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NOTE

Solid Methane on Triton and Pluto: 3- to 4-μm Spectrophotometry

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We report the first observations of a deep absorption feature centered near 3.25 μm in the reflectance spectra of Triton and the Pluto/Charon system (3.25/2.2 μm albedo ratio = 0.28 ± 0.07 on Triton and 0.04 ± 0.10 on Pluto/Charon). The absorption is probably due to solid methane, which is either the dominant surface species or is present in intimate mixture with (or underlies) a very transparent material (such as N_2 frost) over most of the visible surface of both objects.

Introduction. Methane was initially identified in the Pluto/Charon system (Cruikshank *et al.* 1976) and on Triton (Cruikshank and Silvaggio 1979), using absorption features in the reflectance spectrum at 1.7 and 2.3 μm. Since then, the physical state (solid or gas) and abundance of the methane has been the subject of much debate.

Cruikshank and Apt (1984) considered Triton's methane absorptions to be due to solid CH_4, but Cruikshank *et al.* (1989) noted that gaseous CH_4 was a better match to the 2.3-μm absorption. Thompson (1989) suggested that Triton's broad but shallow CH_4 features shortward of 1 μm indicated solid or gaseous CH_4 overlain by a neutral scattering layer of haze or surface particulates. A weak feature of 2.16 μm was tentatively identified with N_2, also of uncertain physical state (Cruikshank *et al.* 1984). Voyager 2 found Triton's atmosphere to be dominated by N_2 with CH_4 as a minor constituent (Broadfoot *et al.* 1989). N_2 is apparently in vapor pressure equilibrium with surface N_2 frost at about 37.5 K, and CH_4 may be undersaturated in the atmosphere. Even if both gases were in equilibrium with their ices at 37.5 K, the CH_4/N_2 molar ratio would be 7.9×10^{-5} (Brown and Zeigler 1980), with a CH_4 gas abundance of 1.1×10^{-4} m-am, far too small to be detected by IR spectrophotometry. The methane features in Triton's spectrum must thus be due almost entirely to surface frost.

In the Pluto system, Charon's surface is dominantly water ice (Marcialis *et al.* 1987, Buie *et al.* 1987). The methane is thus largely restricted to Pluto itself, but its physical state is not yet settled. Methane gas abundance determinations have been hampered by the imprecision of the random band models necessitated by the complexity of the absorption bands shortward of 3 μm (Fink *et al.* 1977, Apt *et al.* 1981, Giver *et al.* 1988). Buie and Fink (1987) used band models to derive a maximum methane gas abundance of 5.6 m-am from the absorptions shortward of 1 μm, attributing the balance of the CH_4 absorption to frost. The deeper absorptions at 1.7 and 2.3 μm have generally been attributed to frost (Soifer *et al.* 1980, Cruikshank and Silvaggio 1980) though without accurate models of gas absorption the evidence has not been conclusive.

The recent stellar occultation of Pluto (Elliot *et al.* 1989) limits the total gas abundance in Pluto's atmo-

TABLE I

1988/89 MEAN GEOMETRIC ALBEDOS

Wavelength range (μm)	Triton	Pluto/Charon
1.22 ± 0.14		0.66 ± 0.01
1.63 ± 0.14		0.52 ± 0.01
2.16 ± 0.20	0.59 ± 0.03	0.37 ± 0.02
2.94 ± 0.11	0.26 ± 0.02	0.29 ± 0.02
3.12 ± 0.11	0.15 ± 0.02	0.11 ± 0.02
3.24 ± 0.11	0.16 ± 0.04	0.02 ± 0.04
3.77 ± 0.33	0.33 ± 0.04	0.19 ± 0.03

[1] Visiting astronomers at the Infrared Telescope Facility, which is operated by the University of Hawaii under contract to NASA.

