

SEARCH FOR NONMETHANE HYDROCARBONS ON PLUTO

TAKANORI SASAKI AND AI KANNO¹

Department of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan; takanori@eps.s.u-tokyo.ac.jp

MASATERU ISHIGURO

Department of Infrared Astrophysics, Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency,
3-1-1 Yoshinodai, Sagami-hara, Kanagawa 229-8510, Japan

DAISUKE KINOSHITA

National Astronomical Observatory of Japan, National Institute of Natural Sciences, 2-21-1 Osawa, Mitaka, Tokyo 181-8588, Japan

AND

RYOSUKE NAKAMURA

Lunar Exploration Division, Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency,
2-1-1 Sengen, Tsukuba, Ibaraki 305-8505, Japan

Received 2004 September 27; accepted 2004 November 18; published 2004 November 29

ABSTRACT

We have carried out infrared high-resolution spectroscopy of the Pluto-Charon system in the L band with the adaptive optics system on the Subaru telescope. The spectrum is dominated by the strong and broad absorption features of methane but includes some additional features. Comparing the spectrum with model calculations, we suggest that absorption features around 3.1, 3.2, and 3.35 μm could be an indication of nonmethane hydrocarbons on Pluto's uppermost surface. Implications of the estimated mass ratio between hydrocarbons for the formation and evolution of Pluto are discussed.

Subject headings: infrared: solar system — Kuiper Belt — planets and satellites: individual (Pluto)

1. INTRODUCTION

Trans-Neptunian objects (TNOs) are thought to be the remnants of icy planetesimals, and Pluto is one of the largest objects among them. Pluto is exceptional, not only in its size but also in its surface composition of N_2 , CH_4 , and CO (Cruikshank et al. 1997). The hydrodynamic escape of Pluto's atmosphere (Trafton et al. 1997) implies that there has been significant surface loss by sublimation for the age of the solar system. In this scenario, surface volatile ices must have been replenished by some reservoir, such as geologic activity as seen on Triton (Stern & McKinnon 2000) and/or infalling TNOs. It has been predicted that nonmethane hydrocarbons (NMHCs) can be generated from methane through photochemical reactions in the tenuous atmosphere (Krasnopolsky & Cruikshank 1999) and cosmic-ray irradiation of the surface (Moore & Hudson 2003). If NMHCs could be detected, then their relative abundances would provide important clues to the primordial volatile inventories of Pluto or the subsequent in situ alteration processes.

Hydrocarbons generally have a fundamental C–H stretching mode in the L band, the absorption of which is much stronger than the overtones in the J , H , and K bands. However, it is difficult to make precise spectroscopic measurements in the L band owing to the high background and variable telluric extinctions. Using SpeX, attached to the Infrared Telescope Facility, Grundy et al. (2002) found CH_4 ice absorption features at 3–4 μm as well as other features around 2.9 and 4.1 μm , which were attributed to H_2O , CO_2 , and/or SO_2 , respectively. The spectral resolution of their data, however, was insufficient to examine the absorption features of hydrocarbons. In this Letter, we present L -band spectra obtained by the Subaru telescope using its adaptive optics (AO) system. The observations and data reduction procedures are described in § 2. Owing to

the higher spectral resolution, we detected several new absorption features. In order to examine the possible carriers, we performed simple model calculations based on Hapke's bidirectional model, which are presented in § 3. NMHCs are the most plausible candidates, and in § 4 we discuss several scenarios for their origin.

