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Ices on the Surface of Triton

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The near-infrared spectrum of Triton reveals ices of nitrogen, methane, carbon monoxide, and carbon dioxide, of which nitrogen is the dominant component. Carbon dioxide ice may be spatially segregated from the other more volatile ices, covering about 10 percent of Triton's surface. The absence of ices of other hydrocarbons and nitriles challenges existing models of methane and nitrogen photochemistry on Triton.

Voyager 2 revealed Triton as a frozen world with a relatively young and highly structured surface almost devoid of impact craters and with evidence of episodes of local and perhaps global melting (1). A tenuous atmosphere of nitrogen and methane supports a tropospheric photochemical

haze layer, discrete clouds, and winds that blow the effluent from at least three active plumes (or "geysers") toward the equator from the south polar region (2). Solid N_2 and CH_4 had been detected on Triton's surface by earlier ground-based telescopic observations (3, 4). The atmospheric pressure of 16 ± 3 microbar N_2 was found to be in approximate vapor pressure equilibrium with the surface ice.

We have continued to observe Triton with ground-based telescopes to probe further details of its composition. In this report we describe the results of our 1991 and 1992 investigations of the reflectance spectrum of Triton obtained with a new infrared spectrometer at the 3.8-m United Kingdom Infrared Telescope Facility on Mauna Kea, Hawaii (5).

Our spectra have significantly higher (250–350) resolving power and signal-to-noise than had been previously achieved. We confirm the presence of the six bands of CH_4 and one band of N_2 that had been seen

in the earlier data, but obtain more precise measurements of the band strengths, shapes, and central wavelengths. The spectra also show absorption bands due to solid CO and CO_2 .

Seen from Earth, Triton is unresolved (subtended diameter <0.2 arc sec), and the telescopic spectra reported here result from sunlight reflected from an entire hemisphere. Reflection from the icy surface of Triton occurs by scattering from individual grains and depends on the grain diameters and refractive indices of the various ice components. Near-infrared spectroscopy probes the uppermost several centimeters of the surface.

In Hapke's (6) model of scattering from a particulate surface, from the real (n) and imaginary (k) indices of refraction of a material one can calculate the reflectance of both multi- and monocomponent surfaces (7). We have used this theory to calculate the radiance factor, which is the reflectance of Triton's surface relative to that of a perfect reflecting lambert surface illuminated and viewed normally, using three different models of the surface ices. The first (checkerboard) model has spatially segregated patches of the four identified ices, and a single solar photon is scattered from a grain of only one kind of ice. The second (salt-and-pepper) model consists of intimate mixtures of ices, in which a photon may be multiply scattered from grains of different composition. In the third kind of model, ices are mixed at the molecular level (for example, CH_4 dissolved in N_2 in a solid solution). We used the optical constants of the pure ices (8) in the spatially segregated and intimate mixture models, and additional data (9) for models of molecular mixtures of CH_4 and N_2 . Laboratory data on the molecular mixes are not yet adequate for our models, and the results reported here pertain only to intimate mixes and spatially segregated components.

With four molecular species identified on Triton's surface, and with the possibilities of spatially segregated pure and mixed ices in various particle sizes, a model fit to the observed spectrum involves many parameters, which are therefore difficult to constrain. In general, larger particles and greater fractional coverage of the surface generate stronger absorption bands, while smaller particles of any constituent will yield weaker bands of all the constituents. In a model fit to the spectrum the behaviors of absorption bands of the four constituents are interrelated, but we first consider each of the components separately.

Molecular nitrogen is the most volatile constituent identified, and gaseous N_2 dominates the atmosphere. Sublimation and condensation of N_2 appear to maintain an

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approximately isothermal surface even on the night side and in the currently dark north polar zone (11). The density-induced N_2 band at $2.15\text{ }\mu\text{m}$ (9) was found in earlier low-resolution spectra (4), but the band shape is more clearly shown in the new data. The $2.15\text{-}\mu\text{m}$ region includes the hydrogen Brackett- γ absorption line in the solar spectrum and in the stellar spectra used for correction of the solar flux and extinction, so special care is required in the processing of the high-resolution Triton data. The peak wavelength of the N_2 band seen in the smoothed spectrum of Triton is $2.1477\text{ }\mu\text{m}$ (4656.1 cm^{-1}) (12), which agrees with the laboratory wavelength of $2.1475 \pm 0.0001\text{ }\mu\text{m}$ ($4656.6 \pm 0.2\text{ cm}^{-1}$) for $\alpha\text{-}N_2$.

