

LABORATORY INFRARED SPECTRA OF CH_2D^+ AND HCCD^+ AND PREDICTED MICROWAVE TRANSITIONS

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ABSTRACT

In order to provide radio-astronomical probes for CH_3^+ and HCCH^+ , which play crucial roles in the chemical evolution of molecular clouds, infrared vibration-rotation spectra of their monodeuterated species have been measured. Rotational transitions of CH_2D^+ and HCCD^+ are predicted.

Subject headings: laboratory spectra — molecular processes

1. INTRODUCTION

According to the current theory of the chemical evolution of molecular clouds based on ion-neutral chemical kinetics (Herbst & Klemperer 1973; Watson 1973, 1976; Dalgarno & Black 1976), the methyl cation CH_3^+ , the acetylene ion HCCH^+ , and the protonated acetylene C_2H_3^+ play pivotal roles in the formation of organic molecules (Prasad & Huntress 1980; Dalgarno 1985; Smith 1987, 1988). The direct radio-astronomical search for their rotational spectra, however, has been hampered by the lack of a permanent dipole moment in the former two ions and the lack of an accurate A rotational constant in the latter (Crofton et al. 1989). In an attempt to provide radio-astronomical probes for the first two carbocations, we have studied high-resolution vibration-rotation spectra of their monodeuterated species CH_2D^+ and HCCD^+ in the infrared region. These isotopic species have effective dipole moments of 0.329 and 0.305 debye, respectively, through the shift of the center of gravity from the center of charge due to the isotope substitution and, hence, allowed rotational transition. The use of such a dipole moment was earlier proposed for H_2D^+ (Dalgarno et al. 1973), and a possible detection of its rotational spectrum in interstellar space has been reported by Phillips et al. (1985), although the validity of the detection has since been contested (Black et al. 1990). The concentrations of those deuterated species are expected to be greater than those calculated from the natural elemental abundance by several orders of magnitude because of the efficient deuterium fractionation in low-temperature molecular clouds (Watson 1976; Hollis et al. 1976).

2. LABORATORY INFRARED SPECTRA

We have observed the high-resolution vibration-rotation spectra of the CH stretching bands of CH_2D^+ (antisymmetric ν_4 band) and HCCD^+ (ν_1 band) using tunable infrared radiation from a difference frequency laser system (Pine 1974) and liquid nitrogen-cooled hydrocarbon plasmas. Details of the experimental arrangement and the plasma chemistry can be found in other papers from this laboratory (Crofton et al. 1988; Crofton et al. 1989). Both spectra were taken using the gaseous mixture of $\text{CH}_4:\text{CD}_4:\text{H}_2:\text{He} = 10:120:100:7000$ with the total plasma pressure of ≈ 7 torr. This ratio, which was chosen after some chemical tests, still showed spectral lines of the normal species to be strongest but also gave those of the mono-

deuterated species clearly. A 6 kHz ac discharge with a current of ≈ 150 mA was used to generate ions and to detect their spectra by the velocity modulation method (Gudeman et al. 1983). Typical observed spectral lines are shown in Figure 1.

2.1. CH_2D^+

The observed ν_4 vibration-rotation band with the band origin 3105.8 cm^{-1} is a typical b -type asymmetric rotor pattern with a large asymmetry ($\kappa \approx -0.231$). All together, 237 spectral lines have been assigned in the region of $3225\text{--}2983\text{ cm}^{-1}$. We have fitted 225 lines to the asymmetric rotor spectral pattern with the standard deviation of 0.0036 cm^{-1} . Molecular constants in the ground state are listed in Table 1. The numbers in parentheses are standard deviations.

2.2. HCCD^+

The observed ν_1 vibration-rotation band with the band origin at 3185.3 cm^{-1} is a typical ${}^2\Pi \leftarrow {}^2\Pi$ transition with large spin-rotational doubling and very small Λ doublings. All together, 87 vibration-rotation-spin transitions have been assigned in the region $3223\text{--}3142\text{ cm}^{-1}$. Forty-one ground-state combination differences have been fitted with the standard deviation of 0.0041 cm^{-1} . The molecular constants of the ground state are given in Table 2.