2. OBSERVATIONS AND DATA REDUCTION

A spectroscopic observation of Pluto was carried out on 2002 May 28 UT near the opposition (R.A. = $17^{\text{h}}05^{\text{m}}33^{\text{s}}$, decl. = $12^{\circ}39'25''$) using an infrared camera and spectrograph (Tokunaga et al. 1998; Kobayashi et al. 2000) with the 8.2 m Subaru telescope in conjunction with its AO system (Takami et al. 1998; Gaessler et al. 2002). We employed a medium-resolution grism with a slit of $0''.3$ width to obtain spectra with a resolving power of approximately 400 at the L band. Pluto itself was used as the reference source for the AO system. The sub-Earth longitude was 40° – 50° , and the separation from Charon was $0''.9$. The slit was set along the position angle of Pluto and the satellite Charon to acquire them simultaneously. The spectra were recorded by nodding the telescope by $3''$ along the slit to subtract the sky emission. The typical seeing size was $0''.3$ – $0''.4$ during the observation, and the total on-source integration time was 2600 s. A nearby G3 V star SAO 141540 (R.A. = $17^{\text{h}}10^{\text{m}}01^{\text{s}}$, decl. = $8^{\circ}31'26''$) was observed as a spectroscopic standard. Special attention was paid to minimize the air mass difference between the Pluto and standard observations and the effect of temporal variation of humidity. Pluto was observed within 1.5 hr before/after the standard star, and the air mass difference was less than 0.035 throughout observations. We discarded all of the data obtained on the next night, as they suffered from rapid and large humidity variations. After bad-pixel correction, sky subtraction, and flat-fielding, we obtained one-dimensional spectra of Pluto by using the NOAO Image Reduction and Analysis Facility aperture extraction package. Since Pluto was clearly separated from Charon with

¹ Current address: Development Technology, Service Business Promotion, Industrial Solution Center, IBM Japan, Ltd., 9-21, Hakozaeki, Nihonbashi, Tokyo 103-0015, Japan.

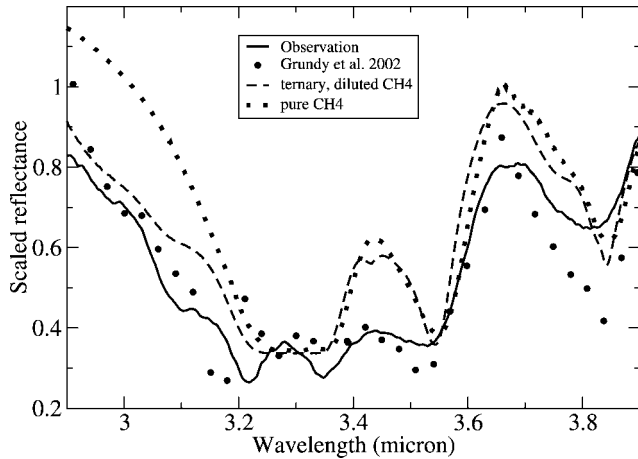


FIG. 1.—Reflectance spectrum of Pluto with the previous low-resolution data (Grundy et al. 2002) and synthetic spectra of intimate ternary mixture of N_2 - CH_4 -CO with the mass ratio 1 : 0.01 : 0.002. The solid curve represents our observation smoothed by taking a running average of 31 pixels ($0.08 \mu\text{m}$). A data point at $3.316 \mu\text{m}$ was removed where the frame-by-frame fluctuation was particularly large owing to very strong telluric absorption. The dotted and dashed curves indicate synthetic spectra for pure CH_4 and for CH_4 diluted in the solid molecular nitrogen, respectively. The grain diameter is 3 cm for N_2 and $100 \mu\text{m}$ for CH_4 and CO. We normalized all the data at $3.58 \mu\text{m}$, and the synthetic spectra were convolved to the same wavelength resolution as the observation.

the FWHM as sharp as 0.4 , the resulting spectrum includes no contamination from Charon. We obtained argon lamp frames at the end of the night to determine the linear dispersion for wavelength calibration. The offset for each frame was corrected by shifting the strongest telluric absorption line at $3.316 \mu\text{m}$ to that of the standard star. The uncertainty in the wavelength calibration is smaller than $0.003 \mu\text{m}$.

3. RESULTS

The spectrum of Pluto is shown in Figure 1 along with the previous low-resolution data (Grundy et al. 2002) and synthetic spectra of a simple ternary intimate mixture of N_2 - CH_4 -CO. As in Nakamura et al. (2000), we employed Hapke's bidirectional model (Hapke 1993) to calculate the spectrum of a uniform half-infinite layer covering the whole surface of Pluto. It should be noted that detailed model calculations are beyond the scope of this Letter because we cannot account for the realistic solid solutions, vertically layered structure, and spatially segregated patches, unlike some previous approaches (Douté et al. 1999; Grundy & Buie 2001). It appears that the shape of the synthetic spectra is dominated by CH_4 because N_2 and CO have no significant absorption features in the wavelength range. Grundy et al. (2002) found a decrease in reflectance below $3.2 \mu\text{m}$ and above $3.95 \mu\text{m}$ with respect to their model prediction. They interpreted the result as the contribution from nonvolatile ices, such as H_2O for the former and SO_2 and CO_2 for the latter. While we cannot confirm the putative band of SO_2 and CO_2 owing to the limited wavelength coverage, our spectrum shortward of $3.2 \mu\text{m}$ is consistent with their results. Our observations show lower reflectance around $3.45 \mu\text{m}$ and additional absorptions around 3.1 , 3.2 , and $3.35 \mu\text{m}$. In order to reproduce the features, we incorporated some NMHCs, namely, C_2H_2 , C_2H_4 , C_2H_6 , and C_3H_8 , into the model calculations. Assuming their mass ratio to CH_4 as 10%, we computed the model spectra in Figure 2. The optical constants were mea-

