydrogen atoms is $64 - 35 = 29$. Thus the possible molecular formula of the compound is C_2H_5Cl .

Problem 11.33: Determine the empirical formula of the compounds containing C, H, O or N unless otherwise indicated corresponding to the exact molecular masses indicated here:

180.0939, 190.9540, (Cl), 334.0873 (S), 109.0528.

Solution From Eq. (11.31), we arrive at the following results:

<i>Molecular mass</i>	<i>Molecular formula</i>
180.0939	C ₄ H ₁₂
190.9540 (mass defect 0.0460)	C ₆ H ₃ Cl ₂ NO ₂
334.0873	C ₁₇ H ₁₈ O ₅ S
109.0528	C ₆ H ₇ NO

Problem 11.34: Deduce the number and type of halogen atoms present in a molecule from the mass spectral data indicated below:

<i>m/e</i>	<i>M</i>	<i>M + 2</i>	<i>M + 4</i>	<i>M + 6</i>	<i>M + 8</i>
Per cent abundance	35	45	11	...	...

Solution The number of peaks is one more than the number of halogen atoms contained in the molecule. Accordingly, the number of halogen atoms = 3 – 1 = 2.

For $n = 2$, the possible combinations of chlorine and bromine atoms are 2 + 0, 0 + 2, 1 + 1.

For Cl = 2, we write from the binominal expansion $(a + b)^n$

$$\alpha = (3 {}^{35}\text{Cl} + {}^{37}\text{Cl})^2 = 9({}^{35}\text{Cl})^2 + 6 {}^{35}\text{Cl}{}^{37}\text{Cl} + ({}^{37}\text{Cl})^2$$

If M is the mass of the molecular ion, M^+ , i.e. $M = ({}^{35}\text{Cl})^2$ then the above expression in terms of M becomes:

$$\alpha = 9M + 6(M + 2) + 1(M + 4)$$

The intensity ratio of the peaks 9:6:1 does not conform to the expected ratio 35:45:11 or 3:4:1.

Thus Cl = 2 is not possible.

for Br = 2, the binomial expansion $(a + b)^n$ yields.

$$\beta = ({}^{79}\text{Br} + {}^{81}\text{Br})^2 = ({}^{79}\text{Br})^2 + 2({}^{79}\text{Br})({}^{81}\text{Br}) + ({}^{81}\text{Br})^2$$

In terms of mass of the molecular ion, we write

$$\beta = M + 2(M + 2) + 1(M + 4)$$

The intensity ratio of peaks, i.e. 1 : 2 : 1 in this case also does not conform to the expected ratio.

Thus Br = 2 is also ruled out.

For Cl = 1 and Br = 1, we write from the binomial expansion $(a + b)^n (c + d)^m$:

$$\gamma = (3 {}^{35}\text{Cl} + {}^{37}\text{Cl})({}^{79}\text{Br} + {}^{81}\text{Br}) = 3({}^{35}\text{Cl}{}^{79}\text{Br}) + 3({}^{35}\text{Cl}{}^{81}\text{Br}) + {}^{37}\text{Cl}{}^{79}\text{Br} + {}^{37}\text{Cl}{}^{81}\text{Br}$$

Collecting the terms where the sum of the superscripts is the same and arranging the resultant terms in the ascending order of the masses, we write

$$\gamma = 3({}^{35}\text{Cl}{}^{79}\text{Br}) + 3({}^{35}\text{Cl}{}^{79}\text{Br}{}^2\text{Br}) + 1({}^{35}\text{Cl}{}^{79}\text{Br}{}^2\text{Cl}) + 1({}^{35}\text{Cl}{}^{79}\text{Br}{}^2\text{Cl}{}^2\text{Br})$$

In terms of mass of the molecular ion, i.e. $M = {}^{35}\text{Cl}{}^{79}\text{Br}$, the above expression becomes

$$\gamma = 3M + 4(M + 2) + 1(M + 4). \quad [4(M + 2) = 3(M + 2) + 1(M + 2)]$$

The intensity ratio of peaks, i.e. 3 : 4 : 1 for Cl = 1 and Br = 1 conforms to the expected ratio. Thus the compound contains one chlorine atom and one bromine atom.

Problem 11.35: Deduce the molecular formulae of the compounds corresponding to the mass spectral data indicated below:

(a)	<i>m/e</i>	90(M^+)	91	92	
	per cent of base peak	100	5.61	4.69	
(b)	<i>m/e</i>	89(M^+)	90	91	92
	per cent of base peak	17.12	0.58	5.36	0.17

(Continued)

(c)	<i>m/e</i>	230(M^+)	232	234	
	per cent of base peak	1.10	2.12	1.06	
(d)	<i>m/e</i>	140(M^+)	141	142	
	per cent of base peak	14.8	1.40	0.85	
(e)	<i>m/e</i>	151(M^+)	152	153	154
	per cent of base peak	100	10.4	32.1	2.9

Solution (a) The per cent abundance of $M^+ + 2$ peak (i.e. 4.69) indicates the presence of sulphur atom in the molecule. Consequently, the contribution of C and H atoms to per cent abundance of $M^+ + 1$ peak

$$= (5.61 - \text{per cent abundance due to sulphur atom}) = 5.61 - 0.78 = 4.83$$

$$\text{Thus, the number of carbon atoms in the molecule} = \frac{4.83}{1.11} = 4$$

or

$$\text{Mass of C and H atoms in the molecule} = 90 - 32 = 58.$$

$$\text{Accordingly, } \frac{58}{14} = 4\text{CH}_2 \text{ groups} + 2\text{H atoms or } \frac{58}{12} = 4\text{Cs} + 10\text{Hs}$$

Thus, the molecular formula of the compound is $\text{C}_4\text{H}_{10}\text{S}$. The compound is dialkyl sulphide $\text{C}_2\text{H}_5\text{SC}_2\text{H}_5$.

An alternative procedure: For a compound containing C and H atoms, the number of hydrogen atoms in the molecule = $(90 - 12 \times 4) = 42$. But it is not possible since the compound contains sulphur atom also. So for a compound composed of C, H and S atoms, the possible number of hydrogen atoms = $(90 - 12 \times 4 - 32) = 10$.

So, the formula of the compound is $\text{C}_4\text{H}_{10}\text{S}$.

(b) Expressing the data as per cent of molecular ion, we obtain

<i>m/e</i>	89	90	91	92
per cent of base peak:	17.12	0.58	5.36	0.17
per cent abundance as	100	3.38	31.3	0.99
molecular ion M^+				

The odd mass number and per cent of $M + 2$ peak relative to that of the percent of M^+ peak indicates the presence of odd number of nitrogen atoms and Cl atom. The number of carbon atoms = $\frac{3.38 - 0.38}{1.11} = 2.7$, i.e. the number should not exceed 2. Accordingly, the residual mass = $89 - 2 \times 12 - 14 - 35 = 16 (= \text{O})$.

Thus, the molecular mass of the compound is C_2ClNO . Note that if $16 \equiv 16\text{H}$ the formula of the compound should be $\text{C}_2\text{ClNH}_{16}$ which is not possible.

(c) **The even mass number and intensity ratio** of M , $M + 2$ and $M + 4$ peaks, i.e. 1 : 2 : 1 indicate that the compound contains even number of nitrogen atoms and two bromine atoms. Accordingly, if number of nitrogen atoms is taken as zero, the residual mass = $230 - 2 \times 79 = 72$. $\frac{72}{14} = 5\text{CH}_2$ groups + 2 hydrogen atoms. Thus, the molecular formula of the compound is $\text{C}_5\text{H}_{12}\text{Br}_2$.

(d)	<i>m/e</i>	140 (M^+)	141	142
	per cent of base peak	14.8	1.40	0.85
	per cent of M^+ peak	100	8.9	5.74

The even mass number and per cent of $M + 2$ peak relative to that of the per cent of M^+ peak indicate the presence of even number of nitrogen atoms and a sulphur atom. If number of nitrogen atoms is zero then

the residual mass is $140 - 32 = 108$. Accordingly, $\frac{108}{14} = 7\text{CH}_2$ groups + 10 hydrogen atoms or the contribution of C and H ions to percent abundance of $M + 2$ peak = $8.9 - 0.78 = 8.12$. Thus, the number of carbon atoms in the molecule = $\frac{8.12}{1.11} = 7$. Accordingly, the molecular formula of the compound is $\text{C}_7\text{H}_{24}\text{S}$. Or for a compound containing S and seven carbon atoms, the number of H atoms = $(140 - 12 \times 7 - 32) = 24$. So the formula of the compound is $\text{C}_7\text{H}_{24}\text{S}$.

(e) Odd mass number of molecular ion and the per cent abundance of $M + 2$ peak, i.e. 32.1 indicate that the compound contains nitrogen and chlorine atoms.

Accordingly, the residual mass = $151 - 35 - 14 = 102$

$$\text{So, } \frac{102}{12} = 8\text{Cs} + 6\text{Hs}$$

Thus, the most probable formula of the compound is $\text{C}_8\text{H}_6\text{Cl N}$.

Since, the base peak is the molecular ion peak, the compound seems to be an aromatic compound with structural formula $\text{CN}(\text{C}_6\text{H}_4)\text{CH}_2\text{Cl}$.

$$\text{Alternative method: Number of carbon atoms} = \frac{10.4 - 0.38}{1.11} = 9.$$

For a compound containing C and H; the number of hydrogen atoms = $151 - 12 \times 9 = 43$

So, the molecular formula of the compound is C_9H_{43} .

But it is not possible since the compound contains Cl and N also. So for a compound containing C, Cl and H, the molecular formula can be written as $\text{C}_9\text{H}_8\text{Cl}$.

The formula contains nitrogen atoms also. Since the atomic mass of nitrogen is equivalent to mass of CH_2 group, the formula of a compound is $\text{C}_8\text{H}_6\text{ClN}$. Or we can start from CH_2 group, i.e. $\frac{102}{14} = 7\text{CH}_2 + 4\text{Hs} = \text{C}_7\text{H}_{18}$ ($\equiv \text{C}_8\text{H}_6$).

(g) General Rules for Writing Molecular Formula There are two general rules that help in writing the molecular formulas of organic compounds, viz., hydrogen rule and nitrogen rule.

(i) Hydrogen Rule According to this rule, organic compounds (containing C, H, O and N) with even molecular mass will have an even number (including zero) of hydrogen atoms. If the molecular mass is divisible by some even numbers, the number of hydrogen atoms must also be divisible by at least one of those numbers. But if the number of hydrogen atoms are divisible by two or more such numbers, the highest divisor will correspond to the minimum number of hydrogen atoms present in the molecule. As examples, CH_4 , $m/e : 16$, H_2NNH_2 , $m/e : 32$, $\text{C}_{17}\text{H}_{35}\text{COOH}$, $m/e : 284$; $\text{C}_6\text{H}_5\text{OH}$, $m/e : 94$; $\text{C}_7\text{H}_{12}\text{N}_2\text{O}_4$, $m/e : 188$; $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_3$, $m/e : 294$, etc.

(ii) Nitrogen Rule The rule has already been stated under the title *The even electron rule*. According to this rule, an organic compound with an even (including zero) number of nitrogen atoms will have an even mass number and if the compound contains an odd number of nitrogen atoms, the mass number will also be odd. This rule applies to all organic compounds containing C, H, N, Si, O, S, As, P, halogens and B. As examples, molecules giving even mass molecular ions are H_2O , $m/e : 18$, CH_4 , $m/e : 16$; H_2NNH_2 , $m/e : 32$; aminopyridine- $\text{C}_5\text{H}_6\text{N}_2$, $m/e : 94$, etc., and molecules giving odd mass molecular ions are NH_3 , $m/e : 17$; $\text{C}_2\text{H}_5\text{NH}_2$, $m/e : 45$, quinoline, $\text{C}_9\text{H}_7\text{N}$, $m/e : 129$, etc.

The nitrogen rule not only applies to molecular ions (i.e. M^+) but to all ions, i.e. fragment ions. However, the fragment ions must contain all the nitrogen atoms of the molecular ion. Thus, the nitrogen rule can also be stated as follows: *An odd-electron ion will have an even/odd mass number provided it has an even/odd number of nitrogen atoms and an even-electron ion will have an odd/even mass number if it contains an even/odd number of nitrogen atoms*. As an example, mass spectrum nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) exhibits a molecular ion peak at $m/e : 123$ and the two ion fragments, namely NO_2^+ and NO^+ , are observed respectively at $m/e : 46$ and 30 , i.e. both these fragment ions appear at even mass numbers. On the other hand, the molecular ion peak in the mass spectrum of 2, 4-dinitrophenol is observed at an even mass number of $m/e : 184$ while the fragment ions ($\text{M}^+ - \text{H}$) and ($\text{M}^+ - \text{H} - \text{CO}$) are observed respectively at $m/e : 183$ and 185 , i.e. both the fragment ions are observed at odd mass numbers as expected according to nitrogen rule. For ready reference, the rule is summarised in Tables 11.14 (a) and 11.14 (b).

Table 11.14(a) Relative parity of A and N for even- or odd-numbered electron neutral species.

Neutral species	Mass number	Number of N atoms	Number of electrons
Molecule] ⁰	even }	even }	even
	odd }	odd }	
Radical] [*]	odd }	even }	odd
	even }	odd }	

Table 11.14(b) Relative parity of m/e and N for even- or odd-numbered electron positively charged species: The nitrogen rule.

Charged species	Mass number (m/e)	Number of N atoms	Number of electrons
Ion radical] ⁺⁺	even }	even }	odd
	odd }	odd }	
Ion] ⁺	odd }	even }	even
	even }	odd }	

Once the molecular formula of the compound is accomplished, the number of unsaturated sites R can be determined by the ring rule.

(iii) Ring Rule According to this rule, the sum total of the number of rings and double bonds in an organic molecule of general formula $C_wH_xN_yO_z$ is given by

$$R = w + 1 + \frac{y - x}{2} \quad (11.45)$$

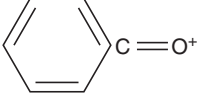
where terms and symbols have their usual meanings. For an even electron ion (M^+), the true value will be followed by 0.5. So in order to obtain the true value, this factor of 0.5 should be omitted.

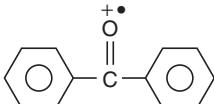
As examples, in case of a compound with molecular formula C_2H_2 ; $w = 2$ and $x = 2$

Therefore, $R = 2 + 1 + \frac{0 - 2}{2} = 2$. Accordingly, there is a possibility of two double bonds in the molecule.

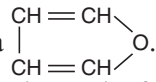
Thus the structural formula of the compound is $HC \equiv CH$. For a molecule of molecular formula C_6H_6 ; $R = 6 + 1 + \frac{0 - 6}{2} = 4$. Accordingly, there is a possibility of one ring and three double bonds. Thus, the molecule is benzene.

For a compound with formula C_7H_5O ; $R = 5.5$. This implies that the molecule gives an even electron ion and the true value of R should be 5. Accordingly, it contains one ring and four double bonds, i.e. the structural formula

of the molecular ion is . For a compound with molecular formula $C_{12}H_{10}CO$, $R = 9$, i.e. two rings

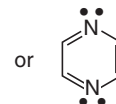
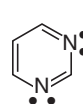
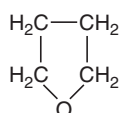
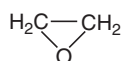
and seven double bonds. Thus, the structural formula of the molecular ion is .

For a compound with molecular formula C_4H_4O , $R = 3$, i.e. one ring and two double bonds. This data fits into

the structural formula .

Similarly, we can arrive at the following results:

Molecular formula Structural formula



Furthermore, the ring rule can also be extended to compounds that contain other elements in addition to C, H, O or N. The number of additional elements is also counted respectively towards C, H, O or N on the basis of principle of corresponding valency. Thus, the number of Si atoms will be counted towards carbon atoms, halogen atoms will be taken as hydrogen atoms, phosphorous atoms will be considered as nitrogen atoms, S atoms will be counted towards oxygen atoms, etc. Thus, the more general formula corresponding to the formula $C_w H_x N_y O_z$ is written as:

I_w, II_x, III_y, IV_z , where, I = C, Si; II = H, halogens; III = N, P; and IV = O, S, etc.

It is to be kept in mind that the above deduction is made on the lowest valence states of the elements and the double bonds formed to elements in higher valence states are not counted. Otherwise we may arrive at negative values and unexpected positive values of double bonds, e.g. $R = 1$ for nitro methane, R is negative for H_3O and equals zero for $C_2H_5SO_2C_2H_5$.

Problem 11.36: Sort out the odd and even electron ions corresponding to the following molecular formulas:



Solution Applying the nitrogen rule [Table 11.14 (b)], we arrive at the following results:

Molecule	Molecular mass	Number of nitrogen atoms	Nature of Ion
CH_4S	Even, 48	Even, 0	Odd, $CH_4S^{+•}$
CH_4	Even, 16	Even, 0	Odd, $CH_4^{+•}$
C_4H_8O	Even, 72	Even, 0	Odd, $C_4H_8O^{+•}$
CH_3Cl	Even, 50	Even, 0	Odd, $CH_3Cl^{+•}$
H_3O	Odd, 19	Even, 0	Even, H_3O^+
C_6H_4ClBr	Even, 190	Even, 0	Odd, $C_6H_4ClBr^{+•}$
C_7H_5ClBr	Odd, 203	Even, 0	Even, $C_7H_5ClBr^+$
C_3H_9SiO	Odd, 89	Even, 0	Even, $C_3H_9SiO^+$
C_2H_5NO	Odd, 59	Odd, 1	Odd, $C_2H_5N^{+•}$
N_2H_4	Even, 32	Even, 2	Odd, $H_4N_2^{+•}$
$C_{29}F_{59}$	Odd, 1469	Even, 0	Even, $C_{29}F_{59}^+$
C_3H_8N	Even, 58	Odd, 1	Even, $C_3H_8N^+$

Note: Even ions are mass spectrometrically active.

(h) Determination of Ionisation Potential of a Molecule and Appearance Potential of an Ion Molecular ion is formed when the energy of the bombarding electron beam equals the ionisation potential of the molecule. The ionisation potential of the molecule consists of energy required to break the chemical bond, the ionisation potential of formed ionised fragment of a molecule, the kinetic and excitation energies of all the fragments formed. With a further increase in the energy of the electrons, excitation of an ionised molecule may lead to dissociation. The latter results in the appearance of ions with smaller masses. Neutral fragments of a molecule may also appear.

The smallest energy of an electron at which dissociation of a molecule occurs with the formation of new ions is called the appearance potential of the ion. These potentials, i.e. ionisation and appearance potentials, can conveniently be measured with the aid of a mass spectrometer.

For the reaction, $R-X + e \rightarrow R^\bullet + X + 2e$; $R^\bullet + e \rightarrow R^+ + 2e$ the appearance potential A_R^+ for fragment R^+ obtained from the molecule RX (i.e. $R-X + e \rightarrow R^+ + X^\bullet + 2e$) is related to the dissociation energy D_{R-X} of the $R-X$ bond and ionisation potential $IP_R^\bullet$ of the radical $R^\bullet$ as

$$A_R^+ = IP_R^\bullet + D_{R-X} \quad (11.46)$$

The intensity of the molecular ion peak ($RX + e^- \rightarrow RX^{+\bullet} + 2e$) grows with the increase in the energy of the bombarding electrons. However, in case of fragment ions, the intensity decreases as the ionising voltage is increased. Thus, it is possible to determine the ionisation potential from the ionisation efficiency energy curve obtained by plotting the intensity of the molecular ion peak as a function of the energy of the impact electrons. When the energy of the impact electrons exceeds the ionisation energy, the fission of the molecular ion occurs leading to fragment ions whose intensities decrease with the increase in the energy of the bombarding electrons. Thus, by extrapolation of the ionisation efficiency energy curve for the molecular ion, the ionisation potential of the molecule can be obtained (Fig. 11.32). When the peak corresponds to the fragment, extrapolation of the ionisation efficiency curve produces the appearance potential of that fragment. It is also possible to determine the bond-dissociation energies from the knowledge of the appearance potentials of fragment ions, which can be determined from the ion-efficiency curve as described above. For example, in order to determine the ionisation potential of N_2 , argon is used as an internal standard. First of all, blank mass spectrum is recorded in order to check the absence of molecular ion peaks at m/e : 28 and m/e : 40 respectively, for N_2 and Ar in the background material. Now the mass spectrum of a mixture of Ar and N_2 is recorded. The intensity of the molecular ion peak of Ar^+ (40) is measured as a function of energy of impact electrons. The electron beam energy is then reduced in steps till the intensity becomes zero. The experiment is repeated a number of times and then from the plot between electron beam energy for $m/e = 40$ (Ar^+) and intensity, the ionisation potential is determined. The standard value of ionisation potential is 15.76 eV. The difference between the standard and observed experimental values of ionisation potential is used to correct the ionisation potential of nitrogen.

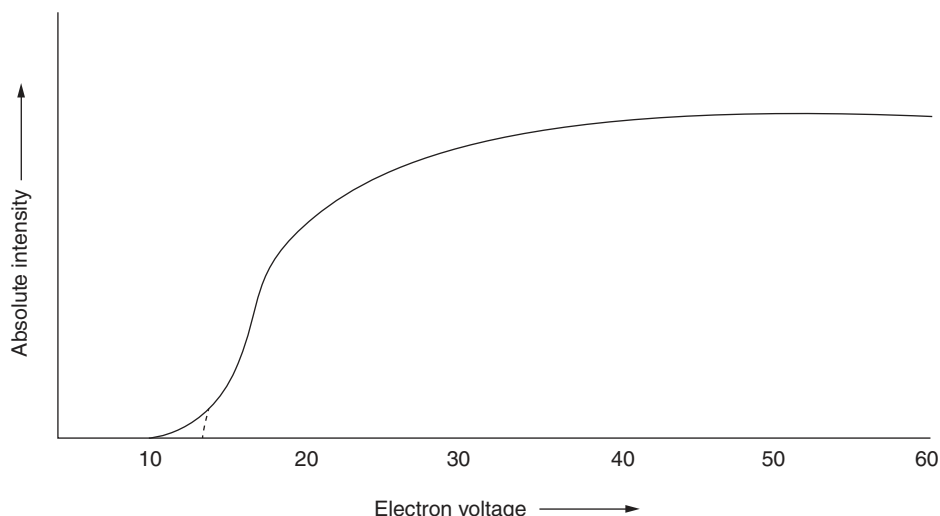


Fig. 11.32 An ionisation efficiency energy curve of a system.

In Eq. (11.46), E_R the kinetic energies of the particles produced; and E_{ex} the excitation energy of the fragments (i.e. electronic, vibrational, and rotational energy of the fragments if they are formed in excited states) being small have been neglected.

The appearance potentials of selected ions in methane measured with the aid of mass spectrometer are given in Table 11.15 and the energies of conversion $R^\bullet + e \rightarrow R^+ + 2e$ and heats of formation of carbonium ions have been listed in Table 11.16. The energy of decomposition of some organic molecules into two univalent radicals at 298 K is listed in Table 11.17 for ready reference.

Table 11.15 Energies of conversion $R^\bullet + e \rightarrow R^+ + 2e$ and heat of formation of carbonium ions.

R^+	Ionisation Potential of radical (eV)	Relative energy of radical conversion (kcal mole ⁻¹)	Heat of formation of ion (kcal mole ⁻¹)
CH_3^+	-	-	262
$CH_3CH_2^+$	-	-	224

(Continued)

Table 11.15 Energies of conversion $R^{\bullet} + e \rightarrow R^+ + 2e$ and heat of formation of carbonium ions—Cont'd.

$\text{CH}_3\text{CH}_2\text{CH}_2^+$	8.69	29.2	216
$\text{CH}_3\text{C}^+\text{HCH}_3$	7.90	11.1	190
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+$	8.64	28.1	207
$(\text{CH}_3)_2\text{CHCH}_2^+$	8.35	21.4	211
$\text{CH}_3\text{CH}_2^+\text{CHCH}_3$	7.93	11.7	181
$(\text{CH}_3)_2\text{C}^+\text{CH}_3$	7.42	0	166

Table 11.16 Appearance potentials of ions when methane is bombarded by electrons.

Reaction	Appearance potential, eV
$\text{CH}_4 \rightarrow \text{CH}_4^+$	13.1
$\text{CH}_4 \rightarrow \text{CH}_3^+ + \text{H}$	14.4
$\text{CH}_4 \rightarrow \text{CH}_2^+ + \text{H}_2$	15.7
$\text{CH}_4 \rightarrow \text{H}^+ + \cdot\text{CH}_2 + \text{H}$	22.7
$\text{CH}_4 \rightarrow \cdot\text{CH}^+ + 3\text{H}$	23.3
$\text{CH}_4 \rightarrow \text{H}^+ + \text{C} + 3\text{H}$	29.4

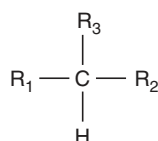
Table 11.17 Energy of dissociation of molecules into two univalent radicals at 298 K (in kcal mole⁻¹).

	H	CH ₃	C ₂ H ₅	C ₆ H ₅
H	104.2	103	98	102
CH ₃	103	86	84	90
C ₂ H ₅	98	84	80	88
C ₆ H ₅	102	90	88	98

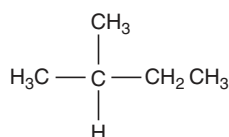
The C—H bond dissociation energy for the aliphatic radical $R_n = \text{C}_n\text{H}_{2n+1}$ in the series R_n-X ($X = \text{H}, \text{OH}, \text{halogen}, \text{C}_6\text{H}_5$, etc.) can be obtained from the expression given below:

$$D_{\text{C-H}} = D(\text{C}_n\text{H}_{2n+1}-\text{H}) = 77.6 + 8.0 \sum 0.4^{k_i} \quad (11.47)$$

where, k_i is the number of C atoms in each of the three radical chains R_1, R_2 and R_3



For the example, in the case of



where, $k_1 = k_3 = 1$ and $k_2 = 2$, the energy values, obtained from Eq. (11.47), for the detachment of an H atom from various hydrocarbons, are in good agreement with experiment.

Such studies can also be extended to inorganic systems. As an example, the mass spectrum of solid Cr_2O_3 shows peaks corresponding to Cr, CrO, CrO_2 , O and O_2 species. The appearance potentials and bond dissociation energies of these species have been determined.

Problem 11.37: The appearance potential of CH_3^+ ion is 14.4 eV. Calculate the dissociation energy of the C—H bond if the energy of ionisation of the $\dot{\text{C}}\text{H}_3$ radical is 9.83 eV.

Solution According to Eq. (11.46), the appearance potential of CH_3^+ ion equals the sum of the bond breaking energy $D_{\text{CH}_3-\text{H}}$ and the energy of ionisation of the radical $\dot{\text{C}}\text{H}_3$. Accordingly, we write

$$A_{\text{CH}_3^+} = \text{IP}_{\dot{\text{C}}\text{H}_3} + D_{\text{CH}_3-\text{H}} \quad \text{or} \quad D_{\text{CH}_3-\text{H}} = A_{\text{CH}_3^+} - \text{IP}_{\dot{\text{C}}\text{H}_3}$$

Substituting the data into the above expression, we get

$$D_{\text{CH}_3-\text{H}} = (14.4 - 9.83) \text{ eV} = 4.57 \text{ eV} = 440.86 \text{ kJ mole}^{-1}$$

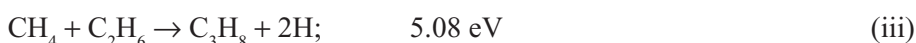
The value of the C—H bond energy obtained by kinetic and photochemical methods respectively is 451.9 and 396.6 kJ mole⁻¹.

The C—H bond energy $D_{\text{CH}_3-\text{H}}$ can also be obtained from the appearance potentials of C_2H_5^+ ion in propane and ethane.

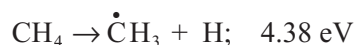
In propane, $A_{\text{C}_2\text{H}_5^+}^{\text{Pr}} = 14.5 \text{ eV}$, and in ethane $A_{\text{C}_2\text{H}_5^+}^{\text{Et}} = 15.2 \text{ eV}$, we write: $\text{C}_3\text{H}_8 \rightarrow \text{C}_2\text{H}_5^+ + \dot{\text{C}}\text{H}_3$; 14.5 eV (i)



It is known from thermochemical data that



The algebraic operation (i) + (iii) – (ii) yields



Thus the value of C—H bond energy, $D_{\text{CH}_3-\text{H}} = 4.38 \text{ eV} = 422.6 \text{ kJ mole}^{-1}$.

