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INTERSTELLAR H_3^+: POSSIBLE DETECTION OF THE $1_{10} \rightarrow 1_{11}$ TRANSITION OF H_2D^+

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ABSTRACT

An interstellar line has been detected in emission at the expected submillimeter wavelength of the $1_{10} \rightarrow 1_{11}$ transition of H_2D^+, the deuterated version of the primary ion (H_3^+) in the favored ion-molecule reaction scheme for interstellar gas phase chemistry. The strength of the line is in approximate agreement with the theoretically anticipated H_2D^+ abundance.

Subject headings: deuterium — interstellar: molecules — molecular processes

I. INTRODUCTION

Since the introduction of the theoretical concept of ion-molecule gas phase reaction chemistry (Herbst and Klemperer 1973; Dalgarno, Oppenheimer, and Berry 1973; Watson 1973) to explain the high molecular abundances in the interstellar medium (ISM), it has been clear that the critically important species is the transient molecular ion H_3^+. The high degree of symmetry of H_3^+ means that there are no strongly allowed rotational transitions which can be observed to determine its fractional abundance, which is believed to be about (1–5) $\times$ $10^{-5}/n_{H_2}$ for clouds of density n_{H_2} cm^{-3} (Prasad and Huntress 1980; Leung, Herbst, and Huebner 1984). However, with the detection of DCN (Jefferts, Penzias, and Wilson 1973), the deuterium-substituted version of HCN, it was recognized that deuterated species were much more easily detected than had been anticipated from the cosmic [H]/[D] ratios. It was pointed out by Dalgarno *et al.* (1973) that H_2D^+ possessed a significant electric dipole moment and that some transitions would be accessible. An effort was therefore mounted to detect the electric dipole allowed rotational transitions of H_2D^+. Some early searches (Angerhofer, Churchwell, and Porter 1978; Phillips *et al.* 1978) were based on a theoretical calculation of the isotopically substituted structure of H_3^+ (Carney and Porter 1974). In particular, the search of Phillips *et al.* (1978) was for the same $1_{10} \rightarrow 1_{11}$ transition reported here; but the theoretical frequencies were not accurate enough to allow a detection at that time, given the limitations of the detection equipment and the problems of observing through a relatively opaque Earth's atmosphere.

Recently, several advances have been made. The theoretical calculation of the H_3^+ and H_2D^+ structures have improved (Carney 1980), and for the first time the detection of their IR spectra became possible (Oka 1980; Amano 1984). The molecular constants of the latter work have made practical a direct laboratory detection of the $1_{11} \rightarrow 1_{10}$ transition by Bogey *et al.* (1984) and by Warner *et al.* (1984), using the magnetic field–enhanced glow discharge technique developed by De Lucia *et al.* (1983). This work provides a precise rest frequency of 372.4213 GHz. Further, the NASA Kuiper Airborne Observatory is available to provide a platform for a telescope well above the bulk of the water vapor in the atmosphere, and the InSb heterodyne receiver used previously by Phillips *et al.* (1978) is now considerably improved. Last, there has been much theoretical and observational work on the deuterium fractionation in interstellar molecules. It has been shown that the ion-molecule reactions

$$H_3^+ + HD \leftrightarrows H_2D^+ + H_2$$

lead to strong enhancement of H_2D^+ and subsequently DCO^+. The work on DCO^+ (Hollis *et al.* 1976; Watson 1976; Wootten, Loren, and Snell 1982; Guélin, Langer, and Wilson 1982; Herbst 1982) has provided much needed information on the likely degree of deuteration of H_3^+ as a function of position within molecular clouds, so indicating the regions to be searched for H_2D^+.

II. OBSERVATIONS

The observations were carried out from the NASA Kuiper Airborne Observatory on the nights of 1985 January 4 and 7. The 91.5 cm telescope provided a diffraction-limited beamwidth of 3′.7. The InSb receiver is similar to that described by Phillips and Jefferts (1974), and provided a noise temperature of about 200 K. The main-beam efficiency was about 55%, as measured by observations of the Moon.

Because of the observing constraints, only two objects were searched sufficiently well to provide meaningful results in terms of the anticipated H_2D^+ line strengths. These were the molecular cloud core regions of NGC 2264 and TMC-1, which were selected on the basis of the DCO^+ observations of

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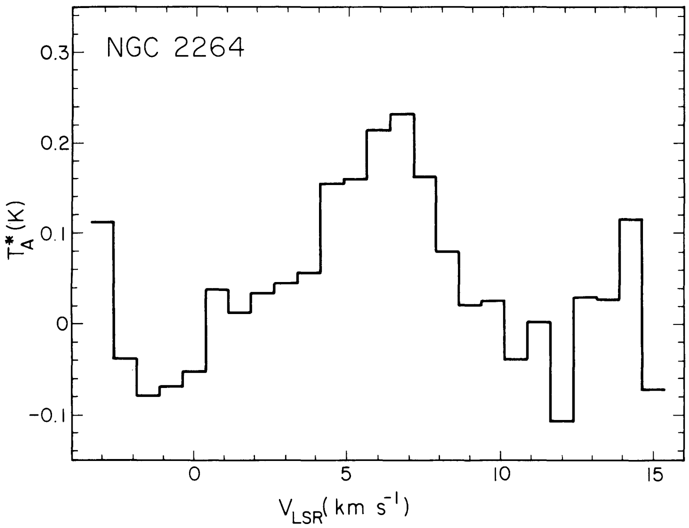

