The Organic Surface of 5145 Pholus: Constraints Set by Scattering Theory

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No known body in the Solar System has a spectrum redder than that of object 5145 Pholus. We use Hapke scattering theory and optical constants measured in this laboratory to examine the ability of mixtures of a number of organic solids and ices to reproduce the observed spectrum and phase variation. The primary materials considered are poly-HCN, kerogen, Murchison organic extract, Titan tholin, ice tholin, and water ice. In a computer grid search of over 10 million models, we find an intraparticle mixture of 15% Titan tholin, 10% poly-HCN, and 75% water ice with $10-\mu m$ particles to provide an excellent fit. Replacing water ice with ammonia ice improves the fits significantly while using a pure hydrocarbon tholin, Tholin α , instead of Titan tholin makes only modest improvements. All acceptable fits require Titan tholin or some comparable material to provide the steep slope in the visible, and poly-HCN or some comparable material to provide strong absorption in the near-infrared. A pure Titan tholin surface with $16-\mu m$ particles, as well as all acceptable Pholus models, fit the present spectrophotometric data for the transplutonian object 1992 QB₁. The feasibility of gas-phase chemistry to generate material like Titan tholin on such small objects is examined. An irradiated transient atmosphere arising from sublimating ices may generate at most a few centimeters of tholin over the lifetime of the Solar System, but this is insignificant compared to the expected lag deposit of primordial contaminants left behind by the sublimating ice. Irradiation of subsurface N₂/CH₄ or NH₃/CH₄ ice by cosmic rays may generate \sim 20 cm of tholin in the upper 10 m of regolith in the same time scale but the identity of this tholin to its gasphase equivalent has not been demonstrated. © 1994 Academic Press, Inc.

INTRODUCTION

Thanks to a combination of spectrophotometric observations, laboratory and theoretical modeling, and spacecraft exploration over the past 2 decades, the once highly speculative notion that organic material is present in the atmospheres and/or on the surfaces of bodies in the outer Solar System has now gained wide acceptance.

The first laboratory simulations of radiation chemistry in CH_4 -containing simulated planetary atmospheres pro-

duced brownish to reddish solids, which Sagan and Miller (1960) proposed may be relevant to the atmospheres of the jovian planets. Sagan (1974) suggested that the reddish haze of Saturn's satellite Titan is composed of such solids. While by that period CH_4 had been detected only in the atmospheres of the jovian planets and Titan, studies of the chemical equilibrium and condensation processes in the low-temperature portion of the solar nebula led Lewis (1971, 1972) to conclude that CH_4 and other simple carbon-bearing molecules should be components of the icy surfaces of some satellites in the outer Solar System, and that the organic chromophores produced from these simple molecules might explain the dark and sometimes reddish surfaces of some outer Solar System objects.

Subsequently, the expected prevalence of CH_4 as a major carbon repository in the outer solar nebula, and its accretion into small bodies, has become a matter of considerable debate. Because of the slow kinetics of conversion to CH_4 at low temperatures, CO might dominate the nebular gas (Lewis and Prinn 1980) but still be converted to CH_4 in protoplanetary nebulae (Prinn and Fegley 1981). As summarized by Thompson *et al.* (1987), small bodies accreted near the distance of Jupiter would not retain substantial CH_4 or CO in any form, while at Saturn's distance CH_4 clathrate can be accreted, at Uranus CO and N₂ clathrates also form, and at Neptune's distance these materials plus pure CH_4 could be accreted into icy bodies.

It is known from direct laboratory experimentation (Thompson *et al.* 1987) that charged particle irradiation of methane clathrate or CH_4/H_2O mixed ices produces an organic solid which, with increasing dose, progressively darkens and reddens. At high doses the material becomes very dark and more neutral in color. Similar results are found for other hydrocarbon ices mixed with water ice, both with and without NH₃ ice (Thompson *et al.* 1987).

Object 5145 Pholus (= 1992 AD) displays a highly eccentric orbit with perihelion at 8.7 AU and aphelion at 32.3 AU. It may be a refugee from either the Kuiper Belt

or the Oort comet cloud. From these heliocentric distances alone, or a hypothetical original formation at 20-40 AU, methane clathrate and/or mixed ices might be expected. Howell *et al.* (1992) and Davies *et al.* (1992) present data suggesting a low geometric albedo (≤ 0.08 and ≤ 0.044 , respectively). For albedos below 0.08 the equilibrium surface temperature of Pholus is then 93 K at perihelion and 48 K at aphelion.

Apart from its unusual orbit, Pholus is of particular interest because of the steepness of its reflectivity at visible and near-infrared wavelengths. It is in fact the reddest object known in the Solar System (see Fig. 1 of Mueller *et al.* 1992). Between 0.44 and 0.96 μ m Pholus increases its reflectivity by a factor of more than five (Binzel 1992, Fink *et al.* 1992). Additional spectrophotometric data is available in the 1.25- to 2.4- μ m region (Davies and Sykes 1992; data displayed by Mueller *et al.* 1992, Davies *et al.* 1993).

The visible and near-infrared properties of Pholus are so extraordinary as seemingly to exclude any plausible mineral or mineral assemblage and most organic solids. By comparing by eye laboratory reflection spectra of organic solids with the reflection spectra of Pholus, several workers (Fink et al. 1992, Mueller et al. 1992, Binzel 1992) have suggested that an acceptable fit can be obtained with organic tholins produced in this laboratory. These workers identified a "UV" tholin made by 2537-Å irradiation of a roughly equimolar mixture of CH₄, NH₃, and H_2S with C_2H_6 in excess and products dissolved in liquid water; and a "spark" tholin produced by spark discharge of an equimolar CH₄/NH₃ mixture with 2.5% H₂O (both mixtures irradiated at roughly STP) as candidates. These are complex organic solids with chemical properties partly characterized (e.g., Sagan and Khare 1971, Khare et al. 1978, 1981, 1986, Sagan et al. 1984, McDonald et al. 1993). One fraction of these tholins consists of a wide range of biologically interesting organic compounds, including-on hydrolysis-biological and nonbiological amino acids. These two tholins have something approaching the slope of Pholus in the visible, but rise too steeply in the near infrared (see relevant figures in Fink et al. 1992, Mueller et al. 1992, and Binzel 1992).

Deferring until later any reservations about the plausibility of such tholins on a very cold, presumably airless world, it is a natural question to ask whether some linear superposition of these and other candidate surface materials on Pholus might produce not just a rough fit, but an excellent fit. The real and imaginary parts of the complex refractive index of many such materials have been measured by our group (summarized in Sagan *et al.* 1995). The main objective of the present paper is to determine whether surface scattering theory and known optical constants of such materials can account for the observed spectrophotometry of Pholus. The



FIG. 1. (a) Spectra of Pholus. When possible the spectra are normalized to unity at 0.55 μ m. The Davies and Sykes (1992) infrared observations use an estimated V magnitude value, 17.2, for the normalization. The Davies *et al.* (1993) spectrum is normalized such that the 1.65- μ m point agrees with the Davies and Sykes (1992) H value. (b) Phase curve of Pholus normalized to 1 at 1.46° phase angle.

present observations also include variation of reflectivity with phase angle, a potentially important additional diagnostic tool. We also explore some aspects of the dependence of model spectra on particle size, compaction, and other parameters.