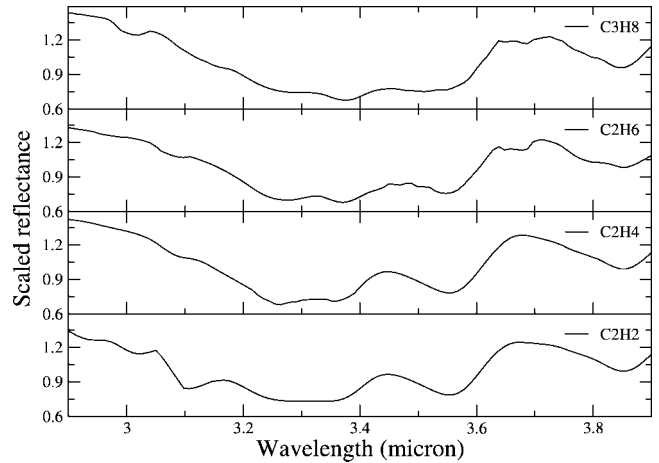


FIG. 2.—Modeled spectra including NMHCs as the fourth component. The fourth components are C_2H_2 , C_2H_4 , C_2H_6 , and C_3H_8 . The model parameters of the basic ternary mixture are the same as those in Fig. 1, and the mass fraction to CH_4 and the grain diameter of the fourth component are 0.1 and $30 \mu\text{m}$, respectively.

sured by Quirico et al. (1999), and the imaginary part is indicated in Figure 3. In Figures 2 and 4, CH_4 is assumed to be diluted in the solid molecular nitrogen. It was found that C_2H_2 , C_2H_4 , and C_2H_6 would produce the $3.1 \mu\text{m}$ absorption if their relative concentration to CH_4 is approximately 10 weight percent. This value should be regarded as the upper limit for C_3H_8 , as the absorption at $3.0 \mu\text{m}$ was not seen in the observed spectrum. Figures 2 and 3 indicate that C_2H_4 and C_2H_6 could be associated with the absorption features around 3.2 and $3.35 \mu\text{m}$. We plotted these two synthetic spectra in Figure 4 for a detailed comparison with the observed spectrum. Adding C_2H_4 as the fourth component, we obtained a better agreement with the observations than the simple ternary mixture model, but there was still a discrepancy between 3.4 and $3.55 \mu\text{m}$. While C_2H_6 improved the fit in this range, there was no clear absorption around $3.65 \mu\text{m}$ in the observed spectrum. In both cases, the observed absorptions around 3.2 and $3.35 \mu\text{m}$ shift toward shorter wavelengths as compared to the model spectra. Quirico et al. (1999) has shown that the dilution of solid N_2 ice causes the shift of methane's absorption. It is possible that other hydrocarbons are affected in a similar way. More laboratory experiments are needed to explore the dilution effect

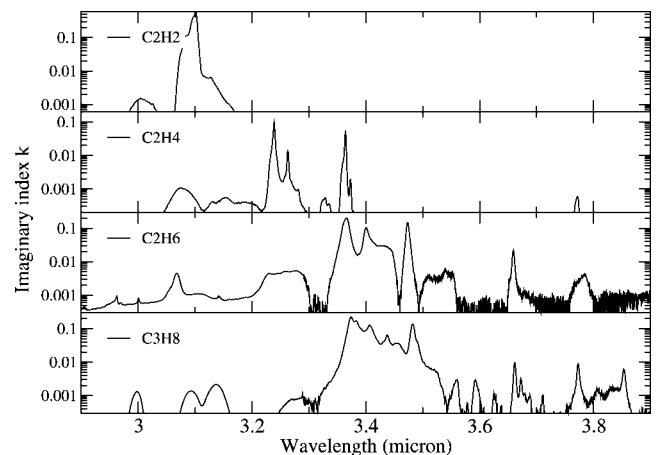


FIG. 3.—Imaginary part of the optical constants of various hydrocarbons (Quirico et al. 1999) used in Fig. 2.

