Titan’s 5 µm Spectral Window: Carbon Monoxide and the Albedo of the Surface

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Received May 13, 1996; revised August 19, 1996

We have measured the spectrum of Titan near 5 µm and have found it to be dominated by absorption from the carbon monoxide 1–0 vibration–rotation band. The position of the band edge allows us to constrain the abundance of CO in the atmosphere and/or the location of the reflecting layer in the atmosphere. In the most likely case, 5 µm radiation is reflected from the surface and the mole fraction of CO in the atmosphere is $q_{\text{CO}} = 10^{+20}_{-10}$ ppm, significantly lower than previous estimates for tropospheric CO. The albedo of the reflecting layer is approximately $0.07^{+0.02}_{-0.01}$ in the 5 µm continuum outside the CO band. The 5 µm albedo is consistent with a surface of mixed ice and silicates similar to the icy Galilean satellites. Organic solids formed in simulated Titan conditions can also produce similar albedos at 5 µm. © 1996 Academic Press, Inc.

1. INTRODUCTION

Because Titan is very faint in the infrared $M$ band, its spectrum there has been observed only recently. The first very low spectral resolution spectrophotometry by Noll and Knacke (1992, 1993) demonstrated that the detected radiation was largely reflected solar radiation, revealed evidence of a strong CO absorption band at 4.7 µm, and opened the possibility of measuring the surface albedo in the continuum outside the CO band. In this paper we report the first moderate spectral resolution ($R = 1500$) observations of Titan in its 5 µm window. These observations allow us to confirm hypotheses raised in our earlier work, obtain a determination of the atmospheric abundance of carbon monoxide that differs from previous estimates, and add an additional datum, the measured 5 µm albedo, to the sparse spectrum that may constrain the composition of Titan’s surface.

Carbon monoxide was discovered in Titan’s atmosphere by detection of absorption lines of the 3–0 vibration–rotation band near 1.6 µm (Lutz et al. 1983). The CO mixing ratio relative to $N_2$ was determined to be between 50 and 150 parts per million (ppm) with a value of 60 ppm for a simple reflecting layer model. A precise determination of the abundance was hampered by uncertainties in the mixing ratio relative to $N_2$ and Knacke (1992, 1993) demonstrated that the detected 60 ± 40 ppm. A reanalysis of this data by Paubert et al. (1984) found a slightly higher abundance of 30–180 ppm. Marten et al. (1988) reobserved the central 0.5 GHz of this line at higher spectral resolution and found it much weaker than expected. The shape of the emission line core was best fit with a CO mixing ratio of $2^{+2}_{-1}$ ppm. However, Gurwell and Muhleman (1995) reobserved the line with
the Owens Valley millimeter array and found a strong line that is fit with a uniform stratospheric CO mixing ratio of 50 ± 10 ppm, consistent with the original results of Muhleman et al. Because of the improved observational technique used by Gurwell and Muhleman, their observation should be regarded as the most accurate.

The 1.5 ppb of CO in Titan’s stratosphere detected by Samuelson et al. (1983) could be maintained in steady state by a CO mixing ratio of 100 ppm in one photochemical model (Samuelson et al.) in closer agreement with the observations of Muhleman et al. (1984) and Gurwell and Muhleman (1995) than with those of Marten et al. (1988). Lara et al. (1996) calculated a new photochemical model and found that their model produces the revised CO mixing ratio of 14±3 ppb (Coustenis et al. 1989a) with an equilibrium CO mixing ratio of 10 ppm. Evidently, considerable uncertainty surrounds the determination of the abundance of carbon monoxide in Titan. Establishing the abundance of CO in Titan’s atmosphere as a function of altitude, however, is required to establish the origin of oxygen containing molecules in Titan’s reducing atmosphere, a question that has wide-ranging consequences including, perhaps, for the atmosphere of the early Earth.

The question of the composition of Titan’s surface has been particularly compelling ever since it was realized that large quantities of organic molecules could precipitate onto its surface (cf. Hunten 1977). Obtaining observational data that could identify the surface composition, however, has proved elusive.

