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The Heliocentric Evolution of Cometary Infrared Spectra: Results from an Organic Grain Model

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Observations of Comets Halley and Wilson reveal an emission feature peaking near 3.4 μm, characteristic of C–H stretching in hydrocarbons. We have previously (Chyba and Sagan 1987a, *Nature* (*London*) 330, 350–353) fit this feature with a simple two-component thermal emission model for dust in the cometary coma (one component corresponding to large, cool, optically thick particles, the other due to smaller, hotter, organic grains) by employing laboratory spectra of the organic residue produced by the irradiation of carbon-bearing ices. This procedure yields optical depths in agreement with limits from spacecraft data. One remarkable result of such modeling is that at ~1 AU emission features at wavelengths longer than 3.4 μm are largely overwhelmed (or "diluted") by continuum emission. The large particle optical depth is ~10^2 times that of the emitting organics, so that, relative to the continuum, only near the continuum minimum can the emitting organics make a significant contribution. At ~1 AU, the 3.4-μm feature is the sole feature near that minimum, lying at the intersection of the curves for particle thermal emission and scattered sunlight. Thus, since as a comet moves away from perihelion the intersection of the scattered solar spectrum and the comet's thermal emission spectrum will move to longer wavelengths, we predicted (Chyba and Sagan 1987a) that the 3.4-μm feature is diluted while those at longer wavelengths are progressively revealed—so long as the comet retains its coma. We now quantitatively develop this model and find agreement with observational data for Comet Halley for certain plausible values of optical constants. Thus the observed heliocentric evolution of the 3.4-μm feature provides information on the composition, and perhaps structure, of the organic grains in Comet Halley. In addition, we argue that the heliocentric evolution of organic features will differ in the cases of thermal emission from small grains and gas-phase fluorescence. Therefore observations of cometary spectral evolution can in principle distinguish between solid or gas-phase origins for these features.

I. THE NEAR-INFRARED SPECTRA OF COMETS HALLEY AND WILSON

Observations of the infrared spectrum of Comet Halley both by spacecraft (Combes *et al.* 1988) and ground-based telescopes (Baas *et al.* 1986, Danks *et al.* 1986, Knacke *et al.* 1986, Wickramasinghe and Allen 1986, Tokunaga *et al.* 1987) reveal an emission feature centered at about 3.36 μm, characteristic of C–H stretching in hydrocarbons. This feature has been interpreted as thermal emission from organic grains in the Halley coma (Wickramasinghe and Allen 1986, Chyba and Sagan 1987a, 1988a), although some contribution to the 3.4-μm feature by gaseous emission is expected

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(Crovisier and Encrenaz 1983, Combes *et al.* 1988). However, Drapatz *et al.* (1987) observed the ~3.2–3.4 μm region of the Halley spectrum at high resolution ($\lambda/\Delta\lambda \sim 1.1 \times 10^4$) and found no prominent line structure typical of gas-phase emission. Moreover, mass spectrometric observations by spacecraft flying through the coma directly demonstrate the presence of organic-rich grains (Kissel and Krueger 1987, Clark *et al.* 1987), although there remains ample room for debate on the detailed composition.

Observations of Comet Wilson (Allen and Wickramasinghe 1987, Brooke *et al.* 1987) also reveal a 3.4-μm emission band which closely resembles the Comet Halley feature for approximately the same heliocentric distance. Again, high resolution ($\lambda/\Delta\lambda \sim 3.3 \times 10^4$) observations in the 3.2–3.3 μm region reveal no prominent line structure in Comet Wilson, although a possible (3σ) detection of methane has been reported (Larson *et al.* 1989). It is remarkable that dynamically old (Halley) and new (Wilson) comets should display such a nearly identical emission feature, a similarity which strengthens the case (Greenberg and Grim 1986, Chyba and Sagan 1987a, 1988a,b, Brooke *et al.* 1987, Johnson *et al.* 1987) for the primordial, although not necessarily the interstellar, origin of cometary organics.

Any proposed identifications of the molecules responsible for the 3.4-μm feature must take into account the absence of organic emission features in cometary infrared spectra at longer wavelengths. The peak position of the 3.4-μm feature itself is indicative of alkanes ($-CH_3$, $-CH_2-$), while substructure indicates the presence of other organics [e.g., aldehydes (–CHO) emit near 3.5 μm]; naively one might expect the presence of these or other plausible classes of organic molecules to result in observable spectral features in the 4.5–8 μm region. For example, alkanes exhibit prominent deformation bands in the 6.8–8 μm region; alkenes and aromatics exhibit (C=C) bands in the 6–7 μm region; and ketones and aldehydes have a carbonyl (C=O) feature near 5.8 μm. Such features are typically present in the transmission spectra of the organic residue of irradiated candidate cometary ices (Thompson *et al.* 1987, Khare *et al.* 1989), for example, in that of the residue of irradiated methane ice clathrate (Fig. 1). Organic solids produced by irradiating N_2/CH_4 gas mixtures exhibit a prominent nitrile or isocyanide (C≡N) feature at 4.6 μm (Khare *et al.* 1984). Yet observations of both Comet Halley (Combes *et al.* 1988, Bregman *et al.* 1987) and Comet Wilson (Lynch *et al.* 1988) in the 5–13 μm range have shown such features to be absent at the $\gtrsim$2% level.

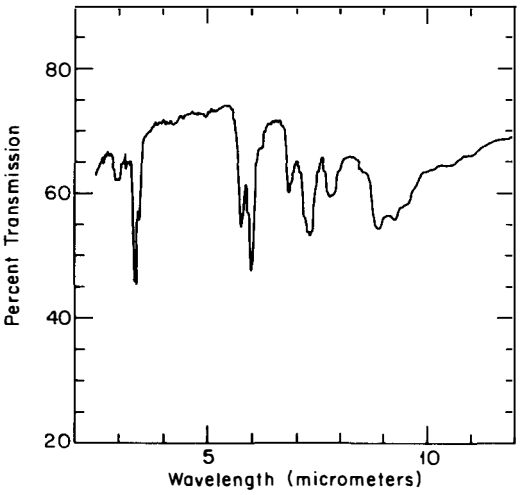

FIG. 1. The 2–12 μm transmission spectrum of the organic residue of irradiated methane hydrate clathrate. See Thompson *et al.* (1987) and Khare *et al.* (1989) for the transmission spectrum of this and other irradiation-produced residues presented on a scale linear in wavenumber.

In a recent model (Chyba and Sagan 1987a,b) for infrared emission by organic grains in the Halley coma, we have explained the absence of these longer wavelength bands as due to the dilution of spectral features by the continuum when such features do not lie near the intersection of the scattered solar and thermal emission curves of the dust in the cometary coma. At

the heliocentric distances of the 5 to 13-μm observations [$\sim$1.3 and $\sim$1.2 AU for Comets Halley (Bregman *et al.* 1987) and Wilson (H. Campins, personal communication), respectively], the 3.4-μm band is the sole feature near the minimum in the continuum. Our model quantitatively demonstrates that it is the only organic feature likely to be observable at these distances. Therefore spectroscopic attempts to rule out certain organic functional groups or polycyclic aromatic hydrocarbons in Comets Wilson or Halley (Bregman *et al.* 1987) appear premature. The presence of absorption features in laboratory transmission spectra does not necessarily require them to be observable in cometary emission, even if the corresponding molecular functional groups are present in substantial abundance.

However, with changing heliocentric distance, the intersection of the scattered solar and thermal emission flux will sweep through the infrared spectrum. Thus, for a comet moving away from perihelion, Chyba and Sagan (1987a) predicted that the contrast between the 3.4-μm feature and the continuum would be gradually suppressed, and spectral features at longer wavelengths progressively revealed, as this intersection moves toward longer wavelengths. In this paper, we present quantitative results of a model for the heliocentric evolution of the Comet Halley infrared spectrum. We expect any comet that displays organic emission features in the infrared to exhibit an analogous evolution with heliocentric distance, although the details of such evolution will vary according to the nature of a given comet's organics (see below). Such spectral evolution should be testable by Earth-based observations and, especially, by future comet rendezvous missions.