3. PREDICTED ROTATIONAL SPECTRA

Predicted frequencies for the rotational transitions of CH_2D^+ in the microwave to submillimeter spectral range are given in Table 3. The error of the prediction (1σ) is 2×10^{-5} of the value. In order to facilitate the laboratory detection of those spectral lines, calculated absorption intensities are given in arbitrary units. We also give the Einstein coefficient for the spontaneous emission. Predicted frequencies for the rotational transitions of HCCD^+ are given in Table 4. The error of the prediction (1σ) is 5×10^{-5} . It is our hope that these results will lead to detection of the microwave lines in laboratories and in space.

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TABLE 1
MOLECULAR CONSTANTS OF CH₂D⁺ IN THE GROUND STATE (cm⁻¹)^a

Symbol	Value	Symbol	Value
A	9.36871 (17)	Δ_{JK}	$3.620 (26) \times 10^{-4}$
B	5.77130 (10)	Δ_K	$2.648 (7) \times 10^{-4}$
C	3.52534 (5)	δ_J	$0.467 (3) \times 10^{-4}$
Δ_J	$1.214 (7) \times 10^{-4}$	δ_K	$3.951 (19) \times 10^{-4}$

^a Numbers in parentheses are 1 σ .

TABLE 3
PREDICTED ROTATIONAL TRANSITIONS OF CH₂D⁺ (MHz)

J	K _a	K _c	J	K _a	K _c	ν (MHz)	I ^a	A _{ij} (s ⁻¹)
3	3	0	3	3	1	5268.85	11.6349	1.0×10^{-10}
5	4	1	5	4	2	8444.64	2.9994	2.0×10^{-10}
7	5	2	7	5	3	9880.13	6.2256	2.1×10^{-10}
9	6	3	9	6	4	10132.75	1.2514	1.8×10^{-10}
2	2	0	2	2	1	23015.95	2.8041	6.3×10^{-9}
4	3	1	4	3	2	34065.77	7.5383	8.5×10^{-9}
10	6	4	10	6	5	36281.06	0.8029	4.7×10^{-9}
6	4	2	6	4	3	38363.03	2.0022	8.2×10^{-9}
8	5	3	8	5	4	38537.88	4.1064	6.6×10^{-9}
1	1	0	1	1	1	67273.71	4.3361	9.6×10^{-8}
3	2	1	3	2	2	101482.82	1.6337	1.1×10^{-7}
9	5	4	9	5	5	114027.76	2.5612	8.8×10^{-8}
5	3	2	5	3	3	116343.38	4.7577	1.2×10^{-7}
7	4	3	7	4	4	119017.21	1.2702	1.1×10^{-7}
2	1	1	2	1	2	201753.99	2.2983	2.9×10^{-7}
4	2	2	4	2	3	251006.92	1.0193	4.8×10^{-7}
10	5	5	10	5	6	265611.26	1.5112	5.6×10^{-7}
6	3	3	6	3	4	273277.08	2.9654	6.0×10^{-7}
8	4	4	8	4	5	276265.59	0.7727	6.1×10^{-7}
1	0	1	0	0	0	278691.62	1.0000	3.0×10^{-6}
3	1	2	3	1	3	398037.70	1.5780	6.1×10^{-7}
5	2	3	5	2	4	466137.32	0.6966	1.3×10^{-6}
2	1	2	1	1	1	490012.30	4.3361	1.3×10^{-5}
7	3	4	7	3	5	502558.71	1.9283	1.7×10^{-6}
9	4	5	9	4	6	513473.21	0.4747	2.0×10^{-6}
2	0	2	1	0	1	534279.91	1.8739	2.8×10^{-5}
2	1	1	1	1	0	624492.58	4.3082	2.8×10^{-5}

^a Intensity is in arbitrary units.

TABLE 2
MOLECULAR CONSTANTS OF HCCD⁺ IN THE GROUND STATE (cm⁻¹)

Symbol	Value	Symbol	Value
B	0.928407 (32)	p	$1.02 (35) \times 10^{-3}$
A	-30.834 (36)	q	$3.31 (31) \times 10^{-4}$
D	$1.055 (57) \times 10^{-6}$		

