Triton: Do We See to the Surface?

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The quantity and physical state of methane and nitrogen in the atmosphere of Neptune's satellite Triton and on the surface are evaluated by means of new telescopic data and laboratory measurements of these volatiles. Methane ice is seen in some spectral regions, indicating that the atmosphere is sufficiently transparent to permit sunlight penetration to the surface. Some of the molecular nitrogen absorption occurs in the atmosphere, though some must occur in condensed nitrogen (liquid or solid) on Triton's surface, or in a thin cloud of condensed nitrogen. The Voyager spacecraft cameras should see the surface of Triton.

Triton is Neptune's largest satellite, and while its intrinsic brightness has long suggested that it is sufficiently large to retain an atmosphere, only in the last decade has it become possible to make spectroscopic observations in the near-infrared where diagnostic bands of expected gases and ices occur. Cruikshank and Silvaggio (*1*) found the 4350-cm^{-1} (2.3-μm) methane band in the spectrum of Triton and deduced that an atmosphere and surface ice deposits must be present. Methane ice and gas both exhibit the 4350-cm^{-1} band and are indistinguishable from one another in spectra with resolution poorer than 30 cm^{-1}.

Seven individual methane bands in the range 2850 to 12500 cm^{-1} (0.8 to 3.5 μm) have now been observed in the spectrum of Triton (*2–4*). In addition, a band of 4650 cm^{-1} (2.15 μm) attributed to the (2-0) density-induced band of molecular nitrogen has been identified (*5*). From absorption coefficients of this band (measured in liquid nitrogen), Cruikshank *et al.* (*5*) deduced that the quantity of N_2 needed on Triton to form this band exceeds that which could exist as a gas, and therefore N_2 must occur in a condensed state on the surface. They further concluded that the 4650-cm^{-1} band was produced in the upper several centimeters of a liquid layer as seen through a transparent atmosphere. The likelihood that condensed N_2 occurs as a solid rather than a liquid was pointed out by Lunine and Stevenson (*6*), from a study of the binary phase diagram of CH_4 and N_2. They favor a model of Triton in which solid CH_4 and N_2 are mixed in a disequilibrium assemblage, perhaps distributed nonuniformly across the surface.

The temperature of Triton's surface is not known from direct observation. If the surface consists of bare rock or a pulverized regolith, the temperature is directly related to the local insolation (*5*), but in the more probable case of a surface rich in condensed methane and other volatiles, the temperature is related in a more complex way to the thermodynamic properties of those volatiles, as noted below. The higher subsolar temperature calculated on the basis of a nonvolatile surface and thermally insignificant atmosphere (pressure at the surface less than a few microbars) is one extreme case, while a fully isothermal surface dominated entirely by volatiles is the lower temperature extreme case. At any plausible temperature of Triton's surface (in the range 40 to 65 K), the vapor pressures of nitrogen and methane are sufficient to ensure at least a tenuous gaseous atmosphere.

In this paper we seek to distinguish gaseous and solid methane on Triton, and to establish the quantity of atmospheric N_2, using telescopic spectra in the near-infrared.

It is unlikely that the atmosphere of Triton is in vapor pressure equilibrium with the volatiles on its surface. Sunlight incident on solid or liquid N_2 in the subsolar regions is transferred to latent heat of sublimation or evaporation, balancing the latent heat released during the freezing or condensation on the dark or weakly lit regions. This distribution of heat by the volatiles tends to isothermalize the surface at a temperature considerably lower than that calculated for insolation at the subsolar point on a nonvolatile surface. The response time of the expected thin atmosphere is sufficiently short that a thicker atmosphere in the subsolar region cannot form, as Trafton (7) has shown. The actual surface temperature depends on the quantity and distribution of the volatiles; Trafton (7) finds that the volatiles should congregate in the polar regions, which are expected to have the same temperature. That temperature, and the areal extent of the polar caps, will vary with the complex seasonal cycle on Triton (*7, 8*), with a concomitant variation in the total atmospheric column abundance and surface pressure.

