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MONODEUTERATED METHANE IN THE OUTER SOLAR SYSTEM

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III. ITS ABUNDANCE ON TITAN

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ABSTRACT

The $3\nu_2$ band of CH_3D has been detected in spectra of Titan recorded at $1.6 \mu\text{m}$ with the Fourier Transform Spectrometer (FTS) at the 4 m telescope of the Kitt Peak National Observatory (NOAO). We have obtained a value of the $\text{CH}_3\text{D}/\text{CH}_4$ mixing ratio of $6.6_{-3.3}^{+6.6} \times 10^{-4}$ from a comparison between the observed Titan spectra and synthetic spectra. This value is ~ 2 times higher than the value measured on Uranus (de Bergh *et al.* 1986) and ~ 6 times higher than on Jupiter and on Saturn (Courtin *et al.* 1984; de Bergh *et al.* 1986). It corresponds to D/H of $1.65_{-0.8}^{+1.65} \times 10^{-4}$, nominally 8 times higher than the most commonly accepted value for the protosolar D/H = 2×10^{-5} (Geiss and Reeves 1981). The value we find on Titan for D/H in methane is comparable to the D/H ratio measured in terrestrial H_2O .

I. INTRODUCTION

The study of CH_3D on Titan presented here is the third in a series of investigations of the $3\nu_2$ band of this molecule in spectra of the outer planets. Lutz *et al.* (1981) reported the probable detection of this band in the spectrum of Uranus. Paper II (de Bergh *et al.* 1986) gave an analysis of the Uranus absorptions, leading to a value of $\text{CH}_3\text{D}/\text{CH}_4 = 3.6_{-1.8}^{+3.6} \times 10^{-4}$.

In 1975, there was a tentative detection of CH_3D on Titan at $8.6 \mu\text{m}$ by Gillett (1975). In 1981, the analysis of *Voyager* spectra at $8.6 \mu\text{m}$ revealed the presence of C_3H_8 emissions at the same wavelength as those of the presumed CH_3D band. Hanel *et al.* (1981) suggested that perhaps there was no contribution of CH_3D to

the emission observed in the *Voyager* spectra at that wavelength. Subsequently Kim and Caldwell (1982) made a more extensive analysis of *Voyager* spectra and evaluated the relative contributions of C_3H_8 and CH_3D to the $8.6 \mu m$ emission by using an emission feature of C_3H_8 at $13.4 \mu m$ for comparison. They obtained a CH_3D/CH_4 ratio of 1.7×10^{-3} .

At about the same time, we reported the detection of absorptions from the $3\nu_2$ band of monodeuterated methane in FTS spectra of Titan recorded in the $1.6 \mu m$ region at KPNO with a spectral resolution of 2 cm^{-1} (de Bergh *et al.* 1981). Our preliminary measurements provided values of the CH_3D/CH_4 ratio that were about ten times lower than the value of Kim and Caldwell (1982). Since then, Kim and Caldwell (private communication) have revised their original estimate downward, and we have recorded new spectra of Titan with an improved spectral resolution and made a correction for a numerical error in the CH_3D partition function that we had used previously (Paper II). The spectrum used in this analysis is the same as the one in which CO was discovered in Titan's atmosphere (Lutz, de Bergh, and Owen 1983). Here we present the results of our analysis of the CH_3D absorption in these spectra.

II. PLANETARY OBSERVATIONS

The set of observations from which the present measurements have been derived consists of spectra of Titan recorded with the FTS at the 4 m Mayall telescope of KPNO for time blocks of about one hour each during the nights of U.T. 1982 June 2-7 with an unapodized FWHM resolution of 1.2 cm^{-1} . We used a circular

aperture 3.75" in diameter. Several spectra have been coadded for the total effective integration time of 7.5 hours, corresponding to a total signal-to-noise ratio of 40:1 (S/σ). In addition, a spectrum of diffused solar radiation was recorded at the same spectral resolution during the same observing run in order to evaluate the contribution from terrestrial and solar absorptions in the Titan spectra.