OBSERVATIONAL DATA

The data being modeled include six spectra in the visible and near-infrared (Fig. 1a), a phase angle brightness curve at 0.55 μ m (Fig. 1b), and upper limits placed on the geometric albedo at 0.55 μ m. The spectra of Fink *et al.* (1992), Binzel (1992), and Davies *et al.* (1993) are continuum measurements which we sample at 0.05- μ m intervals and use the scatter in measurements at nearby wavelengths as the uncertainty. Mueller *et al.* (1992) report two sets of photometry using VRI and BVRI filters. The errors for the VRI set is reported in Mueller (1992) and adopted for the BVRI data. A comparison of the Davies and Sykes (1992) JHK measurements with the Davies *et al.* (1993) continuum shows the K filter sitting on the edge of two absorption bands which makes this point poorly suited for modeling with a single wavelength. As dropping this point leaves a single J-H measurement partially overlapping the Davies *et al.* observations, the Davies-Sykes points are not used in model fitting.

The phase angles of the observations range from 0.4° to 6.2° with three of the four visible observations showing a pattern of increasing slope with increasing phase angle (Mueller et al. 1992, Binzel 1992). Hoffmann et al. (1993) suggest an uneven tholin distribution on Pholus's surface so that different slopes are seen at different rotational phases, but this is ruled out by observations showing a V-R independent of rotation to a level of ± 0.02 mag (Buie and Bus 1992). Binzel (1992) proposes the different slopes are caused by the use of different standard stars. However, the BVRI and VRI observations of Mueller et al. (1992) both use Landolt (1983) standard stars yet differ significantly in slope, with V-I colors of 1.34 ± 0.04 and 1.51 ± 0.04 , respectively. This difference is much larger than the ± 0.02 uncertainty in the standard stars (Landolt 1983). It could possibly be explained if the V and I observations were made more than 1 hr apart. The doublepeaked, 0.17-mag, 10-hr lightcurve (Buie and Bus 1992) has an average variability of 0.07 mag hr⁻¹. Even a short lapse of time will have a significant effect on the measured colors. The BVRI observations, which show the shallowest slope, however, were made as to minimize rotational effects (D. Tholen, private communication, 1993). If this is a real effect, then, and not due to the many possibilities mentioned, phase reddening will be a strong constraint on our results.

The Fink *et al.* (1992) spectrum does not agree with the phase reddening pattern. Despite being obtained at the same phase angle (1.4°) as the *VRI* photometry by Mueller *et al.* (1992), the Fink *et al.* spectrum has a significantly greater slope. To check the consistency of these two data sets, the Fink *et al.* data were rescaled using its upper error bar at 0.55 μ m and plotted in Fig. 2. The resulting slope is still steeper than that of Mueller *et al.*, but it is clear that a good fit to the Mueller *et al.* data will also be a good fit to the Fink *et al.* data. Because it has the smaller error bars and is therefore the stronger constraint, we use the Mueller *et al.* spectrum in what follows.

Buie and Bus (1992) made high time resolution observations of Pholus in order to determine its rotation period and amplitude variation. Having done so, they were able to remove rotation effects and determine how Pholus's V magnitude varies with phase angle (Fig. 1b). Their coverage is from 0.6° to 4°. Extrapolating to 0° and using a diameter of 140 km for Pholus (as reported by Howell *et al.* (1992)) they calculate a geometric albedo of 0.08 (agreeing with Howell *et al.*). Davies *et al.* (1992) report a diameter of 189 km and an albedo of 0.044. Because of



FIG. 2. Comparison of the Fink *et al.* (1992) (filled symbols) and Mueller *et al.* (1992) (open symbols) observations, both made at a phase angle of 1.4°. The Fink *et al.* spectrum has been rescaled such that the top of its 0.55- μ m error bar is 1. The Fink *et al.* spectrum is much redder than that of Mueller *et al.* The Fink *et al.* error bars, however, are large enough to accommodate any good fit to Mueller *et al.*

the possibility of a narrow opposition effect, the Buie and Bus extrapolation could significantly underestimate the zero phase brightness. Therefore, our constraint on absolute brightness is set at 1.46° phase angle, which appears unaffected by an opposition effect. Because of the uncertainty in the diameter and albedo, our only constraint is that the reflectance be less than 0.08 at this reference point.

MATERIALS AND COMPUTATIONAL METHODS

In Table I are listed the six candidate surface materials initially investigated in this study. In addition to water ice are five complex organic solids which have at least some claim to relevance to the outer Solar System: kerogen, Murchison organic extract, ice tholin, poly-HCN, and Titan tholin. Type II kerogen is the only one of these of biological origin. Kerogen has been suggested as a

 TABLE I

 Candidate Surface Materials Used to Model Pholus's Spectrum

Material	Abbreviation	Optical constants reference		
Poly-HCN	Н	Khare <i>et al</i> . 1994		
Type II Kerogen	K	Khare et al. 1990		
Murchison organic extract	Μ	Khare et al. 1990		
Ice tholin	Ι	Khare et al. 1993		
Titan tholin	Т	Khare <i>et al.</i> 1984		
Water ice	W	Warren 1984		
Ammonia ice ^a	Α	Sill et al. 1980		

^a Ammonia ice is not used in the main computer grid search. In later discussion, it is used as an alternative to water ice.

surface analogue for dark material on the D asteroids (Gradie and Veverka 1980). Type II kerogen exhibits optical constants similar, over most of the visible and near infrared spectrum, to those of insoluble organic residue from the Murchison Type II carbonaceous chondrite (Khare *et al.* 1990). Ice tholin is the organic residue left after charged particle irradiation of a $1:6 C_2H_6: H_2O$ intimate ice mixture. Its optical constants have been measured by Khare et al. (1993). Ice tholin is a generic hydrocarbon-water ice irradiation residue that should closely resemble residues from CH₄ plus H₂O clathrates or mixtures in outer Solar System environments (Thompson et al. 1987, Khare et al. 1989). "Polymeric" HCN (henceforth poly-HCN) is an organic solid produced from HCN which has been suggested to be widely distributed through the outer Solar System (Matthews 1992). Optical constants of poly-HCN have recently been measured (Khare et al. 1994). Titan tholin is an organic solid made by plasma discharge through a 9:1 N_2 : CH₄ atmosphere, simulating the observed atmosphere of Titan. Its optical constants (Khare et al. 1984) match within the probable error the ultraviolet, visible, and near and middle infrared spectrophotometry of Titan (Sagan et al. 1992). The optical constants of materials produced by irradiation may well be a function of radiation dose (Thompson et al. 1987), although the irradiation time scale of Titan tholin was chosen for experimental convenience and Titan tholin optical properties do not seem to be a strong function of dose.

Cruikshank *et al.* (1991) display the visible and near infrared bihemispheric reflectance spectra of four tholins—two of them, our spark and UV tholins used by several observers in their comparison with Pholus. The other two are Titan tholins. For technical reasons, the optical constants of spark and UV tholins have not yet been measured. All have very steep reflectivity slopes through the visible and near-infrared. We will use Titan tholin to represent all three of these tholins in the present paper.

For surface scattering calculations we use the model of Hapke (1981, 1984, 1986). Hapke's derivation represents the ratio of scattered intensity I to incident flux F as the sum of two terms: a singly scattered component that includes phase effects and a multiply scattered component that assumes isotropic scatterers. Hapke (1984) incorporates corrections to take into account surface roughness and integrates the reflectance equation over the illuminated and visible portion of a sphere observed at a phase angle g. The resulting equations (Eqs. (62)–(68) of Hapke 1984) describe the scattering behavior of full disk observations of planetary objects. We do not reproduce these equations here but instead present a small phase angle approximation to them that ignores surface roughness:

$$\frac{I}{F} = \frac{\omega p(g)}{8Q_{\rm E}} \left[1 + B(g)\right] + \left\{\frac{r_0}{2} \left(1 + \frac{r_0}{3}\right) - \frac{\omega}{8}\right\}, \quad (1)$$

where

$$r_0=\frac{1-\sqrt{1-\omega}}{1+\sqrt{1-\omega}},$$

and

$$B(g) = B_0 \left[1 + \frac{\tan(g/2)}{h} \right]^{-1}$$

We describe each parameter below. In the end a computer grid search over all free parameters is performed.