II. EMISSION BY ORGANIC GRAINS IN THE COMA OF COMET HALLEY

A variety of plausible cometary materials exhibit C–H stretching features near 3.4 μm, including the organic residue of candidate cometary ices irradiated by charged particles. Higher resolution spectroscopic observations will be required in the future to understand the nature of the organic material responsible for cometary emission. For now, tentative identifications must rest on additional evidence, including a plausible account of the origins of the organic material, a plausible model for the infrared emission of this material, and a demonstration that this conjunction of material and model not only matches the 3–4 μm spectrum, but also does not yield additional emission features where none is observed (Chyba and Sagan 1987b).

We have embarked on an experimental survey of diagnostic spectral features for the organics produced by irradiation of a variety of hydrocarbon and ammonia-bearing ices (Thompson *et al.* 1987, Khare *et al.* 1988), and are beginning an examination of other (e.g., CO and CO_2) ices as well. We have argued that the laboratory synthesis of the organic residue well simulates certain types of pre- and post-accretion radiation processing experienced by cometary ices. As an example of one such organic remnant, we have considered the residue, after evaporation of the ices, of irradiated low-occupancy methane hydrate clathrate (Chyba and Sagan 1987a, 1988a). There is evidence from the Giotto ion mass spectrometer for methane in the Halley coma with a production rate $\sim$2% that of water (Allen *et al.* 1987), and in cometary ices, clathrates are thermodynamically favored (Delsemme 1976). A possible 3σ spectroscopic detection of CH_4 in Comet Wilson has been reported (Larson *et al.* 1988), equivalent to $[CH_4]/[H_2O] \sim 0.04$. However, by no means do we insist on methane clathrate as the only plausible candidate ice yielding radiation-processed organics. Rather, a comparison of experimentally determined spectra with observed cometary emission features may allow certain otherwise plausible ices to be excluded as candidates for the origins of cometary organics (Khare *et al.* 1988).

In addition to the variety of plausible C- and N-rich ices which may contribute to irradiation-produced cometary organics, there is also a range of radiation environments which must be considered (Chyba and Sagan 1988c). We have argued (Chyba and Sagan 1987a, 1988c) that while some of the emitting organic dust in the Halley coma will be due to fragments of the observed low albedo crust, most is probably jetted from the cometary interior, with organics thus due mainly to processing by radionuclides (Draganić *et al.* 1984) and pre-accretion irradiation. Strazzulla *et al.* (1983) have shown that low-energy cosmic rays should totally polymerize C-containing ices in interstellar grains on timescales less than dust cloud lifetimes. Ultraviolet irradiation in the interstellar medium may also play an important role (Greenberg and Grim 1986).

Deriving a simple two-component model for emission from dust in the Halley coma (Chyba and Sagan 1987a), we used the laboratory-determined transmission spectrum (Thompson *et al.* 1987) of the organic residue of irradiated methane hydrate clathrate to fit the Halley spectrum in the 3–4 μm range, as observed by Wickramasinghe and Allen (1986) for 31 March 1986 (heliocentric distance $R = 1.16$ AU, geocentric distance $\Delta = 0.549$ AU; all heliocentric and geocentric distances cited in this paper are from the ephemeris of Yeomans (1986)). This model fits the 3.4-μm feature, provides optical depths in good agreement with those determined by spacecraft observations, and accounts for the absence of features at longer infrared wavelengths, despite their presence in the transmission spectrum of the organic residue.

Our model predicted an observed infrared flux given by

$$F_\lambda = C_\lambda + \Omega\tau'_\lambda B_\lambda(T_r) + \Omega\tau B_\lambda(T_c), \quad (1)$$

where C_λ was the scattered solar flux, Ω the telescope solid angle, τ the optical depth of the blackbody continuum emitters (at temperature T_c), $\tau'_\lambda = \beta(a/\lambda)\ln(t_\lambda^{-1})$ the optical depth of the submicron (radius $a \sim 0.1$ μm) organic emitters (temperature T_r), and t_λ the transmissivity of the laboratory sample (given by Fig. 1, with maximum transmissivity set equal to 100%). β and τ were free parameters varied to provide a best (χ^2) fit to the data. β and τ have clear physical interpretations and are tightly constrained by spacecraft and ground-based data, as discussed below.

Several minor improvements have since been made to the model summarized by Eq. (1). For purposes of comparison with the Wickramasinghe and Allen observations of 31 March 1986, Chyba and Sagan (1987a) took the scattered solar flux C_λ to be given directly by the flux measured that night in two wavelength windows between 1.5 and 2.5 μm. This procedure slightly overestimates the solar contribution to F_λ, as there is also a minor contribution to the flux measured at these short wavelengths by the final two B_λ terms in Eq. (1). We therefore now adopt the following procedure: For each value of β and τ examined in the χ^2 minimization, we subtract from C_λ at 0.1 μm intervals over the 1.5–2.5 μm range the two small B_λ contributions. We then perform a linear regression [$\log(F_\lambda)$ vs $\log(\lambda)$] to obtain the scattered solar curve (i.e., with the B_λ contributions removed) for this choice of β and τ. This avoids a double counting of the B_λ contributions at short wavelengths and also results in a better fit to observations in the 3 μm region (Fig. 2). No attempt is made to model a possible band at 3.05 μm, which may be due to O–H absorption (Combes *et al.* 1988). Thus, we now write

$$F_\lambda = S_\lambda + \Omega\tau_\lambda B_\lambda(T_r) + \Omega\tau B_\lambda(T_c), \quad (2)$$

where S_λ, the scattered solar continuum, is given at any λ via the above regression. We also now set $\tau_\lambda = \gamma(2\pi a/\lambda)\ln(t_\lambda^{-1})$, where γ differs from the previously employed β by a factor 2π, so that the usual $2\pi a/\lambda$ Mie theory dependence is explicitly displayed. In addition, we have recognized a multiplicative error in the values of β and τ'_λ reported

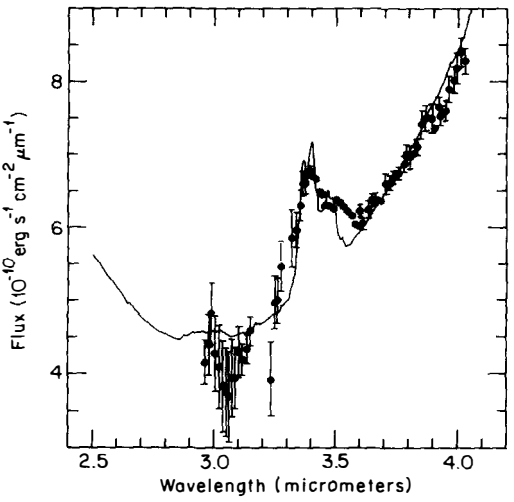

FIG. 2. Our best fit (continuous curve) to the 3–4 μm 31 March 1986 spectrum of Comet Halley (Wickramasinghe and Allen 1986), using a temperature T_r = 450°K appropriate to Titan tholin optical constants, and the spectrum of Fig. 1. The 3.4-μm feature lies almost at the minimum of the scattered solar flux (declining from the left) and blackbody thermal emission (rising to the right). The best fit for T_r = 560°K, appropriate to glassy carbon optical constants, is nearly identical to that shown here. A possible 3.05-μm feature is not modeled.

in Chyba and Sagan (1987a). The values cited there should instead have read $\beta = 3.7 \times 10^{-4}$ and $\tau'_\lambda = 3.6 \times 10^{-6}$ (giving $\tau'_\lambda/\tau = 2.6 \times 10^{-2}$ at $\lambda = 3.4$ μm); these changes do not affect other reported results in any way.

Equation (2) requires a choice of temperatures T_c and T_r. T_c may be determined empirically from observations of continuum emission in the Halley coma. Wickramasinghe and Allen (1986) find that the Halley spectrum in the 3–4 μm range (exclusive of the emission feature at 3.4 μm, and a possible O–H absorption feature at 3.05 μm) is best fit by $T_c = 350 \pm 10$°K. This temperature is ~25% hotter than the temperature of a blackbody at that heliocentric distance, presumably due to the presence of submicron grains in the coma. The temperature T_r of the submicron organic emitters, as a function of heliocentric distance and grain size, may be found via Mie theory calculations using the optical constants of laboratory-produced organic residue or other candidate materials. Hanner (1986) and Lamy and Perrin (1988) have performed such calculations for an organic residue ("Titan tholin") produced by sparking 10% CH_4 in a nitrogen atmosphere (Khare *et al.* 1984). [We stress that Titan tholin is an unlikely material for cometary grains; it was selected by these authors because it is an organic irradiation residue the optical constants of which are well-characterized (Khare *et al.* 1984).] Taking a typical particle size for presumed spherical emitting organic grains in the Halley coma to be ~0.1 μm then gives T_r = 450°K at 1.16 AU. By contrast, Mie calculations for 0.1-μm glassy carbon grains (Hanner 1983) yield T_r = 560°K at 1.16 AU. T_r = 560°K is also close to the temperature given by Mie calculations for biologically derived organic grains of radius 0.1 μm (Wallis *et al.* 1987). If cometary grains are highly porous and nonspherical these temperatures would be higher, and particles as large as tens of microns in size might be much hotter than expected for a blackbody (Greenberg and Zhao 1989).