Triton's southern hemisphere is approaching an extreme summer (maximum southern excursion of the sun) at the present time, and indeed there is some evidence that the atmosphere has changed as recently as about 1984 (*9*). Methane bands in infrared spectra obtained in 1986 are distinctly weaker than they were in 1980, although Trafton (7) predicts that warming in the southern hemisphere should significantly increase the observed CH_4 column abundance. In addition, precise measurements in 1987 of the brightness of Triton (at 8900 Å wavelength) as it orbits Neptune show no variation greater than about 2%, whereas similar measurements a decade earlier gave marginal evidence for a variation on the order of 6% (*10, 11*). We return to the implications of these observations below.

Interpretation of the spectrum of Triton has been hampered by a lack of theoretical and laboratory data on both methane and nitrogen at the appropriate low temperatures, leaving ambiguities as to the state of both substances (*5, 6*). We present here some new infrared spectra of Triton obtained in 1988, together with new laboratory data on methane that are relevant to the low temperature expected on the satellite. In addition, progress has been made in understanding the spectral properties of nitrogen in the context of Triton (*12*).

Spectra of the 4350-cm^{-1} region were obtained in 1987 and 1988, but of the 5880-cm^{-1} region in 1988 only. Data for both years in the 4350-cm^{-1} region are shown because of the possibility of secular changes, as pointed out by Cruikshank *et al.* (*9*). The two Triton spectra shown in Fig. 1 are considered to be identical within the observational errors, including the apparent differences at the extreme long and short wavelength ends of the spectra where systematic effects of correction for the terrestrial atmosphere are not fully reflected in the one-sigma standard error bars shown in the plot (*13*).

It is insufficient to compare Triton data with room-temperature methane gas spectra because of the pressure and temperature dependence of the shape of the methane spectrum. A previous attempt (*2*) to model

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the low-temperature spectrum of methane on the basis of room-temperature absorption coefficients met with only limited success. To improve estimates of the gas phase absorption of methane at the low temperature of Triton, Giver *et al.* (*14*) determined absorption coefficients and Malkmus band model pressure coefficients for sets of laboratory spectra at temperatures of 112, 188, and 295 K in the regions 4010 to 4660 cm^{-1} and 5400 to 6200 cm^{-1}. Integration of the absorption coefficients over the 4350-cm^{-1} region resulted in total band intensities in agreement with Fukabori *et al.* (*15*). To our knowledge, there is no published total intensity for the region 5400 to 6250 cm^{-1}, but the work reported here and by Giver *et al.* (*14*) is in good agreement with the Q branch data at 6000 cm^{-1} at several temperatures by Sarangi and Varanasi (*16*). In the 1988 work of Giver *et al.* (*14*) and for this work, the band model coefficients were extrapolated to T = 55 K and reflecting layer model spectra were computed for a resolution slightly higher than that of the Triton spectra.

Most laboratory reflectance spectra of methane ice or frost show the bands completely saturated, but Fink and Sill have published a reflectance spectrum of a thin film that shows unsaturated bands (*17*). We have processed this spectrum to reduce the resolution to that compatible with the Triton data (about 32 cm^{-1}).

In Figs. 1 and 2 we compare the laboratory ice and model spectra of gaseous methane with the telescopic data for Triton. The methane spectra are computed with a Malkmus reflecting layer model with the absorption and pressure-broadening coefficients for methane extrapolated to T = 55 K. The models assume that the effects of nitrogen as the broadening gas are the same as self-broadening by CH_4. At the resolution afforded by the laboratory data, methane ice bands can be clearly distinguished from the gas bands both in position (for the bands near 5880 cm^{-1}) and in shape (the bands near 4350 cm^{-1}). The new Triton data in principle offer the possibility to distinguish the contributions to the spectrum by methane ice and gas, and to make a more quantitative estimate of nitrogen absorption.