PARAMETERS AND THE GRID SEARCH

The single scattering albedo, ω , contains all the information on the composition of particles and how absorbing/ reflecting they are. We compute ω from the known *n* and *k* values (optical constants) of the candidate materials for a sphere of equivalent diameter *D* using Eq. (24)of Hapke (1981). We adopt Hapke's formulation of $\omega = Q_s$, where $Q_s = f(n, k, D, s)$.

Surface optical constants are modeled by intraparticle mixtures of three candidate materials-i.e., each particle is assumed to be composed of three components in varying proportions. Extensive impact gardening should be capable of producing this type of mixture. The impact, in addition to shattering the surface, will produce an expanding compressional wave that may also fuse particles together. After many resurfacing time scales, the particles will become homogeneous. The peak of the mass distribution of micrometeorites at 1 AU occurs at 10⁻⁵ g (Grün et al. 1985). Assuming the same peak in the outer Solar System with impact velocities ≤ 10 km sec⁻¹, craters will be several centimeters across and several millimeters deep (Melosh 1989). Using a spatial mass density of 10^{-22} g cm⁻³ found at 1 AU (Grün *et al.* 1985) but possibly also valid out to 18 AU (Humes 1980), the resurfacing timescale is ~ 1000 years. Allowing for even two orders of magnitude uncertainty in the flux or typical particle mass, the outer millimeter of regolith will be extensively gardened over time scales much shorter than the age of the Solar System.

Intraparticle mixtures are simulated by calculating a weighted mean of the indices of refraction. A linear mixing relation for k is equivalent to maintenance of the Beer-Lambert absorption laws for concentration-dependent absorption in continuous dielectric media. Strictly speaking this requires the materials to be mixed on a scale substantially less than that of the wavelength. Particle or

"salt-and-pepper" mixtures in which the single scattering albedos are calculated for each component and then averaged (Hapke 1981) and areal or "checkerboard" mixtures in which the reflectances are averaged were investigated, both with a single set of parameters (particle size, phase function, etc.) used for each component, but neither produced models of the quality found with intraparticle mixtures.

With six materials from which to choose (Table I), 20 three-component combinations are examined. The weights for each component are varied from 0 to 1 in 0.05 steps with the constraint that the weights sum to unity. In reporting these mixtures an abbreviation is used of the form ABC = a/b/c where A, B, and C are the component abbreviations given in Table I and a, b, and c are the mixture weights, or fractions. For example, HTW = 10/ 20/70 is 10% poly-HCN, 20% Titan tholin, and 70% water ice.

Because Hapke theory is based on geometric optics, there is a restriction on how small the particles can be. When the wavelength being used approaches the particle diameter, physical optics start to take over. Calculations by Hansen and Travis (1974) show this breakdown to occur at $x = \pi D/\lambda \approx 10$, setting a lower limit of $D_{\min} \approx 3\lambda_{\max}$. There is no physical upper limit. Since Hapke theory is nonlinear in particle size, in our computational protocol D was varied logarithmically with values of 0.8-2.0 with steps of 0.1. This corresponds to particle sizes of 6 to 100 μ m.

The scattering coefficient, s, measures the density of internal scatterers in the particles. Multiplying by the particle diameter, D, gives the mean number of scattering events a photon experiences in passing through the particle. High densities make the particle brighter. This effect is strongest for dark particles since a near-surface scatter will allow light to leave the particle without much absorption. Hapke and Wells (1981) found $s = 600 \text{ cm}^{-1}$ for their cobalt glass samples with particle sizes of 25–150 μ m, so sD was in the range of 1.5–6. Clark et al. (unpublished) found that for sD \leq 0.3 this parameter did not affect their fits for a glass sample, but larger values degraded fit quality. Somewhat arbitrarily, we set sD equal to the intermediate value of 1.0. We consider the effect of this parameter on our fits later.

Using the mixture components, mixing ratios, particle size, and the fixed scattering coefficient, the single scattering albedo, ω , of the surface particles is calculated.

The particle phase function, p(g), is in principle computable from the particle shape, size, and complex refractive index m = n - ik, but in this paper is parameterized in the simple form $p(g) = 1 + b \cos g$. The exact functional form is not an important factor because of the limited phase angle coverage. Over the 6° of observations, p(g) will vary by less than 1% and serves mainly as a factor determining the relative contribution of the singly and multiply scattered light. In effect, then, the unknown parameter is p(0), although we continue using b as the searched parameter.

Particulate surfaces generally show a brightening as the phase angle approaches zero, called the opposition effect. Replacing a different characterization in his 1981 paper, Hapke (1986) describes the opposition effect as a preselection process, where photons that travel unscattered into the surface layer through a series of aligned holes (several particle layers deep) are statistically much more likely to escape along a nearly parallel path. Hapke et al. (1993) have shown that the alternative explanation, coherent backscattering off wavelength-sized roughness on individual particle surfaces, is a significant contributor and in fact dominates the Moon's opposition effect. Our treatment of the opposition effect is heavily based on experimental results, so the Hapke (1986) model should be valid regardless of the dominant contributor. The opposition function B(g) introduces h, the compaction parameter, related to the amount of empty space in the material $(h \propto -\ln v)$, where v is the void fraction of the surface), and B_0 , which determines the strength of this effect.

Since the observations being modeled were made at different wavelengths with a significant albedo variation, the question arises whether the parameters b, B_0 , and h can be assumed constant over the spectrum. Very little work has been done on this question. Prior tests of Hapke theory with laboratory samples (Clark *et al.* unpublished) have intentionally avoided small phase angles, where the opposition effect is important, in order to limit the number of free parameters; and in the cases where an opposition effect is modeled in planetary observations, only a single wavelength is used (Thomas *et al.* 1987, Helfenstein and Veverka 1987, Veverka *et al.* 1987).

Only two sets of research involving multiwavelength observations of the opposition effect and phase function are known to the authors. The first is the original test of Hapke theory by Hapke and Wells (1981). Hapke later modified his model of the opposition effect so his derived values need to be corrected. In the small phase angle limit (which is almost always valid for Earth-based observations of outer Solar System objects), Hapke's original backscatter function simplifies to $B(g) = B_0[1 - (3g/2h)]$. Comparing this to his updated version for B(g), one sees that B_0 is unchanged but there is a factor of 3 difference between the old and the new h.

The second is a study by Oehler (1993). He examined samples of silicates and dark organics (kerogen and Murchison) in the visible and near-infrared. For each sample at each wavelength, h, S(0), p(g), and ω were derived. The parameter S(0), which was introduced in Hapke (1986) and described as the fraction of light scattered from near the upper surface of the particles, is related to B_0 via $B_0 =$



FIG. 3. Dependence of the Hapke parameters, (a) p(0) and (b) B_0 , on single scattering albedo, ω . An albedo independent p(0) and a linearly decreasing B_0 are used in our model. Crosses (Oehler 1993): solid line, basalt; dotted, Murchison; short dash, kerogen; long dash, olivine 3; dash-dot, dunite/soot. Boxes (Hapke and Wells 1981): solid line, 37-74- μ m cobalt glass; dotted, <37- μ m cobalt glass, packed; short dash, <37- μ m cobalt glass, sifted.

 $S(0)/\omega p(0)$. Ochler's observations show complex behavior for large ω . Since Pholus is a dark object, we consider only the data for $\omega < 0.8$.