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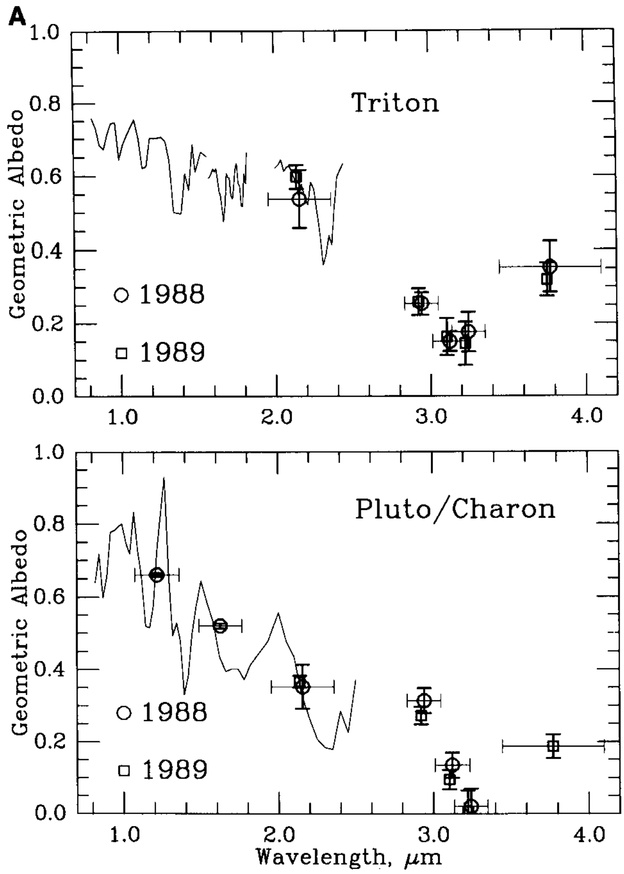

FIG. 1. The spectra of Triton and Pluto from 1 to 4 μm. Vertical error bars are 1-σ formal uncertainties while the horizontal bars indicate the bandwidth (FWHM) of each filter. Solid lines indicate the best available spectra at shorter wavelengths: for Triton, from 1988 (Cruikshank *et al.* 1989) and (shortward of 1.5 μm) 1980/81 (Cruikshank and Apt 1984); and for Pluto, 1979 (Soifer *et al.* 1980, Cruikshank and Silvaggio 1980) and 1982 (Cruikshank and Brown 1986). These spectra have been approximately scaled to match our K photometry. (A) 1988 and 1989 observations shown separately (1989 points offset slightly in wavelength for clarity). (B) Model comparisons to combined 1988 and 1989 data. The dashed line shows a laboratory spectrum of an extremely fine-grained CH_4 frost spectrum at 60 K (Fink and Sill 1982): because of instrumental effects in this FTS spectrum, the true depth of the frost 3-μm feature is probably greater than shown. The light solid line shows an apparently coarser-grained CH_4 frost, with reported grain size <10 μm and temperature of 77 K (Smythe 1975). Both are arbitrarily scaled. The two CH_4 Gas model spectra on the Pluto plot assume one-way vertical CH_4 abundances of 0.64 and 13.1 m-am, and represent the range of possible gaseous CH_4 abundances on Pluto. All CH_4 spectra are smoothed to similar spectral resolution. The CH_4 frost is the best match to the 3.25-μm absorption feature on both bodies, though a difference in the shape and depth of the feature indicates differences in frost abundance and/or grain size between Triton and Pluto.

sphere. Assuming pure methane, the inferred CH_4 abundance varies between 13 m-am (if the inferred extinction layer has low normal optical depth and overlies a deep clear atmosphere, and Pluto's density has the high value of 3.0 g cm^{-3}) and 0.64 m-am if the surface is immediately below the deepest level probed by the occultation. The abundance of methane gas is smaller if other gases are present (e.g., Yelle and Lunine (1989).