Muhleman et al. (1990) observed radar reflections from Titan that appear to rule out thick oceans of liquid ethane on the surface. In the infrared, the first evidence of an opportunity to study the surface was the observation of variability in Titan in the standard infrared J, H, and K filters by Cruikshank and Morgan (1980), though the full implications of these observations were not appreciated for more than a decade. A reevaluation of these data by Noll and Knacke (1993) showed evidence of systematically higher albedos on Titan’s leading hemisphere. Griffith et al. (1991) laid the basis for much of the recent work on the near-IR lightcurve by showing that the haze optical depth is sufficiently low that in windows of low gas opacity at 1.3, 1.6, and 2.04 μm the surface can be detected. Additional observations of lightcurves (Lemmon et al. 1993, 1995; Griffith 1993; Coustenis et al. 1995) and direct images of albedo features (Smith et al. 1996) have shown that windows of low opacity also occur at 0.94 and 1.07 μm. The relatively high albedos extracted from near-IR observations are incompatible with even thin global deposits of liquid ethane (Griffith et al. 1991). However, different investigators do not agree on the surface albedos in the near-IR windows. Some observers have suggested surface compositions of dirty water ice similar to Callisto (Griffith et al. 1991) or Hyperion (Coustenis et al. 1995). However, Lemmon et al. (1995) do not find evidence for the strong 2 μm ice band.

The new observations presented here address both the question of the abundance of carbon monoxide in the atmosphere and the surface composition of Titan.

### 2. OBSERVATIONS

We observed Titan in July 1992 and in July 1993 with the CGS4 cooled grating spectrograph at the United Kingdom Infrared Telescope on Mauna Kea, Hawaii. All observations were made using a 1.5” slit, a 75 line/mm grating, and a 300 mm focal length camera. With this arrangement and with the 58 × 62 InSb array then installed, the instrument covered 0.2 μm at each grating setting with a resolving power of R = 1500 at 4.9 μm. The observations are summarized in Table I and the data obtained are shown in Fig. 1.

Observing conditions were good on 20 July 1992 but were less so on 12 July 1993 as can be seen in the increased noise for data taken on that night. Nevertheless, the two data sets agree to within their errors near 5.0 μm where the two spectra overlap. The phase angle of Titan was 1.9° and 3.8° at the times of our 1992 and 1993 observations, respectively.

We reduced the data using the FIGARO data reduction software at the Joint Astronomy Centre. Wavelength calibration was accomplished by taking spectra of argon or krypton lamps and fitting a dispersion curve to the observed line centers. Flux calibration was achieved by observations of infrared standard stars. Residual sky background was fitted with a polynomial in selected rows and was then subtracted from the array. We centered Titan on row 29 of the array at the start of each observation. We chopped and nodded the telescope 9 arcsec along the slit in a standard pattern. The data extracted from row 29 were used in the final spectra.

The spectra were substepped to eliminate possible effects of bad pixels. The data have been rebinned to increase

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TITAN’S 5 μm SPECTRUM

FIG. 1. (a) The spectrum observed on 20 July 1992 (triangles) and 12 July 1993 (diamonds) is compared to a series of model spectra. Model spectra assume a reflecting layer fixed at Titan’s surface with an albedo of 0.072. The lowest dashed curve has a CO mole fraction of 60 ppm. Successively higher curves correspond to 20 ppm (dotted), 10 ppm (solid), 5 ppm (dotted), and 2 ppm of CO (dashed). (b) The same spectrum is compared to a series of model spectra where the CO mole fraction has been fixed at 60 ppm and the location of the reflecting layer is varied. The lowest dashed curve corresponds to a reflecting layer at the surface, or a pressure level of 1.5 bar. Successively higher curves correspond to reflecting layer pressure levels of approximately 1.2 bar (dotted), 0.9 bar (solid), 0.7 bar (dotted), and 0.5 bar (dashed). The albedo was fixed at 0.072 for all model curves shown.

the signal to noise (S/N) per displayed data point. We rebinned over two resolution elements in the 1992 data and over two to six resolution elements in the noisier data from 1993. For this latter data set, we rebinned points located between strong terrestrial absorption lines. We did not include data near the terrestrial lines in our final spectrum.