FIG. 1*a*

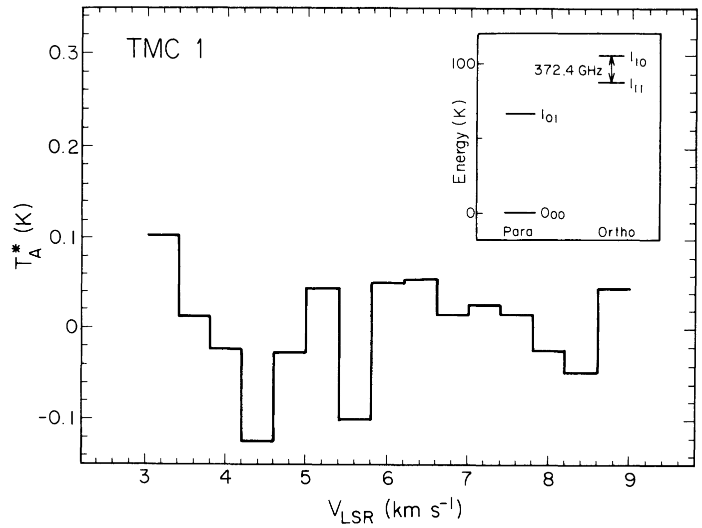

FIG. 1*b*

FIG. 1.—(*a*) A spectrum taken in the vicinity of the H_2D^+ line, toward the molecular cloud NGC 2264. The velocity scale has been established using a rest frequency of 372.4213 GHz. Individual channels are spaced by 0.75 km s^{-1}. (*b*) A spectrum taken in the vicinity of the H_2D^+ line, toward TMC-1. Channels are spaced by 0.4 km s^{-1}. Inset is the energy-level diagram for the lower lying H_2D^+ transitions.

Wootten, Loren, and Snell (1982) and Guélin, Langer, and Wilson (1982). Spectra were taken by sweeping the klystron local oscillator under computer control and by alternating integrations on-source with those located 12′ east and west of the source for NGC 2264 and 10′ northeast of the DCO^+ peak for TMC-1. The positions observed corresponded to the NGC 2264 (0,0) position of Guélin, Langer, and Wilson (1982), $\alpha = 6^h38^m25^s$, $\delta = 9°32'29''$ (1950.0), and their TMC-1 $(-5, 7)$ position, $\alpha = 4^h38^m15\overset{s}{.}8$, $\delta = 25°42'45''$ (1950.0).

Observed spectra are shown in Figure 1. For NGC 2264 a line is detected at a strength of 230 mK for T_A^*, where the antenna temperature has been corrected for losses in the telescope, residual atmospheric opacity, and the beam efficiency. The feature was observed in the spectra taken in each of two separate flights. For TMC-1 no line is detected, and an upper limit (2σ) of about 120 mK is estimated. The spectral resolution is 0.75 km s^{-1} for NGC 2264 and 0.4 km s^{-1} for TMC-1.

Assuming a line frequency of 372.4213 GHz gives a line central velocity of about 6.5 km s^{-1} in NGC 2264. This is agreement with the DCO^+ $(1 \to 0)$ spectrum of Guélin, Langer, and Wilson (1982), which is centered in the 6–7 km s^{-1} range. The line width here is about 3.8 km s^{-1} which is comparable to the DCO^+ $(1 \to 0)$ line width of about 3.2 km s^{-1}. The telescope beamwidth here is about 3′.7, as compared with 2′.5 for the DCO^+ $(1 \to 0)$ data, so a slightly larger region is being sampled.

III. DISCUSSION

The ion-molecule reaction mentioned above provides strong deuteration only when the cloud kinetic temperature is below about 30 K (Watson 1976; Herbst 1982; Smith, Adams, and Alge 1982), so that cool, dense clouds are favored. However, the 1_{10} energy level must be populated for the $1_{10} \to 1_{11}$ transition to be seen in emission.

The excitation of the 1_{10} level in interstellar clouds may be significantly affected by the presence of the two equivalent hydrogen nuclei in H_2D^+, which produce radiatively noninteracting rotational ladders of ortho and para states, just as for H_2CO (see Fig. 1*b*). The 1_{11} level is the ground state of ortho-H_2D^+ and therefore has no radiative transition to any para state, including the true rotational ground state, 0_{00}. To what extent can the relative ortho-para populations be affected by collisions of various kinds?