The 3- to 4-μm spectral region provides a new win-

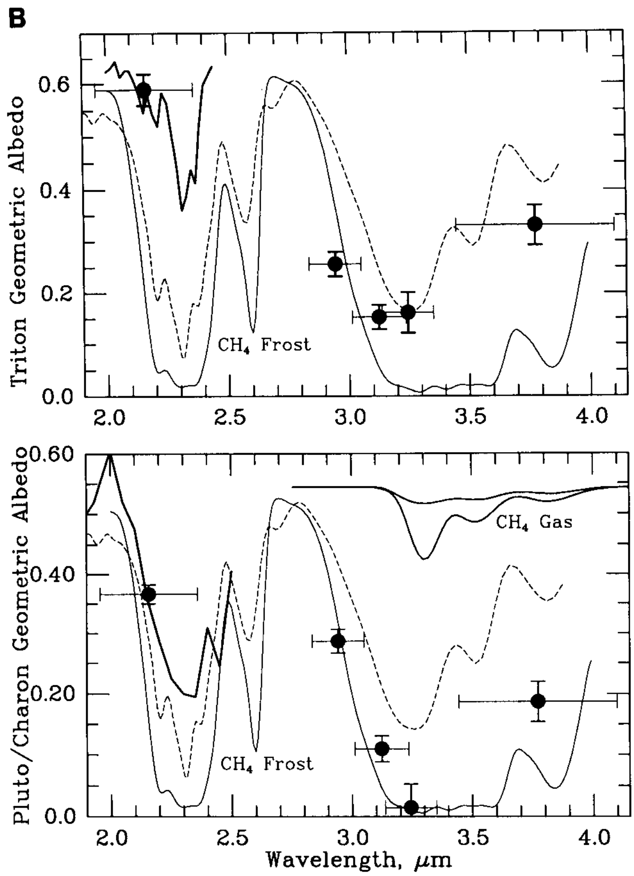

FIG. 1—*Continued*

dow on the nature of Triton and Pluto. It contains the ν_3 fundamental CH_4 absorption, centered at 3.31 μm, which is stronger than any of the shorter-wavelength overtone bands studied previously. Models that account for this band will be better constrained than those using shorter wavelength data alone, because they will include bands with a wider range in intrinsic strengths. The 3.31-μm CH_4 absorption band is simpler than those at shorter wavelengths and unlike them, has quantum assignments for enough of its constituent lines to allow accurate modeling of the gas spectrum at outer solar system temperatures. The 3-μm region is also the best part of the spectrum to search for water ice, which has its strongest absorptions here. The only previous observations in this region are 1978 broadband measurements at 3.5 μm (L) and 3.7 μm (Lebofsky *et al.* 1979). Accordingly, we have obtained new low-resolution 3- to 4-μm spectra of both bodies.

Observations. We used the 3.0-m Infrared Telescope Facility on Mauna Kea, Hawaii, with a standard InSb detector ("RC-2"), standard J, H, K, and L′ filters, and three narrow-band filters covering the 3-μm region (Table I). Apertures used varied from 4 to 8 arcsec, and total exposures in the narrow-band filters ranged from 30 to 80 min. UT dates, objects, and observers were: 1988/06/09,22,23, Triton, Spencer and Buie; 1988/06/28,29, Pluto, Buie, 1989/06/02,24,25, Triton and Pluto, Spencer.

For Triton in 1988, between K and 3.24 μm, we used the solar analog 58 Oph [also used by Cruikshank *et al.* (1989)] to monitor extinction and to model the solar illumination on Triton. We also measured the K magnitude of 58 Oph by reference to other IRTF standards. Taking the K magnitude of the Sun to be −28.25 (Campins *et al.* 1985) we determined geometric albedos for Triton using the Voyager radius of 1350 km (Smith *et al.* 1989). We obtained an L′ geometric albedo for Triton by direct calibration against IRTF standard stars, using an L′ magnitude for the Sun of −28.27 (interpolated between the L and M values in Campins *et al.*).

The 1988 Pluto data were reduced with respect to the standard star "87 Primary" used for mutual event observations (Tholen *et al.* 1987), and converted to geometric albedos using the solar analog 16 Cyg B and IRTF standard stars and assuming an effective Pluto/Charon combined radius of 1288 km (Tholen and Buie 1988). 1989 data for both objects were reduced with respect to 58 Oph.

Agreement between the 2 years is excellent for both objects (Fig. 1A). Figure 1B and Table I show the combined 1988 and 1989 data. Triton shows a broad absorption centered near 3.2 μm, and Pluto, while brighter at 2.95 μm, shows a sharper and deeper feature centered near 3.24 μm, where we did not detect the planet at all.

Interpretation: Atmospheric contribution. Voyager observations have ruled out significant CH_4 gas absorption on Triton, but the possibility remains open on Pluto. We thus determined the possible contribution of gaseous CH_4 to Pluto's 3.2-μm absorption, using a line-by-line spectrum synthesis program (Kunde and Maguire 1974). Methane line parameters are from the 1986 HITRAN database (Rothman *et al.* 1987). Line intensities were derived from lab spectra recorded between 160 and 296 K (Toth *et al.* 1981). The strongest CH_4 transitions are good to 2% but weaker lines may be in error by 15 to 50% at 58 K. The model assumes a clear atmosphere overlying a diffusely scattering uniform spherical planet. Monochromatic transmittances are convolved to a spectral resolution of 50 cm^{-1}. We have ignored Charon in the model spectra, as it is probably extremely dark between 2.9 and 3.3 μm due to its water ice surface and thus will contribute little to the combined spectrum.