Figures 3a and 3b graph p(0) and $B_0 vs \omega$ using the data from both Hapke and Wells (1981) and Oehler (1993). The graphs suggest a constant p(0) and a linear dependence of B_0 on ω as a first approximation. An additional study by Mustard and Pieters (1989) also suggests a relatively stable p(0) over wide albedo ranges. The large scatter in slopes obtained from linear fits to B_0 for each sample in Fig. 3b (-4.3 for Murchison, -0.6 for kerogen) makes the selection of a single representative slope very subjective, but this is preferable to the introduction of an additional free parameter. The median slope is ~ -1 , so we adopt the form $B_0 = \kappa - \omega$ and search over values of κ .

The parameter, h, as modeled by Hapke (1986), is solely a description of the soil structure, so no wavelength dependence should be present; Hapke and Wells (1981) explicitly require this. Oehler (1993), however, makes no such assumption and derives it. For a wide range of albedos, h is nearly constant with significant deviations only when ω approaches either 1 or 0. Despite the small dependence at low albedo, we treat h as a constant.

The choice of test values for b, κ , and h comes from Figs. 3a and 3b, a survey of results obtained from other bodies (Table II), and their physically allowed values. The majority of values of κ fall in the range of 1 to 2.5 so we search this range in 0.25 increments. Values of hrange from 0.008 to 0.12. Because the smaller values of h occur for icy bodies which may be appropriate for Pholus, we focus on the smaller values of h. A crude search using 0.01, 0.03, and 0.05 is initially performed. If fits are found at these values, the search is widened to fill in the gaps and to extend to larger values if necessary. A similar crude search is performed for b. Physically, b can be in the range -1 to +1. We search the range -0.9 to +0.9in 0.2 increments, and perform a finer search after locating fits.

Hapke's reflectance theory assumes a surface of large and closely spaced particles, thereby making diffraction negligible. As a first-order correction for diffraction we include in Eq. (1) the extinction efficiency, $Q_{\rm E} = 1 +$ Q_d , where Q_d is the diffraction efficiency given by $Q_d =$ $\exp(-n_e \langle \sigma \rangle L'')$, where n_e is the effective particle density, $\langle \sigma \rangle$ is the mean geometric cross section ($\pi D^2/4$), and Lⁿ is the length of the diffraction cone (~1.4 D^2/λ) (Hapke 1981). The effective particle density can be related to the compaction parameter as derived by Hapke (1986) giving $Q_{\rm d} = \exp(-5.65hD/\lambda)$. To use Hapke theory at the limit of geometric optics ($\lambda \approx D/3$), then, diffraction must be included unless $h \ge 0.1$ so that $Q_{i} \le 1$, but this is usually not the case. Because diffraction scatters light into a narrow cone in the forward direction it does not contribute light at small phase angles and the single scattering term

 TABLE II

 A Sampling of Hapke Parameters for Other Planetary Objects

	p(0)ª	h۴	ĸb	Source
Moon				
Disk-integrated	1.68	0.07	2.22	Helfenstein and Veverka 1987
Dark regions	1.51	0.12	1.28	Helfenstein and Veverka 1987
Average regions	1.70	0.06	2.09	Helfenstein and Veverka 1987
Bright regions	1.71	0.05	2.16	Helfenstein and Veverka 1987
Titania				
Disk-integrated	2.47	0.018	1.35	Veverka et al. 1987
Dark regions	2.65	0.011	1.41	Thomas et al. 1987
Average regions	NA	0.020	NA	Thomas <i>et al.</i> 1987
Bright regions	2.75	0.008	1.55	Thomas <i>et al.</i> 1987
Umbriel	1.88	0.061	2.65	Helfenstein et al. 1988

^a p(0) is the phase function value at zero phase and can be >2 with the Henyey-Greenstein phase function.

^b See Table III for definitions.

 TABLE III

 Model Parameter Definitions and Grid Search Values

ParameterSymbolRangeGrid sMixing Ratios-0-10.05Particle Diameterlog D0.8-2.00.1Phase function coefficientb-0.9-0.90.2 ^a $p(g) = I + b \cos g$ 00Opposition surge coefficient κ 1.0-2.50.25 $B_0 = \kappa - \omega$ 000.01-0.050.02Scattering coefficient sD 1-Surface roughness \overline{H} 25°-				
Mixing Ratios— $0-1$ 0.05 Particle Diameterlog D $0.8-2.0$ 0.1 Phase function coefficientb $-0.9-0.9$ 0.2^a $p(g) = I + b \cos g$ Opposition surge coefficient κ $1.0-2.5$ 0.25 $B_0 = \kappa - \omega$ Compaction parameterh $0.01-0.05$ 0.02 Scattering coefficient sD 1—Surface roughness \overline{H} 25° —	Parameter	Symbol	Range	Grid size
Particle Diameterlog D $0.8-2.0$ 0.1 Phase function coefficientb $-0.9-0.9$ 0.2^a $p(g) = I + b \cos g$ Opposition surge coefficient κ $1.0-2.5$ 0.25 $B_0 = \kappa - \omega$ Compaction parameterh $0.01-0.05$ 0.02 Scattering coefficient sD 1-Surface roughness \overline{H} 25° -	Mixing Ratios	_	0-1	0.05
Phase function coefficient b $-0.9-0.9$ 0.2^a $p(g) = I + b \cos g$ 0Opposition surge coefficient κ $1.0-2.5$ 0.25 $B_0 = \kappa - \omega$ 0Compaction parameter h $0.01-0.05$ 0.02 Scattering coefficient sD 1 $-$ Surface roughness \overline{H} 25° $-$	Particle Diameter	$\log D$	0.8-2.0	0.1
Opposition surge coefficient κ 1.0-2.50.25 $B_0 = \kappa - \omega$ 0000Compaction parameter h 0.01-0.050.02Scattering coefficient sD 1-Surface roughness \overline{H} 25°-	Phase function coefficient $p(g) = I + b \cos g$	b	- 0.9-0.9	0.2 ^a
Compaction parameterh $0.01-0.05$ 0.02 Scattering coefficient sD 1-Surface roughness \overline{H} 25° -	Opposition surge coefficient $B_0 = \kappa - \omega$	к	1.0-2.5	0.25
Scattering coefficient sD 1 — Surface roughness \overline{A} 25° —	Compaction parameter	h	0.01-0.05	0.02 ^a
Surface roughness \overline{H} 25° —	Scattering coefficient	sD	1	—
	Surface roughness	$\overline{\theta}$	25°	-

^a Used for initial crude search. The grid size was cut in half after locating the best mixtures.

in Eq. (1) gets reduced by a factor of Q_E . The multiply scattered component is unchanged from Hapke's treatment because in order for diffracted light to contribute at small phase angles it must survive a physical scatter with another particle which causes the Q_d term to cancel out.

The surface roughness parameter, $\overline{\theta}$, which is not shown in Eq. (1), is an angle measuring the size of surface deviations away from horizontal. This parameter has very little effect at small phase angles for dark surfaces (Helfenstein *et al.* 1988). Therefore, a typical value of 25° is assigned to it (cf. Helfenstein and Veverka 1987).

Our final parameter list for a single kind of particulate material with known n and k is then b, D, h, and κ . For three-component mixtures which we will use to fit the Pholus spectrum, a semi-infinite layer will be characterized by six parameters. The ranges and grid sizes of these parameters are summarized in Table III.