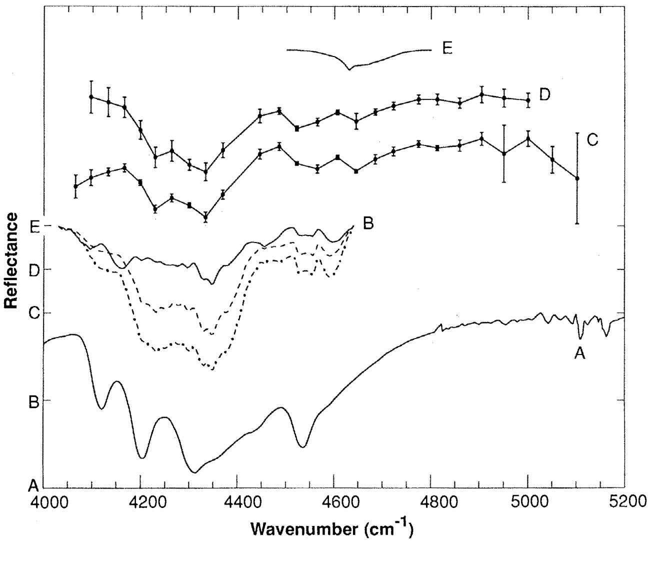

Fig. 1. Reflectance spectra of Triton obtained in 1987 (curve C) and 1988 (curve D), with spectra of methane frost (curve A), methane gas (curve B), and nitrogen (curve E) for comparison. All spectra are normalized to 1.0 at the continuum. The three nested spectra (curve B) are atmospheric model calculations from extrapolated laboratory observations of methane gas, and correspond to the following conditions: solid line, 12.5 m-amagat pure CH_4 with surface pressure P_s = 0.086 mbar, the saturated CH_4 vapor pressure at T = 59 K; dot-dash line, 2.9 m-am CH_4 plus N_2 with P_s = 17 mbar, which assumes saturated vapor for both gases at T = 55 K; dashed line, 1.45 m-am column abundance of CH_4 plus N_2 to give P_s = 9 mbar, corresponding to saturated vapor for both gases at T = 53 K. These and the methane frost spectra are shown at spectral resolution 32 cm^{-1} for direct comparison with Triton, in which the spacing of the individual data points approximately corresponds to this resolution. The N_2 spectrum (curve E) is computed from McKellar's (*12*) absorption coefficients for an average absorption depth of 0.135, corresponding to 0.83 amagat of N_2.

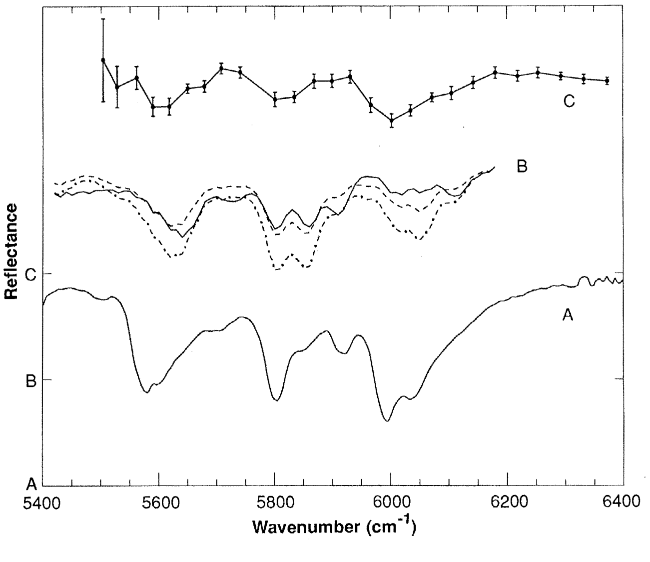

Fig. 2. Reflectance spectrum of Triton (curve C) obtained in 1988, with a laboratory spectrum of methane frost (curve A) and Giver's model calculations for methane-nitrogen gas mixtures (curve B) for comparison. All spectra were normalized, as in Fig. 1. The spectral resolution of the synthetic and laboratory spectra are reduced to 32 cm^{-1}. The three traces in curve B represent the same conditions as in Fig. 1.