(i) Latent Heat of Vaporisation The latent heat of vaporisation of liquids can be determined by making use of Clausius–Clapeyron equation:

$$\ln p = \frac{-\Delta H_{\text{vap}}}{RT} + \text{constant} \quad (11.48)$$

where, p = vapour pressure of the liquid

ΔH_{vap} = latent heat of vaporisation of the liquid

R = gas constant

T = temperature (K)

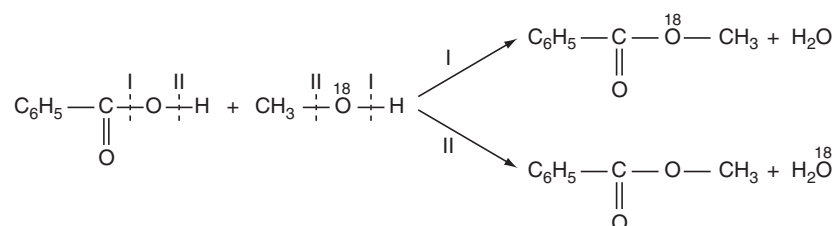
The value of p can be obtained from the peak height in mass spectrum. Thus, by studying the change in peak intensities as a function of sample temperatures, one can determine the value of ΔH_{vap} . The plot of $\ln p$ or intensity of positive peak XT against $\frac{1}{T}$ will be a straight line with slope

$(m) = \frac{-\Delta H_{\text{vap}}}{R}$. From the slope, we get

$$\Delta H_{\text{vap}} = m \times R \quad (11.49)$$

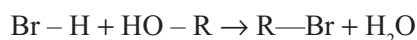
Similarly, one can also determine the heat of sublimation (ΔH_{sub}) of solids by studying the change in peak intensities as a function of sample temperatures since intensity of peaks in a spectrum is directly proportional to the pressure of the sample in the ion source. The sample placed in a reservoir is made to enter the source through a small hole by diffusion only. A sufficient amount of sample is kept in the thermostated cell so that the solid phase is always present in the cell. Such studies also show the formation of n -mers in the vapour over some high melting solids. For examples, monomers and dimers are produced in the vapour over sodium, potassium and cesium chlorides while monomers, dimers and trimers are observed in the vapour over lithium chloride. MoO_3 has been found to consist of trimer, tetramer, and pentamers. The individual heats of sublimation of the dominant gaseous species have also been obtained by utilising the Clausius–Clapeyron equation.

(j) Reaction Mechanism Mass spectrometric determinations of molecular mass to less than one mass unit have been applied to the investigation of reaction mechanisms. Isotopic labelling of a reacting molecule (most frequently deuterium replacing hydrogen, or ^{18}O replacing ^{16}O) enables the change in position of individual atoms during reactions to be determined from an examination of mass spectra of the various products, e.g. two mechanisms are possible of the esterification of benzoic acid by methanol.



According to Mechanism I, the bond between the acyl and hydroxyl is severed in the acid molecule, and the bond between hydrogen and oxygen in the alcohol molecule is broken; according to Mechanism II, the bond between the hydrogen and the oxygen in the acid is ruptured, while in the alcohol molecule, the break occurs between the alkyl and the hydroxyl.

It is very difficult to make a choice between these two mechanisms on the basis of theoretical hypotheses or analogies, because instances are known where the alcohol or acid behaves according to each of the above-mentioned mechanisms, e.g. alcohols react with hydrogen halides according to the only one possible mechanism that is depicted by II.



On the other hand, in a number of esterification reactions, the $\text{RO}-\text{H}$ bond is broken according to Mechanism I.

This problem has been solved by carrying out the reaction in CH_3OH enriched with heavy isotope ^{18}O and studying the reaction by mass spectrometry or by radiometric method. The mass spectrum of the reaction products reveals that the highest-mass molecular ion from the benzoic ester produced occurs at 156, indicating that some ^{18}O has been incorporated into this molecule. The molecular ion for H_2O occurs at a mass number 18, which indicates no incorporation of ^{18}O . As neither the ester nor the water can exchange ^{18}O directly with $\text{CH}_3^{18}\text{OH}$ at any significant rate, we can conclude that the esterification reaction takes place by Route I. Path II would require ^{18}O incorporation into water rather than the ester.

Thus we can establish the mechanisms of chemical reactions simply by labelling a particular atom (a slight enrichment would suffice) and then by locating it by using mass spectrometry alone.

(k) Structural Elucidation of Natural Products The improvement in the mass spectrometric techniques such as direct introduction system, resolution, sensitivity, etc., has made this technique very useful for the structural elucidation not only of small molecules but also of high molecular mass natural products such as proteins and peptides, sugars, lipids, alkaloids, terpenes, nucleic acids, etc. In this section we have introduced the structural elucidation of some natural products, namely peptides, sugars, nucleosides, glycerides and carotenes.

(i) Structural Elucidation of Peptides Before describing the methodology for determining the sequence of amino acid units in peptides, it is nice to comment on the mass spectra of amino acids, the basic units of peptides and proteins.

(ii) Mass Spectra of Amino Acids For an organic compound to be amenable to mass spectrometric analysis, it must be sufficiently volatile. It is for this reason that amino acids are converted into their methyl or ethyl esters; the amino group can be reacted to give trifluoroacetyl derivatives, trimethylsilyl derivatives, etc. The structural formulas and molecular masses of the important amino acids of the proteins are recorded here in Table 11.18 for ready reference.

Table 11.18 The most important amino acids of the protein.

Trivial name	Abbreviation	Formula (Molecular mass)
Glycine	Gly	$\text{NH}_2\text{CH}_2\text{COOH}$ (75.07)
Alanine	Ala	$\text{NH}_2\text{CH}(\text{CH}_3)\text{COOH}$ (89.10)
Valine	Val	$\text{NH}_2\text{CH}(\text{CH}(\text{CH}_3)_2)\text{COOH}$ (117.15)

Table 11.18 The most important amino acids of the protein—Cont'd.

Leucine	Leu	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{CH}_2\text{CH}(\text{CH}_3)_2 \\ (131.18) \end{array}$
Isoleucine	Ileu	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{H}_3\text{C}-\text{CH}-\text{C}_2\text{H}_5 \\ (131.18) \end{array}$
Aspartic acid	Asp	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{CH}_2\text{COOH} \\ (133.11) \end{array}$
Asparagine	Asn	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{CH}_2\text{CONH}_2 \\ (132.13) \end{array}$
Glutamic acid	Glu	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{CH}_2\text{CH}_2\text{COOH} \\ (147.13) \end{array}$
Glutamine	Gln	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{CH}_2\text{CH}_2\text{CONH}_2 \\ (146.15) \end{array}$
Ornithine (+)	Orn	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \\ (132.16) \end{array}$
Lysine	Lys	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \\ (146.19) \end{array}$
Arginine	Arg	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2\text{CH}_2\text{NH}-\text{C}-\text{NH}_2 \\ \quad \quad \quad \\ \quad \quad \quad \text{NH} \\ (174.20) \end{array}$
Serine	Ser	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{CH}_2\text{OH} \\ (105.10) \end{array}$
Threonine	Thr	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{CH}(\text{OH})\text{CH}_3 \\ (119.12) \end{array}$
Cysteine	CySH	$\begin{array}{c} \text{NH}_2\text{CHCOOH} \\ \\ \text{CH}_2\text{SH} \\ (121.16) \end{array}$
Cystine	CySSCy	$\left(\begin{array}{c} \text{NH}_2-\text{CHCOOH} \\ \\ \text{CH}_2\text{S}- \end{array} \right)_2 \\ (240.30)$
Methionine	Met	$\begin{array}{c} \text{NH}_2-\text{CHCOOH} \\ \\ \text{CH}_2\text{CH}_2\text{SCH}_3 \\ (149.21) \end{array}$
Phenylalanine	Phe	$\begin{array}{c} \text{NH}_2-\text{CHCOOH} \\ \\ \text{CH}_2\text{C}_6\text{H}_5 \\ (165.19) \end{array}$

(Continued)

Table 11.18 The most important amino acids of the protein—Cont'd.

Tyrosine	Tyr	$\begin{array}{c} \text{NH}_2-\text{CHCOOH} \\ \\ \text{CH}_2\text{C}_6\text{H}_4\text{OH}-n \\ (181.19) \end{array}$
Tryptophan	Try	$\begin{array}{c} \text{NH}_2-\text{CHCOOH} \\ \\ \text{H}_2\text{C} \text{ (indole ring)} \\ (204.23) \end{array}$
Proline	Pro	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \quad \\ \text{H}_2\text{C} \quad \text{CHCOOH} \\ \backslash \quad / \\ \text{NH} \\ (115.13) \end{array}$
Hydroxyproline	Hyp	$\begin{array}{c} \text{HOH C}-\text{CH}_2 \\ \quad \\ \text{H}_2\text{C} \quad \text{CHCOOH} \\ \backslash \quad / \\ \text{NH} \\ (131.13) \end{array}$
Histidine	His	$\begin{array}{c} \text{NH}_2 \text{ CH COOH} \\ \\ \text{H}_2\text{C}-\text{C}=\text{CH} \\ \quad \\ \text{N} \quad \text{NH} \\ \backslash \quad / \\ \text{CH} \\ (155.16) \end{array}$

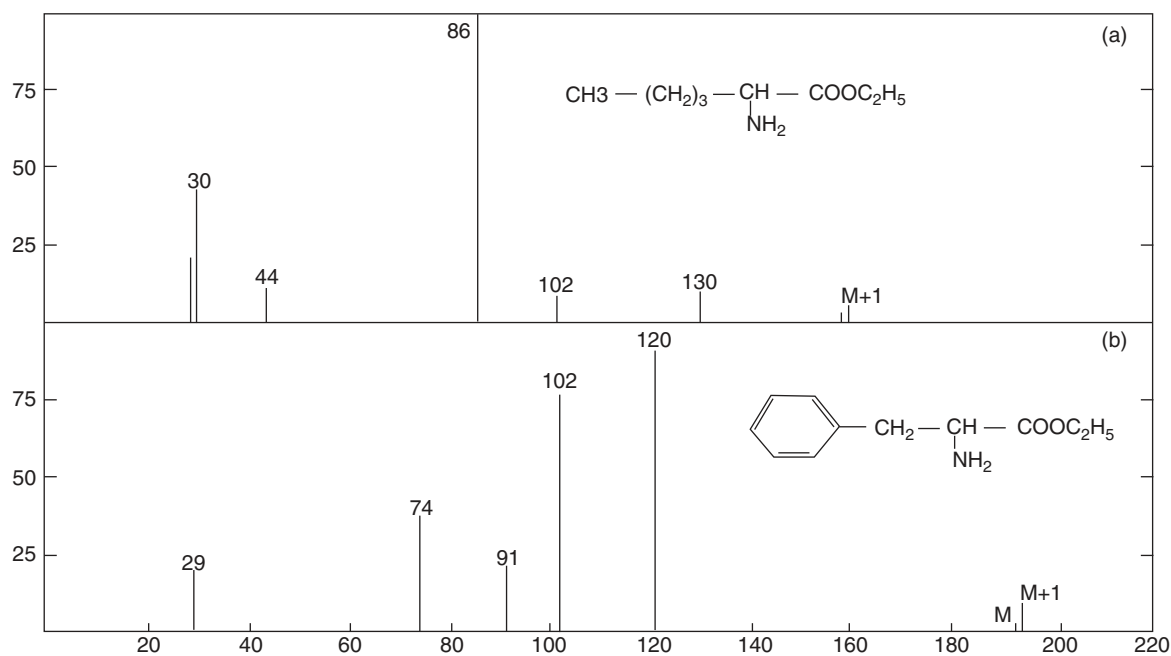


Fig. 11.33 The spectra of ethylesters of (a) norleucine, and (b) phenylalanine.

Let us now examine the mass spectra of amino acids as examples, the acids chosen are norleucine and phenylalanine. The molecular mass of the former is 131 and that of the latter is 165. The mass spectra of ethyl esters of the two acids have been shown in Fig. 11.33(a) and (b). The major peaks in the mass spectra of both the acid esters are listed below.

						$M^{\bullet}$	$M^{\bullet} + 1$
m/e	30	44	86	102	130	159	160
Norleucine:							
Peak height (in mm)	16	4	35	2.5	3.5	0.5	1.5

group which results in the formation of a linear ion, whose positive charge is localised at the C-terminal ester bond, and the N-terminal bond is protected by the acyl residue. Further fragmentation of this ion proceeds with the successive elimination of amino acid residues with transfer of the positive charge along the chain. The mass spectrum of the methyl ester of *N*-decanoylpropyl-alanyl-alanyl-valine (Fig. 11.34) exhibits major peaks at m/e : 524, 493, 394, 323, 252 and 155 amu. The fragmentation of the ester of *N*-acetylated oligopeptide may be depicted by the following scheme.

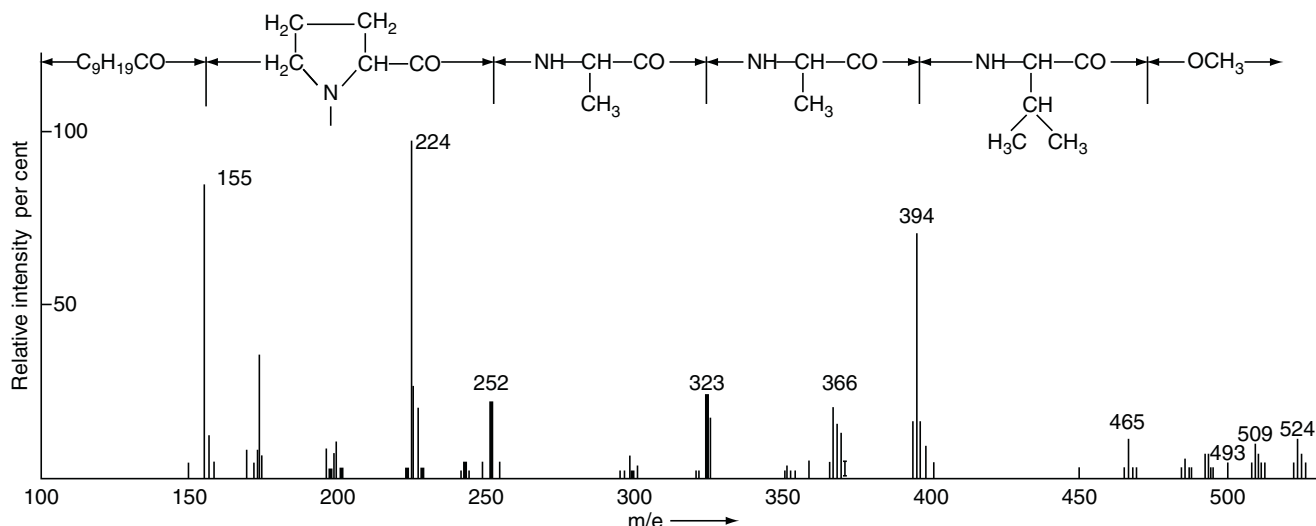
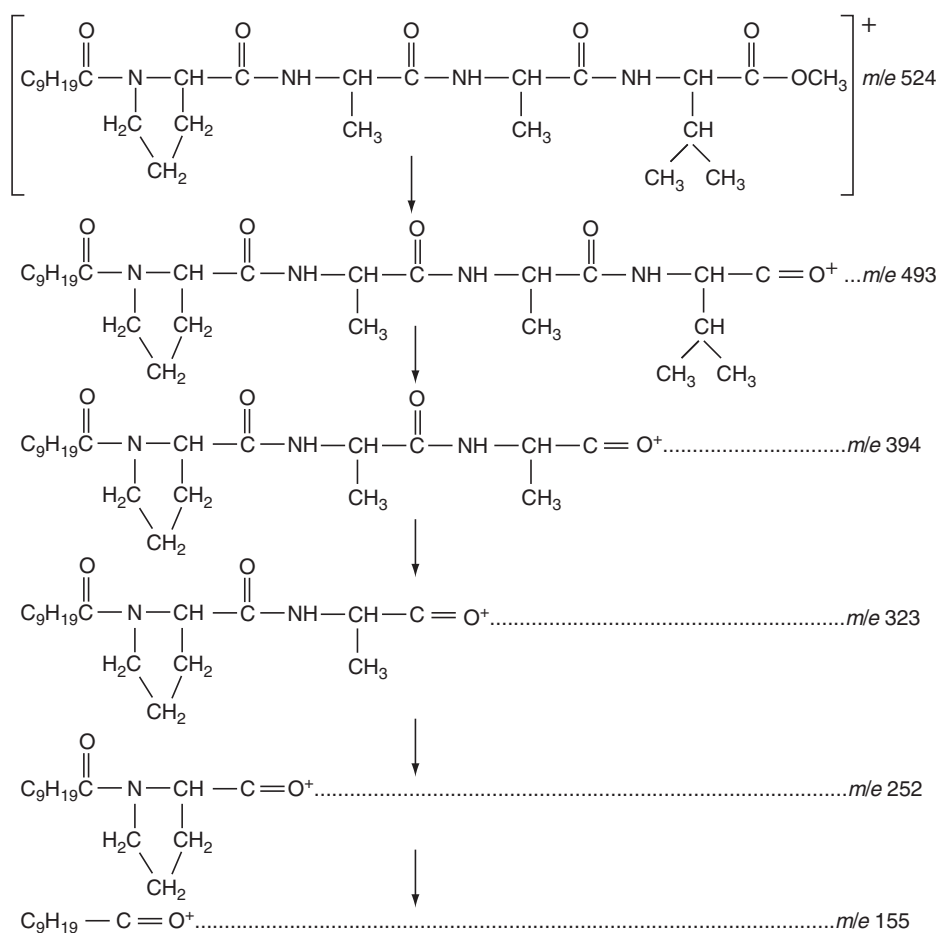
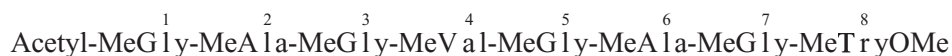


Fig. 11.34 Mass spectrum of methyl ester of *N*-decanoylpropyl alanyl-alanyl-valine.



Thus, if the amino-acid composition of the oligopeptide under consideration is known, the amino-acid sequence in the peptide chain can be established from its mass spectrum. Let us now examine a peptide derived from the silk fibroin in relation to the amino-acid sequence in it. It is found to be an octapeptide and contains four different types of amino acids, namely four molecules of glycine, two of alanine, and one each of valine and tryptophan. The mass spectrum of *N*-acyl peptide methyl ester of this octapeptide shows the main characteristic

peaks at m/e : 832, 610, 539, 454, 383, 270, 199 and 144 amu. The examination of the spectrum reveals that the fragmentation of the peptide fits into the following scheme.



The amino acids are represented by numbers.

Mass	Amino acid sequence
832	1-8
610	1-7
539	1-6
454	1-5
383	1-4
270	1-3
199	1-2
114	1

Peptides having 8 to 9 amino-acid units have successfully been studied by this technique. 10 μg quantity of the sample is sufficient for such studies.

Problem 11.38: The parent peak mass of an peptide has been measured relative to the parent peak in the spectrum of dibromobenzene (236.8638). The measured ratio of unknown mass/reference mass is found to be 1.001197. Calculate the exact mass of the peptide and deduce the molecular formula of the peptide.

Solution Exact molecular mass of the peptide = $\left[\frac{\text{Unknown mass}}{\text{Reference mass}} \right] \times \text{Exact mass of reference}$
 $= 1.001197 \times 236.8638 = 237.1474.$

For a compound containing C, H, N and O; from Eq. (11.44), we get

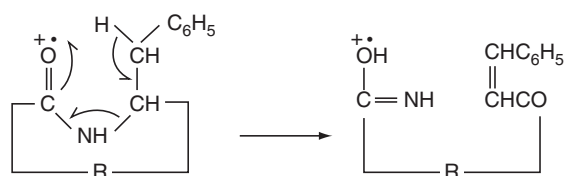
$$\begin{aligned} \text{Number of Hs} &= \frac{0.1474 + 0.0051 \times 2 - 0.0031 \times 3}{0.0078} \\ &= \frac{0.1474 + 0.0102 - 0.0093}{0.0078} = 19 \end{aligned}$$

Accordingly, the compound contains 2Os, 3Ns and 19Hs. So the molecular formula of the compound is written as $\text{C}_x\text{H}_{19}\text{N}_3\text{O}_2$.

Now, the mass due to x carbon atoms in the peptide = $237.1474 - (19 \times 1 + 3 \times 14 + 2 \times 16) = 237.1474 - 93$
 $= 144 \equiv \frac{144}{12} = 12\text{Cs}.$

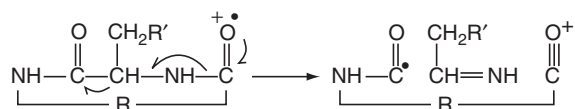
Hence, the molecular formula of the peptide is $\text{C}_{12}\text{H}_{19}\text{N}_3\text{O}_2$.

In cyclic peptides, a ring opening is followed by fragmentation. As an example, at a phenylalanine residue, transfer of hydrogen leads to an open-chain ion as indicated below:



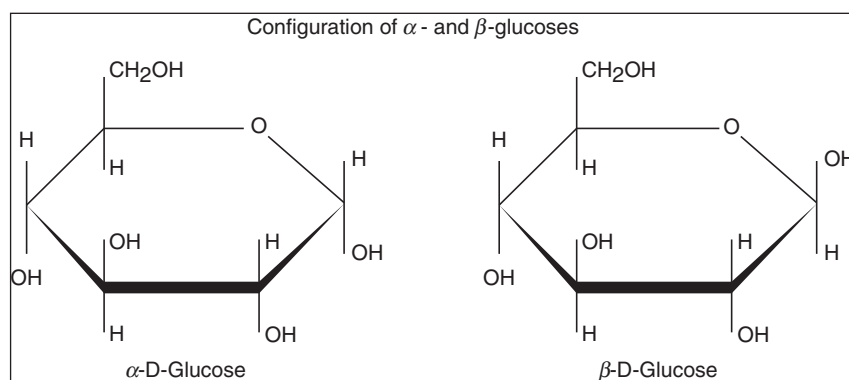
Here, R = remainder of the chain.

The ring opening can also occur at a position adjacent to a bulky amino-acid side chain giving rise to a radical ion. This is attributed to the release of excess vibrational energy as rotational energy.

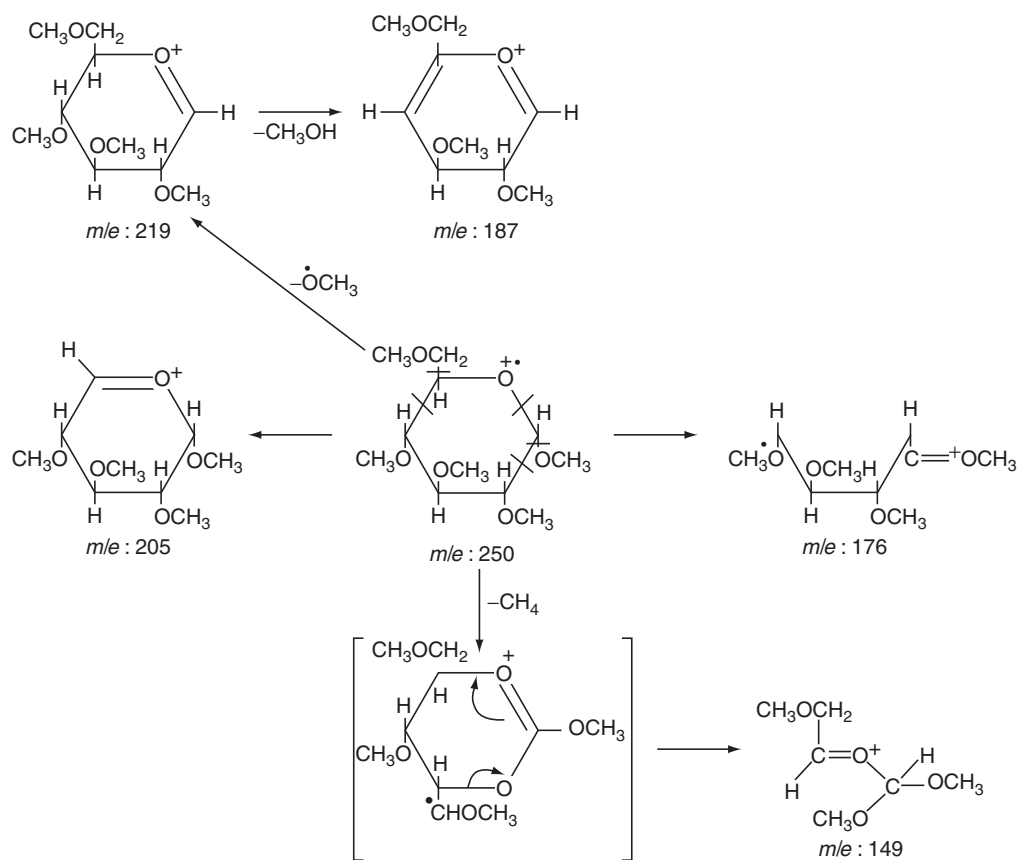


The ions obtained after ring opening can undergo further fragmentation, as described for linear peptide derivatives. The structure of the cyclopeptide alkaloid pandamine has been confirmed by mass spectrometry.

(iv) Structural Elucidation of Derivations of Sugars Just like amino acids and peptides, sugars are nonvolatile and hence as such can't be studied by mass spectrometry. Due to this reason, sugars are converted into methyl esters or acetates. The configurations of α - and β -glucoses are given here in the box for ready reference.

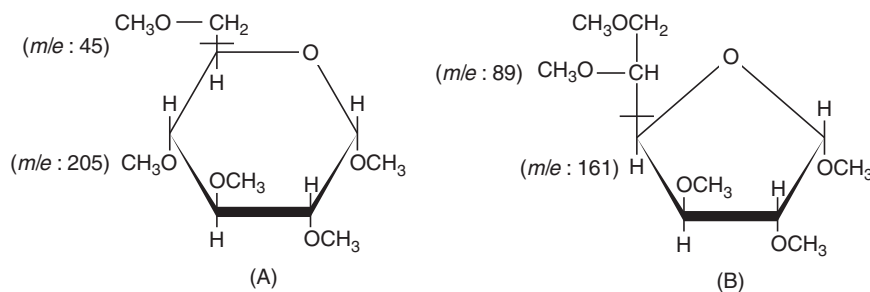


These two stereoisomers of glucose, which differ only in the configuration of carbon-1 (for aldoses, of carbon-2 for ketoses), are known as anomers (the α - or β -anomers). The above formulas represent the anomers of D-glucose. This method of assignment of monosaccharide to the α - or β -series is however applicable only in those cases if there is no other pair of hydroxyl groups on one side of the plane of the ring (in the *cis* position). The NMR method is not only used for the assignment of a monosaccharide to the α - or β -anomers (the D-series) but also for the determination of the equilibrium between α - and β -anomers in solution. The chemical shift for the protons of the glycoside hydroxyl of α - and β -monosaccharides varies markedly: for α -anomers (the D-series), the shift is 5.2δ , while for the β -anomers it varies within the range of 4.55 – 4.8δ . The significant peaks in the mass spectrum of methyl ester of glucose are observed at m/e : 219, 205, 187, 176 and 149. Fragmentation of molecular ion of monosaccharide occurs by several paths simultaneously, giving rise to several series of characteristic ions; the most important fragmentation routes for the methyl ester of glucose are presented by the following scheme:



The scheme shows that all the fragmentations proceed by a single route involving β -fissions, and that the variety of fragmentation routes is because of the large number of functional groups in the sugar molecule.

The mass spectrum of a methylated monosaccharide in the first place gives information about the number of carbon atoms in the carbon chain of the sugar since an ion of maximum mass number ($M - 31$) is formed with the expulsion of the glycosidic $\text{CH}_2\text{OH}(\text{CHOH})_3 - \underset{\text{H}}{\text{C}}=\text{O}$ methoxy radical ($-\dot{\text{O}}\text{CH}_3$) from the ring of the molecular ion ($m/e : 250$) and has a mass equal to 219 in the case of a hexose. In case of pentose the molecular ion peak is observed at $m/e : 206$ while the ($M - 31$) peak is observed at $m/e : 175$. Thus in monosaccharides, the ($M - 31$) rule can be fixed a criterion to identify the hexoses, pentoses, tetroses $\text{CH}_2\text{OH}(\text{CHOH})_2 - \underset{\text{H}}{\text{C}}=\text{O}$, etc. Secondly, the mass spectrum makes it possible to measure the size of the oxide ring in sugar derivatives since various characteristic peaks are obtained in pyranose (A) and furanose (B), for example, the rupture of side chain from the ring (β -fission):

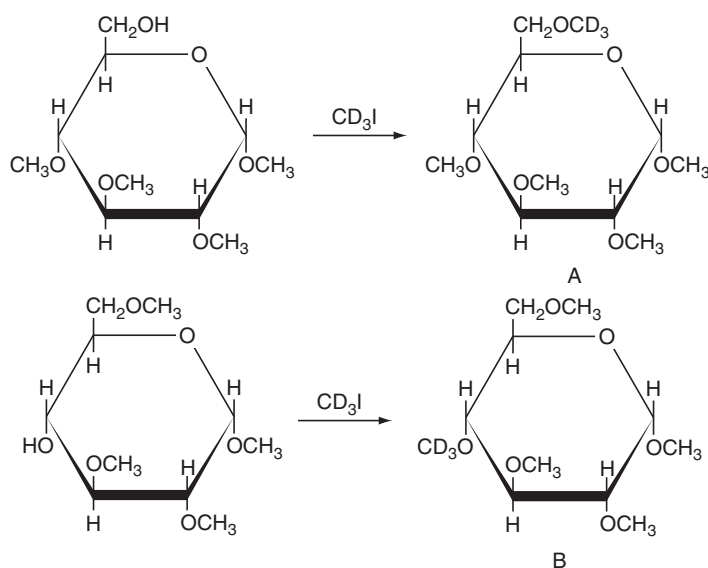


System	m/e	$M^+ - \text{mass loss}$
(A)	205	250 - 45
	45	250 - 205
(B)	161	250 - 89
	89	250 - 161

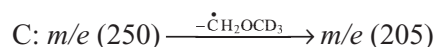
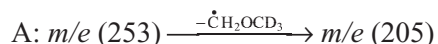
It is also possible to determine the structure of a large number of sugar derivatives by mass spectrometric analysis. The elucidation of the structure of partly methylated sugars is of great importance since they are obtained in the determination of the structure of polysaccharides by the methylation method. In order to know the site of free hydroxyl groups in partially methylated monosaccharide, they are treated with deuterated methyl iodide to replace the free hydroxyl groups by the deuteromethoxy groups. The incorporation of three deuterium atoms per hydroxyl group will manifest itself in the mass spectrum, the m/e values in the deuterated compound will increase by three units compared with the starting partially methylated monosaccharide. Thus, from a simple comparison of the mass spectrum of undeuterated monosaccharide with that of the deuterated monosaccharide, one can draw a conclusion as to the locations of free hydroxyl groups in the starting partially methylated derivatives. For example, the methylglycosides of 2, 3, 4-trimethyl glucose and 2, 3, 6-trimethylglucose give deuterio methyl derivatives A and B.