III. COMPARISON WITH SPACECRAFT RESULTS

Given choices for T_c and T_r, we vary τ and γ in Eq. (2) to minimize χ^2; our best fit to the 31 March 1986 observations is shown in Fig. 2. The resulting values of τ and τ_λ may then be compared with spacecraft-determined filling factors for the Halley coma. For T_r = 560°K (glassy carbon), we find $\tau = 1.5 \times 10^{-4}$ and $\gamma = 2.4 \times 10^{-5}$, giving $\tau_\lambda = 1.5 \times 10^{-6}$ at $\lambda = 3.36$ μm, or $\tau_\lambda/\tau = 1.0 \times 10^{-2}$. τ_λ is sensitive to the choice of T_r; at a temperature appropriate for Titan tholin, T_r = 450°K, we find $\tau = 1.5 \times 10^{-4}$ and $\gamma = 1.5 \times 10^{-4}$, giving $\tau_\lambda = 9.1 \times 10^{-6}$ and $\tau_\lambda/\tau = 6.1 \times 10^{-2}$. It must be emphasized that neither the optical constants for glassy carbon nor those of Titan tholin are necessarily appropriate for the organic residue of an irradiated carbon-bearing ice, so these temperatures and τ_λ/τ ratios should be thought of only as indicators of a plausible range of

values. In particular, irradiated ice residues typically show a strong absorption in the 3.4 μm region (Khare *et al.* 1988), which Titan tholin and glassy carbon do not. To our knowledge, measurements of the optical constants of an ice residue over a wavelength range sufficient to allow Mie theory calculations have never been performed. Such measurements (which, for ice residues, pose difficult experimental problems) are of considerable importance, and are being pursued by our group.

Chyba and Sagan (1987a) compared τ to the geometrical filling factor $A_{WA} = 1.9 \times 10^{-4}$ for the dust in the field of view of the Wickramasinghe and Allen (1986) aperture. A_{WA} is calculated by integrating over the telescope aperture the dust fluence as a function of mass and nucleocentric distance determined by the spacecraft Giotto (McDonnell *et al.* 1986, 1987), convolved with a model for the density–radius relationship for Halley dust (Divine *et al.* 1986), correcting for heliocentric distance. The interim assessment of the Halley dust distribution (McDonnell *et al.* 1986) used for this calculation by Chyba and Sagan has since been finalized in a slightly different form (McDonnell *et al.* 1987), so that A_{WA} must now be reassessed. The current best values for the Giotto-observed dust fluence indicate a mass distribution index $\alpha \approx -0.85$ [where the number of particles having mass greater than m is given by $N(>m) \propto m^{\alpha}$] for $m < 10^{-8}$ kg, above which the exponent changes to $\alpha \approx -0.54$. McDonnell *et al.* consider two upper limits to which the mass integration may be extended, 10^{-3} and 1 kg. The first of these corresponds to the upper limit needed to give a total mass sufficient to account for the observed deceleration of the Giotto spacecraft. The second is chosen to yield a dust/gas ratio of 1 : 1; it is not an observation-based quantity, although larger dust particles than those encountered by Giotto may well exist in the Halley coma. Depending on which choice is made, one finds $A_{WA} = 9.4 \times 10^{-5}$ (for 10^{-3} kg) or $A_{WA} = 1.5 \times 10^{-4}$ (for 1 kg.). As cometary dust emission is known to be highly time-variable [emission from Halley has been observed to deviate from an overall R^{-4} law for infrared flux by as much as a factor of 7 over a few days (Gehrz and Ney 1986), and there were 2 weeks between the Giotto flyby and the Wickramasinghe and Allen observations], the agreement between A_{WA} and the optical depth τ required by our model is excellent.

It is more difficult to compare quantitatively the optical depth τ_λ found for the emitting organic grains with the spacecraft results. Submicron grains in the Halley coma certainly contribute to the 3.4-μm feature, but much larger particles might also contribute if the grains are sufficiently fluffy (Greenberg and Zhao 1989). The Giotto-determined dust distribution can be integrated to find the percentage of the coma filling factor due to grains smaller than a certain radius. Using the latest (McDonnell *et al.* 1987) results for the distribution observed along the Giotto trajectory, one finds that dust particles with radii ≤ 1 μm contribute between 2.8 and 4.4% of the total filling factor, depending upon whether the integration is continued to 1 or 10^{-3} kg, respectively. Similarly, grains with radii ≤ 10 μm contribute between 25 and 40% of the total filling factor. More recently, however, Perry *et al.* (1988) have re-examined the Giotto data, in light of discrepancies between the spacecraft results and ground-based observations made shortly before encounter. Taking into account the dependence of grain outflow velocity on size, they conclude that the change in the value of the exponent α at 10^{-8} kg may have been an artifact of variations in the level of dust production at the nucleus. They therefore recommend that modeling of the Halley coma should not include the large mass excess actually observed by Giotto, but rather that the small-particle exponent ($\alpha \approx -0.85$) should be extended through the larger sizes. If this recommendation is followed, one finds that submicron grains contribute ~6% of the filling factor, while

grains ≤ 10 μm contribute $\sim 50\%$. These results are independent of whether the integration range extends to 10^{-3} or 1 kg, as the large negative exponent α in this case guarantees that particles larger than 1 g contribute almost negligibly to the coma filling factor. Finally, it should be noted that these results make use of the Divine *et al.* (1986) density–radius distribution, which assumes that the smallest coma particles have densities approaching 3 g/cm^3, with density dropping with increasing size up to a large-particle limit of 0.8 g/cm^3. To test the sensitivity of the above results to alternate density–radius models, we have convolved the Giotto-measured mass fluence with a dust particle density 0.8 g/cm^3, taken to be independent of particle size. We find that the resulting filling factors differ little from those cited above.

The range of optical depths τ_λ found above for the emitting organic grains, $\tau_\lambda/\tau = 0.01$–0.06, may be compared with upper bounds placed on this ratio by the fraction A_f of the total coma filling factor determind from Giotto data for dust grains with radii less than 1 and 10 μm, viz., A_f (≤ 1 μm) = 0.03–0.06 and A_f (≤ 10 μm) = 0.25–0.5. Only some portion of A_f is due to organic grains, but this component appears large: Some 84% of Halley's dust contains carbon (Jessberger *et al.* 1988), and Kissel and Krueger (1987) have interpreted Vega mass spectrometer data to mean that most Halley dust consists of a chondritic core coated with an organic mantle.

τ_λ and A_f cannot be directly compared, however. In general, the absorption optical depth of the organic emitters at a wavelength λ is given by

$$\tau_\lambda = \int \tau(\lambda, a) da, \qquad (3)$$

with

$$\tau(\lambda, a) = \int n(a) \pi a^2 Q_{abs}(\lambda, a) dl, \qquad (4)$$

where $n(a)$ is the number density for particles of radius a, and $Q_{abs}(\lambda, a)$ is the dimensionless absorption efficiency factor for these particles at wavelength λ. The integral in Eq. (4) is taken along the line of sight through the coma. For optically thick grains, $Q_{abs}(\lambda, a) \approx 1$, so that the optical depth is just the geometrical filling factor. Thus τ can be compared directly to A_{WA}, as was done above. For grains with $a \lesssim \lambda$, however, Q_{abs} may be either greater or less than 1, typically becoming very small for $a \ll \lambda$. To compare τ_λ with the Giotto-determined filling factors A_f, we need Q_{abs} at $\lambda = 3.4$ μm throughout the range of interest in a. Most simply, τ_λ could be approximated by the expression $\tau_\lambda/\tau \approx \overline{Q}_{abs} A_f$, where $\overline{Q}_{abs}$ is some "typical" value of Q_{abs} for the emitting organic grains over the appropriate range of grain radii.