3. ANALYSIS

Titan’s spectrum shown in Fig. 1 can be described as a relatively flat continuum with a flux density of ≈70 mJy, a sharp absorption edge that begins at about 4.92 μm falling quickly to a barely detectable flux of ≈15 mJy by 4.87 μm and shorter wavelengths. The uncertainty in flux per point in the rebinned data is ≈ ±10 mJy. A few points deviate from the simple behavior described, for example, points near 4.83 and 4.91 μm. Given the relatively low S/N in the unbinned data it would not be surprising to find a few points deviating by as much as these outliers, but it is also possible that these points trace real features in the spectrum. Additional observations are required to determine the reality of possible narrow spectral features.

Both major features of the spectrum we observe, the flat continuum and the sharp absorption edge, are inconsistent with thermal emission from a blackbody (see Fig. 3, Noll and Knacke 1993). The possibility that the 5 μm radiation is predominantly thermal can be ruled out with confidence. On the other hand, the spectrum can be well matched by models of reflected sunlight and atmospheric gas absorption which we describe below.

We produced synthetic spectra for comparison with the data using a multi-layer, line-by-line radiative transfer program (Noll 1987). We used a Voyager temperature–pressure profile with eighteen 6- to 8-km-thick layers extending from the surface at 1.5 bars to an altitude of 130 km and a pressure of 5.6 mbar. We included lines from CO and CH3D from the HITRAN92 molecular line compilation (Rothman et al. 1992). Models were computed from 1900–2200 cm⁻¹ with a step size of 0.1 cm⁻¹. Line wings of the Voigt profiles were truncated at 1000 × the pressure-broadened line half-width appropriate for each layer. Tests with the cutoff at 10,000 × the half-width showed no significant change to the spectral shape, but significantly smaller cutoffs did. All models were computed with an airmass factor, η = 4, appropriate for two-way transmission through the atmosphere of an unresolved disk. (Tests using an exponential integral formulation, 2Ee(2τ), in place of e⁻²τ, resulted in entirely negligible changes to the models.) We report molecular abundances in our models as mole fractions (qX = Px/Ptotal) rather than mixing ratio relative to N2 in order to avoid uncertainties in the mole fraction of N2.

Given the apparent simplicity of the spectrum, we chose to compute models with a minimum of free parameters. In addition to the mixing ratios of CO and CH3D, we varied the pressure and albedo of the reflecting layer in our models. We found that CH3D has virtually no effect
on the spectrum longward of 4.7 \mu m for any reasonable abundance of CO, so we fixed its mole fraction at qCH₃D = 11 ppm (Coustenis et al. 1989b). Of the three remaining free parameters, we varied one at a time while keeping the other two fixed. CO was assumed constant with altitude. The results of this process for two series of models are shown in Fig. 1.

A series of models with the reflecting layer fixed at Titan’s surface and with differing CO mole fractions is shown in Fig. 1a. All models were computed with an effective albedo of 0.072. The lowest curve shows the effects of CO absorption when the abundance preferred by Lutz et al. (1983), 60 ppm, is used. The model spectrum lacks the sharp rise and flat continuum characteristic of the observed spectrum. Reducing the mole fraction of CO causes the absorption to steepen and shift to shorter wavelength, toward the band center, and produces much better-fitting model spectra, as shown. For the albedo of 0.072 used in Fig. 1a, the best fitting model is the one with qCO = 10 ppm. Models with 5 and 20 ppm produce somewhat better fits than shown if the albedo is allowed to vary, with good fits having albedos of 0.06 and 0.09, respectively. Models with more than 20 ppm do not reproduce the apparent flat continuum with any albedo. Models with less than 5 ppm CO have the absorption edge at too short a wavelength.