The spectra cover a usable spectral range of 6100–6700 cm^{-1} , but the present analysis is restricted to 6413–6483 cm^{-1} . Since there was little or no contribution from telluric absorption, the coadded spectrum of Titan could simply be divided by the Doppler-shifted solar spectrum to remove all extraneous lines.

III. ATMOSPHERIC MODEL FOR TITAN

We first computed synthetic spectra of Titan which included only CH_4 absorptions. We searched for atmospheric models that would provide a reasonable agreement with the observations of these CH_4 features. The synthetic spectra of Titan included the 610 lines of CH_4 detected in our laboratory spectra. The intensity measurements for these lines and the "rotational assignments" are the same as the ones which were used to generate the spectra of Uranus (Paper II). The pressure-broadening coefficients for the CH_4 - N_2 collisions were assumed to be 0.064 $\text{cm}^{-1}/\text{atm}$ for all CH_4 lines with a temperature dependence of T^{-1} (Varanasi, Giver, and Valero 1983a). Since no region in the Titan spectrum is entirely devoid of absorptions, the definition of the continuum level in the observed spectrum is difficult and somewhat subjective. In each of our spectra we defined the continuum level as the minimum level above the region of the weak absorption near 6345 cm^{-1} that

provided a best fit between the computed and observed spectra.

In our search for the simplest atmospheric model that would best reproduce the observed spectrum, we found that neither a clear atmosphere above a reflecting layer, nor a homogeneous scattering atmosphere, would provide a satisfactory agreement at $1.6 \mu\text{m}$. Assuming a continuum albedo of 0.7 (Fink and Larson 1979), we obtained a best fit for isothermal, uniform-pressure models with an isotropically scattering cloud layer of optical thickness $\tau = 0.23$ in an otherwise clear atmosphere. No CH_4 was required above the cloud layer. CH_4 absorptions are quite broad and tend to favor atmospheric models in which the average pressure is on the order of 0.7 atm or more. The best agreement between synthetic and observed spectra was obtained with an integrated methane column abundance of 2200 m-amagat at an "average" temperature of 85 K in the atmosphere between the cloud layer and the reflecting surface. For comparison, the methane column abundance derived by Fink and Larson (1979) from the integrated band absorptions at 6400 and 7900 cm^{-1} under the assumption of a clear reflecting layer model is 1700 ± 400 m-amagat.

We also computed synthetic spectra for models in which the pressure and temperature were allowed to vary with altitude. As in the case of the constant temperature and pressure models, we used various cloud properties and methane abundances. The partial pressure of methane was constrained at each atmospheric level by its saturated vapor pressure. The temperature-pressure structure we assumed is the one derived from the *Voyager* observations by Lindal *et al.* (1983). Whatever percentage of CH_4 was used, the line profiles in the synthetic spectra were

always much shallower than the observed ones. We found that this effect was caused by the absorption which occurs above the methane condensation level; i.e., a part of the atmosphere that we assumed free of any particles that scatter significantly at $1.6 \mu\text{m}$. Allowing for subsaturation of CH_4 above the condensation level does improve the fit with the observations. The less CH_4 we assume above that altitude level, the better is the agreement. However, we know that a minimum amount of CH_4 must be present above the condensation level, since it was detected in emission at $8 \mu\text{m}$ by the *Voyager* IRIS experiment (Hanel *et al.* 1981). Furthermore, its presence is required by the observation of hydrocarbons produced by methane photochemistry in the satellite's upper atmosphere (Strobel 1982). Therefore, it is probably necessary to assume not only subsaturation of methane above the methane cloud, but also the possibility of an even more complex altitude distribution for the scattering particles throughout the atmosphere.

A more thorough study of various scattering models with different vertical distributions of CH_4 and of scattering particles must be undertaken. For such a study, it will be extremely useful to investigate also the profiles of the CO lines which we detected in the same Titan spectrum (Lutz, de Bergh, and Owen 1983). This simultaneous study of two constituents of the Titan troposphere, one with a uniform vertical distribution (CO) and the other with a nonuniform distribution (CH_4), should be most informative.