Q_{abs} may be calculated from Mie theory if the optical constants (complex refractive index $n_c = m - ik$, where m is the real and k the imaginary part of the refractive index) are given. Although such constants are not known for ice residues at 3.4 μm, we can delineate a plausible range of values by considering m and k for Titan tholin and glassy carbon. At $\lambda = 3.4$ μm, n_c for Titan tholin (interpolated from Khare *et al.* 1984) is given by $m = 1.65$ and $k = 0.041$; glassy carbon at this wavelength (interpolated from Edoh 1983) has $m = 2.93$ and $k = 1.01$. Wickramasinge (1973) has compiled Mie theory results for extinction and scattering efficiencies, Q_{ext} and Q_{sca}, over a wide variety of m and k values. Employing the relation $Q_{abs} = Q_{ext} - Q_{sca}$, we use his tables for $m = 1.7$ and $k = 0.05$, and $m = 3.0$ and $k = 1.0$, to approximate the efficiency factors for Titan tholin and glassy carbon, respectively, over a range of values for $x \equiv 2\pi a/\lambda$. At $\lambda = 3.4$ μm, these x-values correspond to particles of definite radii a. Our results are summarized in Table I. We see that Q_{abs} for glassy carbon is typically >1 for particles with radii in the range ~ 0.3–3 μm, wherease Q_{abs} for Titan tholin ~ 0.1–1 over the same range of a. We can thus conclude that the values $\tau_\lambda/\tau \sim 10^{-2}$ required by our model are consistent with the spacecraft-determined values $A_f \sim 0.03$–0.5, at least given the large range of uncertainty in A_f

TABLE I

APPROXIMATE EFFICIENCY FACTORS FOR TITAN THOLIN AND GLASSY CARBON AT 3.4 μm

Particle radius $a(\mu m)$	$x \equiv 2\pi a/\lambda^a$	Q_{abs}, Titan tholin[b]	Q_{abs}, glassy carbon[c]
0.1	0.2	0.009	0.1
0.25	0.5	0.05	0.5
0.5	0.9	0.1	1.7
1.0	1.9	0.4	1.5
2.0	3.7	0.8	1.2
2.7	5.0	0.9	1.1

[a] x evaluated at $\lambda = 3.4$ μm.

[b] At 3.4 μm, Titan tholin has $n_c = 1.65 - 0.041i$ (Khare *et al.* 1984); Wickramasinghe (1973) lists $n_c = 1.7 - 0.05i$.

[c] At 3.4 μm, glassy carbon has $n_c = 2.93 - 1.01i$ (Edoh 1983); Wickramasinghe (1973) lists $n_c = 3.0 - 1.0i$.

and Q_{abs}. Agreement is more easily obtained with glassy carbon optical constants than with those appropriate for Titan tholin. Optical constants for an actual ice residue over the crucial wavelength range, as well as a better knowledge of the fluffiness of cometary grains, are critical to performing this calculation more definitively.

IV. HELIOCENTRIC EVOLUTION OF COMETARY EMISSION FEATURES

Green *et al.* (1986) have shown that the Halley continuum spectrum over the range 1–20 μm as a function of heliocentric distance R (measured in AU) is well fit by a combination of scattered sunlight and blackbody emission at a temperature

$$T_c = 329R^{-0.53}, \quad (5)$$

a relation derived from observations of a number of comets. This value of T_c is ~15% lower than that found both by Wickramasinghe and Allen (1986) for the 3–4 μm region, and by Bregman *et al.* (1987) for the range 5–13 μm. This discrepancy may be explained as due to the different wavelength ranges being fit: as increasingly longer wavelengths are considered, the contribution due to small, hot grains in the coma becomes less and less significant. Indeed, Tokunaga *et al.* (1988) have also recently determined a relation similar to Eq. (5) for Comet Halley, finding that color temperatures defined by the flux ratio 4.8 μm/7.8 μm are ~15% higher than those derived for 7.8 μm/12.5 μm data, which are in turn ~15% hotter than equilibrium blackbody temperatures. Thus the continuum over the range 2–12 μm is expected to be best fit by a temperature higher than that given by Eq. (5). Indeed, our own numerical investigations show that our model cannot fit the Wickramasinghe and Allen observations well for temperatures outside the range 350 ± 10°K. Therefore, for consistency with the results of Wickramasinghe and Allen and Bregman *et al.*, we take the temperature of the continuum emitters at 3–4 μm to be given by

$$T_c = 350(R/1.16)^{-0.53}. \quad (6)$$

The exponent is close to that (−0.50) expected for a gray body in thermodynamic equilibrium.

Thus it is possible to model Halley emission over the range 2–12 μm using the model given by Eq. (2). The continuum optical depth $\tau \sim 10^2$ times the optical depth due to the emitting organics (τ_λ), so that only near the minimum in the continuum radiation can an organic emission feature achieve good visibility relative to the continuum. At 1 AU, the 3.4-μm feature is the sole feature near that minimum, lying near the intersection of the scattered solar and 350°K blackbody curves. However, as the comet moves away from perihelion, the intersection of the scattered solar spectrum and the comet's thermal emission spectrum will move to longer wavelengths. Thus, relative to the continuum, we expect the 3.4-μm feature to be diluted and those at longer wavelengths progressively revealed, as the minimum in continuum emission sweeps through the infrared spectrum toward longer wavelengths.

Of course, this evolution is only relevant at those heliocentric distances R at which the comet retains its coma. Water ice is expected to vaporize in the solar radiation field for $R \lesssim 3$ AU (Delsemme 1982) and, indeed, it is at this distance that comets typically develop an obvious, extended coma.

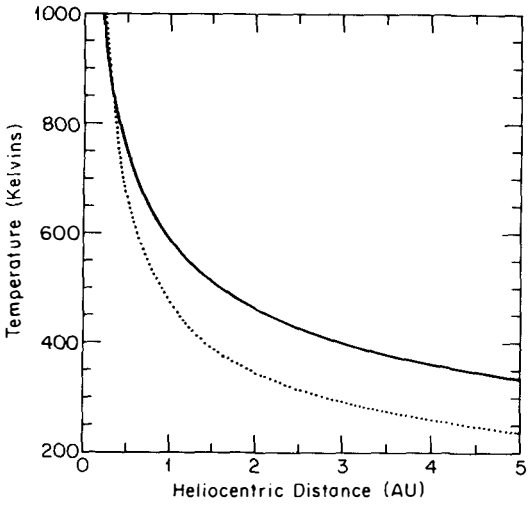

FIG. 3. The temperature of 0.1-μm grains as a function of heliocentric distance for glassy carbon (solid line) and Titan tholin (dotted line) optical constants. Titan tholin results are from Lamy and Perrin (1988) and Hanner (1986). Glassy carbon results are given by Hanner (1983) for $R < 2$ AU, and are extremely well fit by the relation $\log T = 2.77 - 0.355 \log R$. This relation is then used to extrapolate out to 5 AU.

However, some comets develop comae at larger distances. Comet Bowell 1980b exhibited an extended dust coma (but no detectable gaseous emission spectrum) for R as large as 7.2 AU (Cochran and McCall 1980). In the case of Comet Halley, there is evidence for a gaseous coma beginning at $R \sim 6$ AU (Green and Morris 1987), and for a coma of dust grains within $R = 5.4$ AU (Hanner 1986).

Using the values of the parameters found in Eq. (2) to provide the best fit to the 3 to 4-μm emission of Comet Halley at 1.16 AU, we can predict the spectrum of the comet at all wavelengths in the range 2–12 μm as a function of heliocentric distance R. We simply evaluate the flux given by Eq. (2), with T_c given by Eq. (6) and T_r taken to be the temperature of 0.1-μm spherical grains found by Mie theory for either glassy carbon (Hanner 1983) or Titan tholin (Hanner 1986, Lamy and Perrin 1988) optical constants at the appropriate R. The temperature of these grains as a function of R is shown in Fig. 3. In addition, it is known that dust production by Comet Halley exhibited an approximate R^{-2} dependence on heliocentric distance (Gehrz and Ney 1986). Thus the two B_λ terms in Eq. (2) are further reduced by this amount. S_λ falls off as R^{-4}, one R^{-2} factor due to reduced dust production, and one due simply to the decreasing angle subtended by each dust particle as a function of increasing R. Note that our model describes the spectral evolution of organic features only; it does not, for example, include emission due to silicates [observed in both Comets Halley (Bregman *et al.* 1987) and Wilson (Lynch *et al.* 1988)] or carbonates [tentatively identified in Comet Halley (Bregman *et al.* 1987)]. Nor does our model include a possible O–H absorption feature near 3.05 μm, as suggested by Combes *et al.* (1988).