Below the transition temperature of 35.6 K , solid N_2 exists in the high-density, cubic α phase, and above that temperature it is in a lower density hexagonal phase denoted β . The spectrum of $\alpha\text{-}N_2$ is characterized by a very narrow double phonon absorption band superimposed on a broad weaker absorption, while the β phase band is broad and shallow with the absorption peak at $2.152\text{ }\mu\text{m}$ (4647 cm^{-1}). Triton shows the broad and shallow band with the peak at the position of the $\alpha\text{-}N_2$ band, although the narrow band is itself not resolved. Within the limitations of the available laboratory data and with the resolution of our Triton data, we suspect the presence of both the α and β phases of N_2 , but additional laboratory and telescopic data are needed to establish the relative fractions on Triton's surface. Both phases may occur if different parts of the surface have temperatures above and below the phase transition temperature (13).

In the absence of reliable optical constants for the wings of the $\alpha\text{-}N_2$ band, we modeled the spectrum using optical constants for $\beta\text{-}N_2$ derived from absorption coefficients observed in centimeter-size crystals grown in the laboratory. The imaginary index of N_2 is several orders of magnitude less than that of the other ices we have identified. This leads to the high computed abundance of N_2 relative to the other components. The N_2 particle size derived using the Hapke model is $\sim 1\text{ cm}$. Solid N_2 anneals rapidly (14), and we view 1 cm as a characteristic scale for the cracking of a locally continuous and transparent ice sheet. Additional laboratory data for $\alpha\text{-}N_2$ are required for more detailed analysis.

Six strong and three weaker methane bands are seen in the Triton spectrum. All of these are found in laboratory spectra of thin films of CH_4 ice in transmission. Curiously, Triton does not show the CH_4 band at $1.48\text{ }\mu\text{m}$ that appears in Pluto's spectrum (15) and in laboratory spectra. Triton's atmosphere contains a trace

amount of gaseous methane (10), and atmospheric models derived from Voyager UVS data (16) suggest that the surface CH_4 is close to saturation or slightly undersaturated relative to the vapor pressure of gas over pure CH_4 ice. Undersaturation of CH_4 would suggest that the methane is not exposed as a free ice, but is complexed in some way with another constituent. Moreover, the central wavelengths of the CH_4 bands in Triton's spectrum are systematically shifted to longer wavelengths by $0.007\text{ }\mu\text{m}$ to $0.014\text{ }\mu\text{m}$ (13 cm^{-1} to 27 cm^{-1}) depending upon the band (17), compared with values measured in the laboratory spectrum of pure CH_4 ice (8); laboratory spectra of thin films of ices condensed from mixed CH_4 (0.25%) and N_2 (99.75%) show a similar shift. Methane is highly soluble in N_2 , and the occurrence of solid solutions of these two (and perhaps other) constituents is not unexpected on Triton, where sublimation and condensation of the volatiles occurs on a seasonal, and possibly a diurnal cycle.

In our models, we have used the optical constants of pure CH_4 , but we have shifted the central wavelengths of the strongest absorption coefficients to correspond to those seen in the Triton spectrum (8).

We have been unable to find a model with a mass fraction in intimate mixtures, or a combination of mass fraction, fractional surface coverage and particle size distribution in spatial mixtures that simultaneously fits the band strengths and shapes in the $1.7\text{-}\mu\text{m}$ and $2.3\text{-}\mu\text{m}$ spectral regions. Mixtures that fit the $1.7\text{-}\mu\text{m}$ region yield excessively strong bands in the $2.3\text{-}\mu\text{m}$ region, more like the CH_4 bands on Pluto. Conversely, mixtures that fit the $2.3\text{-}\mu\text{m}$ region show too little absorption around $1.7\text{-}\mu\text{m}$. Those intimate mixture models that fit best have an abundance of 0.05% CH_4 relative to N_2 .

Despite the incomplete fit of the model to the Triton spectrum, two lines of evidence lead to the conclusion that CH_4 is a minor component of the surface ice relative to N_2 : the very low ($< 1\%$) abundance of CH_4 derived directly from the band strength is supported by the wavelength shift of CH_4 bands in a matrix of N_2 containing less than 0.5% CH_4 (17). (Because we see only the shifted CH_4 bands and no indication of CH_4 bands at their normal wavelengths, we conclude that virtually all of the methane on the satellite's surface is incorporated in the N_2 .)