Based on these considerations we adopt a CO mole fraction of 10 ppm with a factor of 2 uncertainty if 5 \mu m radiation is reflected from Titan’s surface. The albedo at the observed phase angle is constrained to fall in the range from 0.06 to 0.09. As we will argue below, we believe that reflection from the surface is more likely than scattering from higher in the atmosphere. We note that improved observations of Titan’s spectrum, particularly from 5.0–5.2 \mu m or longer, could significantly reduce the uncertainty of both quantities by providing a tighter constraint on the range of allowed albedos. It is worth pointing out that the albedo we infer for the surface at 5.0 \mu m is higher than the broad M-band albedo (Noll and Knacke 1993) due to the fact that the latter measurement includes the strong CO absorption band over a large fraction of the filter bandpass.

We also computed a series of models in which we fixed the tropospheric CO abundance at 60 ppm (Lutz et al. 1983). In Fig. 1b we show the effects on the spectrum of moving the reflecting layer from the surface at 1.5 bar to successively lower pressures of P \approx 1.2, 0.9, 0.7, and 0.5 bar (z \approx 5, 10, 14, and 20 km). The model fits are qualitatively similar to the series of models in Fig. 1a. From these models we can conclude that if the tropospheric mole fraction of CO is near 60 ppm, then the radiation cannot be reflected from the surface. For the simple reflecting layers we used, the scattering layer must be located between 0.7 and 1.2 bars with 0.9 bars as the best fit, although we believe this to be an unlikely model (see below).

4. DISCUSSION

From the model fits in Fig. 1 it is clear that with our spectrum alone we cannot distinguish between scattering from the surface with \approx 10 ppm CO and models with a reflecting cloud layer above the surface and higher abundances of CO. However, it is possible to constrain the problem by turning to other observations. We could assume that the CO abundance is well known from previous observations in the near-IR and mm wavelengths. Unfortunately, the conflicting determinations described above make this a risky assumption. The abundance determination most relevant to the 5 \mu m spectrum is that of Lutz et al. (1983) who found the tropospheric abundance to be 60 ppm with a simple reflecting layer model. However, this determination depended on the use of a scaled Uranus spectrum as a substitute for the lack of laboratory-measured CH₄ line parameters in this portion of the spectrum, a less than optimal situation. If we accept any value of CO greater than \approx 20 ppm, then we are forced to conclude that Titan has an optically thick (at 5 \mu m) scattering cloud located well above the surface.

The existence of an optically thick cloud at 5 \mu m is at odds with a number of observations that suggest Titan’s atmosphere is not optically thick at shorter wavelengths. The existence of a regular lightcurve (Cruikshank and Morgan 1980, Noll and Knacke 1993, Lemmon et al. 1993, 1995, Griffith 1993, Coustenis et al. 1995) in windows between CH₄ bands confirms models that predict low haze optical depth in the infrared (Griffith et al. 1991, Toon et al. 1992). Direct imaging of Titan at \approx 0.94 \mu m shows clear albedo features with a bright region on Titan’s leading hemisphere (Smith et al. 1996) in agreement with lightcurve data. The increasing amplitude of the lightcurve going from 0.94 to 2 \mu m noted by Lemmon et al. (1995) supports the expectation that the haze optical depth decreases with wavelength with a 1/A dependence. For a CO mole fraction of 60 ppm, the cloud layer would be 6–18 km above the surface, well below Titan’s tropopause where most of the organic haze particles should condense, somewhat lower than the 17–30 km altitude range for a possible thin global CH₄ haze (Lindal et al. 1983), and higher than the 3.5 km limit on possible ethane condensation clouds (Lunine et al. 1983). Eshleman et al. (1983) concluded from the Voyager radio occultation data that global methane condensation clouds were unlikely. These observations all suggest that at 5 \mu m radiation is reflected from Titan’s surface. Thus, we conclude that the models in Fig. 1a are the most relevant to Titan and that the mole fraction of CO in Titan’s troposphere is qCO = 10^{1.1} ppm.

