ON THE POSSIBLE DETECTION OF CH$_3$D ON TITAN AND URANUS

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ABSTRACT

Based on the analysis of a new band of CH$_3$D near 6425 cm$^{-1}$, possible identification of it in Fink and Larson's (1979) spectra of Titan and Uranus is proposed.


I. INTRODUCTION

Although its relationship to the D/H ratio is clouded by the deep atmosphere chemistry which determines fractionation processes, monodeuterated methane, CH$_3$D, has been a successful tool in detecting the presence of deuterium on Jupiter (Beer and Taylor 1978), on Saturn (Fink and Larson 1978), and possibly on Titan (Gillett 1975).

Previous observations of CH$_3$D have been confined to studies of the $v_2$ fundamental band centered near 2200 cm$^{-1}$ and to the $v_6$ vibration centered near 1161 cm$^{-1}$. The molecular properties of $v_2$ and $v_6$ have been quite well studied in the laboratory (Tarrago et al. 1976; Pinkley et al. 1977; Sarangi and Varanasi 1975), but other known transitions have not been nearly so well studied.

II. OBSERVATIONS AND RESULTS

We are involved in an intensive laboratory program, surveying the spectrum of CH$_3$D from the visible into the far-infrared (Lutz, de Bergh, and Maillard 1981; Danehy et al. 1977; Lutz, Danehy, and Ramsay 1978; Lutz et al. 1981) under various pressure path length and temperature conditions.

In addition to those announced previously in the near-infrared (Danehy et al. 1977), we have found three new, simple, and apparently parallel bands. One of them, centered near 6425 cm$^{-1}$ and possibly associated with the second overtone of the C-D stretch $v_2$, is ideally situated in the 1.6 $\mu$m window of the outer planets. Lutz, de Bergh, and Maillard (1981) have carried out a rotational analysis of this band up to $J = 12$, and we have determined the line strengths of many of the component ($J, K$) lines from a single spectrum recorded at room temperature at a pressure of 10 torr and for a path length of 64 m.

Fink and Larson (1979) have recorded new interferometric spectra of Saturn, Titan, and Uranus near 1.6 $\mu$m (6400 cm$^{-1}$) at a nominal resolution of 3.6 cm$^{-1}$, reproduced here as Figure 1.

One of the features Fink and Larson used to probe the CH$_4$ content of the outer planet atmospheres was the absorption near 6400 cm$^{-1}$ which they ascribed to a new CH$_4$ band. Since we had measured line strengths as high as $7 \times 10^4$ cm$^{-1}$ m-amagat$^{-1}$ for several of the CH$_3$D lines near 6425 cm$^{-1}$, it occurred to us that, even in cosmic abundance, the previously unknown and strong 6425 cm$^{-1}$ band of CH$_3$D could significantly compete with the very weak methane absorption in that region and thus confuse the interpretation of the planetary spectra, as well as the laboratory measurements. It also seemed possible that the strong differences between the laboratory spectrum and that of Titan and of Uranus seen near 6425 cm$^{-1}$ may not purely be caused by temperature effects of the methane spectrum but could be evidence of CH$_3$D in the atmospheres of these outer solar system objects. No other molecule seemed to be as likely a candidate, based on the near-infrared survey of possible constituents of outer planet atmospheres by Fink and Larson (1978).

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We have studied the weak absorptions of laboratory methane in this region and identified the lines of the 6425 cm$^{-1}$ band of CH$_3$D in natural abundance. Figure 2 shows a short section of the spectrum of CH$_4$ obtained at Kitt Peak with a total column density of 7.93 m-amagat (15 torr, 434 m at 295 K) with assignments for the Q-branch lines according to the analysis of Lutz, de Bergh, and Maillard (1981). Based on the line strengths for the CH$_3$D band determined from the Meudon spectrum, we have deduced a normal CH$_3$D/CH$_4$ mixing ratio of $5(\pm 1) \times 10^{-4}$ in terrestrial methane.

Our terrestrial mixing ratios are in agreement with values obtained using mass spectroscopic techniques. At our request, the Gollob Analytical Service and M. Javoy at the Université de Paris have determined mixing ratios of $6 \times 10^{-4}$ and $5.5 \times 10^{-4}$, respectively, on different samples. Although the precision of these mass spectroscopic measurements is high, we estimate the accuracy of the mixing ratios to be about $\pm 20\%$ because of the uncertainty in the equilibrium distribution of the deuterium in the samples.