The shape of the Triton absorption from 4100 to 4600 cm^{-1} is not well matched by the methane ice spectrum, which is dominated by the strong Q branches. Instead, the Triton spectrum is more nearly matched in shape and band strength by CH_4 gas or CH_4 pressure broadened by N_2. Of the three atmospheric model spectra (B) shown in Fig. 1, that with 1.45 meter-amagat (m-am) column abundance of CH_4 pressure broadened with N_2 (dashed line) is the best approximation to the Triton spectrum. This quantity of methane and nitrogen corresponds to surface pressure P_s = 9 mbar, the saturation values at T = 53 K. In order to match the band strength with pure CH_4 gas, the column abundance would have to exceed 12.5 m-am, as is seen in Fig. 1. Such a large quantity would appear to violate the measurement of 1.7 ± 0.7 m-am CH_4 in the 8900 Å band on Triton by Apt *et al.* (*4*) and the upper limits of about 2 m-am by other investigators (*18*). Therefore, this band appears to form largely in the atmosphere from gaseous absorption, but not from a thin atmosphere of pure CH_4.

Conversely, in the 5880-cm^{-1} region, the prominent features evident in the CH_4 ice reflectance spectrum appear in the Triton data. While neither pure gas nor pure CH_4 ice appear to be a complete match to the Triton spectrum, a combination of the two can provide a satisfactory fit. In this spectral region the absorption coefficient of CH_4 is approximately ten times less than in the 4350-cm^{-1} region. Therefore, the 5880-cm^{-1} band complex forms deeper in the atmosphere, and solar photons of this frequency may penetrate all the way to the surface of Triton where they encounter methane ice and are absorbed accordingly.

Relatively prominent Q branches in the methane spectrum, as seen at the low resolution of the Triton spectrum, can arise either by absorption in solid methane, as in ice on the surface or suspended crystals in a cloud, or in methane gas at a pressure greater than several tenths of a bar. The latter case is apparently precluded by the low surface temperature expected on Triton as noted above, and according to recent calculations by McKay *et al.* (*19*), who found that in a "warm" model that incorporates photochemical haze, $T_s = 58$ K and the corresponding surface saturation vapor pressure for nitrogen is only 53 mbar. "Cold" models by McKay *et al.* yield surface temperatures with corresponding gas pressures of only a few millibars. Those models do not include haze formation through CH_4 condensation.

While Triton spectra of yet higher spectral resolution are desirable to distinguish with complete certainty between solid and high-pressure gaseous methane, the present data strongly support the contention that we are measuring the spectrum of sunlight that is in part reflected from the surface of the satellite in the 5880-cm^{-1} region. Alternatively, under physical conditions not fully explored, solid methane may occur as haze particles in the lower atmosphere, and the ice signature seen in the 5880-cm^{-1} region may arise there.

The absorption coefficient of the density-induced (2-0) band of N_2 in the original paper about nitrogen on Triton (*5*) was taken from a measurement in liquid nitrogen. That value of 6.8×10^{-9} cm^{-1} am^{-2} is about two times the value measured by Shapiro and Gush (*20*), in gas at room temperature. McKellar (*12*) has observed this band at $T = 97.5$ K, finding that the peak absorption coefficient is 3×10^{-8} cm^{-1} am^{-2}. From McKellar's discussion of the temperature dependence of the peak absorption coefficient, the appropriate value for $T = 58$ K (found for the surface in the models of McKay *et al.* (*19*) is about 6×10^{-8} cm^{-1} am^{-2}, or about a factor of 9 larger than the value used by Cruikshank *et al.* (*5*). Lower temperatures imply yet larger values of the absorption coefficient.

Using the new absorption coefficients for cold gaseous nitrogen and the measured absorption depth on Triton of about 13% of the estimated continuum intensity, we calculate a nitrogen gas density of 0.83 amagat using equation 5 of Cruikshank *et al.* (*5*) modified to use an air mass factor of 4 rather than 3, with an assumed Triton gravitational acceleration of 98 cm s^{-2} and $T = 58$ K. This is the quantity of gaseous N_2 required to produce the observed absorption band at 4650 cm^{-1}. For $T = 58$ K the corresponding surface partial pressure is 180 mbar, which exceeds the vapor pressure of N_2 at the plausible maximum surface temperature of 64 K (*5*), and is substantially in excess of the $P_s = 53$ mbar in the "warm" model of McKay *et al.* (*19*). Furthermore, it is much greater than the surface pressure in the limiting isothermal case of Trafton (*7*) in which formation and evaporation of polar caps buffer the atmosphere at a pressure characteristic of the lower overall temperature of Triton's surface.