The mass spectra of the deuterated compounds are, compared with that of 2, 3, 4, 6-tetramethylglucose C, the parent compound; the fragmentation scheme of which has already been discussed earlier for ready reference.

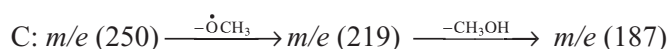
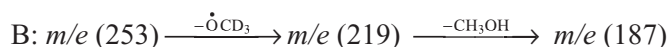
$$\begin{array}{l}
 m/e \left\{ \begin{array}{l}
 A \dots 222 \quad 205 \quad 190 \quad 176 \quad 173 \quad 162 \quad 152 \\
 B \dots 222 \quad 208 \quad 187 \quad 179 \quad 173 \quad 162 \quad 149 \\
 C \dots 219 \quad \boxed{205} \quad \boxed{187} \quad 176 \quad 173 \quad 159 \quad 149
 \end{array} \right. \\
 173 = (205 - \text{CH}_3\text{OH}), \quad 159 = (187 - \text{CO})
 \end{array}$$



A simple examination of the spectral data indicates that the spectra of compounds A and B not only differ from one another but also from the parent compound C; the m/e values for a number of ions in A or B have grown by three units as compared to their counterparts in C as expected. The peak at m/e equal to 205 in the parent compound C appears at m/e : 208 in the deuterated derivative B and remain unchanged from A which shows that fragmentation in the deuterated derivative A occurs at carbon atom 6 according to the following scheme:

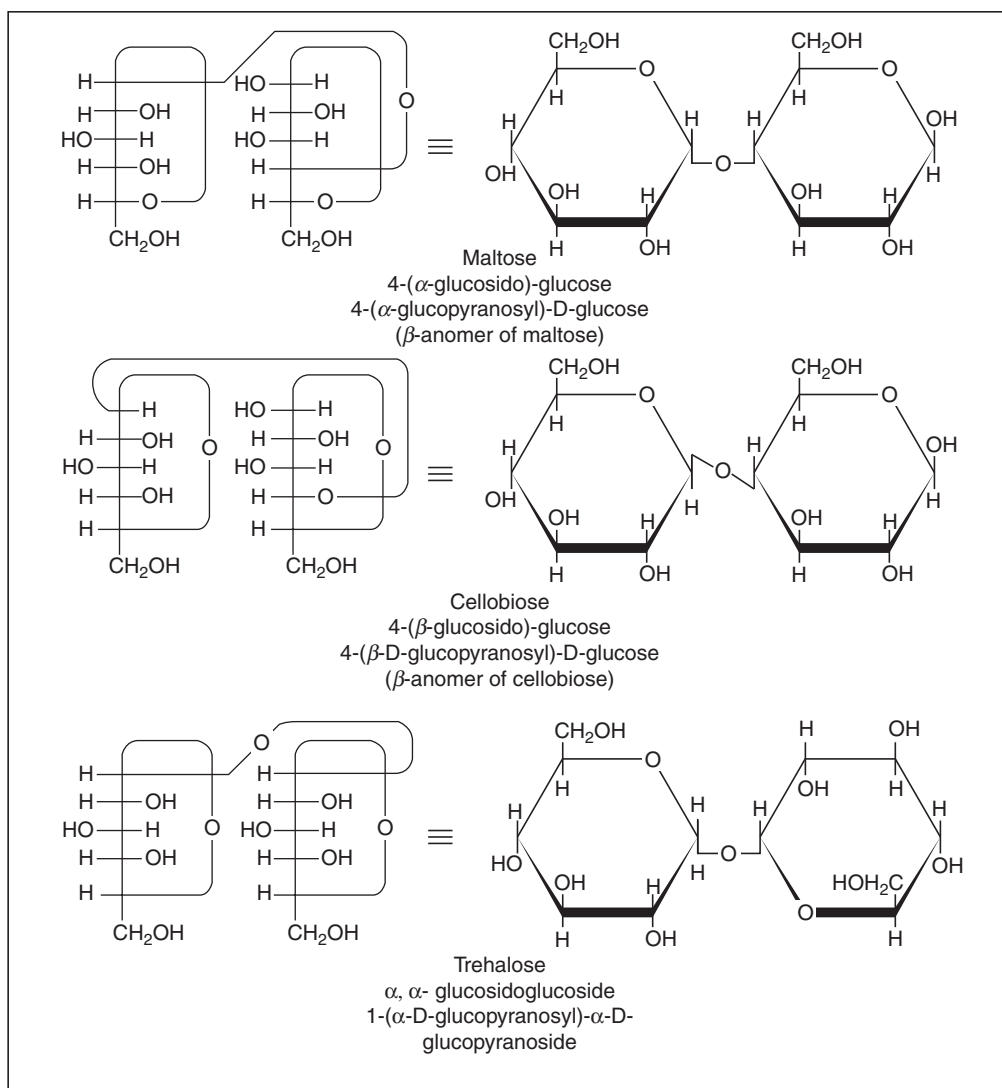


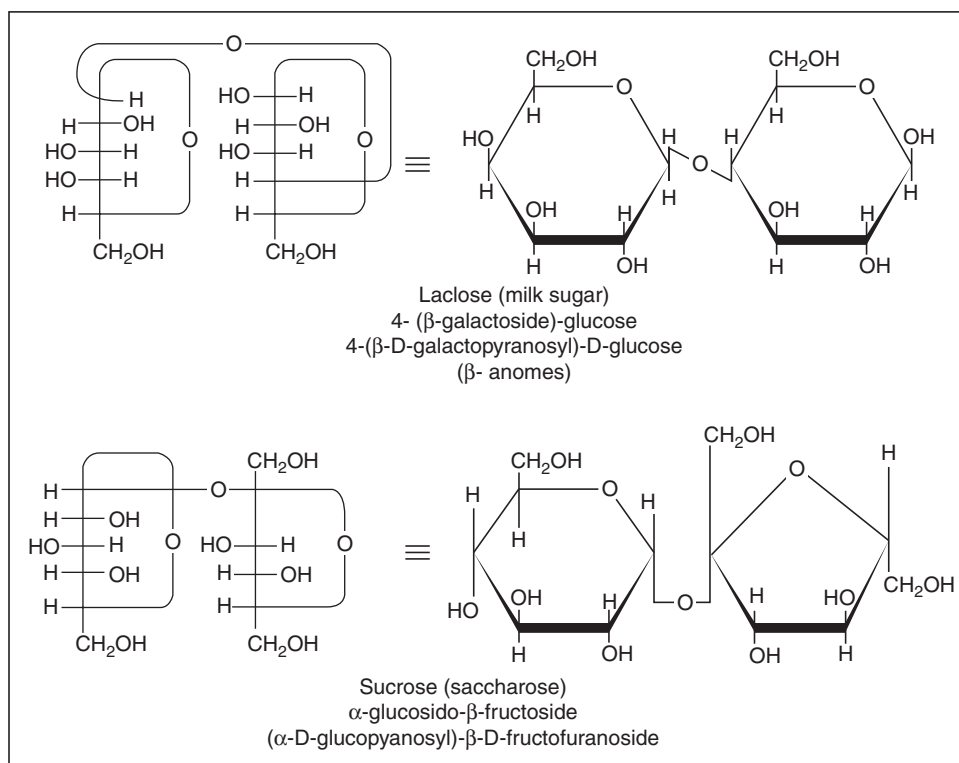
Hence, the site of deuteromethoxy group in the deuterated derivative A is at carbon atom 6. Contrary to this, a simple comparison of the mass peak at m/e : 187 in the parent compound with its counterpart in A and B reveals that the fragmentation in the deuterated derivative B occurs at carbon atom 4 according to the following scheme.



Hence, the deuteromethoxy group is situated at carbon atom 4 in the deuterated derivative B.

The complicated problems encountered in the investigation of structure of carbohydrates have also been solved by mass spectrometric analysis. For example, the structure of disaccharides can now be determined from mass spectral data alone since a number of peaks in the mass spectra of disaccharides (listed here in the box) with different types of bonds between monosaccharides can be differentiated.



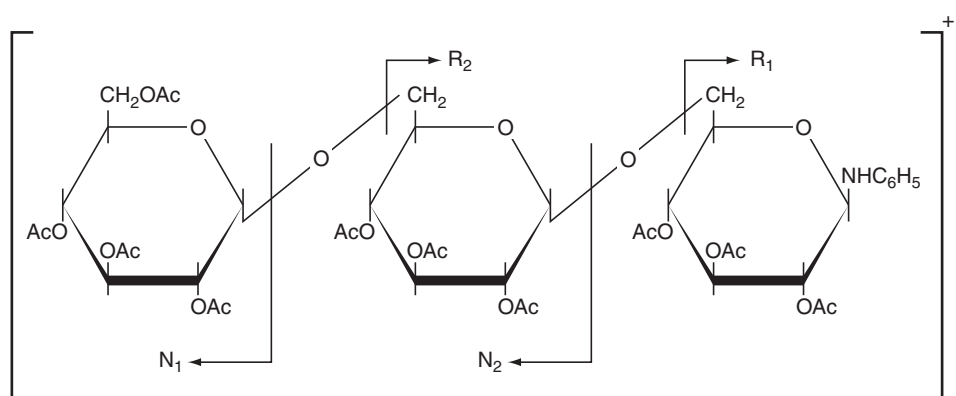


The electron impact mass spectrum of the anilide formed by the treatment of the acetate of an oligosaccharide shows a stable molecular ion at m/e equal to 999. The first act of fragmentation of the molecular ion proceeds with the subsequent elimination of the monosaccharide units from the reducing end (series R) or from the non reducing end of the chain (series N) giving rise to primary fragments given here.

<i>m/e (non reducing end):</i>	331 ⁺	288 ⁺	380 ^{••}
<i>m/e (reducing end):</i>	364 ⁺	288 ⁺	347 ^{••}

Thus, the mass spectrum of anilide of acetate of oligosaccharide will exhibit peaks at m/e values indicated;

$$m/e : 999 (M^{+•}), 380^{+•}, 364^{+}, 347^{+•}, 331^{+}, 288^{+}$$



Further, one can differentiate between isomeric glucosylglucoses (molecular mass = 454) from mass spectra.

For example, some characteristic peaks of methylated isomeric glucosyl-glucoses containing 1 → 6 and 1 → 4 bonds are indicated below:

Methylgentiobiose	<i>m/e :</i>	—	353	—	—
(1 → 6 bond)					
Methylcellobiose	<i>m/e</i>	380	—	305	161
(1 → 4 bond)					

Data reveal that we can differentiate between gentiobiose (1 → 6 bond) and cellobiose (1 → 4 bond), etc.

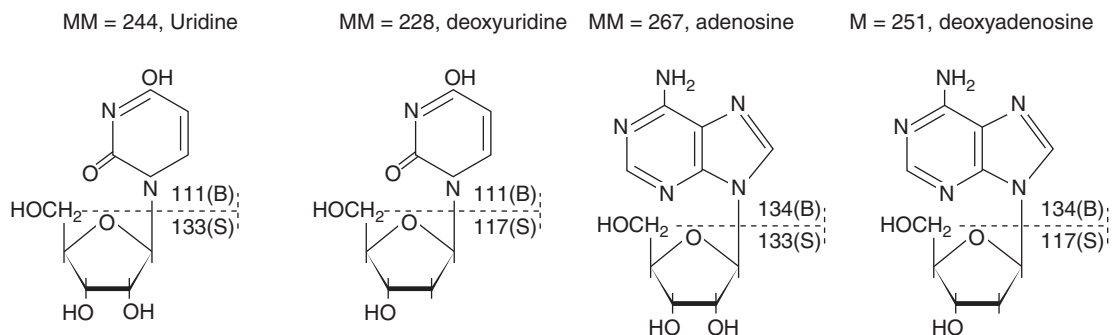
Differences in the mass spectra arise from the different routes of fragmentation of disaccharides caused by breakdown of the reducing monosaccharide unit since this unit is replaced by the non reducing monosaccharide in different positions at carbon atoms 6, 4, etc.

In conclusion, we can state that by identifying each fragment mass and suitably following them, one can establish the sequence of monosaccharide units in the oligosaccharide chain. The primary fragments split into smaller fragments, the structure of which depends on the type of glycosidic linkage. Thus mass spectral data enables not only to determine the sequence of monosaccharide units in the chain but also the nature of bond between them by differentiating $1 \rightarrow 6$ bonding units from $1 \rightarrow 4$ bonds, etc. Thus one can accomplish the entire structure of oligosaccharides from mass spectral data alone.

(v) Structural Elucidation of Nucleosides Mass spectra of deoxyribosides are recorded by the direct introduction of the sample into the ion source and the fragmentation pattern is shown in scheme 1. The pyrimidine or purine residue (B) yields a prominent peak at $m/e : M - 1$. Sometimes rearrangement processes involving one or two hydrogen atoms give rise to peaks at $m/e : B + 1$ and $B + 2$ respectively. These are removed preferentially from hydroxyl group as indicated by the spectra of the O, N-per deuterio derivatives. Thus, the relative intensities of $B + 1$ and $B + 2$ peaks can be fixed a criterion to differentiate between ribosides and 2'-deoxypentosides, while their mass indicates the identity of the base.

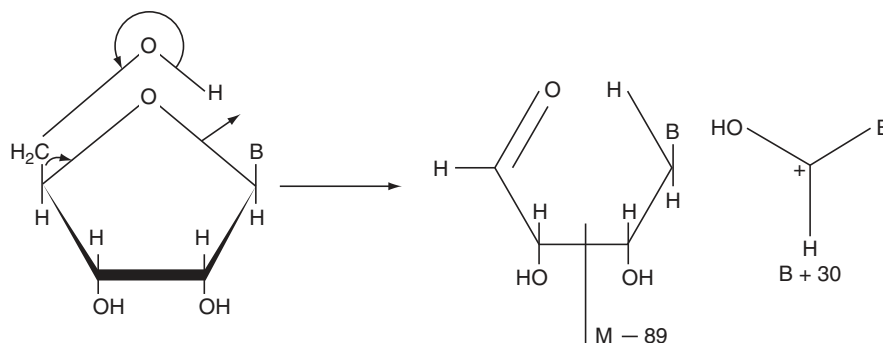
The mass of the sugar fragment gives rise to a peak at $m/e : 117$ in deoxypentosides and at $m/e : 133$ in pentosides. The ribose fragment generally is less abundant than the 2'-deoxyfragment.

Scheme 1: Mass spectra and fragmentation pattern of some nucleosides



<i>m/e</i> (peak height) 244 (1 mm)	<i>m/e</i> (peak height) 228 (1 mm)	<i>m/e</i> (peak height) 267 (3 mm)	<i>m/e</i> (peak height) 251 (3 mm)
M - 89 (3 mm)	M - 89 (2 mm)	M - 89 (16.5 mm)	M - 89 (11 mm)
B + 30 (9 mm)	—	B + 30 (26 mm)	B + 30 (3.9 mm)
133 (S) (24 mm)	117 (S) (34.5 mm)	133 (S) (1 mm)	117 (S) (2 mm)
113 (B + 2H) (34.5 mm)	113 (B + 2H) (5 mm)	136 (B + 2H) (26 mm)	136 (B + 2H) (11 mm)
112 (B + H) (7 mm)	112 (B + H) (16 mm)	135 (B + H) (34.5 mm)	135 (B + H) (34.5 mm)

Peaks at lower mass ($< m/e : 100$) are mainly due to fragments of sugar moiety. The higher mass peaks at $m/e : M$, $M - 18$ (loss of water), $M - 89$ and $B + 30$ are of interest. The loss of 89 mass units is indicated by the following mechanism.

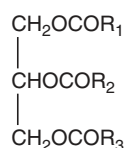


Thus, the 5'-deoxynucleoside fails to exhibit a peak at $M - 89$ due to the absence of 2'-hydroxy group. The mass spectrum of bacterial RNA, in which the methyl group of methionine-methyl- d_3 is incorporated into

thymine riboside shows a fragment peak at 129 instead of 126 ($B + H$) indicating thereby the incorporation of the intact CD_3 group.

The trideuterated riboside of 6-methyl-aminopurine shows a peak at m/e : 152 instead of 149 ($B + H$) for the normal compound.

(vi) Structural Elucidation of Triglycerides Triglycerides are esters of glycerol with structural formula:



Glyceride of stearic acid, called tristearin is found in Ox tallow. For this glyceride, $R_1 = R_2 = R_3 = C_nH_{2n+1}$, and $n = 17$. For glycerides of palmitic acid called tripalmitin; $R_1 = R_2 = R_3$ and $n = 15$. Sources of these glycerides are mutton, coconut oil, etc. Note that cow butter in addition to the glycerides indicated above contains glycerides of butyric acid and other glycerides of even number of carbon atoms between $n = 4$ and $n = 15$. Cephalin an phosphatide is a diglyceride of fatty acid is found in brain. It is contained in many animals and plants (egg, liver tissue, soya bean, etc.) In this compound, $R_3 = -P(=O)(O^-)O-CH_2-CH_2-N^+H_3$ the

mass spectra of pure glycerides help to elucidate the structure of unknown glycerides. The principal fragmentation pattern of a glyceride with general formula (A) is shown in Fig. 11.35.

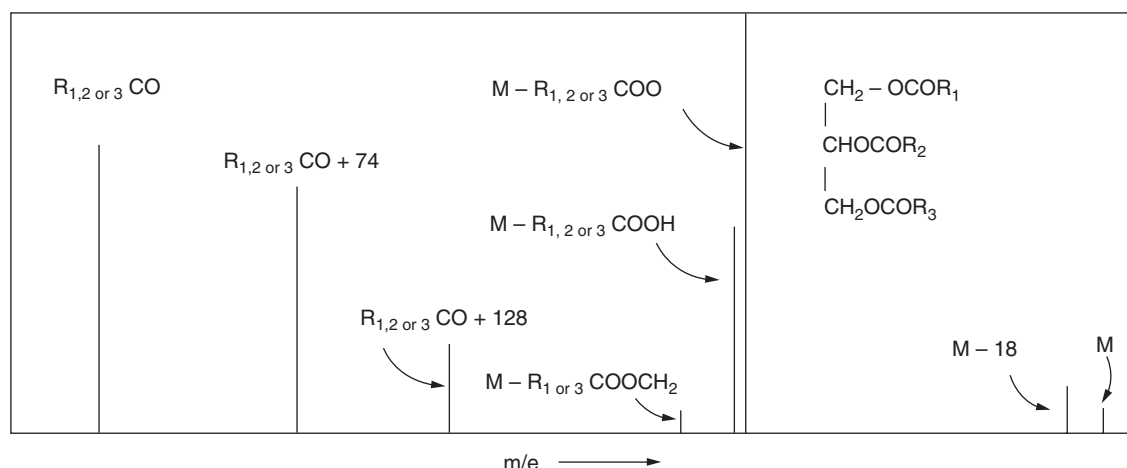


Fig. 11.35 Cracking pattern of triglycerides.

The base peak ($M - R_{1,2,3}COO$), in most cases, is due to the loss of acyloxy group from the complete molecule. In mixed triglycerides, i.e. $R_1 \neq R_2 \neq R_3$, a peak is observed by the loss of each acyloxy group present in the molecule. Peaks corresponding to $M - R_{1,2,3}COOH$ ions are also distinguishable in the mass spectra. The second-most intense peak is usually that of the positively charged acyl ion. A peak corresponding to each fatty acid present in the molecule is observed. The peaks of smaller intensity 14 mass units lower are associated with $M - R_{1,2,3}COO$ peak. One of these peaks, $M - (R_2COO + 14)$ is much smaller than the $M - R_1COOCH_2$ and the $M - R_3COOCH_2$ peaks. These compounds also show a set of peaks at m/e : 74 and 128 higher than each acyl ion peak.

All the triglycerides always show peak at $M - 18$. The presence of a metastable peak corresponding to this transition suggests that this is mainly due to ionic fragmentation and not to thermal cracking. These observations led to infer that a complete structural analysis of triglycerides containing straight-chain fatty acids can be carried out from their mass spectral data.

As an example, let us now deduce the structural formula of a triglyceride from its mass spectral data. The exact molecular mass of hydrogenated optically active allene-containing tetraester triglyceride isolated from the seed oil of sapium sebiferum is 920.801. Deduce the structural formula of the glyceride from its mass spectral data indicated below.

m/e	Peak height (in mm)
920	< 1
748	< 1
637	12

(Continued)

(Continued)

607	7
593	1
425	3
395	9
371	3
341	5
297	3
267	13
171	3.4
155	18.5

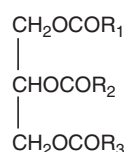
The number of hydrogen atoms in the molecule = $\frac{0.801 + 0.0051 \times 8}{0.0078} = 108$

Thus, the empirical formula of the compound can be written as $C_xH_{108}O_8$.

Since molecular mass = 920, the number of Cs = $\frac{920 - 108 - 16 \times 8}{12} = \frac{684}{12} = 57$,

Accordingly, the formula of the compound is $C_{57}H_{108}O_8$.

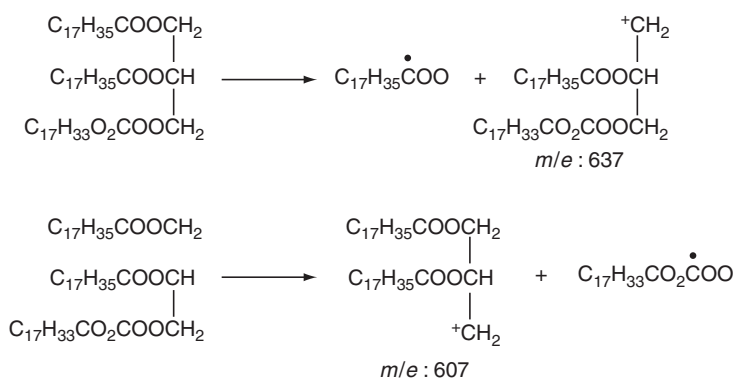
The general formula of the triglyceride can be written as



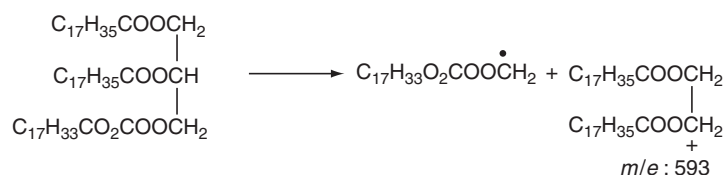
where,

$$R's = C_n H_{2n+1}.$$

Now the problem is to find the nature of R_1 , R_2 , and R_3 from the mass spectral data. The parent peak of the hydrogenated triglyceride is observed at m/e : 920. The peak at m/e : 155 is due to the acyl group ($C_9H_{19}CO$) derived from decanoic acid while at m/e : 297 is due to the intact ($C_8 + C_{10}$)-acyl fragment, i.e. $C_{17}H_{33}O_2CO$. The peak at m/e : 267 is attributed to the acyl group derived from stearic acid is $C_{17}H_{35}CO$. The peaks at m/e : 341 and 395 are respectively due to the fragments 74 and 128 mass numbers higher than the acyl group originating from stearic acid, i.e. $C_{17}H_{35}O_2CO + 74 = 341$ and $C_{17}H_{35}CO + 128 = 395$. The peaks at m/e : 371 and 425 correspond to the fragments 74 and 128 mass numbers higher than the intact ($C_8 + C_{10}$) acyl group originating from decanoic acid, i.e. $C_{17}H_{33}O_2CO + 74 = 371$ and $C_{17}H_{33}O_2CO + 128 = 425$. The absence of peaks at m/e : $C_9H_{19}CO + 74$ and $C_9H_{19}CO + 128$ suggests that decanoic acid is not esterified to the glycerol moiety. The two peaks at m/e : 637 and 607 are respectively attributed to the fragments remaining after acyloxy loss of stearic acid and the 18-carbon diester moiety, i.e.

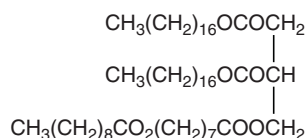


The peak at m/e : 593 is attributed to $920 - C_{17}H_{33}O_2COOCH_2$. This suggests that the $C_8 + C_{10}$ group is esterified to a primary hydroxy group of glycerol, otherwise the peak at 593 should appear at $593 + 14 = 607$ mass number.



The peak at $m/e : 748$ corresponds to $\text{M}-(\text{C}_9\text{H}_{19}\text{COOH})$. Elimination of acid occurs via McLafferty rearrangement.

Accordingly, the final structural formula of the hydrogenated triglyceride is

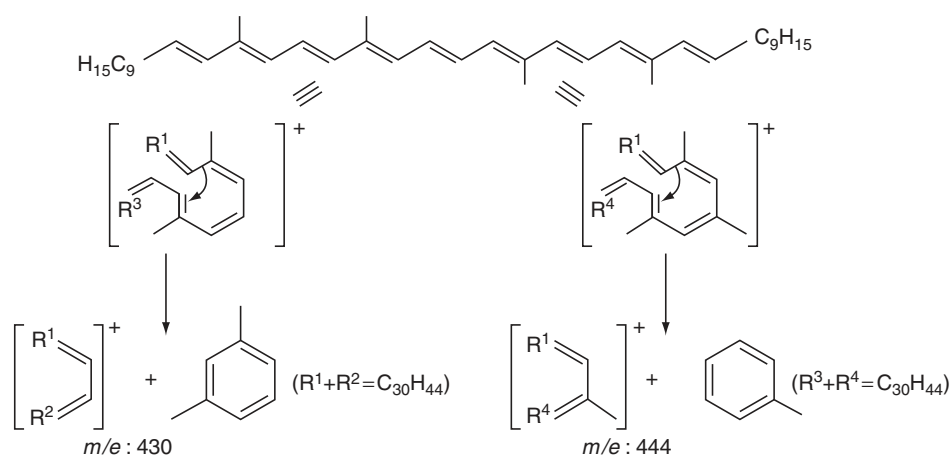
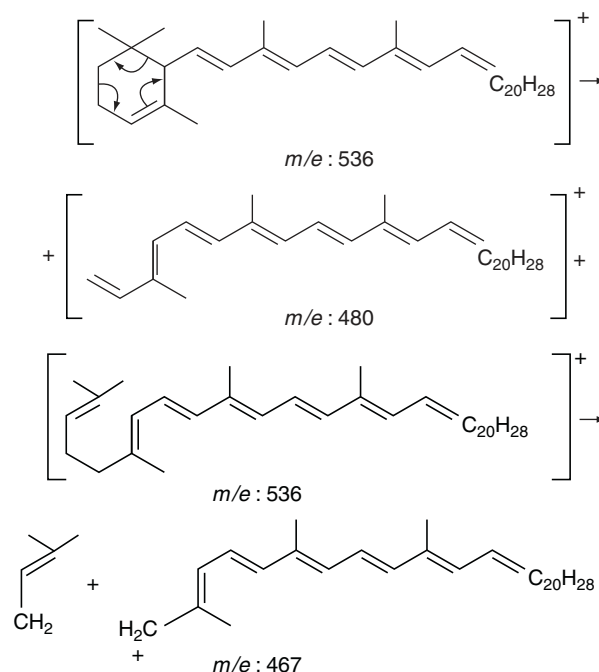


(vii) Structural Elucidation of Carotenes The mass spectra of six isomeric carotenes and of lycopene show an intense molecular ion peak at $m/e : 536$ ($\text{C}_{40}\text{H}_{56}$). The peak at $m/e : 480$ is shown by all isomers containing the α -ionone ring. The peak appears due to 'retro-Diels' reaction.

The open-chain isomers (γ and δ -carotene and lycopene) exhibit a peak at $m/e : 467$ due to the rupture of the doubly allylic bond; the charge is again kept by the polyene fragment. Strong peaks ($m/e : 430$ or 444) are observed due to elimination of toluene or xylene from the middle of the polyene chain. The thermal production of toluene and xylene from carotene is well known.

Thus the isomers of carotenes containing the α -ionone ring and the open-chain isomers can be differentiated on the basis of their mode of fragmentation. The former will exhibit a peak at $m/e : 480$ while the latter will show a peak at $m/e : 467$.