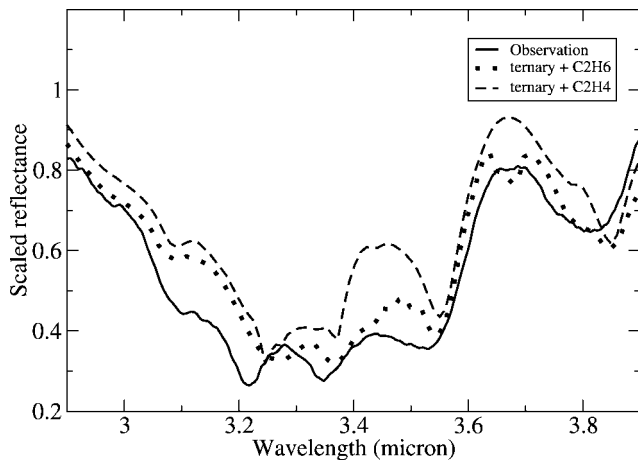


FIG. 4.—Reflectance spectrum of Pluto with the modeled spectra. The solid curve shows our observation as shown in Fig. 1. The dashed and dotted curves represent the synthetic spectrum with $C_2H_4 : CH_4 = 1 : 30$ and $C_2H_6 : CH_4 = 1 : 10$, respectively. While C_2H_6 gives better agreement with the observation between 3.4 and 3.55 μm , the narrow absorption feature at 3.65 μm is absent.

more quantitatively. Figure 4 demonstrates that another component is needed to strengthen the absorption around 3.1 μm . Moore & Hudson (2003) found that HCN forms in the solid phase, with infrared absorption features at 3.04 μm , when nitrogen ices containing methane are irradiated by cosmic rays. Unfortunately, we cannot make quantitative model calculations because the optical constants of HCN are not available. We added C_2H_2 as an alternative fifth component in the model calculation. The resulting spectrum matches the observed spectrum quite well, as shown in Figure 5.

If we simply extend the wavelength coverage for the model calculations, the resulting synthetic spectra would exhibit detectable absorptions in the *J*, *H*, and *K* bands. So far, however, NMHCs have not been definitely identified in the *J*, *H*, or *K* bands. This discrepancy could be explained by a strong concentration of NMHCs at the uppermost surface. While previous observations in the *J*, *H*, and *K* bands have “seen” the underlying materials rather than the very thin surface layer, our *L*-band observations probe a shallower surface with deep absorption, resulting in enhanced contribution from the surface layer. Nondetection of the spectroscopic signatures of NMHCs at shorter wavelengths implies that they exist as a veneer. It is worth noting that Nakamura et al. (2000) suggested the existence of solid ethane from their *K*-band spectra taken at a similar sub-Earth longitude to our observations in the *L* band. The veneer of NMHCs might be related to the lateral surface inhomogeneity of Pluto’s surface (Buie et al. 1997; Grundy & Fink 1996; Douté et al. 1999; Young et al. 2001a).

4. DISCUSSION

Among numerous TNOs, Pluto and Triton have a distinctive surface composition, including solid N_2 , CH_4 , and CO , which reflects the fact that only these two objects are large enough to retain such very volatile ices (Brown & Calvin 2000). On the other hand, Krasnopolsky (1999) estimated that a 500 m thick N_2 layer has been lost from the surface since the formation of the Pluto-Charon system. Although N_2 could be the dominant form of nitrogen in the outer protoplanetary disk (Womack et al. 1992; Owen et al. 2001), it is unlikely that such pristine N_2 survived the accretional heating and formed such a thick layer

