NOTE

Detection of Gaseous Methane on Pluto

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We obtained Pluto’s spectrum using the CSHELL echelle spectrograph at NASA’s IRTF on Mauna Kea, on 25–26 May 1992, with a spectral resolution of 13,300. The spectral range (5998–6018 cm⁻¹, or 1661.8–1666.9 nm) includes the R(0) and the Q(1)–Q(9) lines of the 2ν₁ band of methane. The resulting spectrum shows the first detection of gaseous methane on Pluto, with a column height of 1.20±0.15 cm⁻² (3.22±0.14 × 10¹⁹ molecule cm⁻²). © 1997 Academic Press

Introduction. This paper presents the first positive detection of gaseous CH₄ in Pluto’s atmosphere. Solid CH₄ has been previously identified in Pluto’s visible and near-IR spectra at resolutions of a few hundred up to 1200 (e.g., Fink et al. 1980; Spencer et al. 1990; Owen et al. 1993). Unfortunately, these observations cannot be used to find the CH₄ mixing ratio in the atmosphere directly, since the spectra of solid and gaseous CH₄ are essentially indistinguishable at these resolutions. Furthermore, the absorption features due to gaseous CH₄ are hundreds of times weaker than those due to solid CH₄, and have not been detected in these spectra. Because Pluto’s atmosphere is expected to be in vapor-pressure equilibrium with the surface, the surface temperature and composition can be used indirectly to estimate the atmospheric CH₄ mixing ratio (X(CH₄)). Near-IR spectra indicate that Pluto’s surface is dominated by frost with 0.5% CO, 1.5% CH₄ (by mass), and N₂ in an intimate mixture (Owen et al. 1993). Assuming the N₂–CO–CH₄ frost acts like an ideal mixture, one finds that X(CH₄) is only 0.0001% to 0.001%. However, Lellouch (1994) points out that Triton’s X(CH₄) is several hundred times greater than that predicted by the ideal mixture that Cruikshank et al. (1993) used to interpret similar spectra of Triton. This can be explained if the N₂–CO–CH₄ frost is nonideal. Lellouch therefore suggests that Pluto’s X(CH₄) is inflated by a similar amount, so that X(CH₄) = 0.1%. Finally, there is recent spectral evidence of pure CH₄ on Pluto’s surface (Schmitt et al., 1994). Pure CH₄ frost would supply more gaseous CH₄ than N₂–CO–CH₄ frost, raising X(CH₄) above the ideal-mixture value. The thermal structure of Pluto’s atmosphere is further evidence that X(CH₄) is larger than the ideal mixture predicts. The temperature of the N₂–CO–CH₄ frost is 40 ± 2 K, from the shape of the N₂ absorption feature at 2148 nm (Tryka et al., 1994), and the brightness temperature of Pluto (which is a global average, including frost-covered and frost-free regions) ranges from 55 K at 60 μm (Sykes et al. 1987; Tedesco et al. 1987) to 35 K at 1300 μm (Stern et al. 1993; Jewitt 1994). In contrast with the cold surface, the atmosphere is 100 K at μbar levels (Elliot and Young 1992), implying a source of heating in the atmosphere. CH₄ can provide the required heating, if X(CH₄) > 0.1% and there is no CO cooling (Yelle and Lunine 1989). For models that include CO cooling, large enough amounts of gaseous CH₄ can still heat the atmosphere (Lellouch 1994, Strobel et al. 1996).

Observations. Both solid and gaseous CH₄ absorb in the near infrared. At sufficiently high spectral resolution, it is possible to distinguish...
between these two phases because narrow rotation–vibration lines are present only in the gas phase. At 5.5 K, solid CH₄ in an N₂ matrix shows narrow bands, but these bands broaden and coalesce by 20 K (Nelander 1985, Bohn et al. 1994), well below Pluto’s frost temperature of 40 ± 2 K (Tryka et al. 1994).

Using the CSHELL echelle spectrograph (Tokunaga et al. 1990; Greene et al. 1993) with NASA’s Infrared Telescope Facility on Mauna Kea on 25 and 26 May, 1992 (UT), we recorded the spectrum of the Pluto–Charon system from 5998 to 6018 cm⁻¹ (1661.8 to 1666.9 nm) at a nominal resolution of 13,300. This spectral range contains the R(0) and Q(1−)–Q(9) lines of the 2v₅ band of CH₄. Pluto’s rotational phase was 0.84 on 25 May (midway between the extremes in Pluto’s visible rotational lightcurve) and 0.97 on 26 May (just before the minimum in Pluto’s visible rotational lightcurve), where zero phase is defined in Binzel et al. (1985), and corresponds to the minimum in the visible lightcurve. Asteroid 532 Herculina and the star 16 Cyg B, a solar analog (Campins et al. 1985; Hardorp 1978), were observed to confirm our correction of solar and telluric features. The dispersion was determined from four lines from CSHELL’s standard Xe, Kr, and Ar lamps. Because the CSHELL employs a circular-variable filter (CVF) to separate out a single order, the wavelength range is small enough that the wavelength is simply a linear function of detector array column.