Independent of the true structure of the atmosphere, the line formation processes for CH_4 and CH_3D and their respective vertical distributions must be very

similar. Consequently, a $\text{CH}_3\text{D}/\text{CH}_4$ mixing ratio derived from the absorptions of these two gases is relatively insensitive to any adopted atmospheric model. In practice, however, it is also important that the absorptions of the two gases are in adjacent spectral regions so that a common continuum level can be adopted for both, as is the case here. Thus it is sufficient to optimize the fit for methane alone, and then to adjust the $\text{CH}_3\text{D}/\text{CH}_4$ mixing ratio (as is discussed in the next section) until a good agreement between observed and synthetic spectra is obtained in the spectral range where the absorptions occur. We have indeed verified by calculation that different atmospheric models which provide reasonable fits with the observed Titan spectrum lead to the same D/H ratio, regardless of the differences among the models. Of the various models we have studied so far, the one that provides the best agreement with the observed CH_4 absorptions in the Titan spectrum is actually the simplest one described above: a single cloud with constant pressure and temperature between the cloud and the surface, with no CH_4 above the cloud. The synthetic spectrum of Titan shown in Figure 1 is based on this model.

IV. MEASUREMENTS OF THE $\text{CH}_3\text{D}/\text{CH}_4$ RATIO

As in the case of Uranus (see Paper II), CH_4 alone could not provide a satisfactory fit with the spectrum of Titan near 6427 and 6452 cm^{-1} in any of the atmospheric models considered. These are the regions of the Q-branch and R2 manifold, respectively, of the $3\nu_2$ band of CH_3D . We therefore computed synthetic spectra corresponding to different $\text{CH}_3\text{D}/\text{CH}_4$ ratios, using the rotational assignments for the $3\nu_2$ band worked out by Lutz, de Bergh, and Maillard (1983) and the

same line intensities used in paper II. The mean $\text{CH}_3\text{D}-\text{N}_2$ pressure-broadening coefficient was assumed to be the same as that adopted for CH_4-N_2 . This assumption is supported by our own preliminary laboratory measurements. The temperature dependence of this coefficient was also assumed to be T^{-1} (Varanasi, Giver, and Valero 1983b). With our single cloud model, we find the best fit to the observed Titan spectrum for a mixing ratio of $\text{CH}_3\text{D}/\text{CH}_4 = 6.6 \times 10^{-4}$, and this fit is shown in Figure 1.

The major sources of uncertainty in this determination lie in the line intensities and broadening coefficients for the CH_4 and CH_3D lines, in the rotational assignments for the lines of CH_4 (see Paper II), and in the placement of the continuum level for the Titan spectrum and the choice of an appropriate atmospheric model. Another source of uncertainty is the difficulty we have in accounting for extremely weak lines of methane that are undetectable in our room-temperature laboratory spectra. These lines nevertheless contribute to the absorptions observed in the spectrum of Saturn (see Paper II) and must, therefore, also contribute to the absorptions in the spectra of Titan. Given all the uncertainties listed above, we believe that we have measured the $\text{CH}_3\text{D}/\text{CH}_4$ ratio on Titan to within a factor of 2.

We have found that the wavelength ranges where the fits between observed and synthetic spectra of Titan are not very good ($6433\text{--}6450\text{ cm}^{-1}$, for instance) are the same as the ranges where the fits between the observed and synthetic spectra of Uranus and of Saturn are not very good. This gives us some hope that we will be able to improve the precision of our CH_3D abundance measurements on Titan

(and also on Uranus and Saturn) when we have a better knowledge of the extremely weak CH_4 absorptions. This knowledge should be achievable by studying very high signal-to-noise ratio laboratory spectra of methane obtained at low temperatures with very long optical paths, if and when such data become available.