Our results are displayed in Figs. 4 and 5. In each we present parallel results for both glassy carbon and Titan tholin optical constants, over the spectral range 2.5–12 μm. Beginning at $\sim$8 μm, however, silicate emission should begin substantially to alter the results predicted here (see below), and beyond $\sim$10 μm the assumption of constant T_c will begin to fail.

Figure 4 shows the predicted spectrum of Comet Halley for six different representative heliocentric distances. (Halley's perihelion distance was 0.59 AU; we have however extended our calculations to 0.3 AU, in anticipation of observations of comets with perihelion distances within several tenths of an AU of the Sun. Our 0.3-AU spectra may serve as predictions for such comets only if their 3.4 μm spectrum near 1 AU resembles that of Comet Halley, however, and if there is no significant thermal or radiation processing of the grains preferentially at small R.) The decrease in overall flux from the comet due to decreased dust production is evident. No account is taken of changing geocentric distance in calculating the overall magnitude of the flux. Thus, the magnitude of the flux in Fig. 4 changes in the manner that would be observed by a co-orbiting spacecraft that maintained a fixed distance from the cometary nucleus.

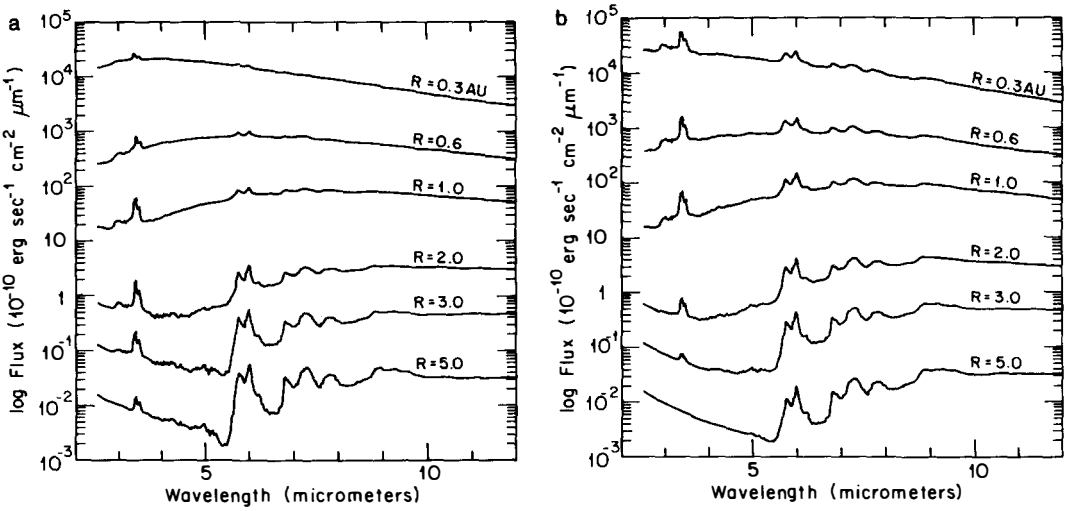

FIG. 4. (a) The 2–12 μm spectrum of Comet Halley predicted by our model for T_r given by glassy carbon optical constants (solid line in Fig. 3) at six different heliocentric distances. Emission features have been exaggerated by a factor of 10 for clarity. The prominence given to successive organic emission features by the minimum in the continuum spectrum as the comet moves to larger heliocentric distances is evident. (b) The same as (a) but for T_r given by Titan tholin optical constants (dotted line in Fig. 3).

As seen in Fig. 4, as the continuum minimum sweeps to longer wavelengths, the ~6-μm feature (present at the level of the 3.4-μm feature in the transmission spectrum of Fig. 1, but greatly suppressed in emission relative to the continuum at ~1 AU) becomes progressively enhanced. We have exaggerated the strength of the emission features in Fig. 4 by a factor of 10, in order to make this evolution more apparent. Note the evolution of the continuum underlying the 3.4-μm feature from thermal emission to scattered solar continuum as the comet moves from R = 0.3 to 2.0 AU. Such an evolution has been observed by Knacke *et al.* (1986) in ground-based observations for Comet Halley moving between R = 1.08 and 1.54 AU. The movement of the continuum minimum toward longer wavelengths with increasing R found in Fig. 4 is in quantitative agreement with continuum measurements for Comet Halley made by Tokunaga *et al.* (1986) over the heliocentric range 0.9–2.8 AU.

In Fig. 5, we divide out the continuum from the predicted cometary emission spectra in order to make evident the evolving strengths of the features relative to the continuum. No exaggeration of emission features is made here. There are important similarities and contrasts between the heliocentric evolution predicted by glassy carbon (solid line) and Titan tholin (dotted line) optical constants. In both cases, the strength of the 3.4-μm feature increases from a low level at 0.3 AU out to a maximum between 1 and 2 AU, then becomes nearly negligible by the time the comet is 5 AU from the Sun. (Of course, the cometary coma may have already disappeared by this heliocentric distance.) Simultaneously, the features at ~6 μm grow from only a few percent above continuum at ~0.3 AU to ~100% over continuum at 5 AU. For best visibility relative to the continuum, observations of the 6-μm or longer wavelength features should evidently be conducted at heliocentric distances greater than 2 AU.

Finally, we note that the 3.4-μm feature increases in strength between 1 and 2 AU in the case of glassy carbon optical constants, whereas it decreases in strength over the

same range of distances for Titan tholin optical constants. This is immediately explicable in terms of the differing heliocentric temperature dependence for these materials as displayed in Fig. 3. Glassy carbon, with a much larger imaginary refractive index, is more highly absorbing than Titan tholin, so that grains of this material reach higher temperatures. The resulting differences in spectral feature heliocentric evolution provide an observational diagnostic of cometary organic composition, as will be addressed in the following section.

V. COMPARISON WITH AIRBORNE AND GROUND-BASED OBSERVATIONS

Observations of Comet Halley in the 5–13 μm range (Bregman *et al.* 1987) at helio-