Therefore, the N_2 band in Triton's spectrum cannot be formed entirely within the gaseous atmosphere because the required gas column abundance cannot be supported at reasonable temperatures of the surface. As discussed by Cruikshank *et al.* (*5*), condensed N_2 must occur on Triton's surface, either as a liquid or a solid, and some of the absorption in the 4650-cm^{-1} band arises from the passage of solar photons through that material. Some absorption may also occur in a haze of condensed nitrogen postulated by McKay *et al.* (*19*).

McKellar's (*12*) admittedly simplified model of Triton predicts that for 13% peak absorption the observed N_2 could occur entirely within a saturated atmosphere for $T = 63$ K, but for the reasons discussed above, and in accordance with the calculations by McKay *et al.* (*19*), the temperature of the surface and lower atmosphere must be at least several degrees colder. We therefore do not concur with McKellar's conclusion, and require absorption in a surface layer of condensed nitrogen.

While the brightness measurements at 8900 Å are consistent with the formation of an optically thick haze of micrometer-size particles in the atmosphere of Triton sometime in the early 1980s, they are also consistent with a globally uniform distribution of condensed volatiles on the surface. An atmospheric haze is not expected to have a significant scattering effect at wavelengths longer than the characteristic particle size. Hazes in planet and satellite atmospheres are the norm rather than the exception, but particle sizes are typically 1 μm or less. Among the small bodies, Titan has an opaque photochemical haze resulting from sunlight on the methane in the upper atmosphere (*21*), and Pluto is now thought to have a weak haze layer, presumably from the same cause (*22*). Rather than the episodic formation of a haze in Triton's atmosphere in the mid-1980s, the observed decrease in methane band strengths may represent a selective removal of methane from the atmosphere on the Earth-directed hemisphere and a deposition on the surface in the colder anti-sun polar region, but such a process would appear to contradict the prediction by Trafton (*7*) as maximum summer approaches in Triton's southern hemisphere.

While Triton's atmosphere very likely supports a photochemical haze, the particle sizes are expected to be less than 1 μm in diameter (by analogy with Titan's haze), and the overall optical thickness is approximately 0.4 (*19, 23*). The haze is therefore essentially completely transparent to photons of wavelength greater than 1 μm (10,000 cm^{-1}). At optical wavelengths, Triton's atmosphere is approximately as hazy as that of Mars at times when no dust storms are in progress; the Voyager spacecraft cameras should see the surface with no difficulty at small observing angles, and should detect the haze at the satellite's limbs.

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Carbon-14 in Methane Sources and in Atmospheric Methane: The Contribution from Fossil Carbon

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Measurements of carbon-14 in small samples of methane from major biogenic sources, from biomass burning, and in "clean air" samples from both the Northern and Southern hemispheres reveal that methane from ruminants contains contemporary carbon, whereas that from wetlands, peat bogs, rice fields, and tundra is somewhat, depleted in carbon-14. Atmospheric $^{14}CH_4$ seems to have increased from 1986 to 1987, and levels at the end of 1987 were 123.3 ± 0.8 percent modern carbon (pMC) in the Northern Hemisphere and 120.0 ± 0.7 pMC in the Southern Hemisphere. Model calculations of source partitioning based on the carbon-14 data, CH_4 concentrations, and $\delta^{13}C$ in CH_4 indicate that 21 ± 3% of atmospheric CH_4 was derived from fossil carbon at the end of 1987. The data also indicate that pressurized water reactors are an increasingly important source of $^{14}CH_4$.