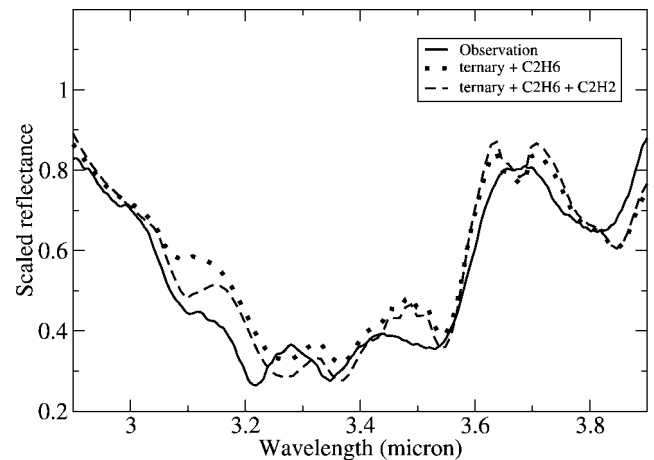


FIG. 5.—The solid and dotted curves are the same as in Fig. 4. The dashed curve shows the spectrum of a mixture of $C_2H_2 : C_2H_6 : CH_4$ with mass ratios 1 : 1 : 10.

near the surface. The surface of Charon is covered by ammonia-water ice mixtures (Brown & Calvin 2000). The absorption features of water ice have been detected on Triton (Cruikshank et al. 2000) and suggested for Pluto (Grundy et al. 2002). It is generally accepted that Triton’s subsurface layer is composed mainly of water ice or ammonia-water ice mixtures (Ruiz 2003) and that Pluto has a similar underlying structure (Busarev et al. 2003) based on its density and solar abundance. Pluto may have a deep internal reservoir that can produce N_2 from more refractory nitrogen compounds and supply it to the surface along with CH_4 and CO . The mass ratio between hydrocarbons derived from our observations would give strong restrictions on the differentiation and migration processes.

Alternatively, Pluto would have acquired the surface volatiles as a late-accreting veneer. Durda & Stern (2000) estimated that approximately 100 10 km sized TNOs have struck Pluto over the last 3.5 Gyr, which corresponds to a uniform layer of 3 m thickness on Pluto. If we decrease the number by a factor of 25, as suggested by recent *Hubble Space Telescope* observations (Bernstein et al. 2004), there has been an inadequate number of impactors to replenish the volatile loss. However, it is likely that impact rates were much higher for the first billion years after solar system formation. Assuming little modification through impacts, we may link cometary compositions with the pristine inventory of Pluto’s surface. TNOs may have delivered the volatiles observed in cometary comae, as they are thought to be precursors of short-period comets.

It is well known that comets contain both CO and CH_4 , as on Pluto’s surface, although CO shows large comet-to-comet variation (Gibb et al. 2003), possibly owing to selective sublimation prior to accretion. In the protoplanetary disk and the interstellar cloud that preceded it, the gas-phase ion-molecule reactions could have yielded C_2H_2 . The reaction of H with C_2H_2 on cold dust grains could have produced C_2H_6 more effectively than C_2H_4 (Hiraoka et al. 2000). In fact, C_2H_2 and C_2H_6 have been found in the comae of Oort Cloud comets (Mumma et al. 1996; Gibb et al. 2003; Kawakita et al. 2003), but detection of C_2H_4 has not been reported to date. The C_2H_6/CH_4 ratio estimated from Figure 5 is consistent not only with Oort Cloud comets but also with the value of the short-period comet 21P/Giacobini-Zinner (Mumma et al. 2000) and the upper limit for interstellar materials (Boudin et al. 1998). Moreover, the

C_2H_2/CH_4 ratio approximately agrees with the values for Oort Cloud comets (Mumma et al. 1996; Brooke et al. 2003). The observed 3.2 and 3.35 μm features could be ascribed to cometary C_2H_6 , not C_2H_4 , and C_2H_2 may be responsible for the absorption at 3.1 μm .

In contrast to the extreme deficit of N_2 in some comets (Cochran et al. 2000; Cochran 2002), TNOs, formed in the colder regions, are thought to contain larger amounts of N_2 owing to entrapment in amorphous ice (Notesco & Bar-Nun 1996; Owen et al. 1999) or in clathrates (Iro et al. 2003). Such TNOs may have delivered intact N_2 to Pluto. Owen & Bar-Nun (1995), however, suggested that the likely maximum value for the initial N_2/CO ratio cannot account for the currently observed N_2 dominance on Pluto. While the vapor pressure over multicomponent ices is not well understood, the composition of surface frost could be generally different from the underlying reservoir layer (Young et al. 2001b). Presumably, the different volatility and/or the escape rate of N_2 and CO led to efficient concentration of N_2 in the surface frost through sublimation-recondensation. The observed relative ratios between less volatile hydrocarbons may place some additional constraints on the models for atmosphere-surface interaction and/or the atmospheric escape.