We show two synthetic spectra in Fig. 1B (bottom). The one with the weaker absorption corresponds to the Elliot *et al.* (1989) pure CH_4 isothermal model with Pluto's surface at 1142-km radius, just below the deepest level probed by the occultation: temperature is 67 K, total CH_4 abundance is 0.64 m-am, and surface pressure is 2.8 μbar. The more absorbing spectrum represents the maximum reasonable gaseous CH_4 abundance on Pluto, with the surface at 1014 km radius, a temperature of 58 K (Sykes *et al.* 1987), a CH_4 abundance of 13.1 m-am, and a surface pressure of 72 μbar. Yelle and Lunine (1989), and Hubbard *et al.* (1990) suggest that Pluto has a warm (106 K) stratosphere above about 1190 km radius, with methane abundance $\leq$ 65 mol%, a total abundance of $\leq$ 0.2 m-am CH_4 at this temperature. A synthetic spectrum generated from this model is very similar to the 1142-km radius pure CH_4 spectrum shown in Fig. 1B. Clearly, the Pluto stellar occultation gaseous CH_4 abundance of $\leq$ 13 m-am can account for only a small fraction of the observed absorption at 3.24 μm.

Interpretation: Surface materials. Gaseous N_2 and CO have no absorption features in the 3-μm region, and most other possible atmospheric species will be frozen out on both bodies, so the 3-μm absorption is presumably due to surface materials. H_2O, CO_2, CO, and NH_3 ices cannot match the observed absorption. CO_2 frost is bright between 2.88 and 3.27 μm, CO has no features between its 2.35- and 4.68-μm absorptions, and though both H_2O and NH_3 frosts have deep absorptions here they are darker at 2.94 μm than at 3.24 μm, unlike Triton or Pluto (Fink and Sill 1982). However, solid methane, thought to be responsible for the shorter-wavelength absorptions, provides a good match to the 3-μm spectrum on Pluto, and also on Triton except for the relative broadness and shallowness of its 3-μm absorption (Fig. 1B). Because the absorption results from a C–H bond, many more complex organic molecules also have an absorption feature near 3.2 μm (Pierson *et al.* 1956), but as these are likely to be less abundant than CH_4, and CH_4 provides a good match to the shorter-wavelength absorptions, we expect that it is also primarily responsible for the 3.2-μm feature.

The shape of the absorption is quite different on each body. Triton is brighter at 3.24 μm, but relative to 2.2 μm is much darker than Pluto at 2.94 μm: the absorption on Triton is shallower, like the shorter wavelength features (Fig. 1A), but broader. The shallowness of Triton's 3.25-μm absorption may indicate decreased frost purity, filling in of the band center by scattering from overlying particulates (Thompson 1989), or a smaller areal coverage of CH_4 frost on Triton (see below). The greater breadth of the Triton feature at 3 μm may indicate a larger grain size than on Pluto, as the breadth (but not the depth) of the Triton absorption is best matched by the coarser grained Smythe frost spectrum. Alternatively, small quantities of H_2O or NH_3, mixed with the CH_4 frost on Triton but not on Pluto, might account for Triton's lower reflectance with respect to K at 2.94 μm.

The depth of the 3.2-μm feature on Triton, relative to the 2.2-μm albedo, is 0.72 $\pm$ 0.07. The lower limit to the absorption depth, 0.65, implies that less than 35% of the 2.2-μm flux comes from material (such as pure nitrogen frost) that does not decrease in reflectivity between 2.2 and 3.2 μm. The remaining $\geq$ 65% of the light probably comes from methane frost or transparent material (such as N_2 frost) with enough intimately mixed or underlying CH_4 to produce the observed 3.2-μm absorption feature. Triton's N_2 atmosphere can only be maintained by the sublimation of a substantial coverage of N_2 frost (probably seasonal) from the sunlit hemisphere (Broadfoot *et al.* 1989, Stansberry *et al.* 1990, Spencer 1990). However seasonal N_2 frost, with a probable CH_4 content similar to the atmospheric abundance of $\leq 8 \times 10^{-5}$, is unlikely to have CH_4 spectral features as strong as the CH_4 absorptions seen on Triton (Spencer 1990). The existence of the atmosphere despite the strong CH_4 spectral signature is thus an important constraint on models of Triton's surface/atmosphere interaction.