MODEL FITS

A grid search is performed using the previously described parameters and value ranges (summarized in Table III). At each grid point predicted reflectances are calculated and compared to the observations. Models with a reflectance greater than 0.08 at $\lambda = 0.55 \ \mu m$ and $g = 1.46^{\circ}$ are rejected. Fit quality of remaining models is measured by calculating the reduced χ^2 s of the five data sets (four spectra and one phase curve). The best fits are then determined by requiring that the model fit each data set better than a limiting χ^2 . In our grid search a liberal limit of $\chi^2_{lim} = 4$ is used. In total, 10 million models are examined. Only 440, or <0.005% of the parameter space, qualified. (An identical search of particle and areal mixture models yielded no satisfactory fits.) The mixture HTW yields the best fits with many parameter fits having $\chi^2_{lim} < 3$; HTW mixtures make up 98% of all fits. The mixing fractions of HTW are very well constrained to 10/15/75 with a $\pm 5\%$ uncertainty. The only other acceptable combination found is HKW with similarly well defined mixing fractions of 15/15/70. A second finer grid search was performed using these two mixtures with the *b*-increment decreased to 0.1 and the *h*-increment decreased to 0.01. Better fits were found for both, but HTW is still the only combination with $\chi^2_{lim} < 3$. Table IV lists the five best models with the reference reflectance and the average χ^2 of the five data sets for both combinations.

The extreme forward scattering of the HKW fits raises the question of whether these are physical results. The phase function embodies the light from two sources: Fresnel reflection and transmission. The effect of diffraction is treated separately in the model so it does not need to be included here. For a surface with randomly oriented particles the reflection phase function should be completely backscattering: $p_r(g) = 1 + \cos g$. Depending on the strength of internal reflections and scattering, the transmission function could be anywhere from isotropic to completely forward scattering. For the materials examined here the real part of the refractive index is such that 10-15% of the incident light is reflected at the surface. This light will always be backscattered. The remaining light will enter the particle and will either be absorbed or be transmitted. For nonabsorbing particles that are completely forward scattering, $p_t(g \approx 0) = 0$, the final phase function at small phase angles will be $p(g \approx 0) =$ 0.2, or b = -0.8. This is typical of the values found for terrestrial snows (Verbiscer 1991). Of course, our particles are strongly absorbing, so this limit should never be reached. Typically, only 10-40% of the incident light is transmitted, giving phase functions p(0) = 1 to 0.4, or b = 0 to -0.6. As this is for the case of no transmitted light being backscattered, extremely forward scattering particles do appear to be unreasonable for absorbing particles. However, this argument is flawed in that it also predicts a phase function strongly dependent on the albedo, which is not observed (Oehler 1993; Mustard and Pieters 1989). However, when combined with the fact that all previous planetary observations have found backscattering surfaces (summarized in McEwen 1991) and the significantly poorer quality fits, we feel confident in rejecting the HKW models in favor of the backscattering HTW models.

Figure 4 graphs the model spectra and phase curve of the best HTW mixture (= 10/15/75, from Table IV) along with the observations (from Fig. 1). Our model does a fair job of recreating both the unusual steep slope and the phase reddening of the observations at $\lambda < 1 \mu m$, as well as matching the phase curve. It has some difficulty in simultaneously agreeing with the Davies *et al.* (1993) infrared spectrum, though. None of the materials we have used so far has a strong absorption feature near 2.25 μm ,

ORGANIC SURFACE OF 5145 PHOLUS

	Mixture ^e		<i>D^b</i> (μm)	b^b	h^b	ĸb	(I/F) _{ref} ^c	χ^2_{lim} ^d	$\chi^2_{avg}{}^e$	
нтw										
0.10	0.15	0.75	10.0	0.8	0.02	1.00	0.077	2.24	2.01	
0.10	0.15	0.75	6.3	-0.4	0.04	2.50	0.078	2.28	1.61	
0.10	0.15	0.75	7.9	0.0	0.03	1.75	0.078	2.29	1.66	
0.10	0.15	0.75	10.0	0.7	0.02	1.00	0.073	2.30	1.96	
0.10	0.15	0.75	6.3	0.6	0.01	1.25	0.078	2.32	1.42	
HKW										
0.15	0.15	0.70	7.9	-0.8	0.01	2.00	0.015	3.67	2.86	
0.15	0.15	0.70	7.9	-0.9	0.02	2.50	0.014	3.77	3.17	
0.20	0.20	0.60	6.3	-0.8	0.01	2.25	0.014	3.87	2.87	
0.20	0.20	0.60	6.3	-0.8	0.01	2.00	0.014	3.88	2.86	
0.10	0.10	0.80	12.6	-0.9	0.02	2.50	0.013	3.90	2.88	

TABLE IV ive Best Fits, Sorted by χ^2_{lim} , of Each "Good" Combination Found in a Computer Grid Searc

^a H, poly-HCN; K, kerogen; T, Titan tholin; W, water ice.

^b See Table III for definitions and searched values.

^c Reflectance at $\lambda = 0.55 \ \mu m$ and $g = 1.46^{\circ}$, constrained to be <0.08.

^d The worst χ^2 of the five data sets. A good model is defined as having $\chi^2_{bm} < 4$.

^e Average χ^2 of the five data sets.



FIG. 4. Comparison of the best poly-HCN (H), Titan tholin (T), and water ice (W) model spectra and phase curve to the data (cf. Fig. 1). The three curves at $0.4-1.0 \ \mu m$ are calculated at the three phase angles of the visible observations and show the same phase reddening. All the data are matched within errors except the absorption at 2.25 μm .

although the 2- μ m absorption can be matched with water ice. There must be an additional material on Pholus that we have not included. We note that a weak 2.2- μ m feature corresponds to the overtone of the strong $-C\equiv$ N absorption fundamental of both poly-HCN and Titan tholin (Khare *et al.* 1984, 1994). This feature has also been reported in the infrared spectra of many objects in the outer Solar System (Cruikshank *et al.* 1991). Stronger features near 2.3 μ m correspond to combinations and overtones of several C-H stretching and bending modes (Cruikshank *et al.* 1993).

Davies et al. (1993) suggest ammonia ice as one possibility because it has strong absorption bands at both 2 and 2.25 μ m, but they note the absence of weaker bands in Pholus's spectrum near 1.5 µm. Sill et al. (1980) measured the optical constants of ammonia ice for $\lambda > 1.4 \ \mu m$ and found the absorption coefficient in the $\sim 1.5 - \mu m$ bands to be a factor of 20 lower than that at the 2.0- and 2.25- μ m bands. These are easily hidden in intraparticle mixtures where a dark material, poly-HCN, dominates absorption, as is the case for the relatively stronger $1.5 - \mu m$ band in water ice. Continuing to restrict ourselves to only threecomponent mixtures, we replace the water ice with ammonia ice (abbreviated A), estimating its visible optical constants such that it maintains its high reflectance in agreement with Hapke et al. (1981), and perform a grid search with an HTA mixture. The results are a significant improvement over the HTW mixtures-mainly because of the 2.25- μ m fit—as can be seen in Fig. 5, which shows the best HTA mixture with $\chi^2_{lim} = 1.4$, and in Table V, which lists the five best HTA models. The ammonia absorption bands are deeper than the observations show,

FIG. 5. Best fit model using ammonia ice (A) instead of water ice in combination with poly-HCN (H), and Titan tholin (T) (cf. Fig. 1). The three curves at $0.4-1.0 \,\mu$ m are calculated at the three phase angles of the visible observations and show the same phase reddening. Because ammonia ice has absorption at 2.25 μ m this model does significantly better than the models using water ice.

suggesting that we have too much ammonia ice. By adding water ice and going to a four-component mixture we can effect a compromise between the HTW and HTA models. We keep the poly-HCN and Titan tholin components at 10 and 15%, respectively, fix all the parameters to that for the best HTA model, and just vary the ammonia ice and water ice mixing fractions. We find that 50% of the surface can be water ice and still retain the 2.25- μ m feature with a model fit as good as, or better than, the threecomponent HTA model.