NMHCs could be secondary products generated from methane. Krasnopolsky & Cruikshank (1999) simulated photochemical reactions in Pluto's tenuous atmosphere and the subsequent precipitation to the surface. C_2H_2 and C_4H_2 have the highest precipitation rates among numerous photochemical products, but C_2H_2 cannot produce the observed 3.2 and 3.35 μm features, and we do not have optical constants for solid C_4H_2 . The precipitation rates of C_2H_4 and C_2H_6 are smaller than those of C_2H_2 and C_4H_2 by an order of magnitude. If the 3.2 and 3.35 μm features are an indication of C_2H_4 and/or C_2H_6 produced by the photochemical reactions, their concentrations relative to C_2H_2 and C_4H_2 must be somehow increased. Moore & Hudson (2003) conducted a systematic infrared study of proton-irradiated N_2 -

rich ices containing CH_4 and CO. They found C_2H_2 , C_2H_4 , C_2H_6 , and C_3H_8 along with HCN and HNC in the irradiated analog materials of Pluto's surface. It should be emphasized that they identified C_2H_6 with absorption at 3.35 μm , but the expected absorption around 3.65 μm was not detected, as in our observation. In addition, HCN is expected to decrease the gap between the models and observation around 3.1 μm . Therefore, we do not rule out the possibility that the observed features were associated with NMHCs produced by in situ surface reactions induced by cosmic-ray irradiation to the original ternary mixture of N_2 , CH_4 , and CO. In either case, thin deposits are vulnerable to micrometeorite impact. The relative mass ratio to the parent methane, derived from our observations, could be a key to understanding the gardening process on Pluto, such as the poorly known dust flux (Krivov et al. 2003) and vertical mixing timescale (Krasnopolsky & Cruikshank 1999).

We have obtained a high-resolution spectrum of Pluto in the *L* band, which indicates unknown absorption features around 3.1, 3.2, and 3.35 μm . Instead of the more refractory ices suggested from previous observations of low spectral resolution (Grundy et al. 2002), we added NMHCs to the model calculations in order to reproduce the observed spectrum. Although we have no definite identification, the comparison of the spectrum and model calculations suggests the presence of a veneer of NMHCs on Pluto, the mixing ratio of which to methane is of the order of 10%. We briefly examined several formation mechanisms that could account for the observed species and their relative ratios to methane.

We thank E. Quirico for providing us with the optical constant data of various ices in electronic form and Y. Abe and Y. Yamashita for their many helpful suggestions and comments. We thank K. Ishibashi, Y. Inoue, and A. Suzuki for supporting the data analysis. We also thank the anonymous reviewer for a constructive review.