The xylene or toluene is produced as follows:



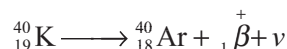
(l) Age of Rocks and Fossils The decay of radioactive elements is independent of the physical and chemical conditions imposed on them. Although the decay of an individual particle from a given nucleus is a random process, the gross decay of many nuclei sample provides a very convenient way of measuring times. If an igneous rock, formed

as a result of volcanic eruption, contained a small amount of uranium-238 with half-life of 4.5×10^9 years, it would steadily decay leaving less uranium-238 and depositing more stable Pb-206 according to the scheme:



By measuring the ratio of uranium to lead in rock samples, an exact time can be determined for the origin of geological deposits on earth and other planets.

Another similar method of dating is the decay of the isotope K-40 into Ca-40 or Ar-40 by the positron emission, i.e.



with the half-life of 1.3×10^9 years. Because it is more readily measured, Ar-40 is most often used to date the geological samples.

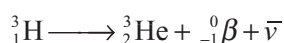
Thus, if the decay rate of ${}^{238}\text{U}$ to ${}^{206}\text{Pb}$, ${}^{40}\text{K}$ to ${}^{40}\text{Ar}$ or ${}^{87}\text{Rb}$ to ${}^{87}\text{Sr}$ is known, and the ratio of the isotopes of one of these pairs (depending upon the nature of the geological deposit) in the reference sample and in the unknown sample under study is determined by mass spectrometry then the age of the minerals and rocks can be estimated.

The other most important method of absolute dating, sometimes called *chronometric dating*, is that of radiocarbon dating. It was developed by the American chemist Willard Libby and his co-workers in 1949. Radiation from space produces neutrons that enter the earth's atmosphere and react with nitrogen to produce the carbon isotope C-14. Since all plants use CO_2 from the atmosphere for growth, a portion of the carbon in plants is radioactive C-14 and the plants are slightly radioactive. When a plant dies, no additional C-14 is taken in, and that within the plant body begins to decay without being replaced. Measurements of the relative amounts of C-14 and C-12 in an organic archeological sample by mass spectrometry provides a sensitive method of dating. Recently, a new approach to radio carbon dating using an Accelerator Mass Spectrometer (AMS) has been developed. AMS directly counts C-14 atoms, rather than counting rates of disintegration. AMS can date a sample as small as a single kernel of grain or a fleck of wood preserved inside a bronze axe socket. This method can date items that are up to 90,000 years old.

Another element that is continuously produced in the atmosphere by cosmic impact is tritium, ${}^3_1\text{H}$. It is formed by neutron collision with ${}^{14}_7\text{N}$ according to



Tritium, the heavy isotope of hydrogen, decays with a half-life of 12.4 years by β decay into the stable helium isotope ${}^3_2\text{He}$:



A small percentage of water contains ${}^3_1\text{H}$ instead of ${}^1_1\text{H}$ and thus by measuring the relative amounts of ${}^3_1\text{H}$ and ${}^1_1\text{H}$ in samples of water by mass spectrometry at various locations, some indication may be obtained as to how long this water was in the form of rain.

We know that the rate of radioactive decay is directly proportional to the number of atoms present at time t ,

i.e.
$$-\frac{dN}{dt} \propto N \quad \text{or} \quad -\frac{dN}{dt} = \lambda N$$

which on integration gives

$$t = \frac{1}{\lambda} \ln \frac{N_0}{N} \quad (11.50)$$

where, $\lambda = \frac{0.693}{t_{1/2}}$, is the decay or disintegration constant, N_0 is the number of radioactive atoms at time $t = 0$, N is the number of radioactive atoms at time t and $t_{1/2}$ is the half-life of the radioactive isotope.

The expression (11.50) when used in mass spectrometry modifies to

$$t = \frac{1}{\lambda} \ln \left[\frac{\text{Ratio of relative abundance of parent and daughter isotopes in the standard sample}}{\text{Ratio of relative abundance of parent and daughter isotopes in the sample under study}} \right] \quad (11.51)$$

To summarise, precise age dating is based on the rate of decay of radioactive nucleids. If the decay rate of ^{238}U to ^{206}Pb ; ^{40}K to ^{40}Ar , and ^{87}Rb to ^{87}Sr is known, and the ratio of one of these pairs is measured, the age of minerals and rocks can be determined. Similarly, the age of the plant fossil is determined from the $^{14}\text{C}/^{12}\text{C}$ ratio in the plant fossil and in the living organisms.

The age of the minerals can also be determined by another method, also based on radioactive decay, known as the isotope dilution method.

Isotope Dilution Method In this method, an element like Li, C or N which has isotopes and whose natural abundance is small cannot be estimated by spiking it with that isotope. This is similar to the radioactive tracer technique.

Let us say, we have to estimate oxygen in a substance A which is in a tracer.

Let the mass of the substance (A) taken be ' a '; oxygen content of it be x per cent.

Let us add enriched oxygen ' b ' or ^{18}O content of m per cent. After equilibration, let ^{18}O content becomes n per cent.

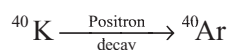
Thus,

$$axn = b(m - n)$$

or

$$x = \frac{b(m - n)100}{na} \quad (11.52)$$

Li in granite has been determined by using Li tracer. In determining the geological ages of minerals, potassium minerals contain argon due to



Since, ^{40}Ar content is very small, it is mixed with ^{36}Ar and by the ^{36}Ar content of the mixture, one can determine the age of the mineral. By the isotope dilution method, one can determine quantities as small as 10^{11} atoms.

Problem 11.39: The mass spectrum of an aged sample of rain water collected from a pond is characterised by the presence of peaks of the isotopic forms of hydrogen ^1HOH and ^3HOH , which are equal to 60 and 0.4 mm respectively, while the mass spectrum of fresh sample of rain water exhibits peaks corresponding to ^1HOH and ^3HOH equal to 50 and 0.6 mm respectively. Calculate for how long this water was in the rain form? The half-life of ^3H is 12.4 years.

Solution Since, $t_{1/2} = 12.4$ years (for ^3H)

$$\text{Therefore, } \lambda = \frac{0.693}{12.4} \text{ yr}^{-1} = 5.58 \times 10^{-2} \text{ yr}^{-1}$$

Substituting the value of λ and the data given in the problem into Eq. (11.51), we obtain

$$\begin{aligned} t &= \frac{1}{5.58 \times 10^{-2} (\text{yr}^{-1})} \ln[(0.60/50)/(0.40/60)] \\ &= \frac{\ln 1.8}{5.58 \times 10^{-2} (\text{yr}^{-1})} = \frac{5.87 \times 10^{-1}}{5.58 \times 10^{-2} (\text{yr}^{-1})} = 10.5 \text{ yrs.} \end{aligned}$$

Problem 11.40: The $^{14}\text{C}/^{12}\text{C}$ ratio in a plant fossil as well as in a living organism has been examined on an isotope ratio mass spectrometer. The $^{14}\text{C}/^{12}\text{C}$ ratio in the former has been found to be 0.617 times than that found in the latter. How old is the plant fossil? $t_{1/2}$ for ^{14}C is 5770 years.

Solution The decay constant λ for $^{14}\text{C} = \frac{0.693}{5770(\text{yr})} = 1.20 \times 10^{-4} (\text{yr}^{-1})$

Substituting the value of λ and the given data into Eq. (11.51), we obtain,

$$\begin{aligned} t, \text{ the age of the fossil} &= \frac{1}{1.20 \times 10^{-4} (\text{yr}^{-1})} \ln \frac{1}{0.617} \\ &= 8.33 \times 10^3 (\text{yrs}) \times \ln 1.620 \\ &= 8.33 \times 10^3 (\text{yrs}) \times 4.82 \times 10^{-1} = 4015 \text{ years} \end{aligned}$$

(m) Quantitative Analysis of a Mixture of Gases The procedure employed in quantitative analysis by mass spectrometry is basically the same as used in infrared spectrometry and in ultraviolet spectrometry. Let us suppose we want to analyse a mixture of four gases, namely N_2 , O_2 , CH_4 and CO_2 . About one cc of the gas sample at NTP is introduced into the mass spectrometer and let its pressure inside the ion chamber be 100 microns ($1 \mu = 10^{-3}$ torr). The mass spectrum will exhibit molecular ion peaks at m/e : 16, 28, 32 and 44. In addition, there will be peaks due to the fragmentation of molecular ions into ions like 12–15 for CH_4 , and 28 for CO_2 . For analysis, peaks are selected on the basis of both intensity and non-interference by peaks of another component. If possible, monocomponent peaks (perhaps of parent ion peaks) are chosen. It is assumed that at the pressure inside the ion chamber (i.e. = 100 μ) there are no ion-molecule reactions (e.g. $CH_4 + CH_4^+ \rightarrow CH_5^+ + CH_3$, etc.) and peak heights represent the original composition. But the direct peak height ratios of monocomponents cannot be fixed as the criterion to determine the composition as these ratios will actually be that of ions and not that of parent molecules. Therefore, peak heights need be standardised with the parent gases. Different molecules have different ionisation energies and different rates of diffusion through molecular leaks. Further peak at m/e : 28 is not due to N_2 alone but has contribution from CO_2 also. So the latter has to be subtracted out in order that the total sum of the contributions of all components of the mixture comes out to nearly 100 per cent. For standardisation, 100 μ of each gas is taken and their peak heights are measured at the respective chosen values of their masses. The peak heights per micron known as the sensitivity factors or parameters (S) are then determined. Thus for CO_2 ($m/e = 44$), if the measured peak height is h_1 , then $h_1 = S_1 p_1$ where p_1 is the partial pressure of CO_2 in microns of Hg, for O_2 ; $h_2 = S_2 p_2$ and for nitrogen, $h_3 = S_3 p_3 = S_1 p_1$ where $S_1 p_1$ is the contribution from CO_2 . Once the sensitivity values of the pure components are known, all the partial pressures due to the components of a mixture of gases can be determined from peak heights. Calculations of sample components become simple if the components of the mixture give spectra with at least one peak whose height is due entirely to the monocomponent.

In general, we can write

$$\text{Sensitivity } (S) = \frac{\text{Height of the analysis peak in the pure compound}}{\text{Pressure of pure compound in the sample chamber}} \quad (11.53)$$

$$\begin{array}{l} \text{Partial pressure due} \\ \text{to each component} \\ \text{of a mixture} \end{array} = \frac{\text{Height of the monocomponent (i.e. analysis) peak in the mixture}}{\text{Sensitivity factor}} \quad (11.54)$$

$$\begin{array}{l} \text{Mole per cent of} \\ \text{each component} \\ \text{in the mixture} \end{array} = \frac{\text{Partial pressure of each component in the mixture}}{\text{Sum of the partial pressures due to all the components of a mixture}} \quad (11.55)$$

If the mixture has no monocomponent peak, then simultaneous equations are set up from the coefficients (per cent of base peak) at each analysis peak. If there are n -components in a mixture, there will be one equation for each compound in the mixture with n -terms.

Let $x_1, x_2, x_3, \dots, x_n$ be the relative contributions respectively of the components $A_1, A_2, A_3, \dots, A_n$ of a gas mixture. If $h_1, h_2, h_3, \dots, h_n$ are the peak heights of the monocomponent peaks at m/e : $m_1/e, m_2/e, m_3/e, \dots, m_n/e$ of the pure compounds $A_1, A_2, A_3, \dots, A_n$, constituting the mixture then we can write

$$\begin{aligned} \left(\frac{m_1}{e}\right)^{\text{mix}} : h_n^{\text{mix}} &= x_1 h_1' + x_2 h_2' + x_3 h_3' + \dots + x_n h_n' \\ \left(\frac{m_2}{e}\right)^{\text{mix}} : h_2^{\text{mix}} &= x_1 h_1'' + x_2 h_2'' + x_3 h_3'' + \dots + x_n h_n'' \\ \left(\frac{m_3}{e}\right)^{\text{mix}} : h_3^{\text{mix}} &= x_1 h_1''' + x_2 h_2''' + x_3 h_3''' + \dots + x_n h_n''' \\ &\vdots \\ &\vdots \\ \left(\frac{m_n}{e}\right)^{\text{mix}} : h_n^{\text{mix}} &= x_1 h_1^n + x_2 h_2^n + x_3 h_3^n + \dots + x_n h_n^n \end{aligned} \quad (11.56)$$

where $(m/e)^{\text{mix}}$ are the respective peaks of the mixture.

The solution of these equations will give the values of $x_1, x_2, x_3, \dots, x_n$. If $S_1, S_2, S_3, \dots, S_n$ are the sensitivity parameters of the respective components of the mixture then the partial pressures due to the constituent components in microns can be obtained by dividing the values of x 's by the sensitivity parameter values S 's.

For fast calculations, a set of equations in terms of each unknown and the analytic masses is obtained by inversion of the coefficient matrix, i.e.

$$x_1 = y'_1(h_1)^{\text{mix}} + y'_2(h_2)^{\text{mix}} + y'_3(h_3)^{\text{mix}} + \dots + y'_n(h_n)^{\text{mix}}$$

$$x_2 = y''_1(h_1)^{\text{mix}} + y''_2(h_2)^{\text{mix}} + y''_3(h_3)^{\text{mix}} + \dots + y''_n(h_n)^{\text{mix}}$$

$$x_3 = y'''_1(h_1)^{\text{mix}} + y'''_2(h_2)^{\text{mix}} + y'''_3(h_3)^{\text{mix}} + \dots + y'''_n(h_n)^{\text{mix}}$$

$$\vdots \quad \quad \quad \vdots$$

$$x_n = y''_1(h_1)^{\text{mix}} + y''_2(h_2)^{\text{mix}} + y''_3(h_3)^{\text{mix}} + \dots + y''_n(h_n)^{\text{mix}}$$

Substituting the values of peak heights from the spectrum of the mixture into the inverse matrix equations, we can obtain the relative contributions of each component of the mixture. The sum of the partial pressures determined should be equal to the total sample pressure, the discrepancy if any would indicate an unexpected component or a change in operating sensitivity.

Many solids like alloy steels, rocks, semiconductor, reactor materials, etc., have been analysed for trace metals and quantities as small as one in 10^9 , i.e. nanogram quantities have been estimated.

A computer program in C++ entitled 'Mole-PER.CPP', based on Gause Jordan method to determine the constituent components of a mixture has also been given and the results of the problems 11.41–11.43 determined manually by simple elimination method are compared with those determined using the program. The values within braces in the tables are from the program.

Problem 11.41: Determine the contents of the components in an alcohol mixture, using the mass spectral data of pure components and the intensities of the peaks in the mass spectrum of the mixture given below. The sensitivity parameters (in divisions/ 10^{-3} torr) for methyl and ethyl alcohols respectively are 8.76 and 17.98.

<i>m/e</i>	<i>Percentage of component</i>		<i>Peak intensity</i>
	<i>CH₃OH</i>	<i>C₂H₅OH</i>	
15	35.48	9.44	
19	0.29	3.13	
27	—	21.62	
29	58.80	21.24	
31	100	100	
32	68.03	1.14	400
33	0.98	—	
43		7.45	
45		37.33	
46		16.23	800

Solution According to the set of Eqs (11.56), we write

$$68.03x_1 + 1.14x_2 = 400$$

$$16.23x_2 = 800$$

where x_1 and x_2 are the relative contributions of methyl and ethyl alcohols respectively.

Solving for x_1 and x_2 , we obtain

$$x_1 = 5.05; \quad x_2 = 49.29$$

In order to determine the mole per cent of the components, we proceed as follows:

Component	Values of x	Sensitivity, (in divisions/micron)	Partial pressure (in microns) $p = x/S$	Mole per cent
CH ₃ OH	5.05	8.76	0.576	17.37
	(5.05)		(0.576)	(17.354)
C ₂ H ₅ OH	49.29	17.98	2.74	82.62
	(49.29)		(2.746)	(82.645)
			$\Sigma 3.316$ (3.323)	

Problem 11.42: Determine the mole per cent of each component in a mixture, using the mass spectral data of pure components and the intensities of the peaks in the mass spectrum of the unknown mixture given below. The sensitivity parameters (in divisions/micron) respectively for methyl, ethyl, *n*-propyl alcohols are 8.76, 17.98, 26.51.

m/e	Percentage of component			Line intensity in the spectrum of the mixture
	CH ₃ OH	C ₂ H ₅ OH	<i>n</i> -C ₃ H ₇ OH	
15	35.48	9.44	3.77	
19	0.29	3.13	0.90	
27	—	21.62	15.20	
29	58.80	21.24	14.14	
31	100	100	100	
32	68.03	1.14	2.25	2600
33	0.98	—	—	
39		—	4.00	3000
43		7.45	3.18	
45		37.33	4.39	
46		16.23	—	800
59			9.61	
60			6.63	

Solution Let x_1 , x_2 and x_3 be the contributions of the methyl, ethyl and *n*-propyl alcohols respectively.

Proceeding as in the above problem, we write

$$2600 = 68.03x_1 + 1.14x_2 + 2.25x_3$$

$$3000 = 4x_3$$

$$800 = 16.23x_2$$

Solving for x_1 , x_2 and x_3 , we get

$$x_2 = 49.29; \quad x_3 = 750, \quad x_1 = 12.58$$

Component	Values of x	Sensitivity (in divisions/ μ)	Partial pressure (in μ); $p = x/S$	Mole Per cent
CH ₃ OH	12.58	8.76	1.43	4.40
	(12.58)		(1.43)	(4.42)
C ₂ H ₅ OH	49.29	17.98	2.74	8.44

(Continued)

Component	Values of x	Sensitivity (in divisions/ μ)	Partial pressure (in μ); $p = x/S$	Mole Per cent
	(49.29)		(2.74)	(8.44)
n-C ₃ H ₇ OH	750	26.51	28.29	87.15
	(750)		(28.30)	(87.13)
			$\Sigma 32.46$ (32.480)	

Problem 11.43: Determine the mole per cent of each component of a gas mixture, using the mass spectra of pure components and the intensities of the lines in the mass spectrum of the mixture given below in the tabular form. The sensitivity coefficients S for n -butane, isobutane, propane, ethane and methane are, respectively, 0.396, 0.464, 0.335, 0.392, and 0.246.

m/e	Percentage of component					Line intensity in the spectrum of the mixture
	n -butane	isobutane	Propane	Ethane	Methane	
15	5.30	6.41	6.19	4.57	85.6	167.3
16	0.12	0.18	0.15	0.08	100	134.2
28	32.6	2.62	59.1	100	—	757.2
30	0.98	0.13	2.20	26.2	—	130.1
31	—	—	—	0.55	—	2.4
43	100	100	22.8	—	—	207.4
44	3.33	3.33	29.0	—	—	145.4
50	1.29	0.89	—	—	—	0.6
55	0.93	0.42	—	—	—	0.7
57	2.42	3.0	—	—	—	2.5
58	12.3	2.73	—	—	—	5.0

Solution Let x_1 , x_2 , x_3 , x_4 and x_5 are the contributions of n -butane, isobutane, propane, ethane and methane respectively.

Proceeding as in the above problems, the base peaks chosen are m/e : 16, 30, 44, 57 and 58.

Accordingly, we write

$$m/e : 16, 134.2 = 0.12x_1 + 0.18x_2 + 0.15x_3 + 0.08x_4 + 100x_5$$

$$m/e : 30, 130.1 = 0.98x_1 + 0.13x_2 + 2.20x_3 + 26.2x_4$$

$$m/e : 44, 145.4 = 3.33x_1 + 3.33x_2 + 29.0x_3$$

$$m/e : 57, 2.5 = 2.42x_1 + 3.0x_2$$

$$m/e : 58, 5.0 = 12.3x_1 + 2.73x_2$$

Solving this set of equations. for x_1 , x_2 , x_3 , x_4 , and x_5 , we obtain

$$x_1 = 0.270; x_2 = 0.615; x_3 = 4.961; x_4 = 4.535 \text{ and } x_5 = 1.3295.$$

Component	x	S	$p = x/S$	Mole per cent
n -butane	0.270 (0.271)	0.396	0.681 (0.686)	2.01 (2.03)
isobutane	0.615 (0.614)	0.464	1.325 (1.323)	3.92 (3.93)
propane	4.961 (4.912)	0.335	14.808 (14.662)	43.82 (43.56)
ethane	4.535 (4.539)	0.392	11.568 (11.581)	34.24 (34.41)
methane	1.3295 (1.329)	0.246	5.404 (5.404)	15.99 (16.05)
			$\Sigma 33.786$ (33.656)	

Program Name: MOLE_PER.CPP**Purpose:** This program in C++ is for quantitative analysis of mixtures by mass spectrometry.**Compiled by:** Hardeep Kaur Randhawa, Assistant Professor, Department of Computer Science and Applications, Kanya Maha Vidyalaya, Jalandhar.

```

#include <iostream.h>
#include <conio.h>
#include <stdlib.h>
#include <iomanip.h>
const int SIZE = 35;
class mol_per
{
    private:
        int n;
        float h[SIZE][SIZE], s[SIZE], x[SIZE], mol_pt[SIZE], par_pr[SIZE];
    public:
        void input_data( );
        void cal_rel_cont( );
        void cal_mol_p( );
        void output( );
};

class out1
{
    int x1, y1;

    public:
        out1 (int i1, int j1) {x1=i1; y1=j1;}
        ~ out1( ) { }
        friend ostream & operator<<(ostream &stream, out1 o1);
};

class out2
{
    int x2, y2;
    public:
        out2(int i2, int j2) {x2=i2; y2=j2;}
        ~ out 2( ) { }
        friend ostream &operator<<(ostream &stream, out2 o2);
};

//Function to enter data
void mol_per:: input_data( )
{
    int i, j;
    cout<<"\n INPUT : \n";
    cout<<"\nEnter the number of constituent components of the mixture (n) : ";
    cin>>n;
    cout<<"\nEnter the coefficients, constant term and the sensitivity for";
    cout<<"each constituent of the mixture : \n\n";
    for (i=0; i<n; i++)
    {
        for (j=0; j<=n; j++)
            cin>>h[i][j];
        cin>>s[i];
    }
}

//Function to calculate relative contributions of the components of a mixture
void mol_per :: cal_rel_cont( )
{
    int k, m, p, q, i, j;
    float temp, temp1, max;
    for (k=0; k<n; k++)
    {

```

```

        max=abs (* (* (h+k)+k) );
        p=k;
        for(m=k+1; m<n; m++)
        {
            if (abs (* (* (h+m)+k) )>max)
            {
                max=abs (* (* (h+m) + k) );
                p = m;
            }
        }
        if(p!=k)
        {
            for (q=k; q<=n; q++)
            {
                Temp1 = * (* (h+k)+q) ;
                * (* (h+k)+q) = * (* (h+p)+q) ;
                * (* (h+p)+q) = temp1;
            }
        }
        temp = * (* (h+k)+k) ;
        if (temp==0)
        {
            cout<<"h["<<k+1<<"] [<<k+1<<"] = "<<temp<<endl;
            cout<<"Division by zero is not permissible"<<endl;
            exit(0);
        }
        for (j=k; j<=n; j++)
            * (* (h+k)+j) = * (* (h+k)+j) /temp;
        for (i=0; i<n; i++)
        {
            if(i!=k)
            {
                temp = * (* (h+i)+k) ;
                for(j=k; j<=n; j++)
                    * (* (h+i)+j) = * (* (h+i)+j) - temp * (* (* (h+k) + j) );
            }
        }
        for (i=0; i<n; i++)
        {
            * (x + i) = * (* (h+i)+n) ;
        }
    } //End of member function cal_rel_cont( )
//Function to calculate partial pressure and molepercent
void mol_per :: cal_mol_p( )
{
    int i;
    float sum;
    sum=0.0;
    for(i=0; i<n; i++)
    {
        * (par_pr+i) = * (x+i) / (* (s+i));
        sum = sum + * (par_pr+i);
    }
    for(i=0; i<n; i++)
    {
        * (mol_pt+i) = (* (par_pr+i) * 100) / sum;
    }
} //End of member function cal_mvl_p( )
ostream &operator<< (ostream &stream, out1 ol)
{
    register i, j;
    stream << "\n";
    for(j=1; j<=ol.y1; j++)
    {
        stream<<"*";
        for(i=0; i<ol.x1; i++)

```

```

        stream<<"-";
    }

    stream<<"*"<<"\n";
    return stream;
}

ostream &operator<<(ostream &stream, out2 o2)
{
    register i2, j2;
    for(i2=1; i2<=o2.x2; i2++)
        stream<<" ";
    stream<<"|";
    for(j2=1; j2<=o2.y2; j2++)
        stream<<" ";
    return stream;
}

//Manipulator to print "Press any key to continue"
istream &cont(istream &stream)
{
    cout<<"\nPress any key to continue :\n";
    getch( );
    return (stream);
}

//Manipulator to clear the screen
ostream &clr_scr(ostream &stream)
{
    clrscr( );
    return(stream);
}

//Function to pause the output
void stop(int i)
{
    out1 ob(25, 3);
    if (i==7 || i==15 || i==23 || i==31)
    {
        cin>>cont;
        cout<<clr_scr;
        cout<<ob;
    }
}

//Manipulator to set the format
ostream &fmt(ostream &stream)
{
    stream.setf (ios::fixed);
    stream.width (10);
    stream.precision (5);
    stream.setf(ios::showpoint);
    return stream;
}

//Function to display output
void mol_per::output( )
{
    Out1 a(25, 3), *pa;
    out2 b03(0, 3), b25(2, 5), b0_10(0, 10), b69(6, 9), b0_13(0, 13), b99(9, 5);
    out2 b57(5, 7), b70(7, 0), b80(8, 0), b78(7, 8), b89(4, 9);
    out2 *pb03, *pb25, *pb0_10, *pb69, *pb0_13, *pb99, *pb57, *pb70;
    out2 *pb80, *pb78, *pb89;
    int i;
    pa = &a;
    pb03 = &b03; pb25 = &b25; pb69 = &b69; pb0_10 = &b0_10;
    pb80 = &b80; pb99 = &b99; pb57 = &b57; pb0_13 = &b0_13;
    pb70 = &b70; pb78 = &b78; pb89 = &b89;
    cin>>cont;
    cout<<clr_scr;
    cout<<"\n OUTPUT : \n";
    cout<<*pa;
    cout<<*pb03<<"Relative Contribution"<<*pb25<<"Partial Pressure"<<*pb57<<"Mole Per cent"
<< *pb70;

```



```

cout<<endl<<*pb0_13<<"x[i]"<<*pb99<<"par_pr[i] (micron)"<<*pb89<<"mol_pt[i]"<<*pb80;
cout<<*pa;
for(i=0; i<n; i++)
{
cout<<*pb0_10<<fmt<<x[i]<<*pb69<<fmt<<par_pr[i]<<*pb78<<fmt<<mol_pt[i]<<*pb80;
cout<<*pa;
stop(i);
}
cin>>cont;
} //End of function output( );
void main( )
{
mol_per obj;
char ch;
cout<<clr_scr;
do
{
obj.input_data( );
obj.cal_rel_cont( );
obj.cal_mot_p( );
obj.output( );
cout<<"\nDo you want to solve any other equation?";
cout<<"Enter y or Y for yes and any other key for no : ";
ch = getche( );
}while (ch == 'y' || ch == 'Y');
}
/*End of the program*/

```

Let us solve problem 11.46 by using this program.

This program accepts a number of components, coefficients, i.e. peak heights of the pure components at a particular selected value of the mass number, the constant term, i.e. the peak height of the respective component in the spectrum of the mixture at the selected mass number, the sensitivity (in divisions/ μ) corresponding to the respective constant. The program displays relative contributions, partial pressures (μ) and composition of the mixture in mole per cent.

The output of one run of the program is given here.

INPUT:

Enter the number of constituent components of the mixture (n) : 5

Enter the coefficients, constant term and the sensitivity for each constituent of the mixture:

0.12	0.18	0.15	0.08	100	134.2	0.396
0.98	0.13	2.2	26.2	0.0	130.1	0.464
3.33	3.33	29.0	0.0	0.0	145.4	0.335
2.42	3.0	0.0	0.0	0.0	2.5	0.392
12.3	2.7	0.0	0.0	0.0	5.0	0.246

Press any key to continue:

Output:

<i>Relative Contribution</i>	<i>Partial Pressure</i>	<i>Mole per cent</i>
x[i]	Par_pr[i](micron)	Mol_pt[i]
0.27169	0.68608	2.03832
0.61417	1.32365	3.93252
4.91207	14.66290	43.56317
4.53997	11.58157	34.40859
1.32957	5.40475	16.05739

Press any key to continue:

Do you want to solve any other equation? Enter y or Y for yes and any other key for no : n

Note:

- While entering the data it should be kept in mind that there should be one blank space between any two consecutive values and at the end of each line of data entry, press Enter.

- This program can handle a mixture containing a maximum of thirty-five components. This number can be increased by changing the value of SIZE.

(n) Nature and Amount of Impurities The mass spectrum of the impure compound, say X , is recorded and the relative abundance of the various peaks is noted. From the positions of the peaks, the nature of impurities in the sample X is accomplished. In order to determine the amount of impurities in the sample X , the impurities in the standard sample are determined by chemical methods and the mass spectrum of the standard sample is recorded. Just by comparing the mass spectral data of the impure compound X with that of its standard sample, the amount of impurities in the impure sample of the compound can be determined.