Carbon monoxide is revealed in our new spectra, where earlier spectra at lower resolution were inadequate to distinguish the narrow (2-0) CO overtone band at $2.352\text{ }\mu\text{m}$ between the two strong flanking CH_4 bands. Although the wavelength of the CO fundamental at $4.7\text{ }\mu\text{m}$ is sensitive to ma-

trix effects (18), experiments by one of us [B.S. (19)] show that the shift of the (2-0) band of CO in a matrix of N_2 is too small to be discerned at the resolution of the Triton data. We cannot therefore say whether CO occurs as a free ice or in a complex with N_2 .

Our analysis of CO uses only the (2-0) band because the higher overtone (3-0) is blended with a CO_2 band, and the still weaker isotopic band at $2.404\text{ }\mu\text{m}$ is in a noisier part of the spectrum. There is also a weak CO absorption coincident with the short wavelength wing of the strong $2.32\text{-}\mu\text{m}$ CH_4 band.

Carbon monoxide ice is highly volatile: at the $\sim 38\text{ K}$ surface temperature of Triton, the ratio of partial pressures $p_{CO}/p_{N_2} = 0.074$ (20), although the atmospheric mixing ratio of CO to N_2 derived from Voyager ultraviolet spectra is in the range 10^{-2} to 2×10^{-4} (21). The disparity between the vapor pressures and the atmospheric mixing ratios suggests that the condensed CO is indeed complexed with another constituent.

The relative fraction of CO to N_2 in the intimate mixture model that best fits the Triton data is 0.1%. From Raoult's law, the CO/N_2 mixing ratio in the atmosphere is then 1.5×10^{-4} (for $T = 38\text{ K}$), which is consistent with the range of values derived from Voyager observations.

Three discrete and narrow absorption bands at 1.966 , 2.012 , and $2.070\text{ }\mu\text{m}$ are seen in laboratory spectra of thin films of CO_2 , and all three are present in our Triton spectra. Another series of four absorption bands appears in the $1.6\text{-}\mu\text{m}$ region; the two strongest of these bands at 1.577 and $1.610\text{ }\mu\text{m}$ appear in the Triton spectrum, although one ($1.577\text{ }\mu\text{m}$) is blended with the (3-0) CO band, as noted above. The shapes of the solid CO_2 bands are distinctly different from the P and R branches in gaseous CO_2 in Earth's atmosphere, facilitating their detection amidst the strong telluric absorptions. We have taken special care to obtain stellar extinction standards at the same air mass as the Triton data and we are confident that the deep absorption features at 2.012 and $2.070\text{ }\mu\text{m}$ are intrinsic to Triton. We suspect that the other features in the region from 2.0 to $2.1\text{ }\mu\text{m}$ are residual absorptions from the telluric CO_2 removal rather than real spectral bands.

Five bands of solid CO_2 are found in the spectrum of Triton after removal of the telluric contribution. In the laboratory experiments of B.S. the $2.070\text{-}\mu\text{m}$ band in the pure ice is shifted to $2.066\text{ }\mu\text{m}$ when CO_2 is dissolved at a concentration of 0.25% in N_2 ; the CO_2 wavelengths on Triton are consistent with the pure ice and not consistent with CO_2 dissolved in N_2 .

Because CO_2 is far less volatile than N_2 it is likely to be spatially segregated, not