V. DISCUSSION

The value of D/H in Titan's atmosphere is derived directly from the $\text{CH}_3\text{D}/\text{CH}_4$ ratio using the stoichiometric relationship:

$$\text{D}/\text{H} = \frac{1}{4}[\text{CH}_3\text{D}/\text{CH}_4] = 1.65_{-0.8}^{+1.65} \times 10^{-4}.$$

This ratio is distinctly higher than the range of values measured on Jupiter and Saturn, $\text{D}/\text{H} = (0.6 - 5.0) \times 10^{-5}$ (Owen, Lutz, and de Bergh 1986). Uranus represents an intermediate case with a range of $\text{D}/\text{H} = (4.5 - 18) \times 10^{-5}$ (de Bergh *et al.* 1986). All of these values are based on ratios of $\text{CH}_3\text{D}/\text{CH}_4$. The situation for HD/H_2 is not yet well defined. Published measurements (for a summary, see Table 2 of de Bergh *et al.* 1986, and the discussion therein), as well as new measurements (Smith, Schempp, and Macy 1987) suggest that on Jupiter and Saturn the D/H ratios derived from this abundance ratio are systematically higher compared with the values derived from $\text{CH}_3\text{D}/\text{CH}_4$. We have proposed that part of this apparent discrepancy may be traceable to contamination by very weak methane absorptions in the regions of the HD lines (Owen, Lutz, and de Bergh 1986), and preliminary laboratory studies by Smith (private communication) seem to support this possibility.

The only other determination of D/H on Titan was made by Kim and Caldwell (1982), using the ν_6 band of CH_3D at $8.6 \mu\text{m}$ by the *Voyager* IRIS instrument (Hanel

et al. 1981). At this wavelength the spectrum is formed predominantly in Titan's stratosphere. Deriving a mixing ratio for $\text{CH}_4/\text{N}_2 = 3.6 \pm 1.1 \times 10^{-2}$, they found $\text{CH}_3\text{D}/\text{CH}_4 = 1.7 \times 10^{-3}$ and $\text{D}/\text{H} = 4_{-1.5}^{+2} \times 10^{-4}$. Subsequent to their analysis, a new temperature-pressure profile for Titan's atmosphere was published by Lindal *et al.* (1983) and new broadening coefficients for ν_6 of CH_3D were obtained by Varanasi, Giver, and Valero (1983c). The net effect of these two changes, plus a small error in their computer code, reduces their original estimate of D/H by about a factor of 2 (Kim and Caldwell, private communication). Their work is thus actually in good agreement with the determination we have made using a completely different band, in absorption instead of emission.

We have discussed the general problem of deuterium abundance in the outer solar system elsewhere in more detail (Paper II and Owen, Lutz, and de Bergh 1986). We agree with Kim and Caldwell (1982) that the enrichment of D/H on Titan must have occurred prior to the formation of the satellite. We believe that Pinto *et al.* (1986) provide quantitative support for this conclusion. They found that all the processes acting to increase the value of $\text{CH}_3\text{D}/\text{CH}_4$ during the evolution of the planet's atmosphere could only achieve an enrichment of 2.2 times the original value. Another factor of 2 may be possible through 500 K catalysis on metallic grains in the proto-Saturnian nebula prior to Titan's formation. This process seems unlikely and in any case fails to produce the observed ratio except for the lower range in the error bars.

Our general conclusion is that bodies in the outer solar system had access

to at least two distinct reservoirs of deuterium: one in hydrogen gas and one in methane frozen on or trapped in solid material. Water and other hydrogen-containing compounds constitute additional reservoirs, depending on how closely the value of D/H which we have measured in primitive ice agrees with the D/H in Titan's atmosphere when the latter is corrected for the possible enrichment by a factor of about 2 that may have occurred since the satellite formed (Pinto *et al.* 1986) and for possible dilution with equilibrated methane in the proto-Saturnian nebula (Prinn and Fegley 1981). The fact that D/H on Titan is so close to the value of 1.5×10^4 found in standard mean ocean water (SMOW) [which may also be enriched by about a factor 2 through several escape processes (Hunten, private communication)] suggests that the primordial methane and water reservoirs may actually have very similar deuterium-to-hydrogen ratios.