Pluto's lightcurve shows that visible-wavelength photons reach the surface (Elliot *et al.* 1989) so it is highly probable that the same is true at 3.24 μm, and that we are seeing surface CH_4 frost rather than, for instance, a CH_4 haze layer. The inference of solid CH_4 on the surface confirms conclusions based on rotational variations in the CH_4 absorptions shortward of 1 μm (Buie and Fink 1987), but it is firmer because of the improved reliability of gaseous absorption models in the 3-μm region, and our new knowledge of the total gas abundance.

Because no other likely surface components (other than more complex organic molecules) drop sharply in reflectivity between 2.95 and 3.25 μm, and Pluto/Charon is very dark at 3.25 μm, most of the 2.95 μm flux comes either from methane ice or a transparent material containing intimately mixed methane ice. The geometric albedo of the Pluto/Charon system at 2.95 μm is 0.29 ± 0.02 (Fig. 1B). Because 21% of the projected area of the system is occupied by Charon, which is probably very dark from 2.95 to 3.25 μm due to its water ice surface, the 2.95-μm geometric albedo of Pluto alone is probably closer to 0.37. If the 2.95-μm reflectivity of the methane frost was 1.0, 37% of Pluto's visible surface would be covered in methane or methane-containing material. More likely, the methane is darker and surface coverage is correspondingly greater.

Conclusions. These observations reveal the deepest absorption feature yet found in the spectra of Triton and Pluto. We identify it as the ν_3 solid CH_4 fundamental. Its great depth suggests abundant CH_4 on the surfaces of both objects. If another species dominates their surfaces, it must contain CH_4 in intimate mixture and have sufficiently long pathlengths for 3.2-μm photons that most are eventually absorbed by CH_4 molecules. On Triton an overlying optically thin CH_4-free scattering layer is also possible.

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REFERENCES

APT, J. A., J. V. MARTONCHIK, AND L. A. BROWN 1981. Comparison of band model and integrated line-by-line synthetic spectra for methane in the 2.3 μm region. *J. Quant. Spectrosc. Radiat. Transfer* **26,** 431–442.

BROADFOOT, A. L., AND 20 CO-AUTHORS 1989. Ultraviolet spectrometer observations of Neptune and Triton. *Science* **246,** 1459–1466.

BROWN, G. N., AND W. T. ZEIGLER 1980. Vapor pressure and heats of vaporisation and sublimation of liquids and solids of interest in cryogenics below 1-atm pressure. *Adv. Cryo. Eng.* **25,** 662–670.

BUIE, M. W., D. P. CRUIKSHANK, L. A. LEBOFSKY, AND E. F. TEDESCO 1987. Water frost on Charon. *Nature* **329,** 522–523.

BUIE, M. W., AND U. FINK 1987. Methane absorption variations in the spectrum of Pluto. *Icarus* **70,** 483–498.

CAMPINS, H., G. H. RIEKE, AND M. J. LEBOFSKY 1985. Absolute calibration of photometry at 1 through 5 μm. *Astron. J.* **90,** 896–899.

CRUIKSHANK, D. P., AND J. APT 1984. Methane on Triton: Physical state and distribution. *Icarus* **58,** 306–311.

CRUIKSHANK, D. P., AND R. H. BROWN 1986. Satellites of Uranus and Neptune, and the Pluto/Charon system. In *Satellites* (J. Burns and M. Matthews, Eds.), pp. 836–873. Univ. Arizona Press, Tucson.

CRUIKSHANK, D. P., R. H. BROWN, AND R. N. CLARK 1984. Nitrogen on Triton. *Icarus* **58,** 293–305.

CRUIKSHANK, D. P., R. H. BROWN, L. P. GIVER, AND A. T. TOKUNAGA 1989. Triton: Do we see the surface? *Science* **245,** 283–286.

CRUIKSHANK, D. P., C. B. PILCHER, AND D. MORRISON 1976. Pluto: Evidence for methane frost. *Science* **194,** 835–837.

CRUIKSHANK, D. P., AND P. M. SILVAGGIO 1979. Triton: A satellite with an atmosphere. *Astrophys J.* **233,** 1016–1020.

CRUIKSHANK, D. P., AND P. M. SILVAGGIO 1980. The surface and atmosphere of Pluto. *Icarus* **41,** 96–102.