To understand why these mixtures fit the data, and to look for possible alternative materials we plot the effective optical constants of the surface in Figs. 6 and 7. Instead of plotting k, though, we plot the product of absorption coefficient ($\alpha = 4\pi k/\lambda$) and particle diameter, which is more conducive to analysis. We also plot the contribution of each component separately. The model dependence on *n* is very weak; *n* serves mainly to set the strength of Fresnel reflection. Changing n will affect the single scattering albedo but only a slightly different slope of k will be required to match the observations. The slope of αD is dominated by Titan tholin at short visible wavelengths, but poly-HCN plays an increasing role at wavelengths longer than green-yellow. In HTW, water ice starts to contribute in the near infrared but is muted by the stronger absorption of poly-HCN. In HTA, ammonia ice provides the two strong absorption bands at 2.0 and 2.25 μ m but elsewhere it is only a nonabsorbing medium.

Titan tholin has an [N]/[C] ratio approaching unity (Sagan *et al.* 1984). Is our Pholus fit improved if we employ pure hydrocarbon tholins? Khare *et al.* (1987) report the optical constants of a number of CH₄-derived tholins and compare them to a large number of high-carbon-content materials such as PAHs and soot. None of the materials by themselves have behavior similar to that of our model. The closest is a tholin produced in a 3% CH₄/25% He/ 72% H₂ gas mixture designated as Tholin α . It is spectrally similar to Titan tholin, but its absorption coefficient does not fall off as fast to longer wavelengths. Substituting it for Titan tholin in the HTW and HTA mixtures improves the fits slightly to $\chi^2_{lim} \approx 1.9$ and 1.2, respectively, from

Mixture ^a		<i>D^b</i> (μm)	b^b	h ^b	κ ^b	(1/F) _{ref} ^c	χ^2_{lim} ^d	$\chi^2_{avg}^e$		
HTA										
0.10	0.15	0.75	6.3	0.4	0.01	1.50	0.071	1.37	1.10	
0.10	0.15	0.75	6.3	0.4	0.01	1.25	0.067	1.45	1.06	
0.10	0.10	0.80	6.3	-0.3	0.01	2.00	0.054	1.45	1.15	
0.10	0.15	0.75	6.3	-01	0.02	1.50	0.063	1.50	1.07	
0.10	0.10	0.80	6.3	-0.2	0.01	1.50	0.053	1.50	1.16	

TABLE VFive Best Fits, Sorted by χ^2_{im} , of the HTA Model

^a H, poly-HCN; T, Titan tholin; A, ammonia ice.

^b See Table III for definitions and searched values.

^c Reflectance at $\lambda = 0.55 \,\mu$ m and $g = 1.46^{\circ}$, constrained to be <0.08.

^d The worst χ^2 of the five data sets.

^e Average χ^2 of the five data sets.





FIG. 6. Optical constants of the model surface composition used in Fig. 4. The broken lines indicate the separate contributions of the three components.

2.2 and 1.4. The parameters are roughly the same as listed in Tables IV and V.

Figures 6 and 7 extend to $\lambda = 5 \mu \text{ min order to compare}$ how the two models may differ at currently unobserved wavelengths. Because of the small particle sizes, we are unable to calculate brightnesses reliably at these longer wavelengths, but the αD graphs do allow a qualitative comparison. Both models predict a very dark surface near 3 μ m, where all of the materials have strong absorption bands. The HTW model has a $3-\mu m$ absorption band with a full width greater than 0.5 μ m while the HTA model has a band only $\sim 0.2 \ \mu m$ wide. Because αD is greater than unity in both models, the absorption depths may not differ greatly between the two models. Beyond 3.3 μ m, the two models differ very little. The ammonia ice returns to being nonabsorbing in the HTA model, leaving poly-HCN to dominate the spectrum. In the HTW model, water ice is as absorbing as poly-HCN, so the poly-HCN features are muted but still present. The narrow 4.6- μ m features of poly-HCN may be discernible in HTA but smeared in HTW.

Our results so far have had two parameters fixed $(sD = 1 \text{ and } \overline{\theta} = 25^\circ)$. We now vary these to see how

they affect the model spectra. In Fig. 8a we take the best HTW mixture from Table IV and for a phase angle of 5.4° compare spectra using $\overline{\theta} = 15^{\circ}$, 25°, and 35°. As seen, this parameter has virtually no effect on the model. Figure 8b compares sD = 0.3, 1.0, and 3.0 for the same model. As stated earlier, this parameter makes dark particles brighter because more light escapes the particle before being absorbed. This is reflected in Fig. 8b by a shallower slope for larger sD, making the near-infrared brightness relatively dimmer because of the larger normalizing brightness. Use of a value other than 1 for sD should not significantly alter our results. A slightly larger (smaller) value could be compensated for by more (less) Titan tholin which controls how dark the particles are near 0.55 μ m, the reference wavelength.

Hoffmann *et al.* (1993) have reported good fits to the Fink *et al.* (1992) Pholus spectrum based on a Hapke model using a particle mixture with Titan tholin, neutrally bright, and neutrally dark materials. The particle sizes are 3, 15, and 5 μ m, respectively. (Our rejection of a particle mixture earlier was based on using a single parti-



FIG. 7. Optical constants of the model surface composition used in Fig. 5. The broken lines indicate the separate contributions of the three components. The visible and near-infrared $(0.4-1.4 \ \mu\text{m})$ estimates of k for ammonia ice are upper limits based on its measured reflectance (Hapke *et al.* 1981) and infrared optical constants (Sill *et al.* 1980).

cle size for all components. Allowing multiple sizes adds free parameters over our intraparticle mixtures.) They do not describe their treatment of phase and wavelength dependence of parameters, so we retain our parameter treatment in checking their results. We replace their hypothetical dark and bright materials with poly-HCN and water ice. Fixing the particle sizes, a grid search is performed and fits made to the Fink et al. spectrum. We confirm excellent fits for a wide range of mixing ratios and phase parameters. When fitting to the other spectra (Mueller et al. 1992, Binzel 1992), excluding the observations at $\lambda > 1 \ \mu m$ because of the 3- μm particles, and the phase curve (Buie and Bus 1992), however, a model even with $\chi^2_{lim} < 15$ is not found. The best fit is shown in Fig. 9. These poor fits arise from an inability to create simultaneously sufficient phase reddening and to continue the steep slope down to $\lambda \approx 0.45 \ \mu m$. Both deficiencies are most evident in the Mueller et al. BVRI photometry, since it has the shallowest slope and a B filter observation. Having only four data points, missing one of them by a



FIG. 8. (a) Dependence of spectrum on $\overline{\theta}$. As stated in the text, surface roughness has very little effect at small phase angles. (b) Dependence of spectrum on sD. The differing slopes come about because larger scattering coefficients make dark particles brighter. By increasing (decreasing) the amount of tholin in the model the normalizing brightness can be lowered (raised) and offset the effect of sD.



FIG. 9. Best fit model found based on the Hoffmann *et al.* (1993) results, but using water ice (W) and poly-HCN (H) as the bright and dark materials in a particle mixture with Titan tholin (T). The particle diameters are fixed at the values used by Hoffmann *et al.* and the remaining parameters search. The three curves at $0.4-1.0 \mu$ m are calculated at the three phase angles of the visible observations. An infrared spectrum is not plotted because the Titan tholin particles have $3-\mu$ m diameters and the geometric optics underlying Hapke theory would be invalid at these wavelengths. This model is incapable of matching simultaneously the $0.45-\mu$ m data and the phase reddening. If we ignore the B photometry of Mueller *et al.* (1992), the remaining data can be fit nearly as well as in our models.

significant amount has a strong influence on the reduced χ^2 . The Binzel spectrum also has a 0.45- μ m problem, but because the model fits the rest of the spectrum well the average χ^2 contribution is small. Ignoring the *B* photometry results in some fits with $\chi^2_{lim} \approx 2.5$.