The abundance of CO that we derive does not agree with any previous measurements of the CO abundance (Table II). In particular, it is significantly lower than the one measurement relevant to the troposphere, the Lutz et
4.8 wavelength observations of Muhleman (1983) measurement of CO lines in the 3±0 band near 1.6 μm. Two theoretical model estimates, one by Samuelson et al. (1983) and recent work by Lara et al. (1996) based on the measured abundance of CO2 at 15 μm and a photochemical model, are indirectly relevant to the tropospheric CO abundance. Samuelson et al. found an equilibrium abundance of CO significantly higher than we measure, but Lara et al. found that the equilibrium mixing ratio of CO in their model is 10 ppm, in excellent agreement with our results. However, these results are model dependent; Samuelson et al. found that an increase in atmospheric CH4 over that assumed in their model would reduce the predicted equilibrium abundance of CO. The millimeter wavelength observations of Muhleman et al. (1984) or Gurwell and Muhleman (1995) and Marten et al. (1988) do not agree with each other and do not agree with our CO abundance. However, millimeter wavelength observations are sensitive to the abundance of CO in Titan’s stratosphere, well above the part of the atmosphere that we sample. The long photochemical lifetime of CO leads to the prediction of CO uniform with altitude (Samuelson et al. 1983). However, a non-uniform distribution of CO (Marten et al. 1988) can be postulated as an explanation of different stratospheric and tropospheric CO abundances.

Understanding the meaning of the observed abundance of CO in Titan’s atmosphere depends on knowing its abundance as a function of altitude, a goal not yet achieved. The important questions that can be asked about CO in Titan are whether it is in steady state in the atmosphere over the age of the Solar System or, instead, the manifestation of a cosmically recent event such as a collision of a large comet. Zahnle et al. (1992) showed that a plausible explanation for the existence of a massive atmosphere around Titan but not Ganymede or Callisto is the lower relative velocity of impactors at Titan that allows it to build up an atmosphere. Collision-generated CO coupled with an efficient sink in the form of the CO2 cold trap (Samuelson et al. 1983) could maintain the atmospheric CO abundance near the equilibrium abundance. It can also be asked whether the source of the observed CO is Titan itself (Owen 1982) or whether it is derived from an exogenic source of oxygen. The firm establishment of a non-uniform vertical distribution of CO with more CO near the surface would favor an endogenic source for CO in the atmosphere.

The situation could be improved with additional observations. In the 5 μm window observations from the ground could improve the spectrum from 5.0–5.2 μm. This would allow an improved determination of both the surface albedo and the CO abundance. It may also be possible to observe the spectrum from 5–7 μm using ISO (Courtin, private communication). Prospects for improving the estimate from the 3–0 band at 1.6 μm depend on improved modeling of recently obtained spectra (de Bergh et al. 1995). Finally, Hidayat et al. (1995) report the observation of CO(1±0), CO(2±1), CO(3±2), and 13CO(2±1) rotational lines which may lead to an improved determination of the abundance of CO at altitudes about 60 km.

If Titan’s surface is composed of water ice and a non-ice component as suggested by some determinations of the near-IR albedo (Griffith et al. 1991), then the 5 μm albedo that we measure may characterize the non-ice component of the surface. Both Roush et al. (1990) and Calvin and Clark (1991) find that Callisto’s spectrum beyond 2.5–3 μm is dominated by the non-ice component. They are able to match features in the spectrum and the albedo level by including serpentine minerals in mixtures of less than 50% H2O ice. As shown in Fig. 2, the albedo of Titan at 5 μm is roughly comparable to that of Callisto in this region.

![Fig. 2. The albedo we derive at 5 μm is plotted (triangle) along with near-IR “surface” albedos (the measured albedo corrected to remove atmospheric absorption) derived by Griffith et al. (1991) (squares), Coustenis et al. (1995) (diamonds), and Lemmon et al. (1995) (stars). There is a marked lack of agreement between the various near-IR albedos. The curve plotted with error bars and no symbols is the infrared albedo spectrum of Callisto’s leading hemisphere (Calvin et al. 1995). As discussed in the text, the 5 μm datum does not rule out ice–silicate mixtures as a possible Titan surface, though other compositions, notably solid organic precipitates, can also match the 5 μm albedo.](image-url)
(Noll and Knacke 1993, Calvin et al. 1995), though the poor agreement of inferred near-IR albedos and the lack of strong diagnostic spectral features limits the predictive power of this comparison. Given the similarities of these satellites in size and density and the prevalence of water ice and silicate minerals in the Solar System, the suggestion that Titan’s surface may be a mixture of ice and silicate minerals is plausible on cosmochemical grounds. However, continuum albedo is a non-unique identifier of possible surface components and, at most, we can only rule out candidate materials. A water ice/silicate mixture similar to that found on Callisto is not ruled out by our 5 μm albedo.