Problem 11.44: In the mass-spectrometric determination of impurities in gallium arsenide, the lines were obtained for singly charged ions with mass numbers (m/e) equal to 16, 56, and 112 and the following values of the signals, respectively, 15, 35, 48 mV. The standard sample of gallium arsenide in which these impurities were determined by chemical means was found to contain 2×10^{-5} , 5×10^{-4} , and 3×10^{-4} per cent of the respective impurities and gave signals at 10, 50 and 72 mV.

Determine the nature of these impurities and their contents in the sample. (in percent).

Solution The peaks at m/e : 16, 56 and 112 in the mass spectrum of gallium arsenide correspond to singly charged oxygen (O^+), iron (Fe^+) and cadmium (Cd^+) ions respectively. We know that the peak height is a measure of the relative abundance of an ion. Accordingly,

$$\text{the amount of } O^+ \text{ in the sample} = \frac{2 \times 10^{-5} \times 15(\text{mV})}{10(\text{mV})} = 3.0 \times 10^{-5} \text{ per cent}$$

$$\text{the amount of } Fe^+ \text{ in the sample} = \frac{5 \times 10^{-4} \times 35(\text{mV})}{50(\text{mV})} = 3.5 \times 10^{-4} \text{ per cent}$$

$$\text{and of } Cd^+ \text{ in the sample} = \frac{3 \times 10^{-4} \times 48(\text{mV})}{72(\text{mV})} = 2.0 \times 10^{-4} \text{ per cent}$$

(o) Reaction Kinetics Mass spectrometry is used for the study of fast reactions, free radicals; equilibrium processes and exchange reactions. By using variable rate of gas flow, the time interval for the disappearance of a precursor ion and for the formation of a daughter ion can be calculated. From the peak height in the spectrum, the concentration of species at different time intervals can easily be calculated. A plot of time t against $\ln(\text{peak height})$ will be a straight line with slope equal to k , the specific rate constant. The activation energy E_a of the process can be determined from the Arrhenius equation,

$$k = Ze^{-E_a/RT} \quad (11.57)$$

provided the experiment is performed at least at two different temperatures, say T_1 and T_2 .

$$\text{Accordingly,} \quad \ln \frac{k_2}{k_1} = \frac{E_a(T_2 - T_1)}{RT_1T_2} \quad (11.58)$$

$$\text{or} \quad E_a = \frac{RT_1T_2}{(T_2 - T_1)} \cdot \ln \frac{k_2}{k_1} \quad (11.59)$$

11.16.2 Biological Applications of Mass Spectrometry

Although EIMS proved to be an invaluable method for the analysis of volatile compounds up to about 1000 Da, it is now possible to use other 'soft' ionisation techniques for analysis of nonvolatile compounds such as proteins, nucleic acids, and other compounds of biological importance with molecular masses up to and in excess 100,000 Da. Techniques such as ESI, IS, MALDI and FAB mass spectrometry have proved to be very potential tools for analysis of protein molecular masses, enzyme-substrate complexes, antibody-antigen binding, drug-receptor interactions, and DNA oligonucleotide sequence determinations. The ions produced by these techniques are separated by quadrupole mass filters, ion traps, time of flight and Fourier transform-ion cyclotron methods. For example, the electron-spray process

proved to be very useful for the molecular mass of macromolecules. The initial droplets produced by the electron-spray process usually have positive charges. Protonated or deprotonated droplets evaporate. In the naked macromolecule ions, entering the mass analyser, this charge is typically manifested as variable states of protonation at proton-accessible sites. The phenomenon results in ions with varying charges in the range +2 up to +40 or even higher. According to the multiple charge theory of Fenn (1989), the different charge states are interpreted as independent measurements of molecular mass and an averaging method based on the solution of simultaneous equations provides accurate molecular mass estimations of macromolecules. The molecular mass so determined from the sequence is the chemical molecular mass, i.e. the average value based on the natural abundance of isotopes. The molecular masses of some typical systems are listed here in Table 11.19.

Table 11.19 Molecular masses of some biological systems.

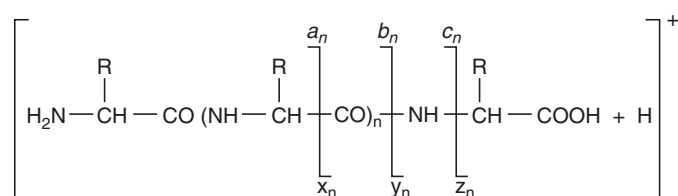
Bimolecule	Molecular mass (Da or amu)	Chares	m/e
Insulin (bovine)	5,730	4–6	950–1450
Cytochrome C (horse heart)	12,400	12–21	550–1100
Alcohol dehydrogenase (horse liver)	39,800	3 2–46	800–1300
α -Amylase(bacterial)	54,700	35–58	880–1550
Conalbumin (Chicken egg)	76,000	49–64	1200–>1500

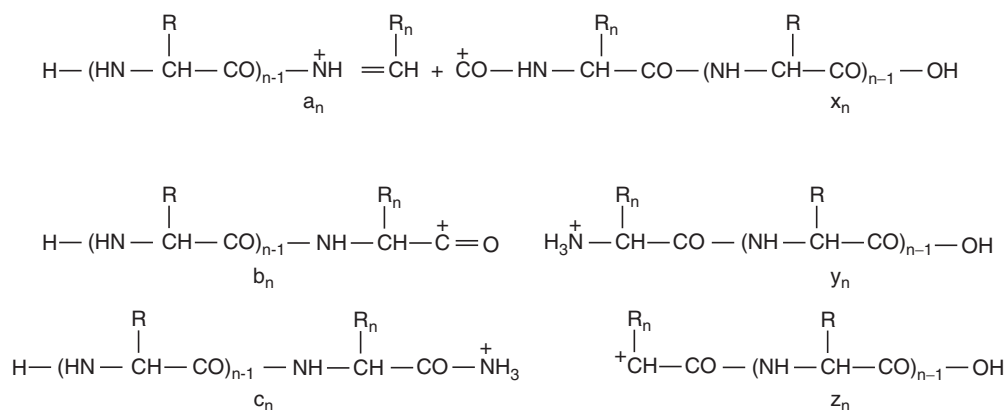
Fragmentation in Proteins and Peptides Proteins and peptides are linear polymers made up of twenty most common amino acids linked with each other by peptide bonds. However, the proteins produced by ribosomes may undergo covalent modifications, called post-translational modifications, after its incorporation of amino acids. Over 200 such modifications have been detected already, and the most important are indicated below:

Post- translational modification	Mass difference (Da)
Methylation	14.03
Propylation	42.08
Sulfation	80.06
Phosphorylation	79.98
Glycosylation	146.14
Carboxymethylation	58.04
Cysteinylation	119.14

The fragments that result are generally analysed by tandem mass spectrometry using soft ionisation techniques.

The first fragments that are identified are produced by cleavage of a bond in the main chain. The cleavage of a bond in that peptide chain can occur in either of three types of bonds $C_{\alpha}-C$, $C-N$ or $N-C_{\alpha}$ which yields six types of fragments that are labelled a_n , b_n and c_n , when a positive charge is kept by N -terminal side and x_n , y_n , and z_n when positive charge is retained by the C -terminal side. The c_n and y_n fragments implicate the transfer of two extra hydrogen atoms, the first one responsible for the protonation and a second one originating from the other side of the peptide. The subscript ' n ' indicates the number of amino acids present in the fragments. Main fragmentation paths of peptides in CID/MS/MS(CID/MSⁿ) are:

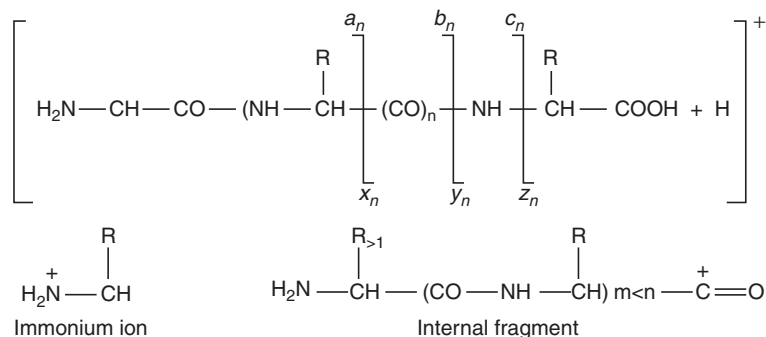




The mass difference between consecutive ions within a series allows one to determine the identity of the consecutive a/a and thus deduce the peptide sequence. There are two exceptions: Leu-Ileu which are isomers; and Gly-Lys, which are isobars. Normally, the spectra show several incomplete series of ions that produce redundant data and make the spectrum very complex.

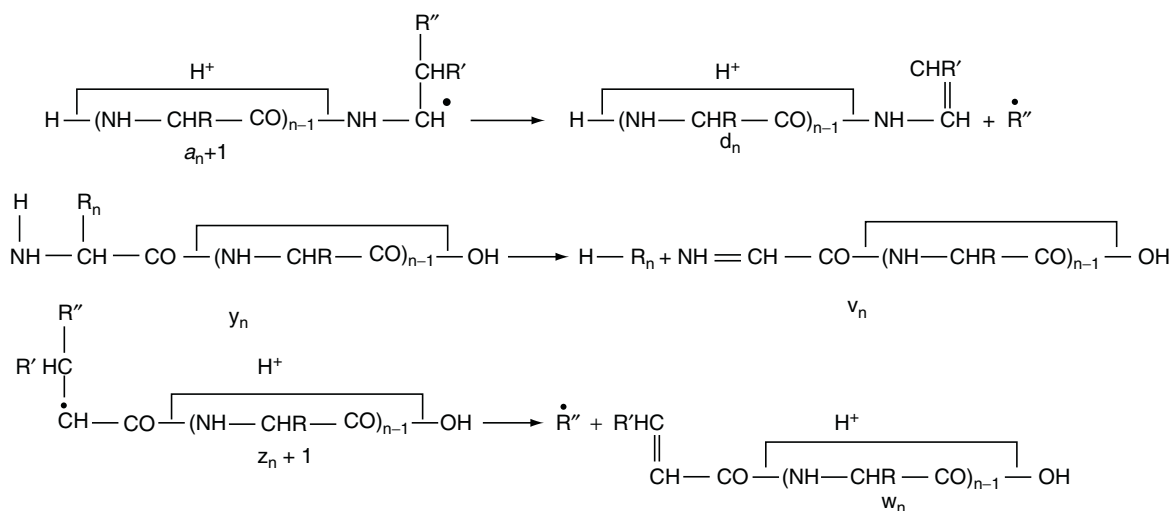
There is also a marked difference between the fragmentation at high and low energies.

Two other types of fragments found in most spectra result from the cleavage of at least two internal bonds in the peptide chain. This type of ions is often only weakly abundant and since they contain more than three or four a/a residues, they appear in the spectrum among the low masses; the exception proline contains imino group is included in a five-atom ring and thus has higher proton affinity than other peptide bonds. The second type of fragments requiring a cleavage of two bonds or a multiple cleavage of peptidic chain appearing among the low masses in the spectrum. These are immonium ions of a/a , labelled by a letter corresponding to the parent a/a code.



In addition to the ions described earlier, three new types of fragments that require the cleavage of the peptidic chain and amino-acid lateral chain are highlighted only in the high energy spectra. These fragments are useful to distinguish between isomers, e.g. Leu-Ileu.

Two of the fragment types originate from the cleavage of the bond between the β and γ carbon atoms of the side chain of a/a . These fragments are denoted by d_n or ω_n , respectively, according to whether the positive charge resides

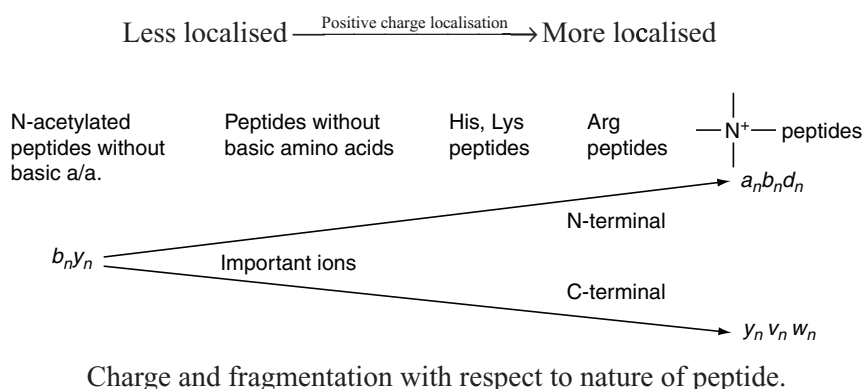


Fragmentation paths yielding the ions characteristic of a/a - a/a lateral chain

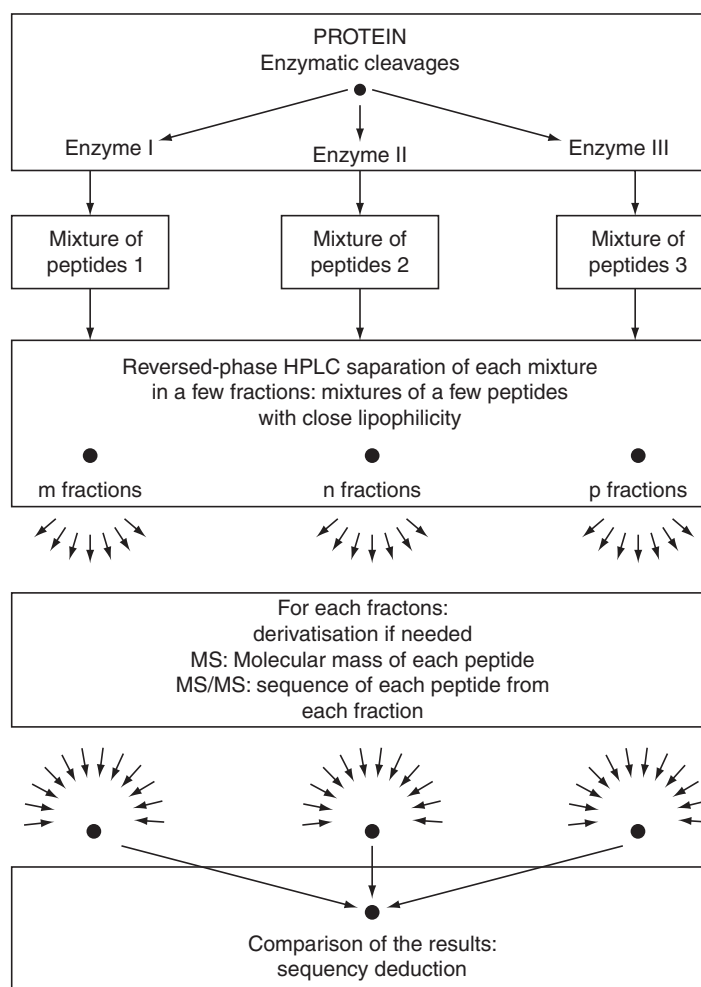
on N-terminal or the C-terminal fragment. They are useful to distinguish between isomers. Amino acids carrying an aromatic group attached to the β -carbon either do not display these two fragments or have very low abundance.

The other type of fragments results from the complete loss of the side chain and is denoted by v_n . This fragment containing the C-terminal moiety is intense for a/a that do not easily yield w_n type fragments. No equivalent containing the N-terminal moiety has ever been observed.

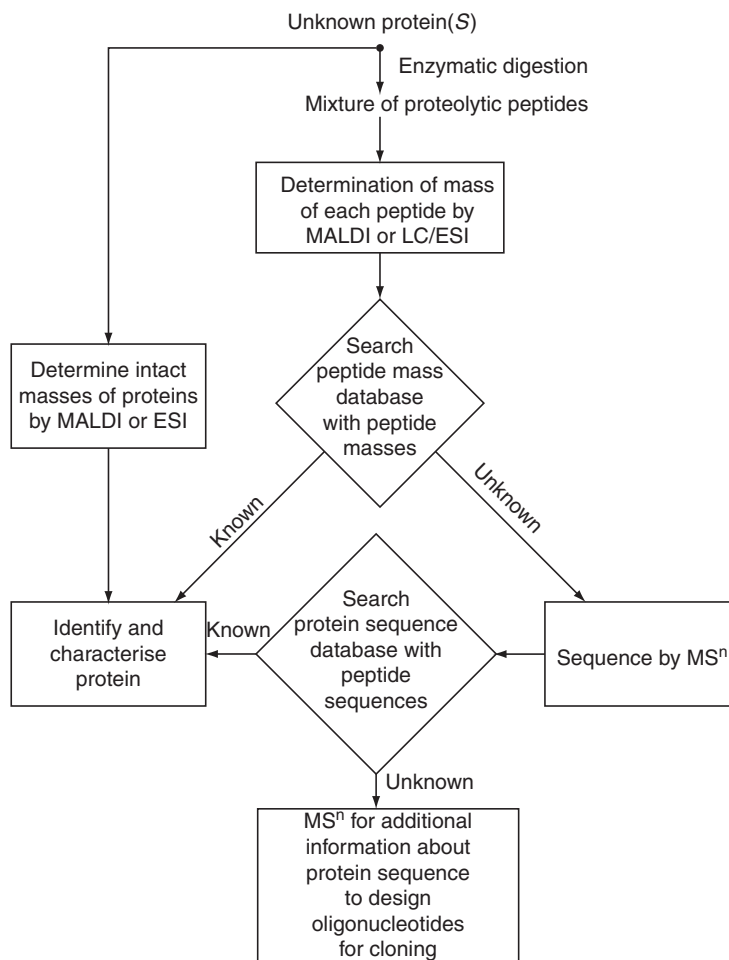
The charge and fragmentation depend upon the nature of the peptide. The rule describing the relationship between the position and charge localisation on the one hand and fragmentation process on the other is



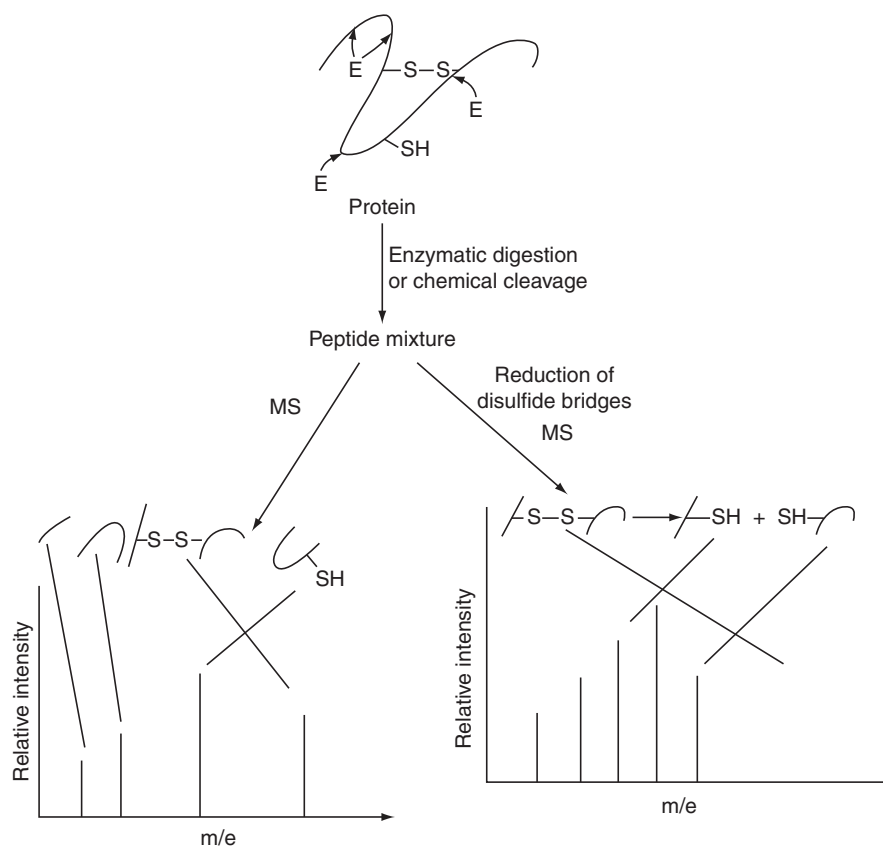
Some of the strategies adopted for identification, sequencing, identification and localisation of post-translation modification, verifying of structure and purity of peptides and proteins are listed here (1-6).



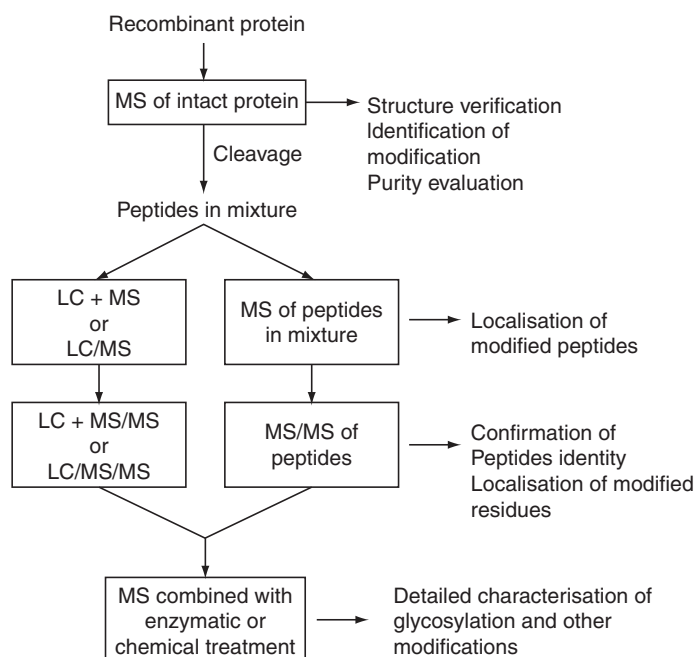
1. Strategy followed in sequencing proteins using mass spectrometry.



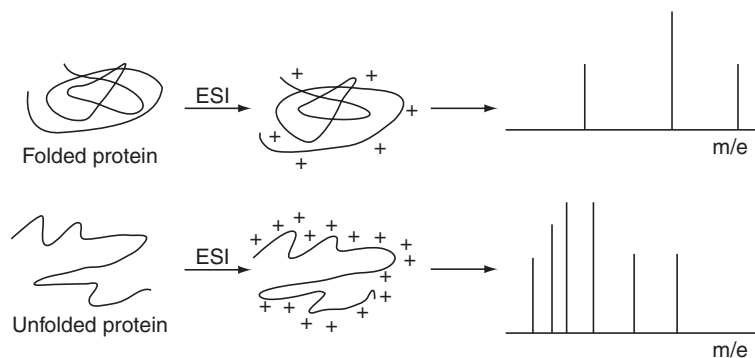
2. Strategy for the identification of proteins based on mass spectrometry.



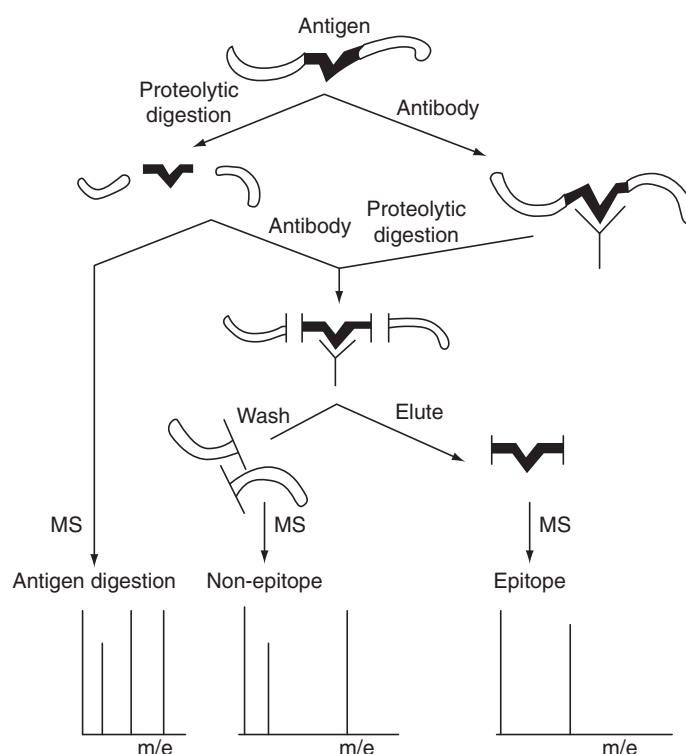
3. Strategy used to locate the cysteines linked by a disulfide bridge.



4. General strategy to characterise recombinant proteins.



5. Characteristic charge distribution of native or denatured protein.



6. Two different methods for the identification by mass spectrometry of an epitope recognised by a given antibody. The selection by affinity for the antibody is performed either before or after the enzymatic cleavage.

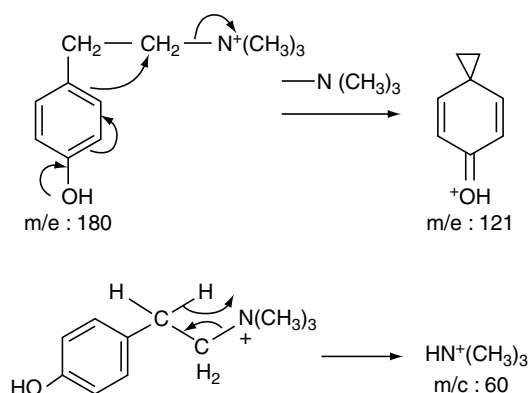
The sequencing and cloning of a protein which inhibits the proliferation of capillary endothelial cells *in vitro* has been achieved by electron spray-tandem mass spectrometry. Sequencing and DNA cloning of a peptide with *m/e*: 699.3 from endothelial cell growth inhibitor carried out by tandem mass spectrometry are compared with the deduced sequence of amino acids here.

Nucleic acid sequence of cloned gene	Deduced amino-acid sequence	Amino-acid sequence obtained by mass spectrometry
ATA GTT GCA ATT	Ileu—Val—Ala—	Lxx—Val—Ala—
AAT GTT CCT AAA	Ileu — Asn—Val—Pro—Lys	Lxx—Asn—Val—Pro—Lys

Here, Lxx is Leu or Ileu.

Electron-spray mass spectra for a synthetic oligonucleotide show major peaks at *m/e* : 709.1 ($M-6H$)⁶⁻, 608.0, 531.6, 472.4, 425.1, 386.3 ($M-11H$)¹¹⁻. Based on the mass spectral data, the sequence of nucleotides in the system has been found to be C—A—T—G—C—C—A—T—G—G—C—A—T—G.

The combination of desorption ionisation and MS/MS allows surface analysis of heterogeneous materials with both good sensitivity and selectivity in the real world also. The direct analysis of plant material is possible by SIMS. The direct detection of the quarternary alkaloid muscarine in fungal tissue is an example. The mushroom tissue is effectively sputtered into the gas phase by the primary ions of Ar⁺. The cation of muscarine shows a peak at *m/e* : 174 as expected. Positive ion MS/MS spectrum of *m/e* : 180 generated from a dried aqueous extract of the cactus *Trichocereus pacacana* by laser desorption mass spectrometry shows two major fragments which arise as illustrated from the quarternary alkaloid candicine. In this cactus, the quarternary compound is present at about 4 parts per thousand dry mass.



SI/LD-MS/MS has been used for the identification and quantitation of modified bases of nucleic acids since SI or LD mass spectrum of modified bases of nucleic acids contain intact ions corresponding to the nucleoside bases, e.g. 7-methylguanosine ($C_{11}H_{15}N_5O_5$, MM = 297) is characterised by the peaks at *m/e* : 282, 166 (base peak) and 149. The quantitation is carried out with *d*₃-labelled internal standard and an additional peak due to deuterated moiety at *m/e* : 169 also appears in the spectrum.

EI-GCMS has proved to be a very powerful tool for the analysis of the branched fatty acids of human skin surface, identification of volatile compounds in human urine, identification of drugs in body fluids such as gastric contents, blood or urine in emergency cases of acute poisoning, etc. For instance if EI-GCMS of the urine samples of an overdose victim shows peaks at *m/e* : 370, 356 and 245, the victim is supposed to have consumed the drug melleril (B) since the peaks are characteristic of parent drug (B) and its metabolites, (A) and (C) (Fig. 11.36).

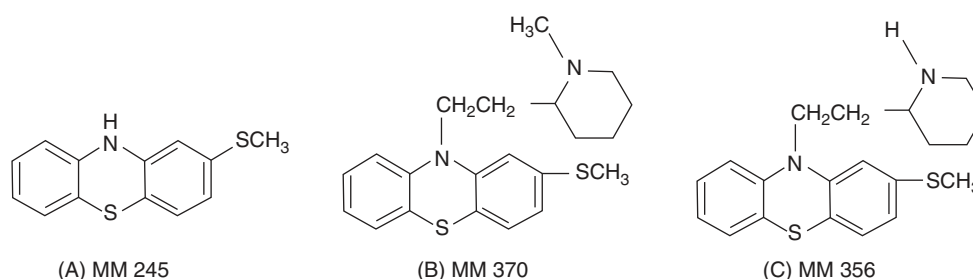


Fig. 11.36 Structures of the drug melleril (B) and two of its metabolites (A) and (C) found in the urine of an overdose victim.

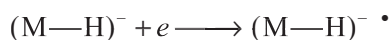
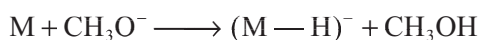
GCMS has also been successfully applied to detect morphine in the bile extract, codeine in the urine extract, amobarbital in the blood sample, etc., of drug addicts.