ELLIOT, J. L., E. W. DUNHAM, A. S. BOSH, S. M. SLIVAN, L. A. YOUNG, L. H. WASSERMAN, AND R. L. MILLIS 1989. Pluto's atmosphere. *Icarus* **77,** 148–170.

FINK, U., D. C. BENNER, AND K. A. DICK 1977. Band model analysis of laboratory methane absorption spectra from 4500 to 10500 Å. *J. Quant. Spectrosc. Radiat. Transfer* **18,** 447–457.

FINK, U., AND G. T. SILL 1982. The infrared spectral properties of frozen volatiles. In *Comets* (L. Wilkening, Ed.), pp. 164–202. Univ. Arizona Press, Tucson.

GIVER, L. P., D. C. BENNER, AND C. B. SUAREZ 1988. Band models of methane gas phase spectra, 2.1–2.5 microns, extrapolated to T = 55 K for analysis of Triton's spectrum. *Bull. Amer Astron. Soc.* **20,** 838.

HUBBARD, W. B., R. V. YELLE, AND J. I. LUNINE 1990. Non-isothermal Pluto atmosphere models. *Icarus* **84,** 1–11.

LEBOFSKY, L. A., G. H. RIEKE, AND M. J. LEBOFSKY 1979. Surface composition of Pluto. *Icarus* **37,** 554–558.

KUNDE, V. G., AND W. C. MAGUIRE 1974. Direct integration transmittance model. *J. Quant. Spectrosc. Radiat. Transfer* **14,** 803–817.

MARCIALIS, R. L., G. H. RIEKE, AND L. A. LEBOFSKY 1987. The surface composition of Charon: Tentative identification of water ice. *Science* **237,** 1349–1351.

PIERSON, R. H., A. N. FLETCHER, AND E. ST. CLAIR GANTZ 1956. Catalog of infrared spectra for qualitative analysis of gases. *Anal. Chem.* **28,** 1218–1239.

ROTHMAN L. S., R. GAMANCHE, A. GOLDMAN, L. BROWN, R. TOTH, H. PICKETT, R. POYNTER, J. FLAUD, C. CAMY-PERYRET, A. BARBE, N. HUSSAN, C. RINSLAD, AND M. SMITH 1987. The HITRAN database: 1986 edition. *Appl. Opt.* **26,** 4058–4097.

SMITH, B. A., AND 64 CO-AUTHORS 1989. Voyager 2 at Neptune: Imaging science results. *Science* **246,** 1422–1449.

SMYTHE, W. D. 1975. Spectra of hydrate frosts: Their application to the outer solar system. *Icarus* **24,** 421–427.

SOIFER, B. T., G. NEUGEBAUER, AND K. MATTHEWS 1980. The 1.5-2.5 μm spectrum of Pluto. *Astron. J.* **85,** 166–167.

SPENCER, J. R. 1990. Nitrogen frost migration on Triton: A historical model. *Geophys. Res. Lett.* **17,** 1769–1772.

STANSBERRY, J. A., J. I. LUNINE, C. C. PORCO, A. S. MCEWEN, AND L. A. SODERBLOM 1990. Zonally averaged thermal balance and stability models for Triton's polar caps. *Geophys. Res. Lett.* **17,** 1773–1776.

SYKES, M. V., R. M. CUTRI, L. A. LEBOFSKY, AND R. P. BINZEL 1987. IRAS serendipitous survey observations of Pluto and Charon. *Science* **237,** 1336–1339.

THOLEN, D. J., M. W. BUIE, AND C. E. SWIFT 1987. Circumstances for Pluto/Charon mutual events in 1987. *Astron. J.* **93,** 244–247.

THOLEN, D. J., AND M. W. BUIE 1988. Circumstances for Pluto/Charon mutual events in 1989. *Astron. J.* **96,** 1977–1982.

THOMPSON, W. R. 1989. Triton: Scattering models and surface/atmosphere constraints. *Geophys. Res. Lett.* **16,** 969–972.

TOTH R. A., L. R. BROWN, R. H. HUNT, AND L. S. ROTHMAN 1981. Line parameters of methane from 2385 to 3200 cm^{-1}. *Appl. Opt.* **20,** 932–935.

YELLE, R. V., AND J. I. LUNINE 1989. Evidence for a molecule heavier than methane in the Pluto atmosphere. *Nature* **339,** 288–290.