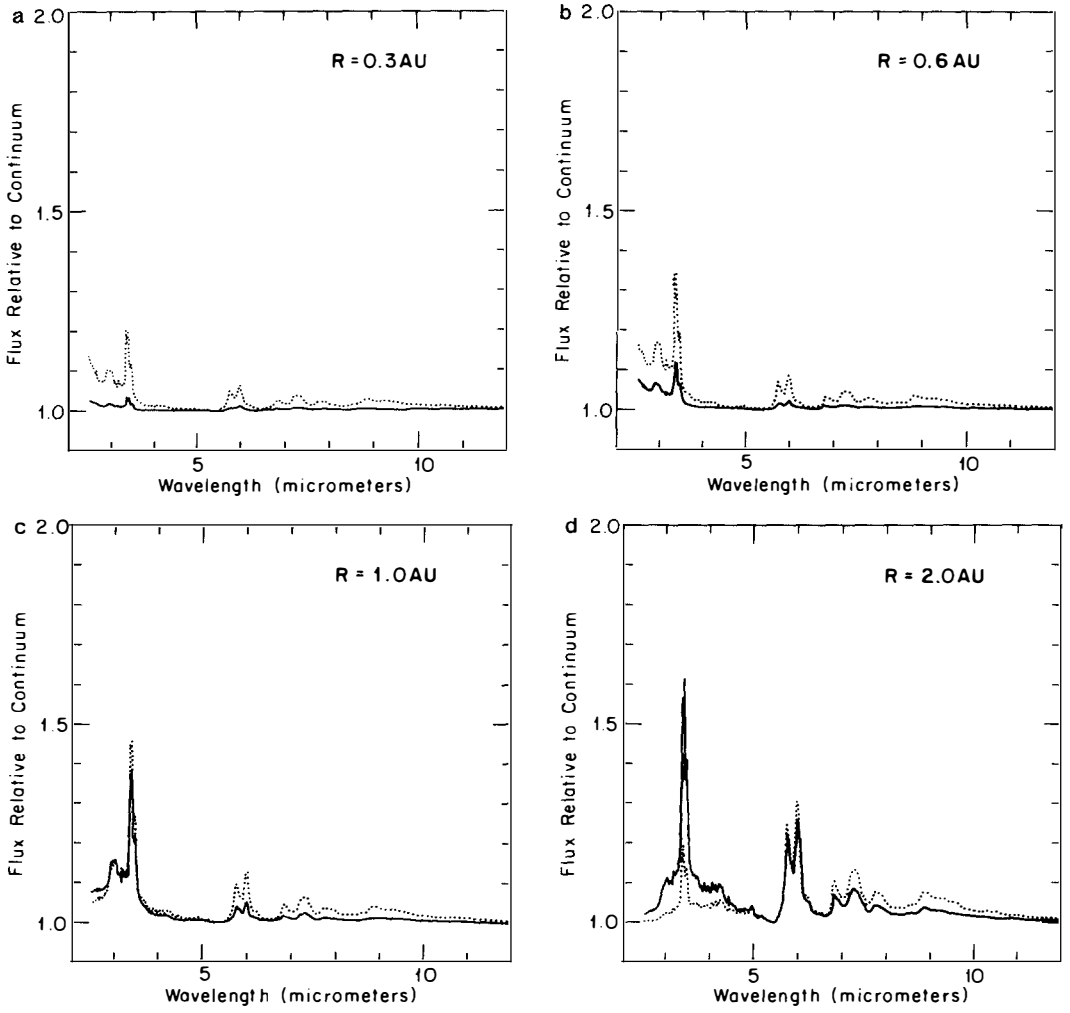

FIG. 5. (a) The 2–12 μm spectrum of Comet Halley predicted by our model at heliocentric distance R = 0.3 AU, after dividing out the continuum. The solid line depicts a model in which the 0.1-μm emitting organics are assigned a temperature T_r appropriate to glassy carbon optical constants. The dotted line assumes a T_r appropriate to Titan tholin optical constants (see Fig. 3). (b) The same as (a) for the case R = 0.6 AU. (c) The case R = 1.0 AU. (d) The case R = 2.0 AU. (e) The case R = 3.0 AU. (f) The case R = 5.0 AU. Note the great suppression of the 6-μm feature (compared to its strength in the transmission spectrum shown in Fig. 1) within $R \sim 2$ AU, and the peaking of the 3.4-μm feature in the 1–2 AU range.

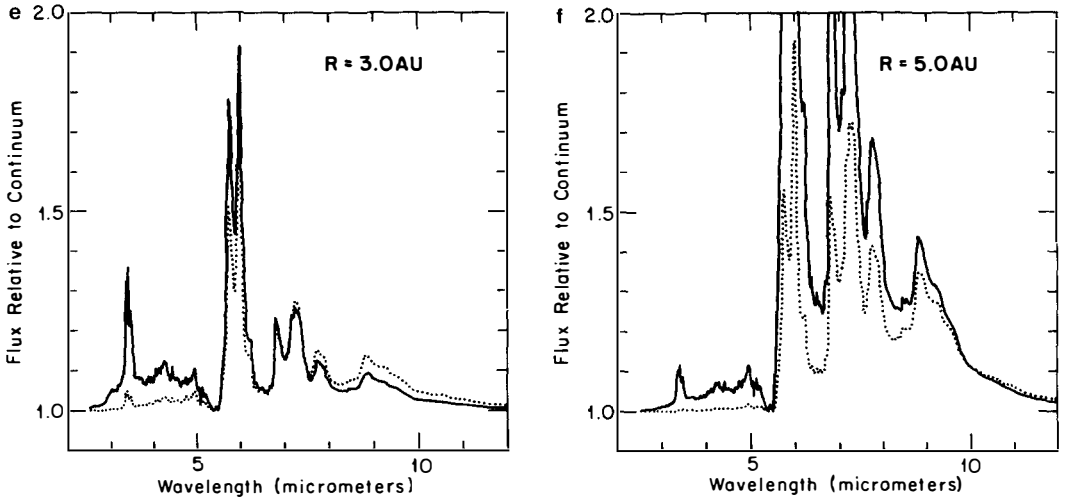

FIG. 5—*Continued, cases* (*e*) *and* (*f*).

centric distance $R \sim 1.3$ AU show a band rising to ~40% above continuum near 9 μm and to ~80% above continuum near 10 μm. This feature is usually attributed to Si–O stretching in small siliceous grains. Figure 5 shows that organic features predicted by our model in the vicinity of 9 μm from 0.3 to 2 AU rise to no more than ~10% above continuum, so Si emission is expected to swamp these features at these heliocentric distances. However, the 10-μm feature in comets typically disappears at larger heliocentric distances (Hanner 1986). At sufficiently large heliocentric distances (e.g., $R \gtrsim 3$ AU) it is therefore possible that organic spectral features near 9 μm could become visible (Figs. 5e, 5f).

Hanner (1986) and Lamy and Perrin (1988) have suggested that the Si feature may not be visible at large heliocentric distances because it is embedded in more volatile material which begins to evaporate only close to the Sun. Especially from the point of view of a Greenberg (1982) core–mantle interstellar grain model for cometary dust, it is interesting to speculate that the silicate material is embedded in a more volatile organic matrix. The correlation, if any, between the 3.4-μm feature and silicate emission in comets is unclear, however. For example, Comets West and IRAS-Araki-Alcock showed Si features in the absence of 3.4-μm features (Tokunaga and Brooke 1988). In addition, while Comets Halley and Wilson showed quite similar 3.4-μm organic features, their Si features differed significantly: Halley had an 11.3-μm feature which Wilson lacked, whereas Wilson displayed a 12.3-μm feature absent in the Halley spectrum (Lynch *et al.* 1988, Campins and Ryan 1988). Moreover, preliminary results for the PIA experiment in Giotto (Clark *et al.* 1987) indicate that ~30% of the "CHON" dust particles encountered by the Giotto spacecraft were, to the limits of detectability, purely organic in composition, rather than organics enclosing a silicate core. In addition, the similarity between the core–mantle interstellar dust model and interplanetary dust particles (IDPs or "Brownlee particles") of possible cometary origin is at best ambiguous. The only "ground truth" we have for cometary dust is the cometary fraction of the IDPs collected by high altitude aircraft in the Earth's stratosphere. But Walker (1988) has concluded that "nothing resembling the Greenberg model has been seen in the study of several hundred IDPs. We therefore doubt that it is a valid picture for typical

cometary particles. . . . Some interstellar material is present but the volume fraction is small. . . ." (See also Brownlee 1988).

The results of our model presented in Figs. 4–5 assume a greatly idealized regularity in the parameters necessary to predict cometary emission spectra. As previously noted, Comet Halley is in fact known to be highly time variable, both deviating from a simple R^{-4} law for infrared flux by as much as a factor of 7 over a few days (Gehrz and Ney 1986), and showing great variability of emission features relative to continuum on successive nights' observations. Similarly, Weaver *et al.* (1987) observed a 40% variation in Halley water molecule production over a space of only 2 hr on 24 March 1986. Thus heliocentric evolution of organic spectral features may well be indiscernible due to stochastic cometary variability, at least in the absence of sufficiently comprehensive observational statistics.

Given this variability, as well as the many uncertainties in our model, it is evident that one can at best make general predictions on the basis of Figs. 4 and 5. Uncertainties in the model include, among others, that the τ_λ/τ ratio appropriate for fitting the 3.4-μm feature on the date of Wickramasinghe and Allen's 31 March 1986 observation cannot be exactly appropriate for other dates; the strength of the 6-μm feature relative to that at 3.4 μm in the transmission spectrum used in the model is expected to vary with radiation dose; CH_4 hydrate clathrate is certainly not the only C- or N-containing ice initially present in a comet; the temperatures 450 and 560°K calculated from optical constants for a gas-phase N-rich product or glassy carbon can only be an approximation to the temperature appropriate to an ice residue; and, finally, the simple two-component model used here is obviously crude. We hope to address some of these dependencies in further experimental work (see also Khare *et al.* (1988) for an initial exploration of some of the relevant parameters).