The reason for this problem is the same as that for Titan tholin by itself not matching Pholus's spectrum—it brightens too fast in going from the visible to near-infrared. The particle mixture of Titan tholin and poly-HCN (or other dark material) obtains a good match for $\lambda > 0.55$ μ m by scaling down Titan tholin's brightening such that the Titan tholin particles are nearly transparent at 1 μ m. The scaling is so large, however, that the Titan tholin particles are almost completely opaque at 0.55 μ m and it becomes very difficult to get much darker at 0.45 μ m. Smaller particles (ignoring the breakdown of geometric



FIG. 10. Best fit model modified from the Hoffmann *et al.* (1993) results (cf. Fig. 9). The Tholin α particles produce the red color beyond 0.55 μ m but become neutral at shorter wavelengths. Kerogen (K) produces the added absorption needed below $0.55 \ \mu$ m. These materials are incapable of matching the absorption bands in the infrared spectrum. Addition of one of the ices (water or ammonia), needed for a good infrared fit, makes the visible and near-infrared fit significantly worse.

optics) would be brighter and, therefore, capable of darkening further but would also become transparent below 1 μ m, making a poor fit at long wavelengths. Replacing Titan tholin with Tholin α , which does not brighten as fast, improves the fit only slightly to $\chi^2_{lim} \approx 12$. The second (or third) surface component, instead of being neutral, needs to add to the absorption at short visible wavelengths. We find a fair match with a 1 : 1 mixture of kerogen and tholin α when both materials have particle diameters of 3 μ m (Fig. 10). It has $\chi^2_{lim} \approx 3.8$. However, because neither of these materials have a 2.0- nor 2.25- μ m feature and the addition of ice worsens the fit, it is not possible to match the infrared spectrum.

Cruikshank *et al.* (1993) claim to have identified a high-[H]/[C] organic solid called asphaltite on Pholus. A priori, we would expect highly irradiated organic solids to have a low [H]/[C] ratio. Their basis for the identification is a weak absorption band at 1.7 μ m, the asymmetric 2.27- μ m absorption seen in the Davies *et al.* (1993) spectrum, and a similarity with Pholus in color and albedo. We find this result suggestive but inconclusive. The substantial error bars on the Davies et al. observations make the 1.7- μ m band identification very subjective; there are similar sized fluctuations throughout the spectrum. An improved infrared spectrum at 2.05-2.45 µm (Cruikshank et al. 1993) shows Pholus's spectrum to be flat to decreasing at $\lambda > 2.3 \mu m$ while asphaltite is increasing. Asphaltite also does not show a 2.0-µm absorption band and, except for the 1.7- μ m band, brightens uniformly over the range 1.4–2.2 μ m while Pholus is equally bright at 1.8 and 2.2 μ m. Finally, asphaltite's visible spectrum appears to suffer from the same problem as tholins alone: flat at the blue wavelengths and too steep at red and near infrared wavelengths. As a pure asphaltite surface is unlikely and Cruikshank et al. do not claim this to be the case, many of these discrepancies can probably be explained by appealing to other materials adding absorption at the appropriate locations, with water ice being a likely candidate. Optical constants for asphaltite are unavailable, so we cannot test this candidate with our model.

GAS-SYNTHESIZED THOLIN ON PHOLUS?

The requirement that Titan tholin (or any other tholin produced in the gas phase) exists on Pholus—as suggested by Fink et al. (1992), Mueller et al. (1992), and Binzel (1992)-presents some difficulty. As synthesized in the laboratory and seen on Titan, Titan tholin is produced in a nitrogen-methane atmosphere. A literal interpretation would require that a N_2/CH_4 atmosphere has existed, and that chemical conversion time scales are shorter than escape time scales. The size of Pholus, 140-200 km (Howell et al. 1992), however, precludes a long-term atmosphere because for all but the lowest temperatures $(\lesssim 10 \text{ K})$ the mean molecular velocity is greater than Pholus's escape velocity. A transient atmosphere would quickly be lost by blowoff. Nevertheless, we examine in detail this and two other situations where tholin production may still take place.

Irradiation of a transient atmosphere by the solar wind. If Pholus has (or had) a near-surface reservoir of frozen nitrogen and methane, as, e.g., Triton does, during near-perihelion periods of increased temperature it would sublimate and produce a transient atmosphere as the molecules expand outward. The rate at which the ice sublimates is given by $Z = p_v(2\pi mkT)^{-1/2}$, where p_v is the vapor pressure of the ice (Delsemme and Miller 1971). Because for Pholus the mean thermal velocity, $\bar{v} = (8kT/$ $\pi m)^{1/2}$, is greater than the escape velocity, very few particles will be moving toward the surface and condensing so the density of the expanding atmosphere will be onehalf the equilibrium density, $n = fp_v/2kT$, where f is the fraction of the surface covered with the volatile ice. Because p_v is strongly temperature-dependent and sublimation requires the absorption of heat, we must include a sublimation term in the energy balance equation $(L_{\odot}/4\pi r^2)(1 - A) = 4\sigma T^4 + fZL$, where L is the latent heat of vaporization. The vapor pressure and latent heat of N₂ and CH₄ ices are calculated using expressions from Brown and Ziegler (1980). For an albedo of 0.05 and a heliocentric distance of 20 AU, an atmospheric pressure of 9 nbar can be maintained with a surface of 10% N₂, but only for a short time. The outer 1 mm ($\rho_{N_2} \approx 0.8 \text{ g cm}^{-3}$) of Pholus will be depleted of N₂ in only 3 hr. A similar depth of methane ($\rho_{CH_4} \approx 0.45 \text{ g cm}^{-3}$) would also be lost in 3 hr. (N₂ sublimation depresses the temperature more than CH₄, so only after all N₂ is lost does CH₄ start sublimating.) Even if the ices were continually replenished (e.g., by loss of outer layers) Pholus would be completely sublimated in ~25,000 years.

At this heliocentric distance the solar wind is delivered at a rate of $\sim 10^{-2}$ erg cm⁻² sec⁻¹ (scaled from Sagan and Thompson 1984). While the average flux at the surface of a rotating spherical object is a factor of 4 lower, the extended atmosphere with a scale height on order of the radius will have a cross section at least 4 times larger than the physical object, so the full flux is used. For a molecular cross section $\sim 3 \times 10^{-15}$ cm² and a number density $\sim 10^{12}$ cm^{-3} , the mean free path, l, of solar wind particles through the atmosphere is a few meters, so all the flux should be deposited in the atmosphere. For a production efficiency $G_{\text{tholin}} \approx G_{-\text{CH}_4} \approx 50(\text{C} + \text{N}) \text{ keV}^{-1}$ (McDonald *et al.* 1993), the CH₄ destruction rate is $\sim 3 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$. In 10⁴ years, $\sim 10^{20}$ molecules cm⁻² would be converted to tholin, potentially a layer 10 μ m thick ($\rho_{\text{tholin}} = 2$ g cm^{-3}). Further from the Sun (or for a higher albedo), the temperature will be less and the lifetime of the atmosphere will be longer due to the slowed sublimation rate. So long as the atmosphere remains thick to the solar wind $(l \leq l)$ R) the amount of tholin produced will increase. When the atmosphere becomes thin, tholin production will drop as $\sim n^3$. (One factor of *n* comes from the declining probability of solar wind interaction and an additional factor of n^2 comes from the declining probability of molecular collisions.) Because the survival times of N_2 and CH_4 will differ and because CH4 is more important in tholin production, we use the CH₄ lifetime (up to the age of the Solar System) as the atmosphere lifetime. Figure 11 plots the amount of tholin produced as a function of distance from the Sun for two albedos. The efficiency of emplacement of the tholin will be determined by sedimentation, fallout from the edge of "jets," and solar wind pressure (which could both eject tholin and force sunward tholin back toward the surface). Even under implausibly favorable conditions, more than 1 mm of tholin is very unlikely.