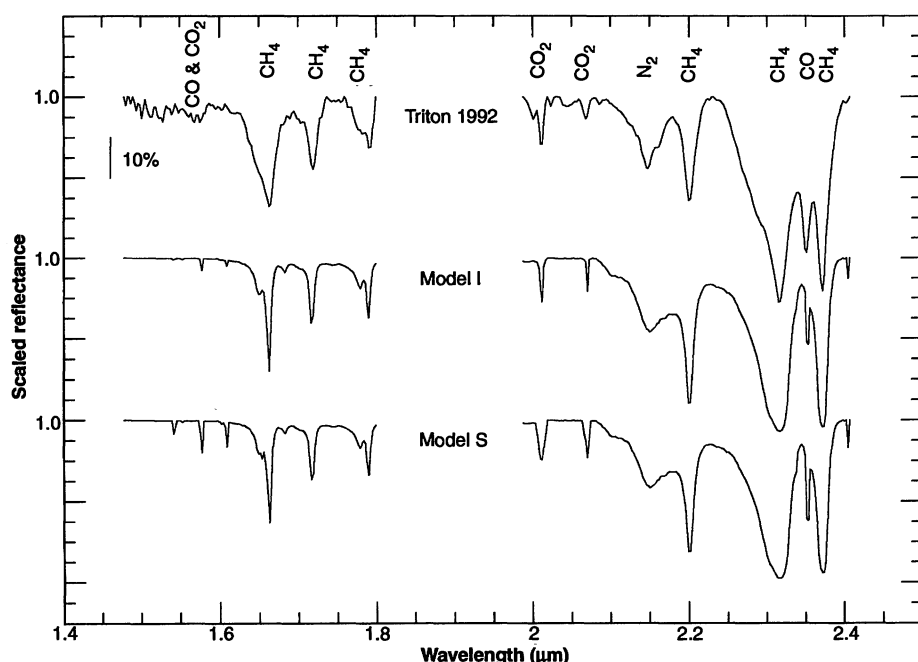


Fig. 1. The infrared spectrum of Triton from 1.47 to 2.41 μm and two Hapke scattering models as described in the text. Model I is a four-component, intimate mix scattering model in which the mass fractions and grain sizes of each component are: N_2 99.75%, 8.0 mm; CO 0.10%, 1.0 mm; CO_2 0.10%, 0.8 mm; and CH_4 0.05%, 0.2 mm. The spectrum and model are plotted as scaled reflectance (normalized to 1.0 at maxima values (8) rather than geometric albedo because the continuum of the Triton spectrum has been flattened by application of several straight line segments. Model S uses the same mix of N_2 , CH_4 , and CO as before (90% of the surface area), but the CO_2 is spatially segregated and constitutes 10% of the visible surface area. The Triton spectrum and the two models are plotted at the same scales (normalized to 1.0 at the continuum) and offset vertically for clarity. The slight mismatch between the position of the 2.35- μm CO band in the Triton spectrum and its position in the model is an artifact of the interpolation scheme used to calculate the real and imaginary parts of the complex optical constants of CO at wavelengths appropriate to the Triton observations. The agreement between the position of the band in the Triton data and the laboratory data is less than the spectral bandwidth of one detector used to obtain the Triton data.

intimately mixed with N_2 . Accordingly, we have calculated models in which an optically thick reflecting surface layer of pure CO_2 is separate from the $\text{N}_2 + \text{CO} + \text{CH}_4$ mixture. These models show that approximately 10% of Triton's surface may be covered with isolated outcrops of CO_2 ice (Fig. 1). Although this is our preferred model, we also show a model in which CO_2 is intimately mixed with the other constituents; the derived relative fraction of CO_2 to N_2 in the intimate mixture model is 0.2%.

The source of the CO_2 is itself an interesting question. One possibility is of reactions between CO and OH , with subsurface H_2O providing the OH radical during impacts. In that case, the CO_2 ice would be expected in association with impact-produced terrain on Triton, a hypothesis that cannot be tested until the next Triton mission.

Using a suite of laboratory reflectance and transmission spectra of numerous ices, we have found no evidence in the Triton data for the following molecules: H_2O , C_2H_2 , C_2H_4 , C_2H_6 , H_2S , CH_3OH , C_3O_2 ,

HCN , and NH_3 . This may provide a constraint on models of Triton's photochemistry. Although none of these molecules can be identified from specific absorption features, the spectrum of Triton exhibits continuum absorption between 2 and 2.5 μm that we have not yet interpreted. We made a special study of H_2O ice, which has very broad absorption bands: Both intimate and molecular mixtures that included water ice produce a negative continuum slope from 2 to 2.5 μm , as is seen in the data, but other calculated absorptions due to water ice are absent. We conclude that any H_2O ice on Triton is buried by N_2 and the three other identified constituents.

Although no specific model mixture exactly duplicates both the relative band depths and continuum shape in the spectra (Fig. 1), all of the calculated mixtures yield similar conclusions (Table 1). For all mixtures the presence of fine-grained material (smaller than about 0.2 mm) masked the N_2 absorption, providing strong limits on the quantity of such material on Triton. The models that best reproduce the obser-

Table 1. Identified bands in the spectrum of Triton.