III. CALCULATIONS AND CONCLUSIONS

We have combined the results of these astronomical and laboratory observations to form the basis of two conclusions:

1. Based on the measurements of the natural abundance ratio of CH$_3$D to CH$_4$ and on the estimated band strength of about 4.4 cm$^{-1}$ m-amagat$^{-1}$ for the 6425 cm$^{-1}$ band of CH$_3$D, it appears that within the region considered by Fink and Larson (1979), in their estimate of the CH$_4$ absorption strength in their laboratory spectrum, approximately 15% is due to CH$_3$D. At their
Fig. 2.—Interferometric spectrum of 7.98 m-amagat CH$_4$ in the region of the 6425 cm$^{-1}$ band of CH$_3$D, recorded at Kitt Peak National Observatory. This spectrum, obtained at room temperature with 15 torr CH$_4$ at a path length of 434 m, shows only the top 13% of the intensity scale. CH$_3$D in its natural abundance is noted with rotational assignments according to Lutz, de Bergh, and Maillard (1981). The resolution of this spectrum is 0.009 cm$^{-1}$, with an obtained signal-to-noise ratio of about 2000:1.

resolution, this contribution would be difficult to detect because of broad rotational distribution of this band of CH$_3$D at room temperature.

2. A very strong absorption is seen in Fink and Larson's spectra of Titan and Uranus near the position of the $Q$-branch of the 6425 cm$^{-1}$ band of CH$_3$D. Because of the similarity of the rotational constants of the upper and lower levels of this band, the $Q$-branch is quite closely packed and, at the resolution obtained by Fink and Larson, would appear very strongly enhanced relative to the $P$- and $R$-branches. Indeed, at 100 K it would correspond to a single, very strong absorption at 6427.5 cm$^{-1}$. This apparent $Q$-branch feature is not obvious either in their laboratory spectrum because of the much higher rotational temperature or in their Saturnian spectrum because of the much lower column density. In Figure 1 we have sketched the relative distribution of the rotational branches for a temperature of 100 K and a resolution of 3.6 cm$^{-1}$ to illustrate the case for Titan and Uranus.

That the increase in absorption in Titan and Uranus is probably due to CH$_3$D rather than to a pure temperature effect in CH$_4$ is further consistent with the much higher resolution spectrum of Saturn obtained some years ago by Connes and Maillard (1974). Using the scattering model of Buriez and de Bergh (1981), we have constructed high-resolution (0.2 cm$^{-1}$) synthetic spectra of Saturn for this region and find that agreement with the Connes-Maillard spectrum is obtained only if most of the unassigned lines of CH$_4$, seen for example in Figure 2, have high $J$-values.

In Figure 3 we show four synthetic spectra of Uranus at a resolution of 3.6 cm$^{-1}$, based on a clear reflecting-layer model for the atmosphere and using intensity measurements of the CH$_4$ lines obtained from several spectra recorded at Kitt Peak. The temperature dependence of the CH$_4$ lines has been deduced from a comparison between synthetic spectra of Saturn and the Connes-Maillard Saturn spectrum.

In the two Uranus synthetic spectra (Fig. 3a), we illustrate the strong temperature effects by comparing pure CH$_4$ absorption at two temperatures ($T = 295$ and 80 K). In Figure 3b we illustrate the effect of CH$_3$D in the atmosphere at a temperature of 80 K by comparing the pure CH$_4$ case with that assuming a CH$_3$D/CH$_4$ mixing ratio of $9 \times 10^{-5}$, corresponding to the canonical interstellar D/H ratio, if the CH$_3$D is not enhanced by fractionation (i.e., a lower limit to the CH$_3$D/CH$_4$ ratio). We have not attempted to match the spectrum of Fink and Larson (1979) because the simplicity of the
model and the complexity of properly accounting for all the very weak absorption in this region make such a detailed comparison very difficult. Rather, we wish to show that CH$_3$D is expected to have a strong influence on the absorption spectrum even at unenhanced levels, and that a search for it at appropriate resolutions and signal to noise should be rewarding.

Confirmation of our proposed identifications of CH$_3$D in Fink and Larson's spectra of Titan and Uranus must await new high-resolution, high signal-to-noise spectra of them; but in the meantime, it is quite clear that a simultaneous study of the CH$_3$D and the weak CH$_4$ lines in this region will lead directly to scattering-independent estimates of the CH$_3$D/CH$_4$ mixing ratios in the outer planets.

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