11.17 NEGATIVE-ION MASS SPECTROMETRY

Recall from sections 11.1–11.4 that when a molecule is subjected to high-energy electrons, a mixture of positive and negative ions as well as neutral species are formed. The energy of the bombarding electron is generally much higher than that of bonds which bind together the atoms in the molecule. Thus when high-energy electrons interact with the molecules, not only does ionisation occur, but bonds are broken and fragments are formed giving rise to ions, other than the intact molecular ion. Positive-ion EI spectra are most commonly recorded because many fewer negative ions are formed by this particular ionisation technique than positive ions. Positive ions are propelled into the analyser by maintaining the ion source at an electrical potential positive relative to the analyser and by focussing with voltages applied to a lens system located between the source and analyser. The repeller electrodes assist in focussing the ions into the analyser. Negative ions and electrons are attracted to the positively charged electron trap. Negative-ion mass spectrometry differs from positive-ion mass spectrometry that in the former, the dominant ionisation processes involved are slow electron attachment and/or dissociative attachment. The slow electrons needed for such attachment processes result mainly from the primary electron bombardment by the following mechanism.



The slow electrons required for the generation of stable carbanion can be obtained by the bombardment of either the sample molecules themselves or by an added gas, such as nitrogen or argon. The masses of negative ions, so produced, are sorted out as a function of their relative abundance. The relative abundance of ions is measured relative to the base peak (i.e. peak of highest intensity which is taken as 100 per cent abundance). Negative ions are not only produced by electron bombardment but by a variety of chemical reactions (observed in the negative chemical ionisation) described in Section 11.3. One of the limitations of negative-ion EI mass spectrometry is its low sensitivity since carbanions formed from most of the organic compounds are unstable. However, negative-ion chemical ionisation and desorption ionisation has solved the problem of low sensitivity to a great extent and these days just like its elder sister, it is promising for molecular structure determination not only of simple organic molecules but also of biological macromolecules, e.g. the negative-ion spectra of electron-loving compounds, namely quinones, trifluoroacetates and nitrocompounds can satisfactorily be scanned by CIMS which otherwise is very hard to scan satisfactorily by EIMS because of high energy of the bombarding electrons. The molecular collisions in the CI process lower down the initial kinetic energy of the bombarding electrons to such an extent that they are easily captured by the anions of the analyte molecule to produce the anion radicals. As an example, the CH_3O^- produced in the CI source behaves as a Brönsted base and deprotonates the sample molecule to generate an anion which captures an electron to give the radical anion.



The study of negative-ion spectra is especially useful in determining ion structures and energetics. Negative metastable ions aid in deducing the structure of molecules. Although multi-charged negative ions of molecules produced in the ionisation process are also well documented but to date no doubly charged negative atomic ions except O^{2-} has been reported. The existence of O^{2-} has been proved by accelerating mass spectrometry (AMS). Using 180-degree magnetic analyser and a Li vapour jet target, it is observed that no O^{2-} with a lifetime longer than 10^{-9} second accompanying the O^- ions are produced. Ca^- , Dy^- , etc., are well known.

Inorganic compounds which contain elements having high electron affinity, i.e. SO_2 , PCl_3 , IClO_3 , etc., or organic compounds containing electron-loving groups, namely F, NO_2 , Cl, etc., are most suited to negative-ion mass spectrometry since derivatisation by such groups would enhance substantially the electron-capturing capacity of the organic compounds. The electron affinities of some molecules, radicals, and atoms are listed in Table 11.20 for

Table 11.20 Electron affinity of some molecules, radicals and atoms.

System	Electron affinity (in eV)/kJ mole ⁻¹
Molecules: Ion formed	
BF ₃ ⁻¹	2.65/255
(p-Benzoquinone) ⁻	1.34/129
(Chloranil) ⁻	2.40/231
(Fluoranil) ⁻	2.27/218
NO ₂ ⁻	3.91/377
O ₂ ⁻	0.45/43
SF ₆ ⁻	1.43/138
(Tetracyanoethylene) ⁻	2.88/278
WF ₆ ⁻	2.74/264
UF ₆ ⁻	2.91/280
Radicals: Ion formed	
CH ₃ ⁻	1.08/104
C ₂ H ₅ ⁻	0.89/86
C ₃ H ₅ ⁻ (Cyclopropyl)	0.344/33.125
C ₆ H ₅ ⁻	2.20/210
CF ₃ ⁻	1.85/179
CCl ₃ ⁻	1.22/117
SiF ₃ ⁻	3.35/323
NH ₂ ⁻	1.12/108
C ₆ H ₅ NH ⁻	1.55/149
(C ₆ H ₅) ₂ N ⁻	1.19/114
PH ₂ ⁻	1.60/154
OH ⁻	1.83/176
CH ₃ O ⁻	0.38/36
CF ₃ O ⁻	1.35/131
SH ⁻	2.19/211
CH ₃ S ⁻	1.32/127
CN ⁻	3.17/305
SCN ⁻	2.17/209
SeCN ⁻	2.64/255
Atoms: Ion formed	
Br ⁻	3.363/324
C ⁻	1.12/108
Cl ⁻	3.613/348
F	3.448/333
H ⁻	0.80/77
*H-(1s ²)	0.747/72
I ⁻	3.063/296
O ⁻	1.466/142
S ⁻	2.07/200

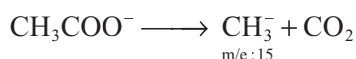
*Quantum mechanical calculation: The electron affinities of most simple alkyl radicals are negative, and consequently the anions are unstable with respect to their radicals.

ready reference. As in positive-ion mass spectrometry, fragmentation of the negative molecular ion occurs with the elimination of neutral molecule or of a free radical. Ions other than M^- , i.e. $[M-H]^-$, $[M-2]^-$, $[M-R]^-$ are also encountered in negative-ion mass spectra of molecules and they assist in accomplishing the fragmentation pattern of molecules. Moreover, negative-ion mass spectrometry is complimentary to positive-ion mass spectrometry.

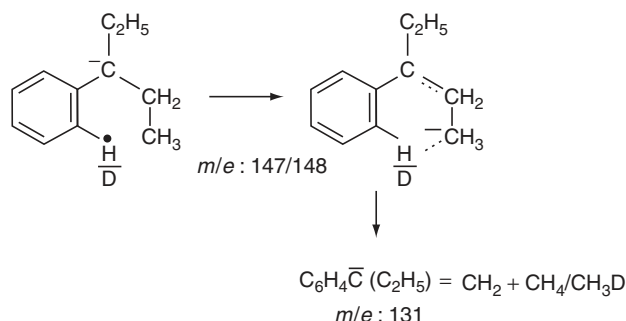
Recently, a new tool based on negative-ion mass spectrometry has been used for the structure determination of unknown molecules. Charge stripping of negative ion yields a decomposing positive ion, which produces a dissociative charge inversion spectrum of the negative ion. This technique allows the study of positive ions not available by conventional ionisation, it provides a fingerprint for the parent positive ion produced in the collision process, and it may be used to determine the structure of the precursor negative ion. Finally, a combination of negative ion spectrum and a charge inversion spectrum may be used as an analytical technique for the structure determination of unknown molecules.

The collision-induced negative-ion mass spectra of some organic compounds are described here.

(a) Hydrocarbons Simple alkanes being weakly acidic are not readily deprotonated even by the strongest base, $-NH_2$. Most of the simple alkyl radicals except $\dot{C}H_3$, $\dot{C}_2H_5$ and $\dot{C}_3H_5$ (cyclopropyl radical) have negative electron affinity so their anions are unstable relative to their respective radicals. But the anions corresponding to $H_3\dot{C}$, C_2H_5 and C_3H_5 can be produced indirectly by decarboxylation of the respective carboxylate ions. As an example,

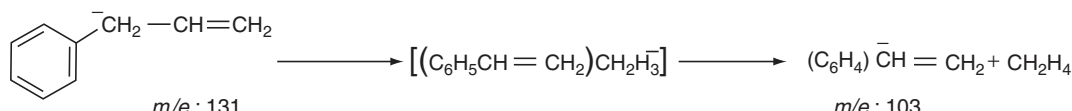


Olefins and benzyl derivatives can readily be deprotonated but benzyl anion undergoes collision-induced deprotonation. The negative-ion mass spectra of (i) $C_6H_5C(C_2H_5)_2$ and its deuterated derivative (ii) $C_6H_4DC(C_2H_5)_2$ show peaks at m/e (i) 147, 131 and (ii) 148, 131. The peak at $m/e : 131$ in the spectra originates from the fragmentation of deprotonated diethylbenzyl anion as follows:



The fragmentation pattern and isotope effect reveal that the loss of methane involves the terminal methyl group and a ring hydrogen; the removal of ring hydrogen is rate determining ($k_H/k_D = 3.75$).

Similarly, the fragmentation of deprotonated 4-phenylbutene occurs to give a peak at $m/e : 103$ with the loss of ethylene.



(b) Aromatic Hydrocarbons Negative-ion mass spectra of benzene, naphthalene and some polycyclic aromatic hydrocarbons are obtained using low-energy electrons. The spectra originate from electron capture with the subsequent expulsion of protons from the hydrocarbon or resonance electron capture or both, i.e.



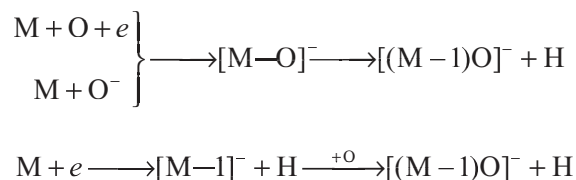
Higher condensed systems, however give M^- ions as base peaks.

Table 11.21 Negative-ion spectral data on some aromatic hydrocarbons.

Compound	Formula	n	Base Peak (m/e)	Other Peaks (m/e)
Benzene	C ₆ H ₆	1	77 (M - 1)	175
Naphthalene	C ₁₀ H ₈	2	127 (M - 1)	126, 125
Anthracene	C ₁₄ H ₁₀	3	178 (M)	177
Phenanthrene	C ₁₄ H ₁₀	3	177 (M - 1)	178, 176, 175
Pyrene	C ₁₆ H ₁₀	4	202 (M)	201
Tetracene	C ₁₈ H ₁₂	4	228 (M)	227

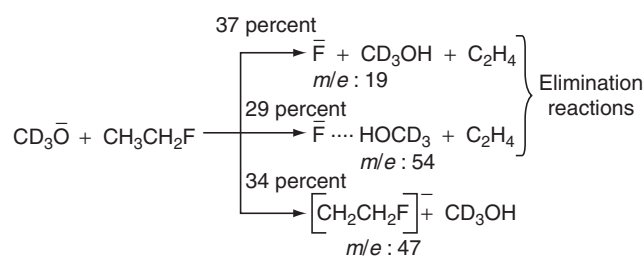
The negative-ion spectral data on some aromatic hydrocarbons have been listed in Table 11.21.

The negative-ion mass spectra of aromatic hydrocarbons also show peak at M + 15. This is attributed to the addition of oxygen atom (present in the ion source) which takes place according to one of the following mechanisms.

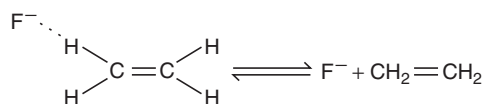


The ease of addition of oxygen atom in the polycyclic aromatic series follows the order: Tetracene > Anthracene > Naphthalene. The peaks at *m/e* (peak height) : 258 (7 mm), 243 (16.5 mm), 228 (35 mm) in the spectra of tetracene correspond to (M + 30), (M + 15) and M⁻ respectively. In case of anthracene, the peaks at *m/e* (peak height): 178 (34 mm) and 193 (7 mm) are attributed to M⁻ and (M + 15) respectively.

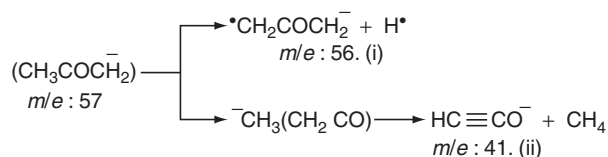
(c) Alkyl Halides The negative-ion mass spectra on the reactions of alkyl halides with strong base in the gas phase reveal that the reactions proceed either via S_N² or elimination mechanism. However in alkyl fluorides, deprotonated species have also been detected. As an example, the reaction of CD₃O⁻ base with ethylfluoride follows the scheme:



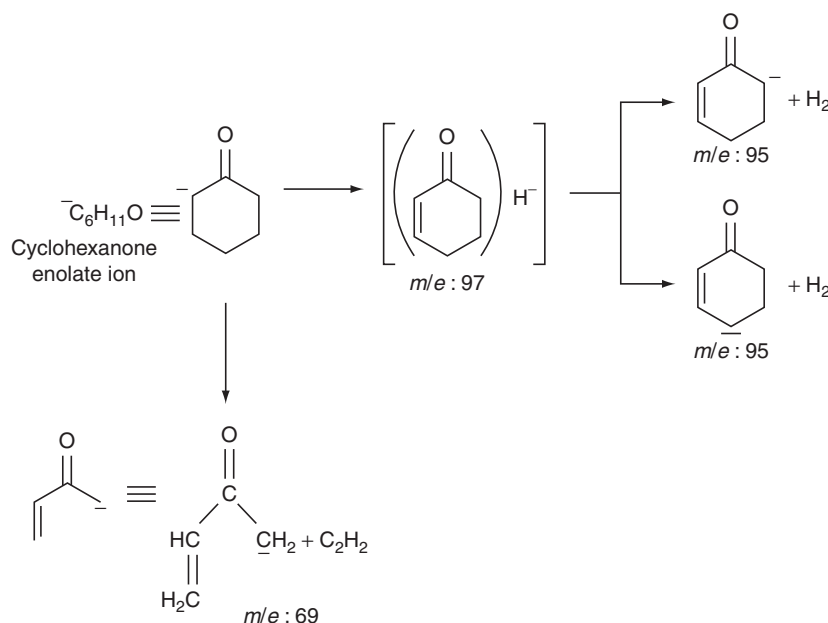
The stability of β-fluoroethyl anion is attributed to the negative or anionic hyperconjugation. The anion will give F⁻ and C₂H₄ on collision activation.



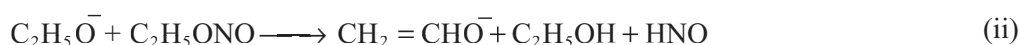
(d) Ketones The negative-ion mass spectrum of deprotonated acetone shows peaks at *m/e* : 57, 56 and 41. The peak at *m/e* : 57 corresponds to the acetate enolate ion (CH₃COCH₂⁻). The other two peaks in the spectrum result from the fragmentation of enolate ion by the following two processes.



The peaks at m/e : 97, 95 and 69 in the mass spectrum of deprotonated cyclohexanone arise due to the following scheme:



(e) Alkyl Nitrites The ion cyclotron resonance (ICR) spectra of alkyl nitrites (RONO) which contain at least one hydrogen substituent on each of the α and β carbon atoms, show peaks corresponding to both RO^- and $(\text{RO}^- - \text{H}_2)$ ions. As an example, in case of ethylnitrite, the $(\text{EtO}^- - \text{H}_2)$ ion at $m/e : 43$ correspond to the enolate $\text{CH}_2 = \text{CHO}^-$ that is produced by the following three processes [(i)–(iii)]



Excited ethoxide
negative ion

The ICR and theoretical studies suggest that the most plausible mechanism for the elimination of H_2 from the ethoxide ion is

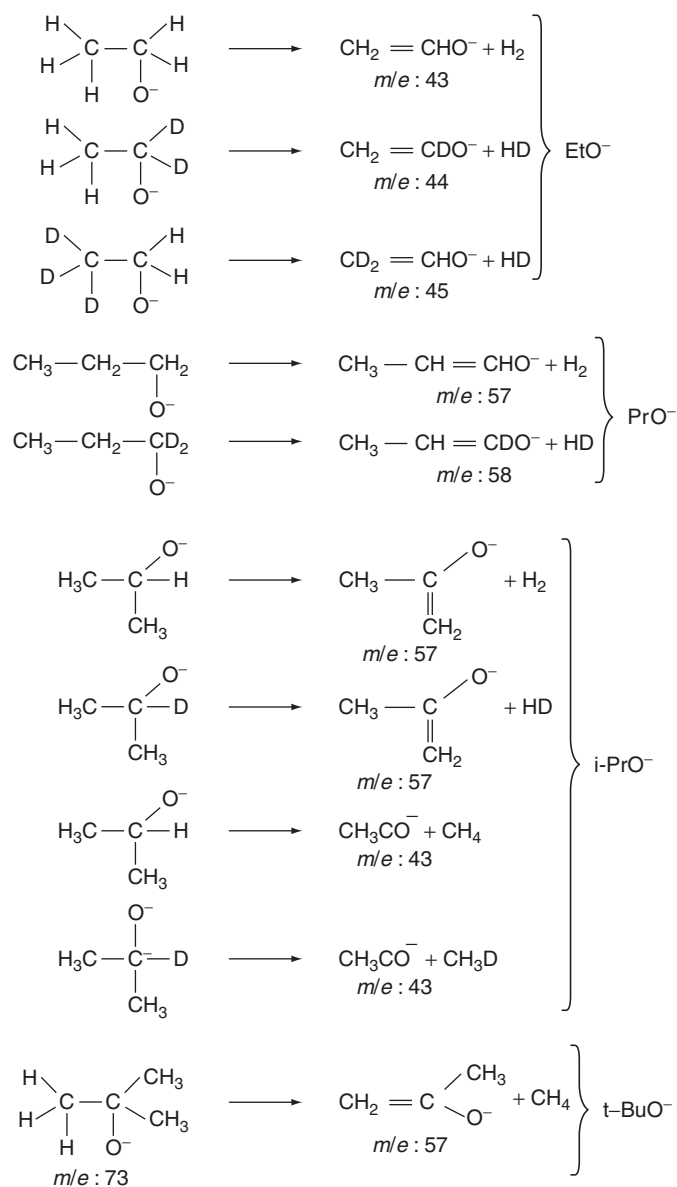


The negative-ion mass spectra of alkoxide ion produced by dissociative secondary electron capture (the energy of primary electron beam being 70 eV) from alkyl and deuterated alkyl nitrites using N_2 as collision gas (since it gives slightly higher isotope effects than those obtained from argon and helium), recorded in Table 11.22 suggest that in cases where losses of H_2 and CH_4 are competitive, the step (i) is always more pronounced than step (ii).

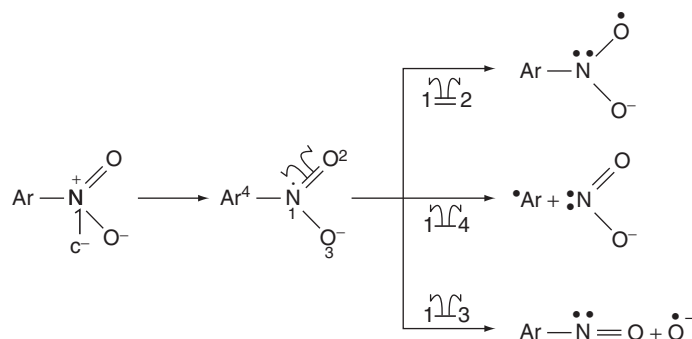
Table 11.22 Collision-induced losses of H_2 and CH_4 from RO^- ions generated from alkyl nitrites.

R in RO^-	Loss(es)	m/e	R in RO^-	Loss(es)	m/e
Me	—	—	CD_3	—	—
Et	H_2	43	CH_3CD_2	HD	44
			CD_3CH_2	HD	45
Pr	H_2	57	$CH_3CH_2CD_2$	HD	58
			$CH_3CD_2CH_2$	HD	58
i-Pr	H_2, CH_4	57, 43	$(CH_3)_2CD$	HD, CH_3D	57, 43
Bu	H_2	71	$(CD_3)_2CH$	HD, CD_3H	62, 46
i-Bu	H_2, CH_4	71, 57			
t-Bu	CH_4	57			
$Me(CH_2)_4$	H_2	69			
Me_3CCH_2	CH_4	55			

The enolate ions are produced by the following scheme:

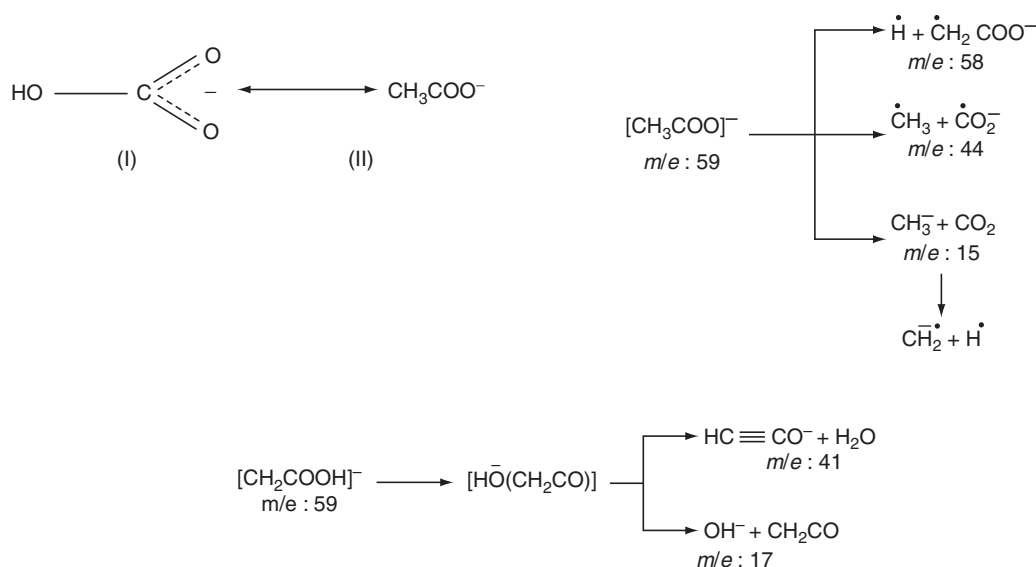


(f) Nitro Compounds The dissociative resonance electron capture negative-ion mass spectra of nitro aromatics are interpreted by the following fragmentation scheme.



The negative ion mass spectrum of nitrobenzene shows peaks at m/e : 123, 46, 16.

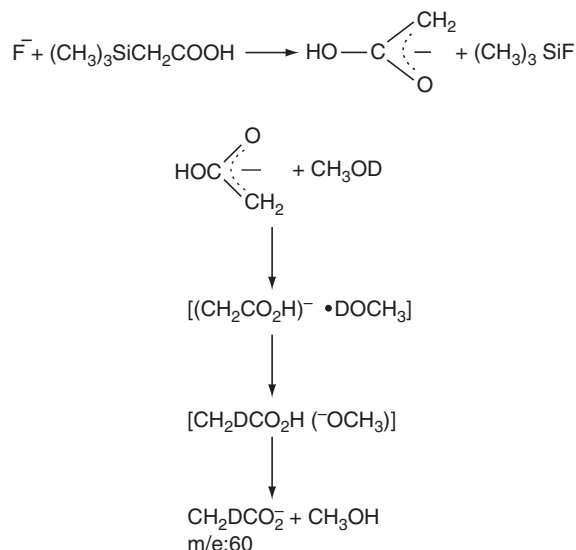
(g) Carboxylic Acids Collision activation negative-ion mass spectra of deprotonated carboxylic acids in the gas phase using He as a collision gas reveal that the deprotonated acids exist as carboxylate and enolate anions in significant amounts. The interconversion of enolate anion (I) to carboxylate anion (II) vice versa occurs under conditions of single collision activation; Both the anions are characterised by their modes of fragmentation. As examples, the single collision activation mass spectra of enolate- and carboxylate anions produced respectively from $(\text{CH}_3)_3\text{SiCH}_2\text{COOH}$ and $\text{CH}_3\text{SiOCOCH}_3$ using $\text{CH}_3\text{O}^-(\text{CH}_3\text{ONO})$ as a deprotonation-inducing base and He as a collision or bath gas show similar peaks but with different per cent abundances at m/e : 59, 58, 44, 41, 17, 15, 14 : These peaks are attributed to the ion fragments formed from the parent anions by the following modes of fragmentation:



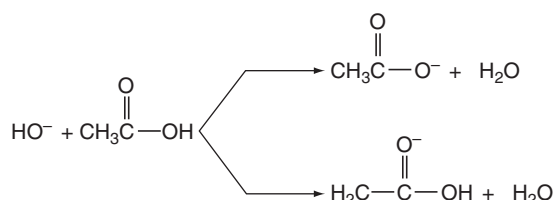
The observed spectra of both the anions are similar so far as their m/e values are concerned. However a minor formation of CH_3^- from (I) and this together with the formation of 41 from (II) implies that the carboxylic acid enolate anion and the acetate anion are interconvertible under identical conditions of collision activation. The I-II transformation is possible only provided the barrier for 1, 3 H^+ - transfer is lower than that for 1, 2 H^+ - transfer. The conversion of a carboxylate anion by 1, 3 H^+ - transfer to the enolate anion prior to fragmentation is a standard reaction of alkyl carboxylate anions (M B Stringer et.al, J. Chem. Soc., Perkin Trans II (1987) 385)

The charge reversal, i.e. positive ion spectra of both the anions, are quite different; m/e values of common peaks in both the spectra are same but their intensities are quite different. Base peak for I appears at m/e : 42 and at m/e : 44 for II. Major ions corresponding to I are CO_2^+ (26 per cent) and HCO_2^+ (65 per cent) while for II are CH_3^+ (31 per cent) and CO_2^+ (100 per cent). This confirms the initial difference between the structures of the two anions.

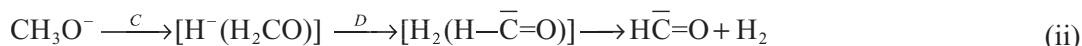
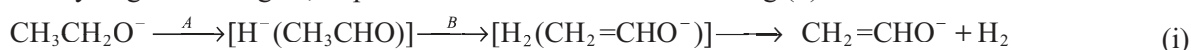
The negative ion mass spectrum of deprotonated $(\text{CH}_3)_3\text{SiCH}_2\text{COOH}$ in the gas phase using F^- as a deprotonation inducing base and in flowing after glow reveals that only enolate ion I is formed and it ($m/e : 59$) reacts readily with CH_3OD to form $m/e : 60$. Acetate anion does not react with CH_3OD under these conditions.



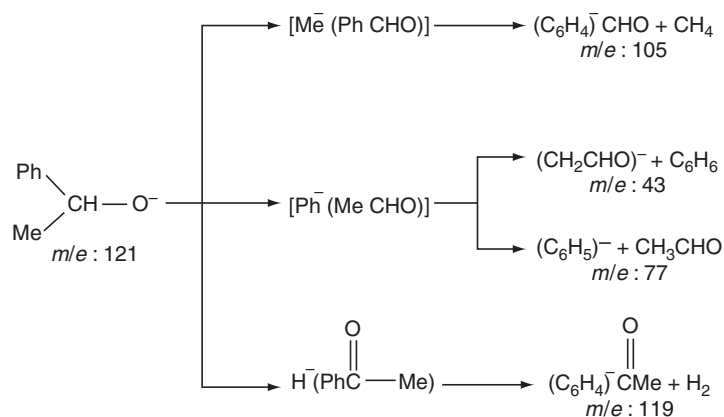
Gas-phase collision-induced mass spectra of deprotonated acetic acid using hydroxide (OH^-) as a deprotonation-inducing base show that significant amounts of the carboxylate and enolate anions are produced. However, the unimolecular I–II transformation does not take place significantly.



(h) Alcohols and Phenols The collision-induced decompositions of simple alkoxides occur with the 1, 2-loss of dihydrogen from alkoxide stepwise. For example, fragmentation of ethoxide takes place via hydride ion-aldehyde complex. Steps A and B are both rate determining (i). The methoxide ion, in contrast, undergoes a low yield 1, 1 elimination of dihydrogen. Here again, steps C and D are both rate determining (ii).



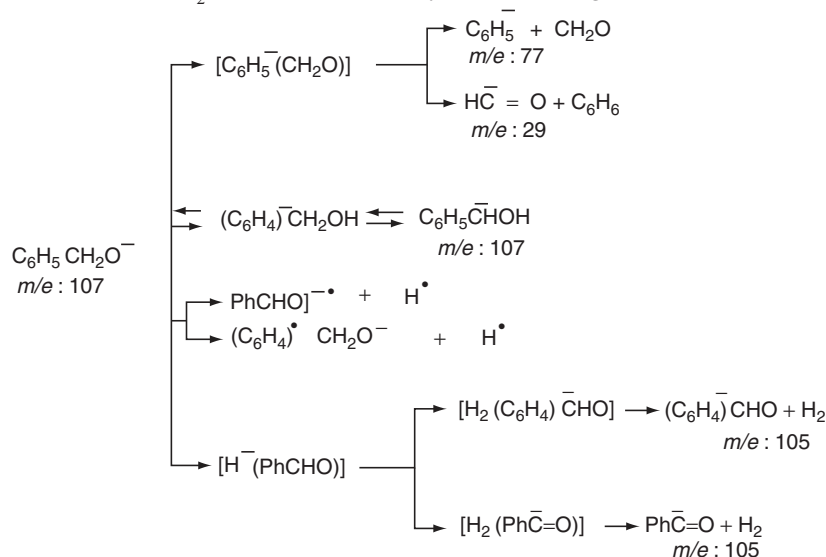
The collision-induced negative-ion spectra of alkoxide $\text{PhCH}(\text{CH}_3)\text{O}^-$ can be interpreted on the basis of decomposition of Wittig product ion $\text{Ph}-\text{CH}(\text{Me})-\text{O}^-$. The Wittig product ion undergoes competitive losses of methane, benzene or aldehyde according to the following scheme.