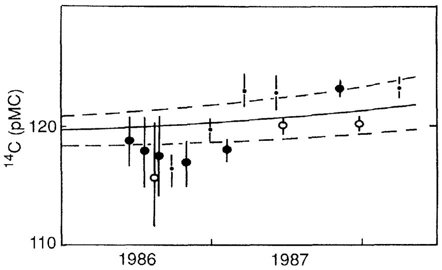

Fig. 1. Atmospheric $^{14}CH_4$ concentration for the sampling period 1986 to 1988. Large data points represent average values and SD for sample series of ocean surface air (Table 2), with the number of samples as in Table 2. Filled circles, Northern Hemisphere data; open circles, Southern Hemisphere data; small data points represent single Northern Hemisphere "clean" land air samples, except for December 1986 (five samples) and March 1988 (two samples). Solid line, model prediction for global average value from one-box model; broken lines, same for Northern Hemisphere (upper) and Southern Hemisphere (lower) average values from two-box model (see text).

METHANE IS A STRONG INFRARED absorber that directly and indirectly affects atmospheric temperature (*1*). It also influences tropospheric and stratospheric ozone concentrations (*2*) and is a major source of stratospheric water (*3*). The atmospheric concentration has more than doubled during the past 200 years (*4*). This increase, mostly attributed to human activities, is about three times as great as the natural concentration variations that occurred between glacial and interglacial times (*5*). The concentration continues to increase by about 1% per year (*6*). Destruction of CH_4 occurs mainly through reaction with OH radicals, and the tropospheric lifetime is 8 to 12 years. Methane is produced bacterially from wet environments (wetlands, rice fields, and tundra) and from ruminants and possibly termites. Additional contributions are from natural gas, coal mining, and biomass burning. The annual production rate and the magnitude of the individual source terms are not well known. Various estimates have come from flux measurements (*7*), atmospheric chemistry (*8*), biostatistical surveys (*9*), and modeling of atmospheric concentration data (*10*).

Derivation of a quantitative budget of CH_4 from ^{13}C, deuterium, and ^{14}C is an approach similar to that proposed for ^{13}C by Stevens and Rust (*11*). If methane from the various sources can be distinguished and characterized isotopically, then in principle a budget can be obtained from comparison of the isotopic composition of source methane to that of the atmosphere. The $^{14}CH_4$ content of the atmosphere is particularly sensitive to the contribution from fossil carbon (^{14}C free), which is thought to come from losses during exploration and distribution of natural gas, from coal mining, and from natural seepage from gas reservoirs. We have measured ^{14}C and ^{13}C in CH_4 from the atmosphere in both the Northern and Southern hemispheres and from various sources and used this data to determine a global CH_4 budget from 1950 to 1987.

Large volume air samples (about 0.5 to 1.5 m^3) were collected into Al gas tanks with three-stage Al air compressors. Methane from ecosystems was sampled in various ways, either retrieved as above from large volume (5 to 10 m^3 and 10 to 20 m^2) flux-box enclosures, from beneath near-surface atmospheric inversion over strong sources (up to two times the background atmospheric CH_4 concentration has been observed over bogs and rice fields), or from bubbles collected with an inverted funnel. Major and minor trace gas concentrations in the samples were measured by gas chromatography. In order to collect other trace constituents (for example, ^{85}Kr), CH_4 and Kr were completely separated from the air samples with adsorption-desorption and gas chromatographic techniques (*12*). The separated CH_4 was then combusted to CO_2 (*13*) and analyzed (*14–19*).

The atmospheric surface air samples were primarily collected over the oceans. We considered land surface air samples to be uncontaminated by local sources if the measured methane concentration did not exceed by more than 3% the one expected for that latitude and time from worldwide measurements (*20*). The atmospheric $^{14}CH_4$ activity increased during the time period covered at a rate of about 2 to 3% per year (Fig. 1). We cannot exclude the possibility that part of the exhibited variability may be seasonal. We detected a small interhemispheric difference of about 3 pMC; the $^{14}CH_4$ activity was 123.3 ± 0.8 pMC in the mid-latitude

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