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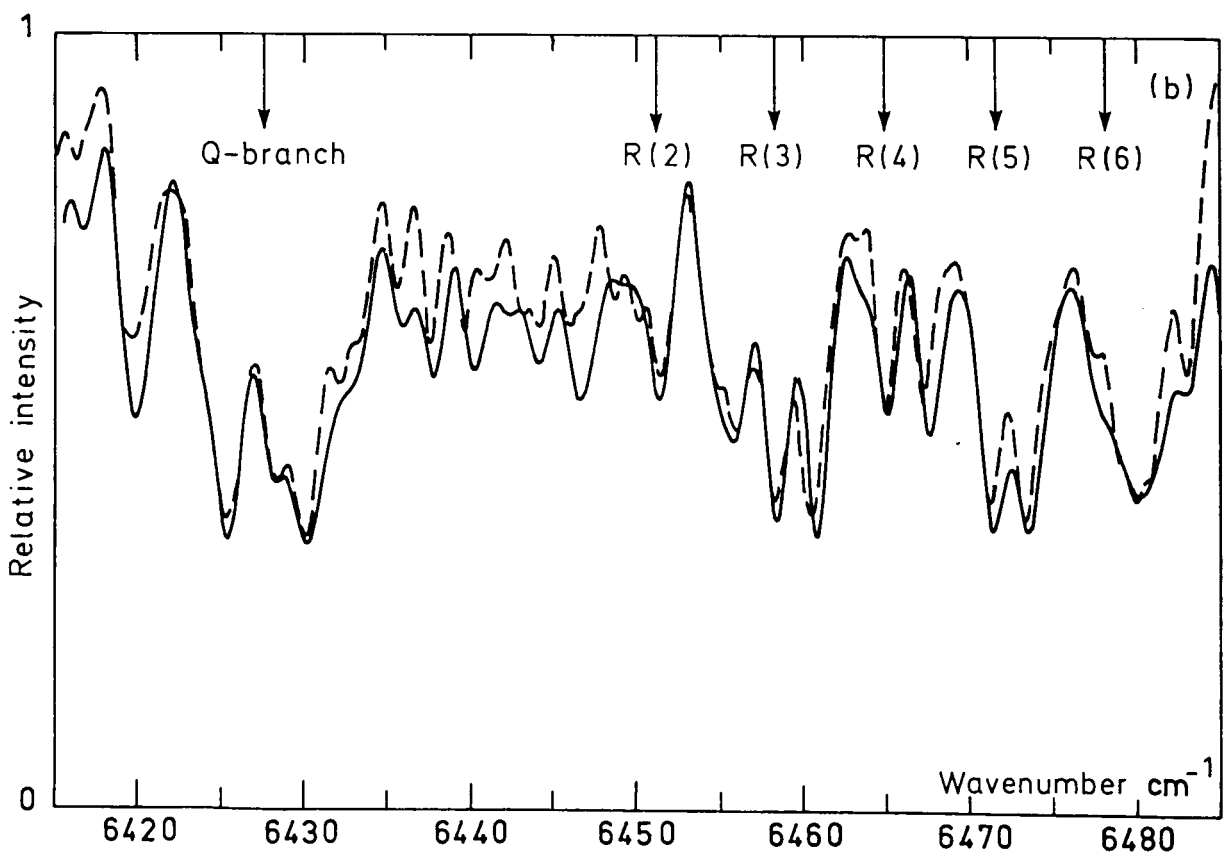
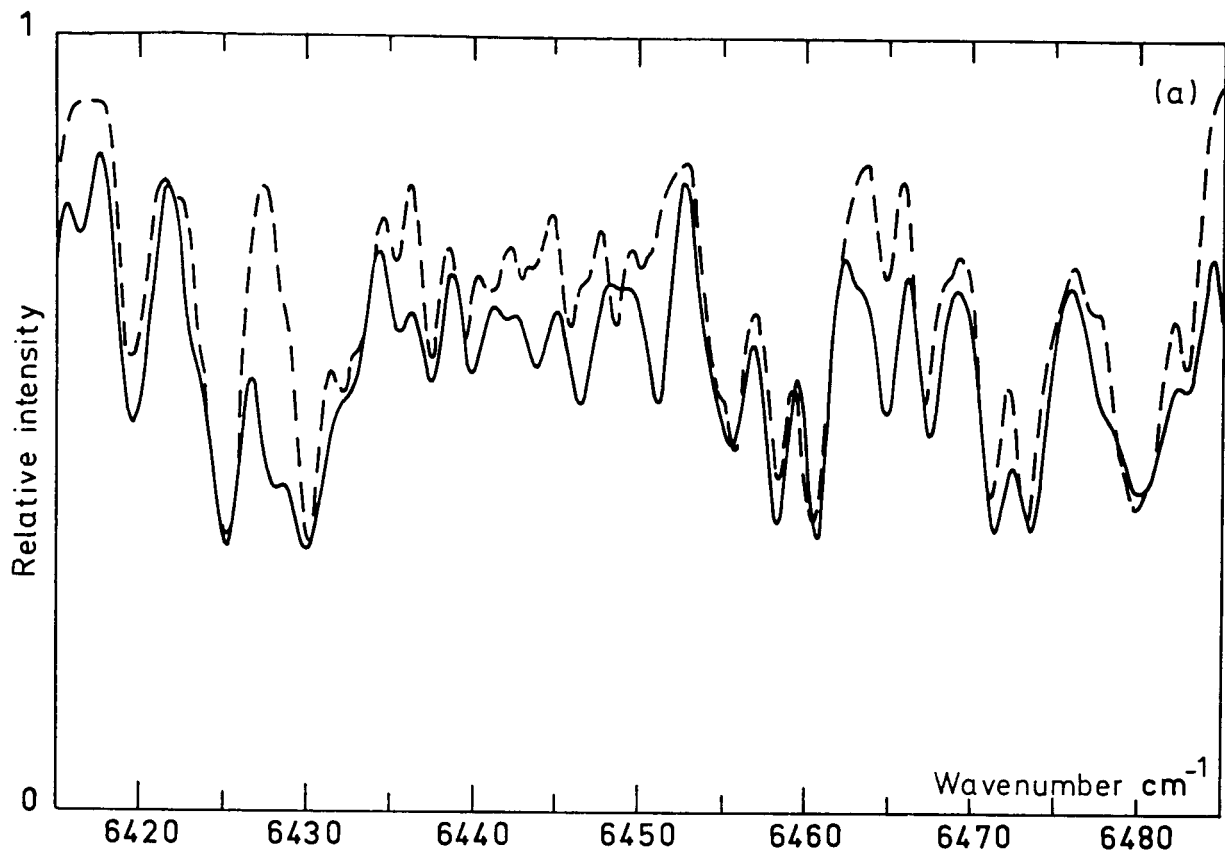
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FIGURE CAPTION

Figure 1. Comparison between observed and synthetic Titan spectra. (a) and (b) Full line: Spectrum of Titan recorded in 1982 June at Kitt Peak National Observatory (NOAO) with the FTS at the 4-m telescope (spectral resolution: 1.2 cm^{-1} , S/N: 40). This spectrum has been divided by the spectrum of diffuse solar radiation recorded during the same run.

(a) Dashed line: Synthetic spectrum of Titan computed as explained in the text for only CH_4 absorptions, based on our nominal atmospheric model (a temperature of 85 K, and a total methane abundance of 2.2 km-atm, at an average pressure of 1 atm, between a cloud layer of optical thickness $\tau = 0.23$ and the surface; no CH_4 above the cloud).

(b) Dashed line: Synthetic spectrum of Titan as shown in (a) but with CH_3D absorptions included: $\text{CH}_3\text{D}/\text{CH}_4 = 6.6 \times 10^{-4}$. The regions of the main $\text{CH}_3\text{D}-3\nu_2$ absorptions are indicated at the top of the figure.



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