Despite predictions of hundreds of meters of condensed liquid methane, ethane, and propane on Titan’s surface over the age of the Solar System (Hunten 1977, Tyler et al. 1981, Sagan and Dermott 1982, Flasar 1983, Lunine et al. 1983), near-IR albedos (Griffith et al. 1991) and high microwave reflectivity (Muhleman et al. 1990) are inconsistent with the presence of even thin global oceans of these hydrocarbons. The large orbital eccentricity of Titan rules out many possible configurations of non-global oceans (Dermott and Sagan 1995). It has been suggested that liquid condensates could exist in saturated layers of a porous Titan regolith (Hunten 1977, Lunine 1991). However, this scenario still leaves the surface covered with 100 m of solid hydrocarbon and nitrile condensates (Lunine 1991). Winds and/or precipitation could produce mixtures of water ice and precipitates.

To test whether hydrocarbon condensates could reproduce the observed 5 μm albedo we consulted model reflectance spectra (Roush 1996, private communication) calculated from the optical constants for Titan tholins (Khare et al. 1984). Models with 100 μm diameter grains have geometric albedos of ~0.05–0.10 in the 4.5–5.2 μm range and are sufficiently dark at near-IR wavelengths to be consistent with derived near-IR albedos. An absorption feature at 4.6 μm, attributable to XCN compounds, is present in all models and results in a shallow positive slope beginning at the center of the feature at 4.6 μm and continuing beyond the 5.2 μm limit of ground-based observations. This feature cannot account for the observed sharp absorption in Titan’s spectrum that we identify as CO. However, the question of whether the shape of the continuum outside the CO band shows evidence of this slope is more difficult to answer. The apparent flatness of the continuum between 4.92 and 5.00 μm is not consistent with the models of Titan tholin reflectance. However, the portion of the continuum sampled is too small for a firm conclusion. An improved spectrum from 5.0–5.2 μm would help determine the slope of the continuum. Also, the models we have compared are a small subset of the range of possible surface models with solid organic material on the surface. The only conclusion that we can reach with existing data is that a surface made up, in part, of condensed organic molecules cannot be ruled out.

One test of the identification of the 5 μm albedo with the non-ice component would be to search for an anticorrelation in the lightcurve at 5 μm with the lightcurves observed at 1–2 μm. The partial lightcurve in the M band published by Noll and Knacke (1993, Fig. 1d) suggests a photometric minimum near an orbital phase of 80°, close to the location of the peak in the lightcurve at shorter wavelengths (Lemmon et al. 1995, Coustenis et al. 1995). Confirmation of this effect with higher S/N observations, especially near greatest western elongation, could be accomplished with current instrumentation. Our attempts to do so over the past few years, however, have been frustrated by poor observing conditions.

5. CONCLUSIONS

We have measured the spectrum of Titan near 5 μm. The spectrum can be well fit with simple reflecting layer models. For models with the reflecting layer at the surface, a condition supported by observations of photometric variations and direct observations of surface albedo features in the near-IR, we derive a CO mole fraction of qCO = 10±1 ppm. This mole fraction does not agree with previous CO abundance determinations and is significantly lower than the previous estimates of the CO abundance in the troposphere. The albedo of the surface at 5 μm is determined to be 0.07±0.02. This is compatible with ice–mineral mixtures similar to those found on the icy Galilean satellites or with a surface covered by solid organic precipitates.

ACKNOWLEDGMENTS

We thank Ted Roush for sharing his calculations of the reflectance spectrum of Titan tholins. This research was supported by Grant NAGW-3392 to the Space Telescope Science Institute and by Grant NAGW-3415 at Penn State Erie from the NASA Planetary Astronomy program. The United Kingdom Infrared Telescope is operated by the Joint Astronomy Centre on behalf of the U. K. Particle Physics and Astronomy Research Council. We thank the staff of UKIRT for its support.

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