TABLE 4
PREDICTED ROTATIONAL TRANSITIONS OF HCCD⁺ (MHz)^a

J ← J	² Π _{3/2}		ν	² Π _{1/2}		ν
	N ← N			N ← N		
$\frac{3}{2} \leftarrow \frac{1}{2}$	2	1 a	85887.04
	2	1 b	85840.30
$\frac{5}{2} \leftarrow \frac{3}{2}$	2	1 a	135250.69	3	2 a	143099.48
	2	1 b	135239.99	3	2 b	143059.84
$\frac{7}{2} \leftarrow \frac{5}{2}$	3	2 a	189403.02	4	3 a	200271.84
	3	2 b	189381.95	4	3 b	200242.56
$\frac{9}{2} \leftarrow \frac{7}{2}$	4	3 a	243603.01	5	4 a	257391.23
	4	3 b	243568.61	5	4 b	257375.28
$\frac{11}{2} \leftarrow \frac{9}{2}$	5	4 a	297859.94	6	5 a	314446.84
	5	4 b	297809.64	6	5 b	314446.80
$\frac{13}{2} \leftarrow \frac{11}{2}$	6	5 a	352180.83	7	6 a	371430.15
	6	5 b	352112.42	7	6 b	371448.21
$\frac{15}{2} \leftarrow \frac{13}{2}$	7	6 a	406570.34	8	7 a	428334.97
	7	6 b	406482.03	8	7 b	428372.93
$\frac{17}{2} \leftarrow \frac{15}{2}$	8	7 a	461030.95	9	8 a	485157.31
	8	7 b	460921.33	9	8 b	485216.58
$\frac{19}{2} \leftarrow \frac{17}{2}$	9	8 a	515563.16	10	9 a	541910.05
	9	8 b	515431.16	10	9 b	541961.89
$\frac{21}{2} \leftarrow \frac{19}{2}$	10	9 a	570165.78	11	10 a	598652.94
	10	9 b	570010.65	11	10 b	598548.16

^a The a and b nomenclature is after the recommendation of Brown et al. 1975.

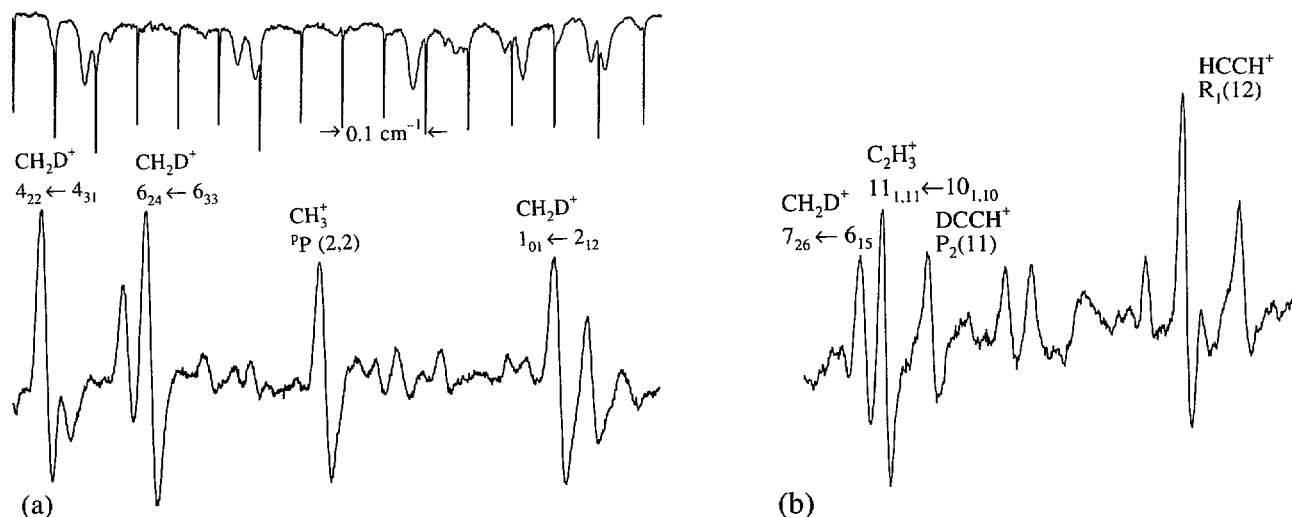


FIG. 1.—Examples of observed spectral lines: (a) CH₂D⁺; (b) HCCD⁺. The upper trace in (a) is the superposition of the ethylene absorption spectrum and Fabry-Perot markers separated by 0.05 cm⁻¹, which is used for frequency measurements. The lower trace contains ion spectral lines with a derivative shape due to velocity modulation. The trace shown in (b) is another frequency region, drawn to the same scale as in (a). The frequencies of the labeled transitions of CH₂D⁺ in (a) are, from left to right, 3086.449, 3086.322, and 3085.835, and the frequency of HCCD⁺ in (b) is 3164.806 cm⁻¹.

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