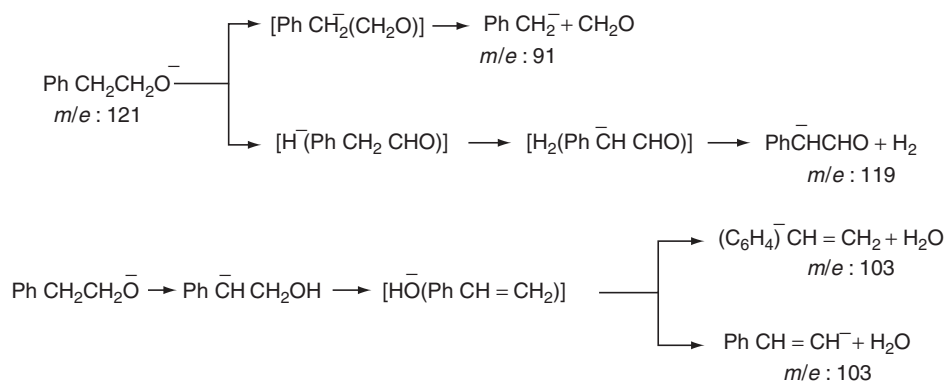
The collisional-induced dissociations of ion PhCH_2O^- (and its deuterated analogues PhCHDO^- , PhCD_2O^- , $\text{C}_6\text{D}_5\text{CH}_2\text{O}^-$) in the gas phase occur with the competitive losses of $\text{H}^\bullet$, H_2 , CH_2O and C_6H_6 . The loss of hydrogen, i.e. H_2 , takes place mainly to form $(\text{C}_6\text{H}_4)^-\text{CHO}$. The *abi initio* calculations show that hydrogen loss occurs by the following mechanism:



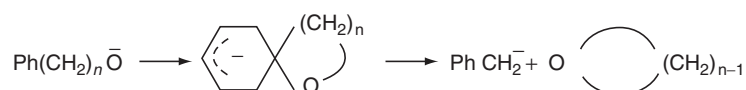
The losses of CH_2O and C_6H_6 are accompanied or preceded by partial phenyl H-benzyl H interchange. The negative-ion mass spectrum of PhCH_2O^- is rationalised by the scheme given below:



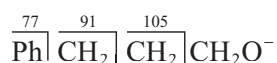
The peaks at $m/e : 121$, 119 , 103 and 91 in the collision activation negative-ion mass spectrum of $\text{PhCH}_2\text{CH}_2\text{O}^-$ (and its deuterated analogues $\text{PhCH}_2\text{CD}_2\text{O}^-$ and $\text{PhCD}_2\text{CH}_2\text{O}^-$) are attributed to the losses of H_2 , H_2O , CH_2O (losses for $\text{PhCD}_2\text{CH}_2\text{O}^-$ are HD , HOD and CH_2O while for $\text{PhCH}_2\text{CD}_2\text{O}^-$ are HD , H_2O , HOD and CD_2O) have been rationalised by the following mechanism of fragmentation.



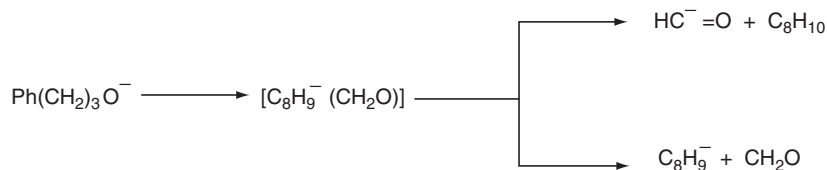
The collision-induced negative-ion mass spectra of ions $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{O}^-$ where, $n = 3 - 5$ being complex, is beyond the scope of this book. The ion $\text{Ph}(\text{CH}_2)_3\text{O}^-$ undergoes many fragmentations including losses of H_2O and CH_2O and loss of H_2 . The loss of H_2 occurs by both 1,2- and 1,3-eliminations. A number of minor fragmentations occurs after partial interchange of phenyl hydrogens and hydrogen at position 2. The first example of specific double-protons transfer is noted, viz. $\text{Ph}(\text{CH}_2)_3\text{O}^- \rightarrow \text{C}_6\text{H}_7^- + \text{CH}_2=\text{CHCHO}$. Ions $\text{Ph}(\text{CH}_2)_n\text{O}^-$ ($n = 2 - 5$) all decompose to produce PhCH_2^- ions; when $n = 3 - 5$ the reactions may involve Smiles intermediates, i.e.



For $n = 3$; peaks result in at $m/e : 77$, 91 and 105 , i.e

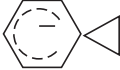


The other peaks are observed at m/e : 135, 133, 117 ($-\text{H}_2\text{O}$), 115, 103, 79 ($-\text{C}_3\text{H}_4\text{O}$), 57 ($-\text{C}_6\text{H}_6$), 43 ($-\text{C}_7\text{H}_8$), 29 ($\text{HC}=\text{O}$). The peaks at m/e : 79 (C_6H_7^-) is formed by a specific double H-transfer, the first such reaction to be reported for negative ions.

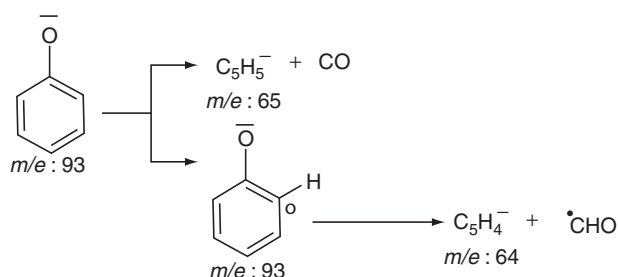


Two possible structures for C_8H_9^- ion are the following:

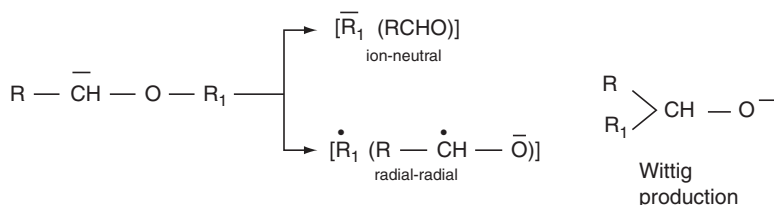
(i) **Ion $\text{PhCH}_2\text{CH}_2^-$** Formed by the direct loss of CH_2O . This seems like a lesser possibility, but may be stabilised by negative hyperconjugation.

(ii) **Spiro ion:**  Mass spectra of C_8H_9^- is still not established,

Simple phenols are little studied. The phenoxide ion itself loses CO and CHO to give the fragment ions as follows:



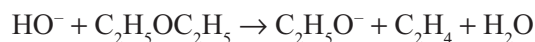
(i) **Ethers** Deprotonated ethers undergo Wittig rearrangement involving either of the ion-neutral or radical-radical intermediates shown in Scheme 1 followed by collision-induced products from the intermediates.



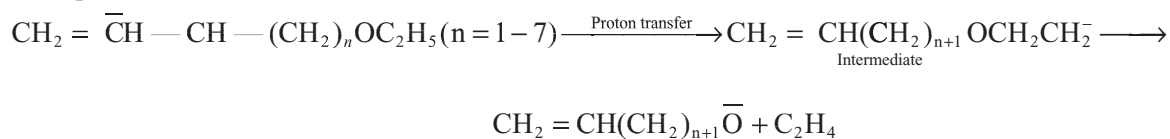
Scheme 1 $\text{R} = \text{C}_6\text{H}_5$ or $\text{CH}_2 = \text{CH}-$, $\text{R}_1 = \text{allyl, benzyl, alkyl, or aryl.}$

In the condensed phase, aldehydes are often by-products of the reaction and the migratory tendency of substituents R_1 is allyl $\approx$ benzyl $>$ methyl $>$ ethyl $>$ phenyl. Since the migratory tendency is in the order of free radical stabilities, it is suggested that the radical pair mechanism is more likely. The collision-induced negative-ion mass spectra of ions $\text{Ph}\ddot{\text{C}}\text{HOR}$ and $\text{Ph}(\text{R})\text{CH O}^-$ ($\text{R} = \text{alkyl or phenyl}$) are similar suggesting thereby that the Wittig rearrangement also occurs in the gas phase. Major fragmentations are best interpreted in terms of the Wittig product ion, i.e. $\text{R}(\text{R}_1)\text{CH}-\text{O}^-$. When R_1 is an alkyl group $>$ Me, the radical-radical intermediate is more pronounced, since the electron affinity of $\text{R}_1 \leq 0$. In view of it let us now see how Wittig rearrangement aids in interpreting the mass spectra of deprotonated ethers in the gas phase.

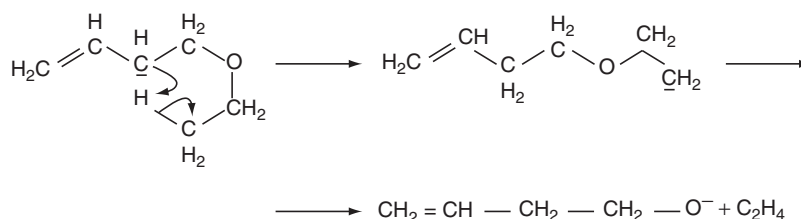
The reaction between simple dialkyl ethers R_2O ($\text{R} \geq \text{C}_2\text{H}_5$) and strong bases in the gas phase undergoes elimination reaction to give alkoxy anion rather than deprotonation process. For example,



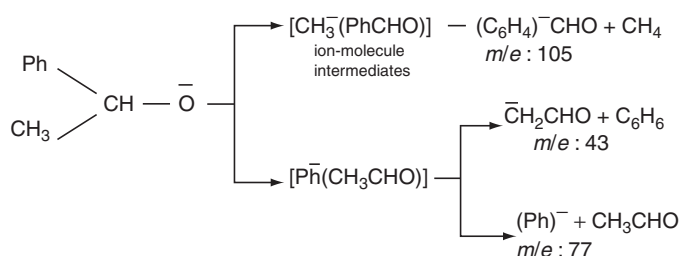
On the other hand, the unsaturated ethers undergo deprotonation at either the allylic or benzylic positions to form carbanions which undergo a number of collision-induced dissociations. For example, in allyl alkylethers, the reaction proceeds as follows:



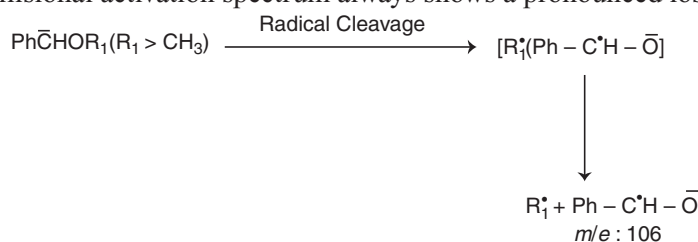
For $n = 1$, the reaction is most pronounced when the proton transfer takes place via six-centre state.



The collision-induced mass spectrum of a Wittig product ion $\text{Ph}(\text{CH}_3)\text{CHO}^-$ (i.e. m/e : 121, 120, 106, 105, 77, 43) suggests that the fragmentation of the ion occurs via ion-molecule intermediates by competitive elimination reactions and via radical cleavage according to the following scheme.

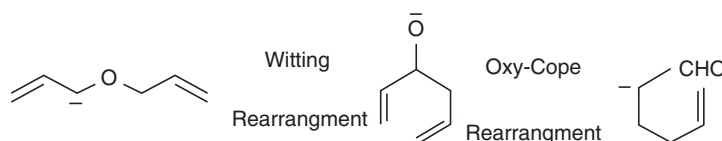


When $R_1 > \text{CH}_3$, the collisional activation spectrum always shows a pronounced loss of R_1 :

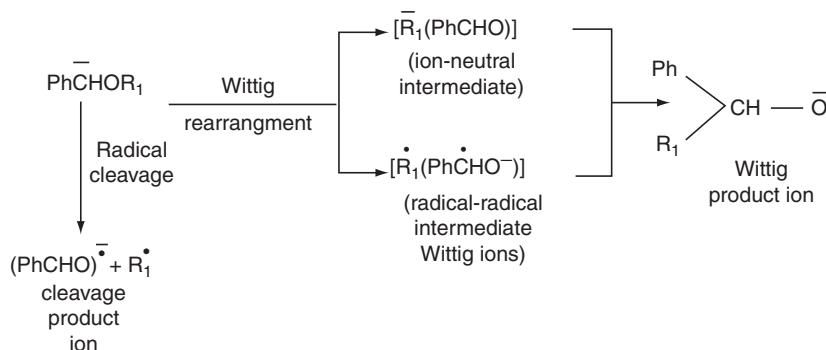


The ion at m/e : 120 corresponds to $(\text{M}-\text{H})^-$.

The deprotonated diallylethers undergo collision induced reactions in the gas phase by 1, 2- and 1, 4-Wittig rearrangements followed by oxy-Cope rearrangement to give the product.

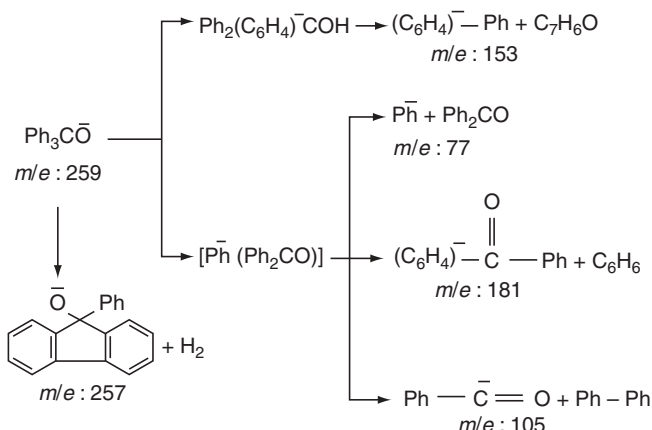


Deprotonated benzyl ethers undergo collision-induced Wittig rearrangement as well as radical scissoring to give respectively Wittig product ion and radical cleavage product ion



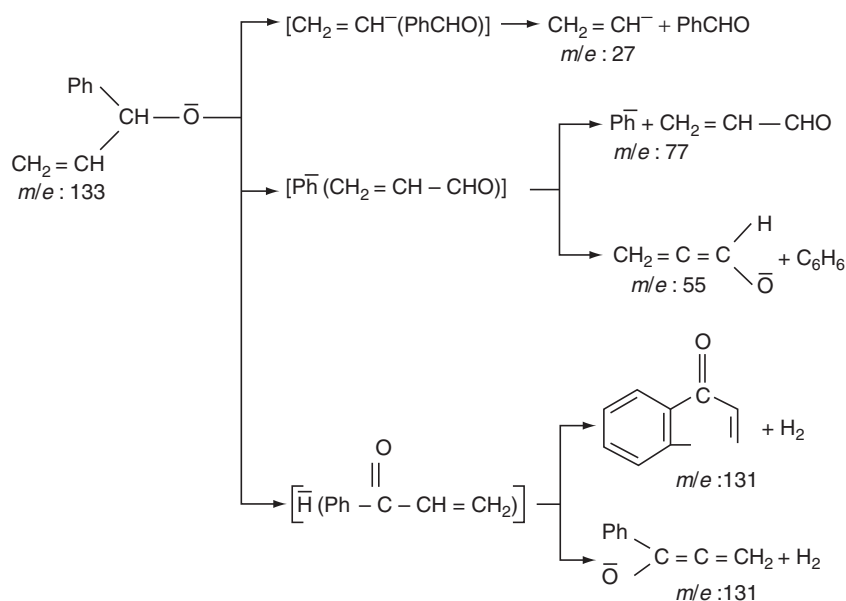
As has already been stated, the similarity between the mass spectra of ions $\text{Ph}\bar{\text{C}}\text{HOR}$ and $\text{Ph}(\text{R})\text{CH}\bar{\text{O}}$ is an evidence for the occurrence of Wittig rearrangement in the gas phase.

Deprotonation of phenyl (diphenylmethyl) ether (PhOCHPh_2) results in the ion PhO^-CPh_2 (I) while that of Ph_3COH gives rise to the ion $\text{Ph}_3\text{C}^-\text{O}$ (II). The collision-induced negative-ion mass spectra of both the anions are very similar except that there is a very low abundance peak corresponding to PhO^- in the spectrum of PhOCHPh_2 . This suggests that the complete fragmentation occurs through Wittig ion according to the following scheme.

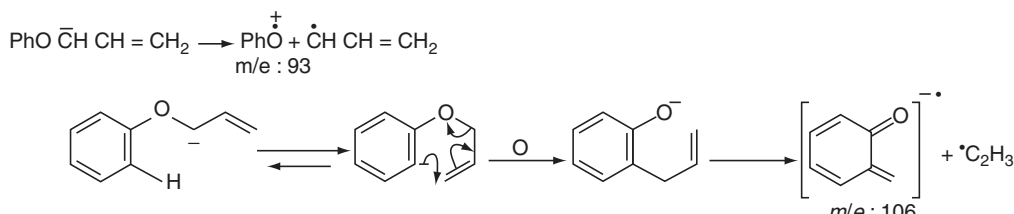


The similarity between the spectra of anions (I) and (II) suggests the collision-induced transformation $\text{I} \rightarrow \text{II}$.

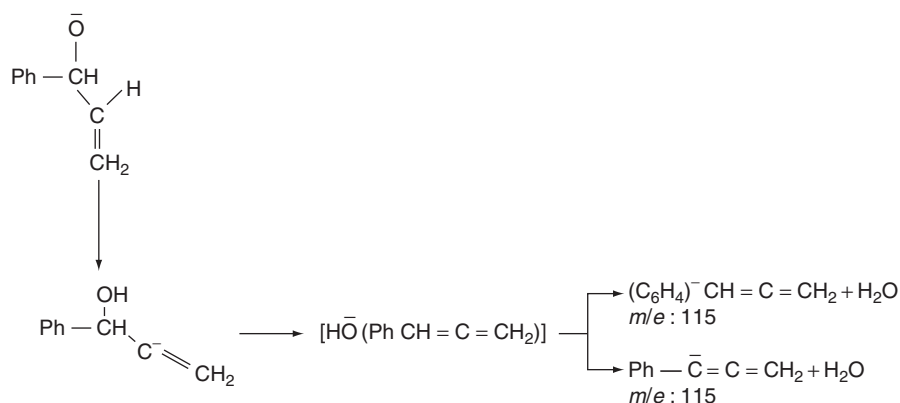
The collision-induced mass spectrum of deprotonated allyl phenyl ether ($\text{PhOCHCH}=\text{CH}_2$) m/e (peak height from common base line in mm) : 133(60), 131(59), 115(50), 106(13), 105(15), 103(15), 93(5), 77(43), 55(22), 27(2.7) is similar to that of $\text{Ph}(\text{CH}_2=\text{CH})\text{CH}\bar{\text{O}}$ to a great extent. The major fragments in the spectra are formed through the Wittig product ion and most fragments follow normal trend. The ions corresponding to the peaks at m/e : 106 and 93 do not appear in the spectrum of the ion $\text{Ph}(\text{CH}_2=\text{CH})\text{CH}\bar{\text{O}}$.



The ions at m/e : 93 and 106 are formed through radical cleavage and Claisen rearrangement respectively.

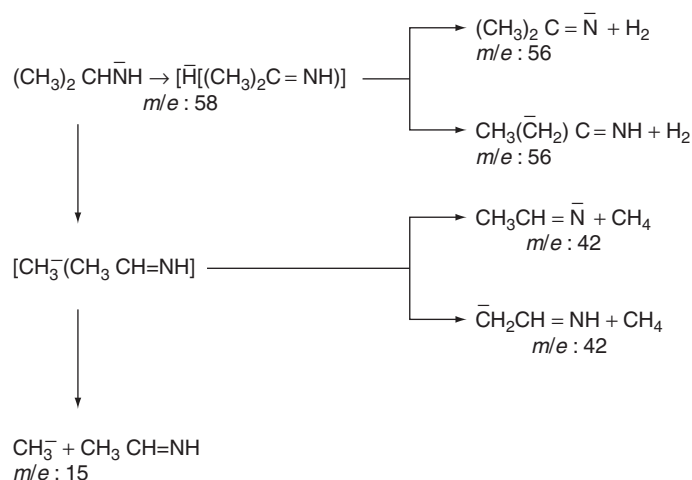


The peak at m/e : 115 corresponds to $(M-H_2O)$ and results in by the following scheme.



The deprotonated spectra of $\text{C}_6\text{D}_5\text{OCHCH}=\text{CH}_2$, i.e. allyl phenyl (d_5) ether fits in the above routes of fragmentation. Moreover, the charge reversal (positive ion) mass spectra of $\text{PhOCHCH}=\text{CH}_2$ and $\text{Ph}(\text{CH}_2=\text{CH})\text{CHO}$ are different but each species has a contribution from the other. This suggests the initial difference in structure of two anions and collision induced transformations of one form to the other form and vice versa.

(j) Amines The collision-activated fragmentation pattern of alkyl N^- ions is similar to that of C^- and O^- species to a great extent. The fragmentation pattern of deprotonated isopropyl amine follows the scheme:

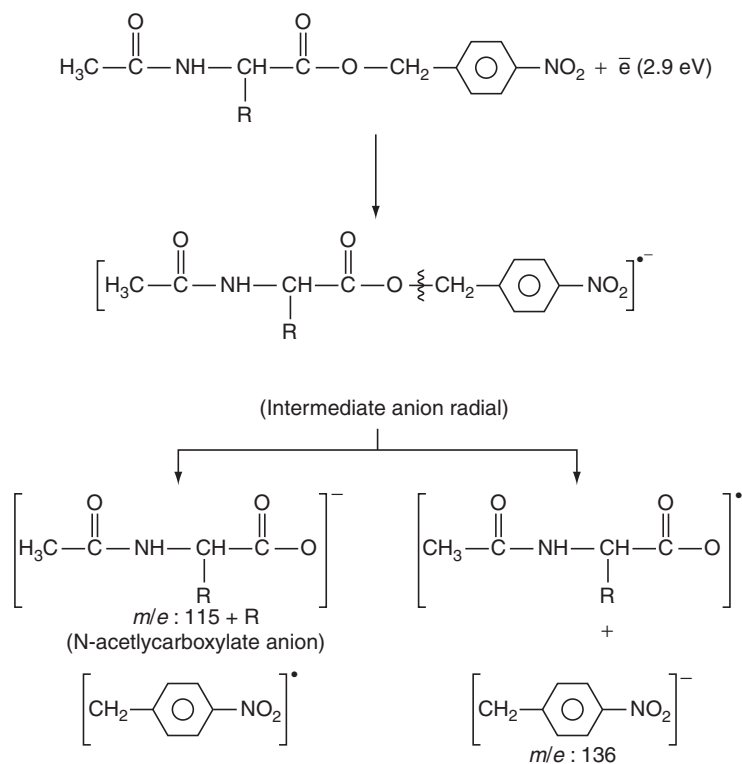


To summarise, in negative-ion mass spectrometry some generalisations regarding the different types of stable carbanions formed in various classes of compounds are listed here in Table 11.23.

Table 11.23 Stable carbanions in various types of organic compounds.

Stable carbanions	Molecular systems
$[\text{M}-\text{H}]^-$	Ketones, aliphatic esters, aldehydes, alcohols, carboxylic acids, mercaptans and steroids.
M^-	Condensed aromatics ($n \geq 4$; n is the number of condensed rings) or same ring systems in which C—H group is replaced by nitrogen atom
$[\text{M}-2]^-$	Condensed aromatics ($n < 4$), compounds such as phenanthradine.
$[\text{M}-\text{R}]^-$	Compounds in which radical R is bound to a heteroatom.
CN^-	Nitriles, lower molecular mass-nitrogen heterocyclics, amines and amides.
NO_2^-	Nitro compounds
Cl^- , Cl_2^-	Chlorinated compounds
S^- , SH^-	Low molecular mass sulphur compounds
Stable carbanions are not readily formed (wide range of weak ion peaks)	Lower molecular mass hydrocarbons, ethers and thiophenes. Not suitable for negative-ion mass spectra

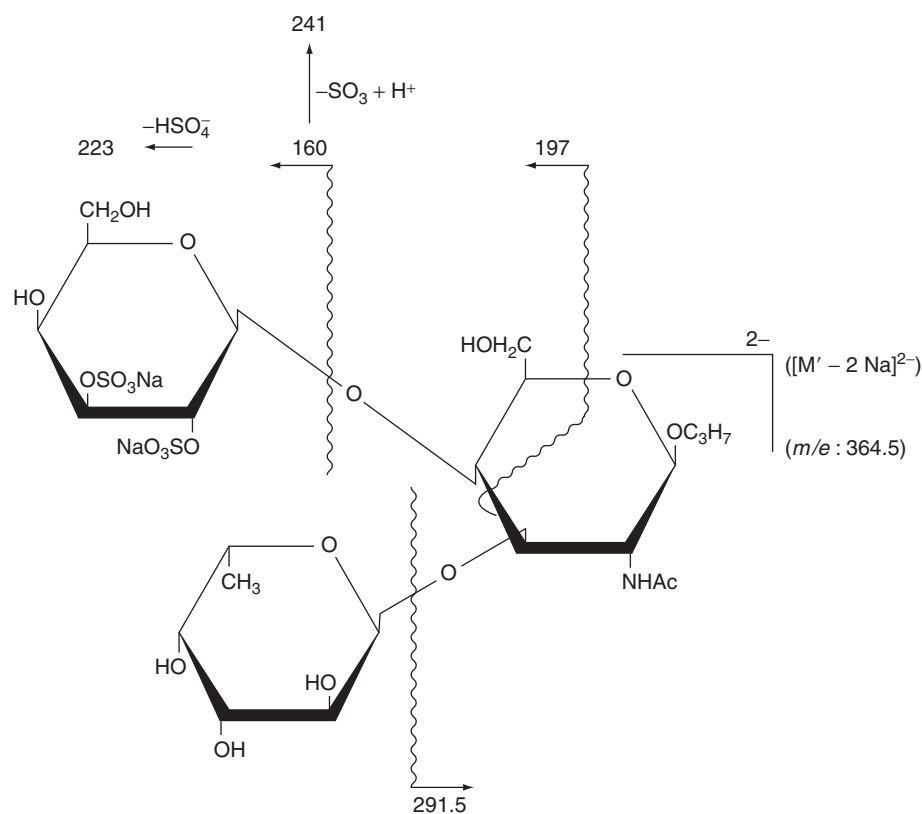
(k) Negative-ion Mass Spectra of Biological Molecules The high-energy electrons cause fragmentation of bioorganic polar molecules and their derivatives due to which it is difficult to observe their negative-ion mass spectra *in vivo* and *in vitro* (especially in intact form). However, this problem has been solved to a great extent by the advent of new ionisation techniques, i.e. chemical ionisation and field ionisation. The derivatisation of molecules is carried out by electron-loving groups in order to enhance their electron affinities. Consequently, the stable carbanions of bioorganic compounds can be produced using low-energy electrons. As already stated in Section 11.4, the minimum energy required for the production of a stable negative ion can be determined from the maximum in the ionisation efficiency curve of the molecular system under study. As an example, let us discuss the EI negative ion mass spectra of *p*-nitrobenzyl-*N*-acetyl amino acid derivatives. The negative ions are produced by the dissociative resonance capture of 2.9 eV electrons as follows:



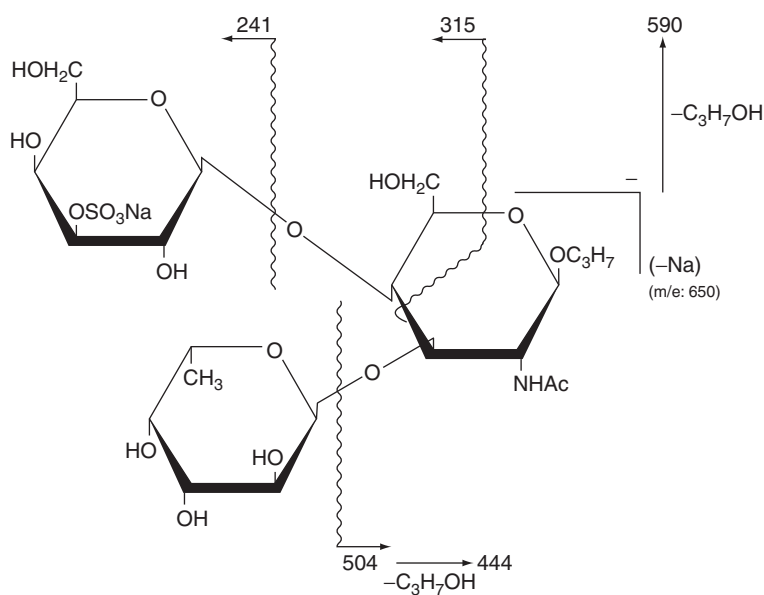
Accordingly, the gas-phase mass spectra of (*N*-acetyl derivatives of) alanine, valine and proline amino acids exhibit peaks at *m/e* values indicated below:

Amino acid	<i>m/e</i> (Relative abundance as percent)
Alanine (R=CH ₃)	130(100), 136(11)
Valine (R=CH(CH ₃) ₂)	158(87), 136(7)
Proline	156(32), – (not observed)

Just like positive ion–soft ionisation–MS/MS, negative ion–soft ionisation–MS/MS proved to be useful for the identification and sequencing of polypeptides and their derivatives, polysaccharides and their derivatives, etc. The nature of the precursor ion depends upon the type of derivatisation. Thus the molecular mass related ions such as (M–H)[–], (M' + Na)[–], (M' – 2Na)[–], etc. (where M and M' have their usual meanings) act as precursor ions. The fragmentation patterns of trisaccharides based on negative ion ESI-CID-MS/MS are given in schemes 1 and 2.