Analysis. We extracted the spectra using the optimal extraction algorithm (Horne 1986), as implemented by IRAF’s APEXTRACT package (Massey et al. 1992). The normalized spectra were combined in weighted means, where the weights were estimated by the scatter in a continuum region. The error in the combined Pluto–Charon spectrum is 7%, based on the propagation of the errors determined for the individual spectra.

At this point, analysis normally proceeds by dividing the object spectra by the standard spectra to remove solar lines, telluric lines, and instrumental effects. However, our standards’ doppler shifts were different from Pluto’s, so the solar lines would not have divided correctly. Instead, we chose to model the Pluto and standard spectra.

The steps in our model of the Pluto–Charon spectrum mimic the physical steps that yield the observed spectrum. Sunlight is absorbed by CH₄ in Pluto’s atmosphere, reflected from the surface, and absorbed again as it leaves Pluto’s atmosphere; it is simply reflected from Charon’s surface. These two components of reflected sunlight then pass through the Earth’s atmosphere, and are absorbed by H₂O and CH₄. Internal reflections in the CVF create an interference pattern (‘‘fringing’’), which causes a low-order undulation in the continuum. Finally, the spectrum is convolved by the slit function as it passes through the instrument (convolution is represented by the symbol ⊗). Putting these all together, the observed normalized spectrum is

\[ M(i) = F(i)G(\lambda) \otimes \left[ T(\lambda) S(\lambda) \left( C + (1 - C) P(\lambda) \right) \right], \]  

where \( F \) is the fringing as a function of pixel \( i \), \( G \) is the slit function, which is approximated by a Gaussian, \( T \) is the telluric absorption, \( S \) is the solar spectrum, \( C \) is the ratio of Charon’s flux to the flux from both Pluto and Charon in the continuum (constant with wavelength), and \( P \) is the absorption due to Pluto’s atmosphere. \( T, S, C \), and \( P \) are between 0 and 1.

Pluto’s CH₄ absorption was calculated on a line-by-line basis, using the 65 lines in the HITRAN database (Rothman et al. 1992) that fell within our spectral range, including one weak line from CH₃. The strongest of these lines are the R(0) and the Q(1−)–Q(9) lines of the 2v₅ band of CH₄. We did not include H₂O, CO, or CO₂, whose lines in this region are 100–1000 times weaker than the CH₄ lines. No other molecules from the HITRAN database had lines listed in this region, including N₂, CH₂, or C₂H₆.

At Pluto’s low pressures, the line shape is the Doppler line shape. Because this is pressure independent, an isothermal atmosphere can be modeled as a single-layer atmosphere. We used a temperature of 100 K, the temperature derived from the stellar occultation for a predominantly N₂ atmosphere (Elliot and Young 1992). The relationship between \( P \) and the vertical optical depth, \( \tau \), depends on the limb darkening. Pluto has no detectable limb darkening at 0.55 μm (Young and Binzel 1994), so we assume no limb darkening at these wavelengths as well. In this case, \( P = 2 E_e(2 \tau) \), where \( E_e \) is the exponential integral. For small \( \tau \), this reduces to \( P \approx 1 - 4 \tau \exp(-4 \tau) \), reproducing the familiar airmass factor of 4. Because only H₂O has been detected on Charon (e.g., Buie et al. 1987), and H₂O is nonvolatile in the outer solar system, we assume that Charon has no gaseous absorption.

The spectra of solid H₂O and CH₄, and therefore the reflectance of the surfaces of Pluto and Charon, do not vary with wavelength over our small spectral range. In particular, the ratio of Charon’s flux to the combined and unattenuated Pluto–Charon flux (C in Eq. (1)) is constant with wavelength. At a rotational phase of 0.75, Charon contributes 15% of the combined Pluto–Charon flux at 1622–1712 nm (through a CVF with a bandpass of 90 nm; Buie et al. 1987). The combined flux varies with wavelength throughout 1622–1712 nm; the combined flux at our wavelength is 62–75% of the combined flux through 1622–1712 nm, and depends on rotational phase (Owen et al. 1993; Ted Roush, personal communication). We assumed that Charon’s contribution, \( C \), ranged from 0.15–0.62 to 0.15–0.75, or 20%–24% of the combined flux.