While tholin production is taking place, the sublimating ice will be producing a lag deposit of whatever impurities preexist in the ice. In order for tholins from the atmo-



FIG. 11. (a) Estimated lifetime of a CH_4 transient atmosphere for a constant sublimation rate. A 10% CH_4 content and a continuous supply of surface ice is assumed. An upper limit of 4.5 Gyr is set. (b) Estimated amount of tholin produced by the solar wind interacting with this CH_4 atmosphere. Because the atmosphere is expanding outward faster than escape velocity, very little of the tholin may ever return to the surface. One millimeter of tholin is a very optimistic upper limit, but would be sufficient to explain the spectrophotometry.

sphere to dominate the spectrum, the lag deposit must be thinner than the tholin deposit. For maximum production, we must assume 10-100 km of methane ice to have been sublimated. The impurity concentration in the ice, therefore, needs to be less than $10^{-7}-10^{-8}$ to produce a lag deposit less than 1 mm thick. Ice this pure is quite certainly unreasonable. Any amount of tholin produced in a transient atmosphere on Pholus could never be anything more than a trace component.

Surface irradiation by the solar wind. When the atmosphere is thin, most of the solar wind flux makes it to the surface where it can irradiate the ice directly. At a distance of 50 AU the surface-averaged solar wind flux is 5×10^{-4} erg cm⁻² sec⁻¹. Thompson *et al.* (1987) find for a 200:1 methane clathrate a solid-phase production efficiency $G_{\text{thoun}} \approx 1-10(C + O) \text{ keV}^{-1}$, an order of magnitude lower than for gas-phase production. This is very similar to the efficiency for pure methane (Thompson *et al.* 1987), so tholin production is insensitive to bulk methane content.

TABLE VI Stability of Sublimating Ices in an Assumed Pholus Regolith with $dp/dz = 4 \mu \text{bar cm}^{-1}$

D' .	T 4	Vapor) µt	pressure par)	Stable depth (cm)		
(AU)	(K)	N ₂	CH₄	N ₂	CH₄	
10	87	3×10^{6}	70000	106	18000	
20	62	90000	260	20000	65	
40	44	330	0.09	80	0.02	
100	28	0.03	10-7	0.001	Surface	

^a An albedo of 0.05 is assumed.

For a production efficiency 5(C + N + O) keV⁻¹, then, the tholin incorporation rate is $\sim 2 \times 10^6$ cm⁻² sec⁻¹, giving a tholin buildup of 7 μ m Myr⁻¹.

The sublimation rate of CH₄ for an albedo of 0.7 is 3 m Myr⁻¹. For the tholin to dominate a lag deposit the ice needs to be pure to a level $\sim 10^{-6}$ which is again unreasonable. Methane clathrate is capable of producing tholin without sublimating and requiring unnatural purities, but the tholin produced is thought to be similar to ice tholin (Thompson *et al.* 1987, Khare *et al.* 1989) which is not a component in the best model mixtures.

Subsurface irradiation by cosmic rays. Solar wind particles can penetrate only to $<0.1 \ \mu m$ (Thompson et al. 1987), so if ice is to be irradiated it must be exposed at the surface. Cosmic rays can penetrate to 10 or more meters (Thompson *et al.* 1987) where volatiles may be in equilibrium with gas trapped in the regolith, and, therefore not sublimating. For a 140-km-diameter object with a 2 g cm⁻³ bulk density and a 1 g cm⁻³ regolith density, there exists a hydrostatic pressure gradient of 4 μ bar cm^{-1} from the weight of overlying material. If the vapor pressure of the ice exceeds the weight of overlying material, a jet will spontaneously form as the gas breaks through to the surface (Hartmann 1993). It is therefore possible to derive the depth at which frozen nitrogen and methane can exist as a function of heliocentric distance (or temperature), ignoring diffusion (Table VI). Regardless of what is happening at the surface, then, cosmic rays could be irradiating CH_4 : N₂ ice mixtures at distances of 40 AU (temperatures <45 K) or CH₄: NH₃ ice mixtures at distances of 20 AU (temperatures <65 K). The energy deposited is roughly 3×10^{-3} erg cm⁻² sec⁻¹ (Thompson et al. 1987). With $G_{\text{tholin}} \approx 5(C + N + O) \text{ keV}^{-1}$, the tholin incorporation rate is $\sim 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$, giving a tholin buildup of 20 cm over 4.5×10^9 years, but distributed throughout the upper 10 m of the object. This constitutes $\sim 2\%$ of the volume of these surface layers. To reach the levels we need on Pholus (10-20%), the outer layers need to devolatilize and concentrate the tholin into a lag deposit. The impurity level of the ice can then be as high as 1% and still have the postaccretion tholin be the major component of the lag deposit. Although they may be very similar, the identity of tholin from gas phase and from solid phase N_2/CH_4 mixtures has not yet been demonstrated.

NEW OUTER SOLAR SYSTEM OBJECTS

Since the discovery of Pholus, two objects have been located beyond 40 AU: 1992 OB, (Jewitt and Luu 1992, 1993) and 1993 FW (Luu and Jewitt 1993). OB₁ is a red object with V-R and R-I colors of 0.6 \pm 0.1 and 1.0 ± 0.2 (Jewitt and Luu 1993), respectively, compared to Pholus's 0.66 and 0.68 (Mueller et al. 1992). 1993 FW has a V-R of 0.4 ± 0.1 (Luu and Jewitt 1993) which makes it only $5 \pm 10\%$ more reflective at R than at V. This is very similar to Chiron which has V-R = 0.37 (Hartmann et al. 1990), or 2% more reflective at R than V. Neither Chiron nor 1993 FW are examined here as their neutral colors do not require extraordinary explanations, unlike Pholus and QB_1 . QB_1 photometry is plotted in Fig. 12. The large error bars on QB₁ make our results for Pholus directly applicable, but also allow a fair match to a pure Titan tholin surface (also plotted in Fig. 12).

CONCLUSIONS

We have found mixtures (HTW and HTA) that are able to reproduce the observations of 5145 Pholus with reasonable parameter values. The two mixtures differ only in their ability to match the infrared data, with ammonia ice providing a better fit than water ice because of the 2.25- μ m absorption band. In our models the poly-HCN and Titan tholin combination is responsible for the steep red visible spectrum that first suggested complex organic



FIG. 12. Two model fits to the 1992 QB₁ observations. The similarity of QB₁ to Pholus makes our models for Pholus directly applicable to 1992 QB₁ (dashed line). The large error bars on the 1992 QB₁ data, however, also allow a much wider range of possibilities, such as a pure Titan tholin surface with 15.8- μ m-diameter particles (solid line).

molecules on Pholus. By themselves the absorption coefficient of Titan tholin is too steep in the near-infrared, while that of poly-HCN is not steep enough in the visible. No tholin with measured optical constants has suitable absorption to match Pholus's spectrum alone nor in a binary mixture with a bright ice. However, very few tholins produced in ice mixtures have had their optical constants measured. Further work in this area is needed in order to predict reliably the type of solids produced by cosmic rays or solar wind particles incident on icy, airless bodies. Of particular interest would be a determination of the optical constants of the organic residue from the charged particle irradiation of CH_4 : NH_3 and N_2 : CH_4 ice mixtures.

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