(i) **Scheme 1** Fragmentation patterns of negative ion ESI-CID-MS/MS of disulphated Le^x -type trisaccharide propylglycoside 2 (M' 775, as the disodium salt) having $(\text{M}' - 2\text{Na})^{2-}$ at $m/e : (\text{M}' - 2\text{Na})^{2-}$ as the precursor ion.



(ii) **Scheme 2** Fragmentation patterns of the negative ion ESI-CID-MS/MS of sulphated Le^x -trisaccharides having $(\text{M}' - \text{Na})^-$ as the precursor ion.

PROBLEMS

1. The mass spectrum of a naturally occurring silicon (Si) sample yields the following data:

Isotopic mass number	Peak height
28	92
29	5
30	3

Calculate the average atomic mass of Si.

[Ans: 28.11]

2. From the mass spectrum of naturally occurring neon, the following data are obtained.

Isotopic mass number	Peak height
20.0	91
22.0	9

Calculate the average isotopic atomic mass of neon.

[Ans: 20.18]

3. The mass spectrum of nitrogen produced from the air is characterised by the presence of the peaks of the isotopic forms of nitrogen $^{14}\text{N}^{14}\text{N}$ and $^{14}\text{N}^{15}\text{N}$, which are equal to 68 and 0.5 mm, respectively. Determine the percentage content of nitrogen ^{15}N .

[Ans: 0.37 per cent]

4. Pick the even and odd electron ions corresponding to the following molecular formulas: CH_2N_2 , $\text{C}_2\text{H}_4\text{O}$, $\text{C}_{10}\text{H}_{23}\text{N}$, $\text{C}_4\text{H}_4\text{N}_2$, $\text{C}_6\text{H}_6\text{BrN}$, $\text{C}_3\text{H}_7\text{Cl}_3\text{Si}$, CH_3NO_2 , CH_3CN .
5. The mass spectrum of nitrobenzene shows the presence of particles with the following mass numbers: 30, 46, 61.5, 77 and 123. Which of the following sets of the products of decomposition of nitrobenzene does this mass spectrum correspond to?

- (a) $\text{C}_6\text{H}_5\text{NO}_2^+$, NO_2^+ , NO^{2+} , C_6H_5^+ , $\text{C}_6\text{H}_5^{2+}$.
 (b) NO^+ , NO^{2+} , C_6H_5^+ , $\text{C}_6\text{H}_4\text{NO}^+$, $\text{C}_6\text{H}_5\text{NO}_2^{2+}$
 (c) NO_2^{2+} , NO^+ , $\text{C}_6\text{H}_5\text{NO}_2^+$, $\text{C}_6\text{H}_5^{2+}$, $\text{C}_6\text{H}_5\text{NO}^+$
 (d) $\text{C}_6\text{H}_5\text{NO}_2^+$, $\text{C}_6\text{H}_5\text{NO}_2^{2+}$, NO^+ , NO_2^+ , C_6H_5^+
 (e) C_6H_4^+ , NO_2^+ , NO^{2+} , $\text{C}_6\text{H}_5^{2+}$, $\text{C}_6\text{H}_5\text{NO}_2^{2+}$

[Ans: (d), $\frac{1}{2}[\text{C}_6\text{H}_5\text{NO}_2^{2+}] = 61.5^+$]

6. Calculate the flight times of singly charged (a) N_2 molecule, (b) O_2 molecule, (c) CO_2 molecule, and (d) Ar^+ ion for drift length of 1 m and acceleration voltage of 2800 V.

[Ans: (a) 7.07 μs ; (b) 7.56 μs ; (c) 8.86 μs ; (d) 8.45 μs]

7. In the radio-frequency mass spectrum of olefin C_2H_4 , there are observed lines corresponding to the ionised molecules and ions indicated below (relative abundance, in per cent):

Radical	...	CH	CH ₂	CH ₃	C ₂ H	C ₂ H ₂	C ₂ H ₃	C ₂ H ₄
Relative abundance in per cent	...	0.7	1.8	0.3	7.3	50	54.5	100

Determine the radio frequencies corresponding to the radicals if the accelerating voltage is 4000 volts and the spacing between the adjacent grids is 1 cm.

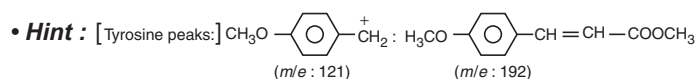
[Ans: 9.04, 8.71, 8.41, 6.52, 6.39, 6.27, and 6.16 MHz]

8. Using the data in Problem 7, determine the cyclotron frequencies corresponding to the radicals if the strength of the applied magnetic field is 15000 G.

[Ans: 3.52, 3.26, 3.05, 1.83, 1.76, 1.69, and 1.63 MHz]

9. The amino acid analysis of a peptide shows the presence of six different amino acids, namely leucine, glutamic acid, glutamine, valine, proline and tyrosine. The hexapeptide has been first acetylated (with acetic anhydride/methanol) and then per methylated (upon treatment with dimethyl sulfoxide anion (CH_2SOCH_3) followed by methyl iodide in order to obtain per methyl-N-acetyl peptide. The mass spectrum of the volatile N-acyl peptide methyl ester exhibits characteristic peaks at m/e : 929 (M^+), 707, 610, 497, 327, 192, 170, 142 and 121. Accomplish the sequence of amino acids in the hexapeptide chain.

[Ans: Leu-Glu-Gln-Val-Pro-Tyr]



The peaks at $m/e : 142$ results via loss of CO from the sequence ion at $m/e : 170$]

10. The values of appearance potentials of C_2H_5^+ ion in ethane and propane are respectively 15.2 and 14.5 eV. What will be the values of ionisation potentials of the $\cdot\text{C}_2\text{H}_5$ radical in ethane and propane if the values of dissociation energies of the $\text{C}_2\text{H}_5-\text{H}$ and $\text{C}_2\text{H}_5-\text{CH}_3$ bonds are respectively 98 and 84 kcal mole $^{-1}$?

[Ans: 10.95 eV, 10.86 eV]

11. The sensitivity coefficients (in divisions/micron) corresponding to the analysis peaks of *n*-, ($m/e : 56$), iso-, ($m/e : 74$), sec-, ($m/e : 45$) and tertbutyl ($m/e : 59$) alcohols are 11.51, 12.05, 26.98 and 20.93 respectively. Determine the relative contributions of the alcohols (in mole per cent) in an unknown mixture of isomeric butyl alcohols from its mass spectral data given below:

m/e : <i>n</i> -butyl alcohol	Percentage component	<i>sec</i> -butyl alcohol	<i>tert</i> -butyl alcohol	percentage of unknown mixture	
56	90.58	2.46	1.02	1.47	126.7
74	0.79	9.06	0.29	—	148.0
45	6.59	5.03	100.00	0.59	322.6
59	0.26	4.98	17.78	100.00	301.5

[Ans: *n*-24.4, iso-25.8, sec-24.8 and tert- 25.0mole per cent]

12. Predict the molecular formulas of the compounds containing C, H, N or O whose exact molecular masses are 60.0210, 45.0214, 102.0678, 190.9540 (Cl), 334.0873(S), 180.0630, and 84.0936.

[Ans: $\text{C}_2\text{H}_4\text{O}_2$, CH_3NO , $\text{C}_5\text{H}_{10}\text{O}_2$, $\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$, $\text{C}_{17}\text{H}_{18}\text{O}_5\text{S}$, $\text{C}_6\text{H}_{12}\text{O}_6$ and C_6H_{12}]

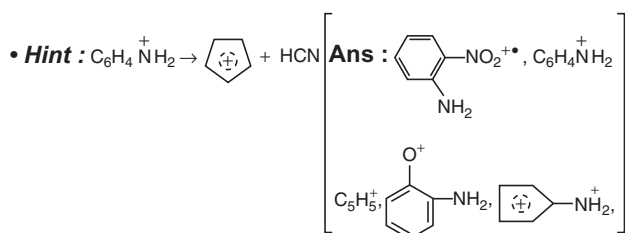
13. A peptide has been found to contain five types of amino acids, viz., Gly (1 molecule), Ala (2 molecules), Val (2 molecules), Leu (2 molecules) and Pro (2 molecules). The mass spectrum of N-acylated (i.e. $\text{C}_{17}\text{H}_{35}\text{CO}$) methyl ester of the nona peptide exhibits major peaks at m/e : 1115 (M^+), 1084, 985, 888, 817, 720, 621, 508, 451, 338

and 267. Determine the sequence of amino acids in the nona peptide.

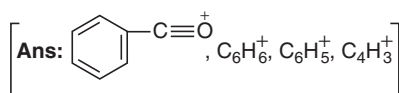
- **Hint:** Stearoyl = $C_{17}H_{35}CO$ (m/e : 267), OCH_3 (m/e : 31). Use the molecular mass data from Table 11.18

[Ans: Ala-Leu-Gly-Leu-Val-Pro-Ala-Pro-Val]

14. The mass spectra of *o* or *m* or *p* nitro-anilines show prominent peaks at m/e : 138 (M^{+*}), 108, 92, 80 and 65. What ions might these peaks correspond to?

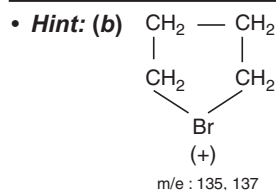


15. The mass spectrum of benzaldehyde shows peaks at m/e : 105, 78, 77 and 51. What ions might these peaks correspond to?



16. Deduce the structural formulas of the compounds corresponding to the mass spectral data indicated below:

(a)	Group	A	B	C	D
	m/e	123, 121, 119, 117	86, 84, 82	49, 47	37, 35
	Peak height (in mm)	1, 20, 45, 48	1, 9, 14	6, 19	6, 24
(b)	m/e	166, 164	137, 135	109, 107	85, 57, 43
	Peak high (in mm)	1, 1	21, 21	3, 3	22, 6, 35



[Ans: (a) CCl_4 and (b) 1-bromohexane]

17. Determine the molecular formulas of the isobaric compounds corresponding to the exact molecular masses indicated below: 31.9898, 32.0375 and 32.0262

Hint: In the first case, mass defect is negative.

[Ans: O_2 , N_2H_4 , CH_4O]

18. Determine the molecular formulas of the isobaric compounds containing C, H, O or N unless otherwise indicated corresponding to the following exact molecular masses: 27.9949, 28.0313 and 28.0061.

[Ans: CO , C_2H_4 , N_2]

19. Deduce the number and nature of halogen atoms present in a molecule from the mass spectral data indicated below:

m/e	M	M + 2	M + 4	M + 6	M + 8
Per cent abundance	27	45	21	3	...

[Ans: 3; Cl = 2, Br = 1]

20. (a) The mass spectrum of an unknown compound has a molecular ion peak with relative intensity 43.27 per cent and a $M + 1$ peak with a relative intensity of 3.81 per cent. What might be the number of carbon atoms in the molecule? (b) Determine the molecular formulas of the isobaric compounds containing C, H, O or N unless otherwise indicated corresponding to the exact molecular masses (amu) given below: 122.1096, 122.0845, 122.0732, 122.0368, 122.0579, and 122.0225(S).

[Ans: (a) 8 (b) $C_9H_{14}O$, $C_7H_{10}N_2$, $C_8H_{10}O$, $C_7H_6O_2$, $C_4H_{10}O_4$, $C_4H_{10}S_2$]

21. Which of the following set of peaks correspond to 1-methoxybutane (a), 2-methoxy butane (b) and 2-methoxy-2-methyl propane (c)

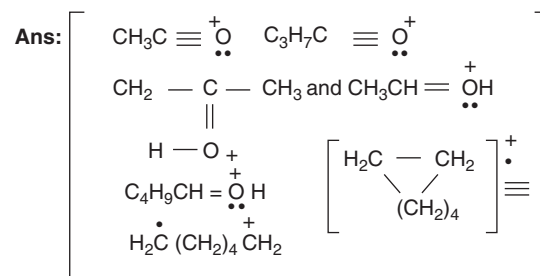
	(A)	(B)	(C)
m/e	Peak height	m/e peak	m/e peak
		height	height
	(in mm)	(in mm)	(in mm)
88	4	88 2.5	88 3
73	45	73 6	56 7
57	14	59 45	45 45

- **Hint:** (C) $CH_3-CH=OH$
 m/e : $M^{+*}-CH_3OH=56$

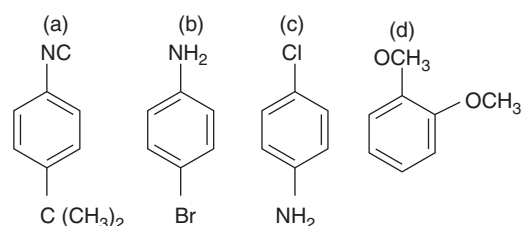
[Ans: (A) $\rightarrow$ (c); (B) $\rightarrow$ (a), (C) $\rightarrow$ (b)]

22. The mass spectra of 2-pentanone and 2-hexanol show prominent peaks at m/e : 43, 71, 58 and m/e : 45, 87, 84 respectively. What ions might these peaks correspond to?

- **Hint:** m/e : $(102 - 18) = 84$; Elimination by OH group of alcohol and a γ -hydrogen.

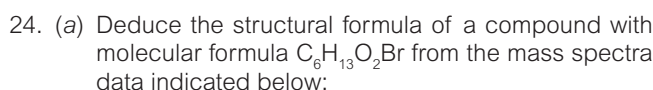


23. Given below are the characteristic peaks of the mass spectra of some aromatic compounds.



Assign these peaks to the ions in the respective molecules.

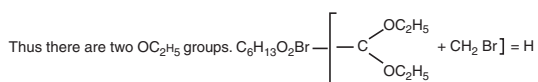
(c) $(M^+ \cdot -H\dot{C}N)$; $(M^+ \cdot -Cl)$; (d) $(M^+ \cdot -CH_3)$,



Metastable peaks: 100.2, 102.2, 54.7.

(b) The mass spectrum of CO_2 shows peaks at m/e : 44, 28, 32, 22, 16, 12. Minor peaks are observed at m/e : 13 and 45. What ions might these peaks correspond to?

- 196 $\rightarrow$ 103 + 93 (= CH₂Br): 54.1, M—C₂H₅ = 167,
M—OC₂H₅ = 151,

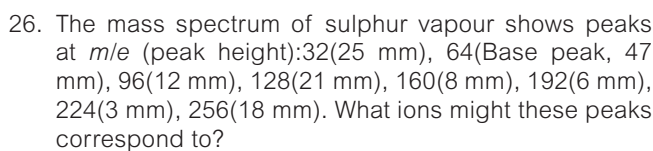
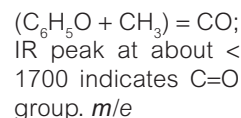


25. Deduce the structural formula of a compound with molecular formula $C_8H_8O_2$ from the mass spectral data given below:

Metastable peaks: 71.6; 45.5. IR shows peak at about $< 1700\text{ cm}^{-1}$.

- **Hint:** $121 \rightarrow 93 + 28 (\equiv \text{CO}) : 71.6$

$M^+ - CH_3 = 121$; Strong molecular ion peak-aromatic component.



[Ans: S^+ , S_2^+ , S_2^+ , ... S_9^+]

- **Hint:** On bombardment with electrons, a puckered ring of 8 sulphur atoms in crystalline sulphur breaks up firstly into chains of atoms; these then successively break to give the various S to S₇ units shown by the mass spectrum, S₈⁺ is the most stable form.



The changes in the viscosity of molten sulphur as temperature rises have been found to be due to the presence of biradical chains which can be detected by ESR technique. The longer the sulphur chains, the more viscous the molten sulphur.

27. The molecular mass of a certain gas, as determined on a high-resolution mass spectrometer is 27.9949. Identify the gas from one of the following compounds which all have molecular masses of about 28:

$$\text{N}_2, \text{C}_2\text{H}_4, \text{H}_2\text{CN}, \text{CO}$$

[Ans. C¹⁶O]

28. The mass spectrum of a compound exhibits significant peaks at m/e : 60 (M^{+}), 42, 31. What might be the structure of the compound?

- **Hint:** $M^{\bullet}-H_2O$; $M^{\bullet}-C_2H_5$, [**Ans:** $CH_2-CH_2-CH_2OH$]

29. The molecular mass of a compound, as determined on a high-resolution mass spectrometer is 32.0375. Identify the compound from one of the following compounds which all have molecular masses about 32.

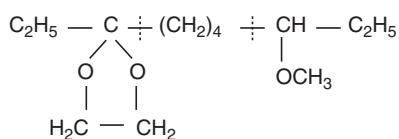
$$\text{O}_2, \text{N}_2\text{H}_4, \text{CH}_4\text{O}$$

[Ans: N_2H_4]

30. Electron spray mass spectrum of arginine in methanol-water (50 : 50) solution containing tetramethyl ammonium iodide shows peaks at m/e : 349(1 nm), 207(4 nm), 175(32 nm), 74(37 nm). What ions might these lines correspond to?

[**Ans:** M_2H^+ , $MCH_3OH_2^+$, MH^+ , $(CH_3)_4N^+$ $M=174$]

31. The significant peaks in the mass spectrum of a compound with structural formula

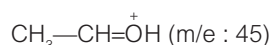
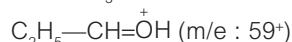
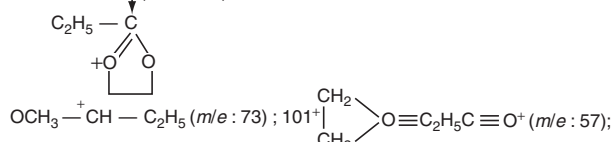
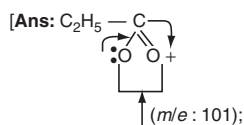
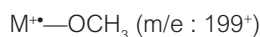


are indicated below:

<i>m/e</i>	230(M ⁺)	201	169	139	101	99	73	57	45
Peak height (in nm)	—	9	2	2	40	3.5	8	7	2

What ions might these lines correspond to?

Hint: The activation energy for formation of highly stabilised oxonium ion *m/e*: 101 is so small that formation of *m/e*: 73 and other primary processes compete very poorly.

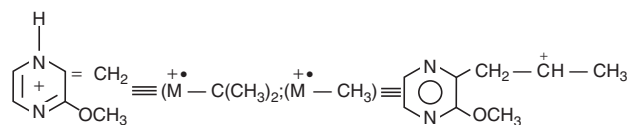


32. Chromatography of the steam volatile bell pepper oil separated a peak which possessed a potent odour, characteristic of bell peppers. The exact molecular mass of the heterocyclic potent odorant, one drop (0.05 ml) of which is sufficient to impart bell pepper flavour to a large swimming pool is 166.1102, (a) Calculate the number of rings, double bonds and the molecular formula of the compound. (b) Deduce the structural formula of the odorant in question from the mass spectral data indicated below,

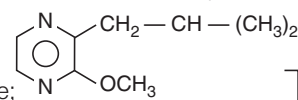
<i>m/e</i> :	166(M ⁺)	151	135	124(base peak)	
	109	95	94	93	81
Peak height	2	12.5	0.8	—	81
(in mm)	1	8	16	9	7

The substituents are ortho to one another in the molecule.

• **Hint:** (M⁺—OCH₃),



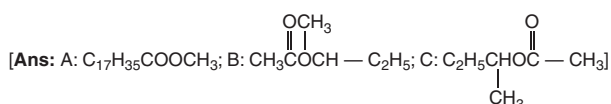
[Ans: (a) 1, 3, C₉H₁₄N₂O]



(b) 2-isobutyl-3-methoxy-pyrazine;

Problem 33 Deduce the molecular as well as the structural formula of the compounds A, B and C from their mass spectral data, i.e. *m/e*, and exact molecular masses indicated below:

A(298.2862)	B(116.0834)	C(116.0834)
298(M ⁺)	116(M ⁺)	116(M ⁺)
267	101	101
239	87	87
237	73	56
225	57	43
223	43	29
211	—	—
209	—	—
197	—	—
195	—	—
59	—	—
31	—	—

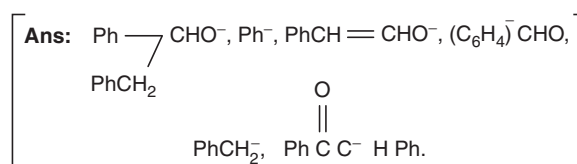


34. Dibenzyl ether undergoes a Wittig rearrangement in the condensed phase, but in the gas phase it forms no stable deprotonated form and no Wittig rearrangement is noted. It reacts with HO[−] to give only PhCH₂[−] most probably by dissociation of unstable PhCH₂OCHPh. The gas phase negative ion mass spectral data of the Wittig product Ph(PhCH₂)CHO[−] (A) and its deuterated analogue Ph(PhCD₂)CHO[−] (B) are indicated below:

A ... *m/e*: 197, 195, 129, 105, 91, 77

B ... *m/e*: 199, 196, 131, 105, 93, 77

What might be ions corresponding to the mass spectral data in question?



35. Mass spectrometric analysis of the vapours in thermodynamic equilibrium with powdered molybdenum trioxide (MoO₃) at 850 K as sampled from Kundsen

effusion cell has shown that the vapour phase consists predominantly of Mo_3O_9 , Mo_4O_{12} and Mo_5O_{15} molecules. Determine the heats of sublimation of tri-, tetra- and pentamers of MoO_3 from the data given below:

Molecular species	Temperature (in K)	Vapour pressure (in atmosphere)
Mo_3O_9	973	1.26×10^{-4}
	914	1.19×10^{-5}
	967	9.0×10^{-5}
Mo_4O_{12}	861	1.64×10^{-6}
	973	6.71×10^{-5}
	913	4.94×10^{-6}
Mo_5O_{15}	905	4.31×10^{-6}
	943	1.74×10^{-6}
	916	2.38×10^{-7}
	908	1.77×10^{-7}

[Ans: $\text{Mo}_3\text{O}_9 = 81$, $\text{Mo}_4\text{O}_{12} \approx 94$ and $\text{Mo}_5\text{O}_{15} \approx 105$ kcal mole⁻¹ at 850 K]

36. The relative abundances and appearance potentials of the principal ions in the mass spectrum of (a) phosphine, and (b) a mixture of phosphine and deuterated phosphines are listed below:

(a)	m/e	70 eV relative abundance	Appearance potential (eV)	Probable Processes
	31	24.1	17.2	—
	32	100.0	13.3	—
	33	21.8	13.2	—
	34	75.2	10.2	—
(b)	m/e	70 eV relative abundance	Appearance potential (eV)	Ionic species
	31	39.8	17.1	—
	32	85.8	13.3	—
	33	100.0	13.1	—
	34	33.8	10.1	—
	35	58.0	10.1	—
	36	47.8	10.2	—
	37	22.9	10.1	—

Fill in the blank columns in (a) and (b) and also compute the heat of formation (ΔH_f°) of the ionic species formed in (a). $\Delta H_f^\circ(\text{H}_2) = 0.0$, $\Delta H_f^\circ(\text{H}) = 52.09$, $\Delta H_f^\circ(\text{PH}_3) = 2.21$ kcal

mole⁻¹.

- **Hint:** $\Delta H_f^\circ(\text{P}^+) = \text{Appearance potential}(\text{P}^+) + \Delta H_f^\circ(\text{PH}_3) - \Delta H_f^\circ(\text{H}_2) - \Delta H_f^\circ(\text{H})$.

[Ans: (a) $\text{PH}_3 \rightarrow \text{P}^+ + \text{H} + \text{H}_2, \rightarrow \text{PH}^+ + \text{H}_2, \rightarrow \text{PH}_2^+ + \text{H}, \rightarrow \text{PH}_3^+$.

- (b) P^+ , PH^+ , PD^+ or PH_2^+ , PH_3^+ , PDH_2^+ , PD_2H^+ , PD_3^+ and ΔH_f° (kcal mole⁻¹): $\text{P}^+ = 346$, $\text{PH}^+ = 308$, $\text{PH}_2^+ = 254$ and $\text{PH}_3^+ = 237$.

37. The equilibrium partial pressures of the gaseous species (viz., Cr, CrO, CrO_2 , CrO_3 , O_2 and O) formed in the dissociative vapourisation of $\text{Cr}_2\text{O}_3(\text{s})$ have been measured mass spectrometrically under neutral and oxidising conditions. The partial pressures of Cr in equilibrium with Cr_2O_3 under both the conditions have been indicated below:

Oxidising condition: (CrO_3^* is formed under this condition only)

T(K)	1890	1911	1942
$P_{\text{Cr}} \times 10^8$ (atom)	3.24	5.91	11.1

Neutral condition (CrO_3^* is not formed under this condition)

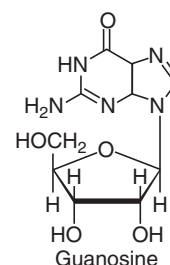
T(K)	1839	1862	1883	1887	1917	1925	1936	1939
$P_{\text{Cr}} \times 10^7$ (atom)	4.30	7.08	10.8	10.8	18.8	22.0	29.0	29.3
	1959	1963	1998	2029	2059			
	39.8	46.0	77.5	119	183			

Calculate the heat of vapourisation of Cr formed by the decomposition of $\text{Cr}_2\text{O}_3(\text{s})$.

- **Hint:** $\ln P = \frac{-\Delta H_{\text{vap}}}{8.3143T} + \text{const}$; ΔH_{vap} is in J mole⁻¹ deg⁻¹.

[Ans: 94.2 kcal mole⁻¹]

38. LD/SI-MS/MS of 7-methylguanosine exhibits peaks at m/e: 282 (intact) and 166 (base peak) in its SI mass spectrum. What might be the ions corresponding to these peaks? The structural formula of guanosine is given below:



Suggested Readings



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Nobel Prizes

Nobel Prize in Physics and Chemistry Related to Molecular Spectroscopy and Structure (1901–2005)

- **1902:** (jointly to) **HENDRIK ANTOON LORENTZ** and **PIETER ZEEMAN** for *influence of magnetic field of magnetism upon radiation phenomena*
- **1914:** **MAX VON LAUE** for *diffraction of X-rays by crystals*
- **1915:** (jointly to) **SIR WILLIAM HENRY BRAGG** and **SIR WILLIAM LAWRENCE BRAGG** for *analysis of crystal structure by X-rays*
- **1919:** **JOHANNES STARK** for *discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric fields*
- **1924:** **KARL MANNE GEORG SIEGBAHN** for his **discoveries and research in the field of X-ray spectroscopy**
- **1930:** **SIR CHANDRA SEKHARA VENKATA RAMAN** for *work on the scattering of light and for discovery of the effect named after him*
- **1952:** (jointly to) **FELIX BLOCH** and **EDWARD MILLS PURCELL** for *development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith*
- **1961:** (divided equally between) **ROBERT HOFSTADTER** for *pioneering studies of electron scattering in atomic nuclei and thereby achieved discoveries concerning the structure of the nucleons*; **RUDOLF LUDWIG MOSSBAUER** for *researches concerning the resonance absorption of gamma radiation*
- **1964:** ***DOROTHY CROWFOOT HODGKIN** was awarded the Nobel Prize for chemistry for her *determination by X-ray techniques of the three-dimensional structure of important biological substances, for example, cholesterol, penicillin, Vitamin B12, and zinc insulin (which contains almost 800 atoms)*
- **1971:** ***G HERZBERG** for *work on electron structure and geometry of molecules particularly of free radicals (molecular spectroscopy)*
- **1981:** The Prize was awarded by one half jointly to **NICOLAA BLOEMBERGEN** and **ARTHUR L SCHAWLOW** for their *contribution to the development of laser spectroscopy* and the other half to **KAI M SIEGBAHN** for his *contribution to the development of high resolution electron spectroscopy*
- **1992:** ***RICHARD R ERNST** for his *contribution to Fourier transform nuclear magnetic resonance spectroscopy*
- **1994:** For *pioneering contributions to the development of neutron scattering techniques for studies of condensed matter* to **BERTRAM N BROCKHOUSE** for the *development of neutron spectroscopy* and **CLIFFORD G SHULL** for the *development of the neutron diffraction technique*
- **2002:** *The prize was awarded by one half jointly to **JOHN B FENN** and **K TANAKA** for *developing soft desorption ionization method for mass spectrometric analysis of biological macromolecules* and the other half to **K WUTHRICH** for his *contribution to the development of nuclear magnetic resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution*
- **2005:** The Nobel Prize was awarded by 2/3rd jointly to **JOHN L HALL** and **THEODOR W HAENNSCH** for their *contribution to the development of laser based-precision spectroscopy including the optical frequency comb technique* while **ROY J GLAUBER** won 1/3rd of the prize for his *contribution to the quantum theory of optical coherence*