It is vital in this analysis to distinguish between CH₄ absorption from Earth’s and from Pluto’s atmosphere. The telluric absorption was modeled with the ATRAN program (Lord 1992), which can calculate atmospheric transmission for any altitude, airmass, wavelength, resolution, and concentration of H₂O, CH₄, and other species. Although telluric H₂O can vary considerably during the night, changing the precipitable H₂O from 1 to 3 mm changed the absorption by an insignificant 1%; we assumed 3 mm H₂O throughout. In one study, telluric CH₄ was found to have a daily variation of only about 0.1% (Khalil et al. 1993), so CH₄ was essentially constant during the two-night run. Therefore, we assumed that the telluric absorption did not vary over the observing run. The mean airmass for each object was the weighted mean of the airmasses of the individual spectra. Pluto spanned 1.1 to 2.3 airmasses, with a weighted mean airmass of 1.25—close to the unweighted mean airmass of 1.29.

The solar spectrum was provided by the KPNO Solar Atlas (Livingston and Wallace 1991). The fringing is well modeled by the first seven parameters in a Fourier series (a constant and three sine–cosine pairs). The nominal dispersion and slit function were determined from CSHELL’s standard lamps. At 1.5 arcsec (6 pixels), our slit was wider than the typical seeing disk, so the position and angular size of the star also contributed to the “slit” function and dispersion. For instance, a seeing disk of 1 arcsec yields an effective resolution of 20,000, and a drift of 0.5 arcsec in the star’s position would offset the wavelengths by 2 columns. An error in the tabulated value for 16 Cyg B’s radial velocity (Wilson 1953) would produce a similar shift.

We used the standards (532 Herculina and the star 16 Cyg B) to confirm our modeling of the solar and telluric lines and to measure the amount of telluric CH₄. In fitting the standard spectra, we allowed the strength and width of the solar lines, the amount of telluric CH₄, the width of the slit function, and the dispersion to be free parameters. We found that the ATRAN program correctly calculated the amount of absorption by telluric CH₄, without modification. Absorption by telluric H₂O occurred primarily at 1663.8–1666.5 nm, which we exclude from the analysis. There are no other important absorbers in the Earth’s atmosphere at these wavelengths. The solar lines we observed in the standards are broader than the solar lines from the KPNO atlas, perhaps because the observables in the HITRAN database had lines listed in this region, including N₂, C₂H₆, or C₂H₄.

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FIG. 1. Pluto data and models. The upper, dashed curve is the product of the solar spectrum and telluric absorption for Pluto’s mean airmass of 1.25. The lower, solid curve is the product of the above spectrum and absorption by Pluto’s atmospheric methane at a temperature of 100 K and a column height of 1.20 cm-A (plus a 22% contribution from Charon, see Eq. (1)). The points represent the observed spectrum of the Pluto–Charon system. The data have been corrected for the low-order interference fringing, and every five points have been averaged. The important lines in the solar spectrum, and the observed rotation lines in the 2ν3 band of CH₄, are indicated below the models. These lines are red-shifted by 0.04 nm relative to telluric CH₄ because of Pluto’s motion.

FIG. 2. Surface pressures. The horizontal line is the observed partial pressure of CH₄ at the surface, if the CH₄ mixing ratio is constant with altitude. If CH₄ were concentrated in the lower atmosphere, the implied surface pressure would be higher. The upper curve is the vapor pressure of N₂ over an intimate mixture of 98% N₂, 0.5% CO, and 1.5% CH₄ (by mass), and should be close to the total atmospheric surface pressure. The lower curve is the vapor pressure of CH₄ over the same mixture. The solid portions on the upper and lower curves show the pressures for a frost temperature of 40 ± 2 K. The middle curve is the vapor pressure of pure CH₄. The upper curve shows that CH₄ is a minor constituent, with a vertically averaged abundance of ~0.1%. If the CH₄ is evenly distributed vertically, it is oversaturated with respect to the N₂–CO–CH₄ mixture by a factor of several hundred, but in equilibrium with pure CH₄ at 41–45 K.
the solar analog, but we attributed this to differences between the spectra of 16 Cyg B and the sun, rather than a problem with the KPNO atlas.

In contrast to the standard spectra, the Pluto–Charon spectrum cannot be explained solely by telluric and solar features. The spectrum consisting only of reflected sunlight and telluric absorption at Pluto’s airmass of 1.25 is the upper, dashed line in Fig. 1. The normalized Pluto–Charon spectrum, binned to 1-nm resolution, is shown as points in Fig. 1. The spectrum shows absorption features at 1665.4–1662.2 nm that are deeper than can be accounted for by the reflected solar spectrum and telluric absorption. To investigate the possibility that this excess absorption was due to an underestimate of Pluto’s airmass, we asked what airmass would be needed to produce these features. The resulting effective airmass, 2.05 ± 0.37, was more than 2σ larger than the actual airmass of the observations.