Ice	Wavelength* (μm)	Frequency (cm^{-1})
N_2	2.148	4655.5
CH_4	1.663	6013.2
	1.719	5817.3
	1.790	5586.6
	2.200	4545.5
	2.316	4317.8
	2.371	4217.6
CO	1.578	6337.1
	2.352	4251.7
$^{13}\text{CO}^\dagger$	2.404	4159.7
CO_2	1.577	6341.2
	1.610	6211.2
	1.966	5086.5
	2.012	4970.2
	2.070	4830.9

*Uncertainty in wavelength is $\pm 0.001 \mu\text{m}$. † Identification in Triton spectrum uncertain.

vational data require both large grain sizes ($\sim 1 \text{ cm}$) and large N_2 abundance ($\sim 99\%$) regardless of the type of mixing.

In this picture, Triton's surface is dominated by the presence of centimeter-sized pieces or large continuous sheets of solid N_2 in which small quantities of CH_4 and other contaminants are dissolved. The surface is probably cracked but intact solid ice. CO and CO_2 may occur sporadically as free ices, although the atmospheric undersaturation of CO suggests that it, too, is incorporated in the N_2 .

The Voyager pictures of Triton show a surface of many different textures and with subtle color variations. The coloration may be due in part to the formation of hydrocarbons and nitriles from the dissociation of CH_4 and N_2 and the subsequent production of chromophores. Photochemical calculations (10) predict that ultraviolet irradiation of Triton's CH_4 and N_2 atmosphere should produce a 6-m layer of C_2 hydrocarbons over the lifetime of the solar system. The fact that we see no trace of these hydrocarbons on the icy surface is therefore puzzling, especially since we do see outcrops of the less volatile CO_2 ice. Perhaps the intermediate compounds, produced on the way to the formation of the dark deposits and the colored terrains are converted sufficiently rapidly to more stable complex substances (for example, by cosmic ray bombardment) that they do not accumulate to detectable levels on Triton's surface (22).

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Surface Ices and the Atmospheric Composition of Pluto

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Observations of the 1.4- to 2.4-micrometer spectrum of Pluto reveal absorptions of carbon monoxide and nitrogen ices and confirm the presence of solid methane. Frozen nitrogen is more abundant than the other two ices by a factor of about 50; gaseous nitrogen must therefore be the major atmospheric constituent. The absence of carbon dioxide absorptions is one of several differences between the spectra of Pluto and Triton in this region. Both worlds carry information about the composition of the solar nebula and the processes by which icy planetesimals formed.

Although Pluto is usually classified as a planet, its closest relative in the solar system appears to be Triton, Neptune's largest satellite. Both of these objects evidently formed from the solar nebula at a distance of ~ 40 astronomical units (AU) from the sun, where temperatures were < 50 K. In this respect, they may be considered huge icy planetesimals that somehow escaped accretion by the giant planets. The lower end of the mass distribution of such objects is represented by the common comets, objects 2060 Chiron, 5145 Pholus, 1992 QB1, and the great comet of 1729 (1). These objects represent an especially primitive stage in the transition from the grains and gas of interstellar clouds to the planets and satellites of the solar system.

We have presented observations of the near-infrared spectrum of Triton (2). We used the same instrumental configuration to study Pluto, without the benefit of Voyager data to provide a context for our work. It is the only planet not yet visited by spacecraft, but its recent occultation of a star (3) and the mutual eclipses and occultations exhibited by Pluto and its synchronously orbiting satellite Charon (4) have helped to define this distant system (5).

Using the cooled grating array spectrometer with the United Kingdom Infrared Telescope, we recorded Pluto's spectrum from 1.4 to 2.4 μm (4160 to 7140 cm^{-1}) at a resolution of 350 on 27 and 28 May 1992 (UT) (6). Previous observations at lower resolution had established that there is solid CH_4 on Pluto's surface (7). Our spectra confirmed the presence of this ice, revealing the same series of strong CH_4 bands seen on Triton. In addition, the (2,0) band of CO at 2.35 μm and the N_2 absorption at 2.15 μm were added, both of which are also present in Triton's spectrum (2) (Fig. 1).

Despite these general similarities, the spectra of Pluto and Triton are not identical. We do not find the solid CO_2 absorptions on Pluto that are so prominent on Triton. In particular, the absence of the strong triad of CO_2 bands near 2.0 μm (2) means that the amount of this ice on Pluto must be less than one-third of the amount that forms the spectrum of Triton. The shapes of the CH_4 bands in the region from 2.0 to 2.4 μm are broader and deeper on Pluto, whose spectrum exhibits an additional CH_4 feature at 1.48 μm that is not

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