Nevertheless, it is instructive to compare quantitatively the predictions of our model with actual observations of the heliocentric evolution of the 3.4-μm feature in Comet Halley. In Table II, we summarize the observations made of this feature for heliocentric distances between 1.08 and 1.96 AU. Column 3 of Table II lists the ratios $F_\lambda^{em}/F_\lambda^{cont}$ of the peak flux F_λ^{em} of the emission feature to the continuum flux F_λ^{cont}. These results are to be compared with the model predictions listed in columns 4–6. Quantifying the error associated with $F_\lambda^{em}/F_\lambda^{cont}$ in column 3 is difficult, as a determination of this ratio requires fitting an underlying continuum to the observed emission feature and a typically small number of neighboring points. However, we estimate typical uncertainties in our determinations of the ratios given in column 3 to be ± 0.1.

The observed flux ratios given in column 3 make the extent of time variability in cometary emission clear. The preperihelion observation of Danks *et al.* (1986) made at $R = 1.11$ AU found the 3.4-μm feature at only the 1σ level. Observations by Wickramasinghe and Allen (1986) on 31 March and 1 April 1986 show a jump in $F_\lambda^{em}/F_\lambda^{cont}$ of ~35% between the 2 nights. Since T_c and T_r in Eq. (2) are virtually unchanged as a comet moves from $R = 1.16$ to $R = 1.18$ AU, this jump must be due to a change in the ratio τ_λ/τ. From Eq. (2), we have $F_\lambda^{em} = S_\lambda + \Omega\tau_\lambda B_\lambda(T_r) + \Omega\tau B_\lambda(T_c)$ and $F_\lambda^{cont} = S_\lambda + \Omega\tau B_\lambda(T_c)$, so that

$$F_\lambda^{em}/F_\lambda^{cont} - 1 = (\tau_\lambda/\tau)A_\lambda, \qquad (7)$$

where

$$A_\lambda \equiv B_\lambda(T_r)/[(S_\lambda/\Omega\tau) + B_\lambda(T_r)]. \qquad (8)$$

[We note that Eqs. (7) and (8), provided S_λ is known, serve to check the consistency of the result τ_λ/τ found by varying χ^2 in Eq. (2).] Since $S_\lambda \propto \tau$, A_λ in Eq. (8) is independent of τ, depending only on T_c and T_r; A_λ for the dates 31 March and 1 April 1986 is thus approximately constant. Dividing both sides of Eq. (7) for 1 April by Eq. (7) for 31 March, we note that A_λ cancels out and we

TABLE II

COMPARISON BETWEEN MODEL AND OBSERVED FLUX RATIOS AT $\lambda = 3.4\ \mu m$[a]

Observation date	Heliocentric distance R(AU)[b]	Observed flux ratio $(F_\lambda^{em}/F_\lambda^{cont})$	Predicted flux ratio $(F_\lambda^{em}/F_\lambda^{cont})$		
			Grains for which $T = 900°K$ at 1.16 AU	Glassy carbon optical constants	Titan tholin optical constants
25 December 1985[c]	1.11	~0[h]	1.5	1.5	1.5
26 March 1986[d]	1.08	1.4	1.5	1.4	1.5
27 March 1986[d]	1.10	1.6	1.5	1.5	1.5
28 March 1986[c]	1.12	1.4	1.6	1.5	1.5
29 March 1986[d]	1.13	1.4	1.6	1.5	1.5
30 March 1986[e]	1.15	1.4	1.6	1.5	1.5
31 March 1986[e]	1.16	1.4	1.6	1.5	1.5
1 April 1986[e]	1.18	1.9	1.6	1.5	1.5
25 April 1986[d,f]	1.54	1.7	1.9	1.7	1.3
19–20 May 1986[g]	1.90	2.2	2.0	1.6	1.2
24 May 1986[f]	1.96	~2[i]	2.0	1.6	1.2

[a] It is shown in Section V that discrepancies between model predictions in columns 4 and 5 and observations lie within the stochastic variability of $F_\lambda^{em}/F_\lambda^{cont}$ observed for Comet Halley.

[b] Ephemeris from Yeomans (1986).

[c] Danks *et al.* (1986).

[d] Knacke *et al.* (1986).

[e] Wickramasinghe and Allen (1986).

[f] Baas *et al.* (1986).

[g] Tokunaga *et al.* (1987).

[h] Feature observed at the 1σ level.

[i] $F_\lambda^{em}/F_\lambda^{cont}$ is difficult to quantify, as the placement of the continuum baseline cannot be made with confidence.

find that the change in $F_\lambda^{em}/F_\lambda^{cont}$ between the two obsevations by the factor $1.9/1.4 \approx 1.4$ requires that τ_λ/τ change by a factor $(1.9 - 1)/(1.4 - 1) \approx 2.3$. Thus we discover that the optical depth of the emitting organic grains may change stochastically relative to the continuum optical depth by a factor of a least 2.3 on timescales of 1 day. Such a sudden increase in τ_λ/τ requires either a sudden increase in the number or the absorption coefficient of the organic grains in the coma; either result seems to imply significant nuclear heterogeneity. Such an outburst of small organic grains implies a change in the exponent α of the Halley dust distribution. This result should therefore also caution cometary modelers against drawing strong conclusions on the basis of the dust mass distribution measured by the Giotto or Vega spacecraft, as these may also be highly time-variable.

We remark that the evident outburst of emitting organic particles on 1 April 1986 coincided with an unusually strong CN-shell expansion at that date (Schlosser *et al.* 1986). This coincidence lends support to the hypothesis of A'Hearn *et al.* (1986) that CN jets in Comet Halley form as the CN dissociates directly from submicron organic dust particles in the coma (see also Lamy and Perrin 1988). In addition to CN jets, Halley exhibited OH outbursts between 24 and 29 March 1986, and 30 March and 4 April 1986 (Silva and Mirabel 1988). These outbursts also coincide with evident outbursts of emitting organics seen in Table II.

The greatest discrepancies between our model results and observations are for 25

December 1985, and for the period from 25 April to 24 May 1986. The lack of an observed 3.4-μm feature on 25 December is a further warning that comparisons between model predictions and observations for Comet Halley infrared emission cannot be expected to be exact when only a small number of observations are available for this highly time-variable object. We know from the dates 31 March and 1 April 1986 that variations in $F_\lambda^{em}/F_\lambda^{cont}$ of a factor $\sim$1.4 occur unpredictably; the observed flux ratio for 25 April is just consistent with the model predictions for Titan tholin (column 6) to within this factor. Model predictions for glassy carbon (column 5) are in perfect agreement with observations on this date. The 19–20 May observations, however, appear to require an increase in $F_\lambda^{em}/F_\lambda^{cont}$ over that predicted by our model by a factor $\sim$1.4 in the case of glassy carbon, and $\sim$1.8 in the case of Titan tholin. In light of the time-variability exhibited by Halley, it is clear that, at least in the case of glassy carbon, changes of this magnitude (equal to that observed between 31 March and 1 April) in $F_\lambda^{em}/F_\lambda^{cont}$ are entirely possible. Thus we conclude that both the general evolutionary trend and quantitative values predicted by our model for glassy carbon optical constants are consistent with observations. Model predictions for Titan tholin optical constants, however, are more evidently discrepant with observations in both qualitative and quantitative respects. Thus the observed heliocentric evolution of the 3.4-μm feature provides information on the optical constants, and by extension the nature of the organic material, in Comet Halley.

Although the predictions shown in column 5 of Table II for our model with glassy carbon optical constants are consistent to within observed stochastic variability with the observational results listed in column 3, the match is far from perfect. In particular, $F_\lambda^{em}/F_\lambda^{cont}$ for glassy carbon optical constants peaks at $\sim$1.5 AU, whereas the observed $F_\lambda^{em}/F_\lambda^{cont}$ for Comet Halley appears to continually rise to $\sim$1.9 AU. Glassy carbon optical constants provide a closer fit to these observations than do those of Titan tholin because of the higher temperatures reached by the former. An obvious question, then, is what temperature emitting organic grains must attain at 1.16 AU in order to reach a peak $F_\lambda^{em}/F_\lambda^{cont}$ $\sim$ 2 at $\sim$1.9 AU. Numerical experiments show that, for particles whose temperature falls off with heliocentric distance as a blackbody, $T_r \sim 900$°K at 1.16 AU best matches the observational data. Results for a model with these temperatures are shown in column 4 of Table II. $T_r \sim 900$°K gives $\tau_\lambda/\tau \sim 5.8 \times 10^{-4}$ for a χ^2 minimum fit to the 3.4-μm feature at 1.16 AU.