Since we could accurately model the telluric absorptions and solar lines seen in the standards, we applied these models to Pluto as well. Holding the strength of the solar lines and the amount of telluric CH₄ fixed, we fit Eq. (1) to the Pluto–Charon spectrum in a least squares sense. We first performed a parameter-space search and investigated χ² (the sum of weighted, squared residuals) as a function of column height, ε. From the χ² for no absorption, we calculated that there is less than a 1% chance that the features longward of 1665 nm are caused by random noise (Press et al. 1988). We find that χ² is a parabolic function of ln(ε), not ε, so we use ln(ε) as the free parameter. This leads to unequal error bars in ε. The best-fit CH₄ column height was 1.20 ± 0.18 cm⁻² (3.22 ± 0.05 bar) for a temperature of 100 K, where we give the 1σ errors. The model spectrum is shown as a solid line in Fig. 1. The difference between the dashed and solid lines is due to absorption by Pluto’s gaseous CH₄.

Discussion. Our detection of 1.20 ± 0.20 cm⁻² of CH₄ confirms that CH₄ is only a minor constituent in Pluto’s atmosphere, as expected from the dominance of N₂ on the surface (Owen et al. 1993), since a pure CH₄ atmosphere would need a column height greater than 23.9 cm⁻² to explain the 1988 stellar occultation (Elliott and Young 1992). If Pluto’s atmosphere had significant scattering by haze, the effective path length would be longer, so that the same absorption could be achieved with less CH₄. Therefore, for a scattering atmosphere, these observations imply an even smaller CH₄ column abundance.

The partial pressure of CH₄ at the surface would be 0.072 ± 0.008 mbar if the CH₄ were evenly distributed in an N₂ atmosphere. This pressure is indicated by the horizontal line in Fig. 2, with the hashed area representing the 1σ error. However, this analysis does not provide information on CH₄’s vertical distribution. For example, if CH₄ were confined below a certain altitude because of photochemical reactions, then the partial pressure of CH₄ at the surface implied by this analysis would be increased.

To find the mean CH₄ mixing ratio, we need to estimate the total atmospheric number density, or, equivalently, the total surface pressure. If the atmosphere is mostly N₂ and in vapor-pressure equilibrium with N₂ frost, then the surface pressure will be V(T)N₂ the vapor pressure of N₂ at the surface temperature. The N₂ vapor-pressure curve is indicated in Fig. 2 by the uppermost curved line (Brown and Ziegler 1980). The 1988 stellar occultation probed down to a pressure of at least 3.25 mbar (Elliott and Young 1992), as indicated by the arrow at 35.25 K. The solid portion of the line reflects the vapor pressure of N₂ at the observed N₂ frost temperature of 40 ± 2 K (Tryka et al. 1994). For a N₂ frost temperature of 40 K, the N₂ surface pressure is 58 μbar. This pressure implies a deep Pluto atmosphere, as first proposed by Stansberry et al. (1994) and investigated for a range of atmospheric structures by Young (1994). Briefly, the pressure at 1215 ± 11 km is 2.38 ± 0.49 μbar (Elliott & Young 1992), or 3.2 scale heights above a 58 μbar surface. Since the scale height below the occultation levels is at least 20 km, a 40 K surface must lie below 1162 km.

For an N₂ surface pressure of 58 μbar, the mean gaseous CH₄ mixing ratio is 0.03–0.45%. According to atmospheric models, 0.1% CH₄ is enough to heat the middle atmosphere in the absence of CO cooling (Yelle and Lunine 1989), but is far less than the 10% needed to raise the temperature in the presence of CO cooling or to reproduce the “kink” in the occultation lightcurve by refraction alone (Lellouch 1994; Hubbard et al. 1990; Strobel et al. 1996).

The mean gaseous CH₄ mixing ratio is several hundred times larger than predicted by an ideal mixture of N₂–CO–CH₄ on Pluto as well as on Triton. Assuming Raoult’s law, the vapor pressure of CH₄ over an ideal mixture of 98% N₂, 0.5% CO, and 1.5% CH₄ (by mass) is 38 times lower than the vapor pressure over pure CH₄. The lowest curve plotted in Fig. 2 is the vapor pressure of CH₄ over the N₂–CO–CH₄ intimate mixture. Since the CH₄ that is mixed with N₂ should have the same temperature as the N₂, the range of 40 ± 2 K is indicated by a solid line on this curve as well. For a surface at 40 K, the partial pressure of CH₄ (assuming the gaseous CH₄ mixing ratio is constant with altitude) is 360 times higher than the vapor pressure of CH₄ over the N₂–CO–CH₄ intimate mixture.

A partial pressure of 0.072 ± 0.008 μbar is consistent with CH₄ vapor-pressure equilibrium over pure CH₄ at 41–45 K, as indicated by the middle curve in Fig. 2. Thus, the overabundance of gaseous CH₄ relative to the ideal mixture lends weight to the tentative identification of pure CH₄ on Pluto’s surface (Schmitt et al. 1994).

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