REFERENCES

- Bernstein, G. M., Trilling, D. E., Allen, R. L., Brown, M. E., Holman, M., & Malhotra, R. 2004, *AJ*, 128, 1364
- Boudin, N., Schutte, W. A., & Greenberg, J. M. 1998, *A&A*, 331, 749
- Brooke, T. Y., Weaver, H. A., Chin, G., Bockelée-Morvan, D., Kim, S. J., & Xu, L.-H. 2003, *Icarus*, 166, 167
- Brown, M. E., & Calvin, W. M. 2000, *Science*, 287, 107
- Buie, M. W., Tholen, D. J., & Wasserman, L. H. 1997, *Icarus*, 125, 233
- Busarev, V. V., Dorofeeva, V. A., & Makalkin, A. B. 2003, *Earth Moon Planets*, 92, 345
- Cochran, A. L. 2002, *ApJ*, 576, L165
- Cochran, A. L., Cochran, W. D., & Barker, E. S. 2000, *Icarus*, 146, 583
- Cruikshank, D. P., Roush, T. L., Moore, J. M., Sykes, M. V., Owen, T. C., Bartholomew, M. J., Brown, R. H., & Tryka, K. A. 1997, in *Pluto and Charon*, ed. S. A. Stern & D. J. Tholen (Tucson: Univ. Arizona Press), 221
- Cruikshank, D. P., et al. 2000, *Icarus*, 147, 309
- Douté, S., Schmitt, B., Quirico, E., Owen, T. C., Cruikshank, D. P., de Bergh, C., Geballe, T. R., & Roush, T. L. 1999, *Icarus*, 142, 421
- Durda, D. D., & Stern, S. A. 2000, *Icarus*, 145, 220
- Gaessler, W., Takami, H., Takato, N., Hayano, Y., Kamata, Y., Saint-Jacques, D., Minowa, Y., & Iye, M. 2002, *Proc. SPIE*, 4494, 30
- Gibb, E. L., Mumma, M. J., Dello Russo, N., Disanti, M. A., & Magee-Sauer, K. 2003, *Icarus*, 165, 391
- Grundy, W. M., & Buie, M. W. 2001, *Icarus*, 153, 248
- Grundy, W. M., Buie, M. W., & Spencer, J. R. 2002, *AJ*, 124, 2273
- Grundy, W. M., & Fink, U. 1996, *Icarus*, 124, 329
- Hapke, B. 1993, *Theory of Reflectance and Emittance Spectroscopy* (Cambridge: Cambridge Univ. Press)
- Hiraoka, K., Takayama, T., Euchi, A., Handa, H., & Sato, T. 2000, *ApJ*, 532, 1029
- Iro, N., Gautier, D., Hersant, F., Bockelée-Morvan, D., & Lunine, J. I. 2003, *Icarus*, 161, 511
- Kawakita, H., Watanabe, J., Kinoshita, D., Ishiguro, M., & Nakamura, R. 2003, *ApJ*, 590, 573
- Kobayashi, N., et al. 2000, *Proc. SPIE*, 4008, 1056
- Krasnopolsky, V. A. 1999, *J. Geophys. Res.*, 104, 5955
- Krasnopolsky, V. A., & Cruikshank, D. P. 1999, *J. Geophys. Res.*, 104, 21979
- Krivov, A., Sremčević, M., Spahn, F., Dikarev, V. V., & Kholshchevnikov, K. V. 2003, *Planet. Space Sci.*, 51, 251
- Moore, M. H., & Hudson, R. L. 2003, *Icarus*, 161, 486
- Mumma, M. J., DiSanti, M. A., Dello Russo, N., Fomenkova, M., Magee-Sauer, K., Kaminski, C. D., & Xie, D. X. 1996, *Science*, 272, 1310
- Mumma, M. J., DiSanti, M. A., Dello Russo, N., Magee-Sauer, K., & Rettig, T. W. 2000, *ApJ*, 531, L155
- Nakamura, R., et al. 2000, *PASJ*, 52, 551
- Notesco, G., & Bar-Nun, A. 1996, *Icarus*, 122, 118
- Owen, T., & Bar-Nun, A. 1995, *Icarus*, 116, 215
- Owen, T., Mahaffy, P. R., Niemann, H. B., Atreya, S., Donahue, T., Bar-Nun, A., & de Pater, I. 1999, *Nature*, 402, 269
- Owen, T., Mahaffy, P. R., Niemann, H. B., Atreya, S., & Wong, M. 2001, *ApJ*, 553, L77
- Quirico, E., Douté, S., & Schmitt, B. 1999, *Icarus*, 139, 159
- Ruiz, J. 2003, *Icarus*, 166, 436
- Stern, S. A., & McKinnon, W. B. 2000, *AJ*, 119, 945
- Takami, H., Takato, N., Otsubo, M., Kanzawa, T., Kamata, Y., Nakashima, K., & Iye, M. 1998, *Proc. SPIE*, 3353, 500
- Tokunaga, A. T., et al. 1998, *Proc. SPIE*, 3354, 512
- Trafton, L. M., Hunten, D. M., Zahnle, K. J., & McNutt, R. L. 1997, in *Pluto and Charon*, ed. S. A. Stern & D. J. Tholen (Tucson: Univ. Arizona Press), 475
- Womack, M., Wyckoff, S., & Ziurys, L. M. 1992, *ApJ*, 401, 728
- Young, E. F., Binzel, R. P., & Crane, K. 2001a, *AJ*, 121, 552
- Young, L. A., Cook, J. C., Yelle, R. V., & Young, E. F. 2001b, *Icarus*, 153, 148