Weak (nonreactive) collisions have "selection rules" which are quite similar to those of radiative transitions and serve mainly to produce thermal or quasi-thermal populations *within* a given symmetry state. However, strong (reactive) collisions involving H_2 and H_2D^+, in which equivalent hydrogen nuclei may be exchanged, can be quite efficient at interconverting the ortho and para states, thereby producing a truly thermal or quasi-thermal population distribution *across* the two symmetry species. In this case the 1_{10} level is about 100 K above the ground state, making the $1_{10} \to 1_{11}$ transition extremely difficult to observe in cold clouds where deuteration is strongest. Of course, thermalization would make higher transitions such as the $2_{20} \to 2_{21}$ at 156 GHz (recently measured in the lab by Saito, Kawaguchi, and Hirota 1985) virtually unobservable. If there is no interconversion between the ortho and para states the 1_{10} level is only 18 K above its effective ground state, the metastable 1_{11} level, and the $1_{10} \to 1_{11}$ transition should be observable even in cold clouds. In addition to the collisional relaxation question, one should also consider the nascent distribution of H_2D^+ among the various quantum states. The resolution of these and other complex questions of interstellar chemistry (such as the ortho/para status of H_2) which impact

TABLE 1

DEDUCED ABUNDANCES

	$N(H_2D^+)(cm^{-2})$	$n(H_2D^+)/n(H_2)$	$n(H_3^+)/n(H_2)$
Thermal:			
NGC 2264 ...	3.1×10^{13}	1.1×10^{-10}	2.3×10^{-9}
TMC-1	$< 6.0 \times 10^{14}$	$< 3.0 \times 10^{-8}$	$< 5.6 \times 10^{-8}$
Statistical:			
NGC 2264 ...	9.3×10^{12}	3.1×10^{-11}	6.7×10^{-10}
TMC-1	$< 1.3 \times 10^{12}$	$< 6.9 \times 10^{-11}$	$< 1.3 \times 10^{-10}$

on the interpretation of these data, is beyond the scope of this *Letter*. Some of these problems will be discussed in a separate paper (Blake *et al.* 1985).

We will try to analyze the data of these observations by means of two alternative assumptions: first, that the H_2D^+ has a "normal" or statistical ortho/para ratio independent of the cloud kinetic temperature, and, second, that this ratio is thermal. Using these assumptions, we estimate that the observations lead to the column densities and the abundances, relative to H_2, for H_2D^+ listed in Table 1. The H_3^+ abundance is deduced from that for H_2D^+ by means of the calculation and assumptions given by Herbst (1982), who, together with Smith, Adams, and Alge (1982), has addressed in detail the problem of deuterium fractionation in clouds of various temperatures. We note that this procedure reproduces the observed DCO^+/HCO^+ ratios in NGC 2264 and TMC-1 to better than a factor of 2. For the statistical assumption a detection should have been possible in TMC-1. For the thermal assumption TMC-1 should not have been detectable in the $1_{10} \rightarrow 1_{11}$ transition of H_2D^+. Some intermediate situation is quite probable.

For NGC 2264 the value for $n(H_3^+)/n(H_2)$ of $(0.7\text{–}2.3) \times 10^{-9}$ is within the range of values which is to be anticipated (Prasad and Huntress 1980; Graedel, Langer, and Frerking 1982; Leung, Herbst, and Huebner 1984).

We now must address the likelihood that the line in NGC 2264 actually is the $1_{10} \rightarrow 1_{11}$ transition of H_2D^+. As noted above, the velocity and width of the line are consistent with those for DCO^+ in NGC 2264, and the strength is consistent with at least partial thermalization of H_2D^+ between its ortho and para states. Partial thermalization explains the absence of emission in TMC-1. It is not possible to exclude completely a chance coincidence of the H_2D^+ frequency with that of some line of another molecule. We have verified that the high-frequency catalogs of Lovas (1984) and of Poynter and Pickett (1984) do not contain any such coincidence. The greatest danger is that the line could be due to some transition of methanol whose more excited states cannot be accurately predicted from its observed spectrum, but a laboratory search of methanol vapor has not revealed any lines at the H_2D^+ frequency (Blake and Pickett 1985). The probability of erroneous identification is greatest in sources such as OMC-1 which contains regions of very high temperature and density and peculiar excitation. However, in a sensitive line-search program in OMC-1 between 215 and 247 GHz, of more than 500 detected lines, only about 20 were not explained by a set of 25 molecules of known spectrum (Sutton *et al.* 1985). Highly excited transitions ought to be very much weaker in a cloud of about 25 K, such as NGC 2264. Given the extreme importance of H_2D^+ to interstellar chemistry and the lack of any other suitable low-lying transition, it seems appropriate to report this initial one-line detection. Presumably a final proof of the identification will rest on many observations of varying temperature regions. This will take a great deal of time, because of the restricted number of observations possible with the Kuiper Airborne Observatory and the close proximity of the 372 GHz H_2D^+ line to the 380 GHz atmospheric water line, making ground-based observations very difficult. In the meantime it is hoped that this report will spur further calculations of H_2D^+ reactions and further astronomical observations.

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