In fact, $T_r \sim 900$°K is probably an overestimate of the temperature required at 1.16 AU to match the data of column 3. For submicron particles, temperature is expected to fall off with heliocentric distance more slowly than for a blackbody, because the long wavelength emissivity of small particles relative to that of a blackbody decreases with decreasing particle temperature (Greenberg 1971). Thus the temperature of submicron grains is expected to fall off as

$$T_r = T_r(R = 1.16\ \text{AU})(R/1.16\ \text{AU})^{-\xi}, \quad (9)$$

where $\xi < 0.5$ (Greenberg and Zhao 1989). Dumont and Levesseur-Regourd (1988) find $\xi \sim 0.33$ from IRAS data on zodiacal dust; if this choice of ξ were appropriate for Comet Halley submicron emitting organics (Greenberg and Zhao 1989), $T_r(R = 1.16$ AU) $\sim$ 825°K would fit the observational results listed in column 3. Such temperatures, higher than those expected for 0.1-μm glassy carbon spheres, may be due in part to a fluffy or fractal grain structure to comet dust (Meakin and Donn 1988). In such particles, flash heating of individual fractal elements by UV photon absorption may lead to temperatures well above those expected for a blackbody. We defer further discussion of these effects to a future publication.

VI. THERMAL EMISSION FROM GRAINS VS. GAS-PHASE FLUORESCENCE

It was first suggested by one of us (M.J.M.) at the workshop *Infrared Observations of Comets Halley and Wilson and Properties of the Grains* (M. Hanner, Ed. 1988) that the heliocentric evolution of organic spectral features will differ in the cases of thermal emission from small grains and gas-phase fluorescence. The observed intensity of a cometary emission feature will be proportional to the total number N of emitters present in that part of the coma subtended by the telescope aperture. N is in turn dependent upon the lifetime of the emitters. Using Mie theory, Wallis *et al.* (1987) have calculated lifetimes for biologically derived organic grains of radius ~ 0.1 μm. Assuming the range of bond energies of terrestrial Type II kerogen to be appropriate for cometary organics, they find that, at 1 AU, the grains experience almost no evaporation within a cometary coma of radius 5×10^4 km, the "nominal" size (McDonnell *et al.* 1987) of the Halley dust coma. [At these heliocentric distances, 0.1-μm grain lifetimes are well in excess of 10^6–10^7 sec; with an outflow velocity ~ 350 m/sec (McDonnell *et al.* 1987), such a grain will travel $\sim 10^6$ km prior to evaporation.] Organic molecular bonds with activation energies $\lesssim 50$ kcal/mole will be disrupted on shorter time scales, but $\lesssim 5\%$ of the bonds in kerogen have strengths below this level. Significant evaporation of 0.1-μm grains on time scales $\sim 10^4$ sec will begin only for heliocentric distances < 0.64 AU or at grain temperatures > 680°K (Wallis *et al.* 1987). Similarly, Combi (1987) has concluded that grain lifetimes are as short as $\sim 10^5$ sec only for grains that are very small ($\sim 10^{-3}$ μm, $\sim 10^{-21}$ g).

These results are in rough agreement with thermogravimetric analyses of the involatile organic residue produced by electron, spark, or UV irradiation of cosmically abundant gases; typical results indicate that the residues are 50% stable at temperatures ranging from ~ 600 to 1200°K (Sagan and Khare 1979, Sagan *et al.* 1984). Since ground-based observations of Comet Halley at heliocentric distances ~ 1–2 AU typically subtend $\sim 10^3$–10^4 km across the coma, particle evaporation is evidently of little importance in evaluating N in the case where organic spectral features are due to thermal emission from grains. Of course, those most volatile organics which do evaporate should themselves contribute to gas-phase fluorescence.

If the organic spectral features are due primarily to fluorescence, however, limits on molecular lifetimes due to dissociation by solar ultraviolet light are of great significance. For example, at 1 AU, unshielded CH_4 and NH_3 lifetimes against UV dissociation are $\sim 10^5$ and $\sim 10^4$ sec, respectively (see Allen *et al.* 1987). CH_4 would contribute prominently to fluorescence near 3.3 μm, and NH_3 near 6 μm (Crovisier and Encrenaz 1983). With a typical gas outflow velocity from the nucleus ~ 1 km/sec (Allen *et al.* 1987), CH_4 and NH_3 molecules should experience significant UV dissociation within a 5×10^4 km dust coma radius. Ground-based observations conducted with aperture sizes large enough to include this molecular dissociation, but small enough to exclude significant organic grain evaporation, are in principle capable of determining which mechanism, grain thermal emission or gas-phase fluorescence, is primarily responsible for the observed cometary organic spectral features. In the simplest approximation, the lifetimes of gas-phase fluorescing molecules will increase as the square of the heliocentric distance R, whereas the lifetimes of thermally emitting organic grains ("infinite" for the purposes of these observations) will remain unchanged. Thus the band strengths predicted by these two mechanisms for the 3.4-μm emission feature differ by a factor R^2 in their heliocentric evolution. To observe this evolution, a sequence of observations over a range of heliocentric distances, with appropriately chosen aperture sizes, would be required.

Of course, the situation is in practice much more complex. For example, the fluorescing of daughter products of dissociated parent molecules (among other complications) must be taken into account. We hope to explore the details of such a more precise treatment elsewhere. In addition, lifetimes of evaporating grains depend both on grain size and on the binding energy of the relevant organics. For example, Lamy and Perrin (1988), choosing a uniform bond energy of 34.5 kcal/mole, find that 0.2-μm grains have lifetimes at 1 AU of $\sim 2 \times 10^5$ sec, traveling $\sim 7 \times 10^4$ km before being completely destroyed. If grain lifetimes are indeed on the order of molecular UV-dissociation lifetimes, heliocentric spectral evolution will not allow a choice between gas-phase fluorescence and solid particle thermal emission. However, given independent reasons to accept the thermal emission model, such evolution would put constraints on grain evaporation lifetimes, and hence, on the nature of the organic bonds present. Finally, it must again be noted that the stochastic variability of a comet's dust emission, if as great as that exhibited by Comet Halley, might well overwhelm the differences between fluorescent and thermal emission described here.

VII. DISCUSSION AND FUTURE OBSERVATIONS

In spite of the many uncertainties discussed above, certain broad conclusions can be drawn. We have demonstrated quantitatively that in the vicinity of 1 AU, spectral features in the 5–8 μm range should be overwhelmed by the continuum while the 3.4-μm feature should be apparent, whereas between 1.5 and 3 AU this relationship will reverse. Thus, for best visibility relative to the continuum, observations which hope to identify organic spectral features beyond 4 μm are preferably conducted at these larger heliocentric distances, placing a premium on early spectral observations of comets as soon as their comae develop (subject, of course, to signal-to-noise limitations). Observations within ~ 2 AU potentially face the dilemma of yielding an uninterpretable null result: no spectral features may indicate a true paucity of molecules with emission features at these wavelengths, or the absence of such features may simply be a result of poor visibility relative to the continuum, the effect described here. The absence of organic spectral features at greater heliocentric distances, however, would begin significantly to constrain the organic composition of the comet in question. In the context of our model, such results would constrain the composition of the ices that are precursors to the organic grains (Khare *et al.* 1988).

Future comet rendezvous missions will be ideally placed to test the predictions of our model. Airborne and ground-based observations are also clearly of great importance. For example, spectral observations in the 5–8 μm range of a cometary coma as the comet moves from 1 to 3 AU would be especially valuable. In addition, observations of a comet approaching perihelion within several tenths of an AU of the Sun could serve to check the near-Sun evolution of the 3.4-μm feature predicted here.

Note added in proof. Danks *et al.* (1987, *Astron. Astrophys.* **184,** 329–332) present the observations described by Danks *et al.* (1986) in refereed form. However, the December observing date and corresponding heliocentric and geocentric distances listed in Danks *et al.* (1987) are in error, whereas those given in Danks *et al.* (1986) remain correct (A. Danks, personal communication). We therefore use the results of Danks *et al.* (1986) in this paper.

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