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Observation of the ν_1 fundamental band of H_2D^+

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The ν_1 fundamental band of H_2D^+ has been observed in absorption in a discharge with a difference frequency laser spectrometer in the range $2830\text{--}3200\text{ cm}^{-1}$. The 27 observed lines are assigned and the transition wave numbers are fit to an effective Hamiltonian to determine the molecular constants. The band origin ($2992.488 \pm 0.016\text{ cm}^{-1}$) and the rotational constants are in good agreement with those from *ab initio* calculations. The dependence of the concentration of H_2D^+ on the D_2/H_2 mixing ratio, which can be used to identify absorption lines of this ion, is discussed.

I. INTRODUCTION

The H_3^+ ion is of key importance in ion-molecule reactions in interstellar clouds.¹ The first high-resolution spectroscopic detection of this ion was made by Oka,² who observed the ν_2 fundamental band around $4.5\text{ }\mu\text{m}$ in absorption in a discharge with a difference-frequency laser as a tunable radiation source. One of the deuterated species of H_3^+ , the H_2D^+ ion, is of particular interest, first because it is considered to play an important role in deuterium fractionation in interstellar molecules,³ and second because it has a permanent dipole moment of about 0.6 D and therefore detection of this species in interstellar space is possible by observations of its microwave transitions.⁴

Carney and Porter⁵ calculated the vibrational frequencies of H_2D^+ as well as of other isotopic modifications. Later Carney⁶ calculated the rotational constants and term values. Shy, Farley, and Wing observed several lines of H_2D^+ using ion-beam Doppler-tuned spectroscopy.⁷ From the Carney and Porter calculations they apparently detected higher- J P -branch lines of the ν_2 and/or ν_3 band, but no definite assignments of these lines have been made and experimental molecular constants were not obtained.

As a first step toward this goal, we have employed the difference-frequency laser system to observe the ν_1 fundamental band. Although the transition moment is smaller than that for ν_3 ,⁵ the ν_1 band is advantageous because it falls in a convenient frequency range for the difference-frequency spectrometer. The wide continuous frequency coverage of the latter is of great value in searching for the widely spread lines of a light molecule such as H_2D^+ , as was demonstrated by Oka² for H_3^+ .

II. OBSERVATIONS

The spectrometer system used in this work was similar to that described in Ref. 8. The H_2D^+ was generated through a modulated dc discharge in a mixture of H_2 and D_2 . As discussed below, the optimum mixing ratio for observation of H_2D^+ was found to be approximately 2.5:1. The total pressure was about 500 mTorr.

The discharge was modulated by adding a switching circuit in parallel with the discharge tube.⁹ The modulation frequency used in this work was about 17 kHz, and the peak discharge current was about 180 mA. The concentration of a

short-lived species generated in the discharge plasma is modulated at the same frequency, with some phase delay depending on the reaction mechanism or the lifetime of the species. The signals were detected with a lock-in amplifier operated at the modulation frequency. With increasing modulation frequency, the noise contributed by the source lasers decreases greatly. Moreover, the method can discriminate between short-lived species and stable reaction products or parent molecules, because the amplitude of the signals from such stable species cannot be modulated effectively. This discharge amplitude modulation method can be used in conjunction with a conventional multitraversal cell, and can then attain higher sensitivity than the single-traversal Doppler velocity modulation method.¹⁰ One disadvantage of this amplitude modulation method is that it does not discriminate ions from short-lived neutral species.

The infrared beam was passed 24 times through the cell, giving an effective path length of about 24 m. The cell was cooled with liquid nitrogen. Figure 1 is an example of an observed signal corresponding to about 0.6% absorption, which leads to an absorption coefficient of $3 \times 10^{-6}\text{ cm}^{-1}$.

The transition wave numbers were measured with H_2CO and C_2H_4 lines as references.¹¹ The accuracy of the measurements is estimated to be about $\pm 0.002\text{ cm}^{-1}$.

During the course of the search, we detected lines of at least two species other than H_2D^+ . One is clearly H_3^+ , and the other is probably HD_2^+ . These observations will be published separately.

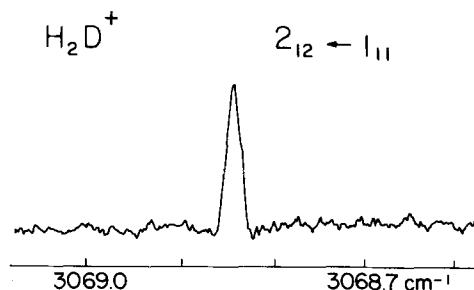


FIG. 1. The $2_{12}\text{--}1_{11}$ transition of the ν_1 fundamental band of H_2D^+ . The signal was recorded with a detection time constant of 0.4 s.

III. RESULTS

The ν_1 mode of H_2D^+ is essentially the H–H stretching vibration, and the fundamental band is a polarized because the a axis is parallel to the C_2 symmetry axis. Before commencing the search, a predicted spectrum was calculated from the rotational constants and vibrational frequencies of Carney and Porter.^{5,6,12} As shown below, the calculated constants turned out to be very close to the observed.

The observed frequencies were readily assigned on the basis of this predicted spectrum, and were subsequently fit with a conventional effective Hamiltonian in a I^rA representation. However, the procedure was not completely straightforward because only $\Delta K_a = 0$ transitions have been observed so far, and the relative energies of levels with different K_a are not well determined. Also, the K -type doubling splittings were not obtained separately for the ground and excited states. For a light molecule of this type the observed transitions are in general limited to relatively low J and K_a states, but rather a large number of higher-order parameters are required for a reasonable fit.

TABLE I. Observed wave numbers of the ν_1 fundamental band of H_2D^+ (in cm^{-1}).

	ν_0	$(\text{O}-\text{C}) \times 10^3$
$3_{13} \leftarrow 4_{14}$	2839.096	26
$2_{11} \leftarrow 3_{12}$	2840.962	2
$2_{02} \leftarrow 3_{03}$	2871.897	-11
$2_{12} \leftarrow 3_{13}$	2874.811	-12
$1_{10} \leftarrow 2_{11}$	2887.370	11
$1_{01} \leftarrow 2_{02}$	2906.523	-13
$1_{11} \leftarrow 2_{12}$	2911.635	-4
$0_{00} \leftarrow 1_{01}$	2946.802	22
$2_{12} \leftarrow 2_{11}$	2952.940	-13
$3_{31} \leftarrow 3_{30}$	2975.064	3
$1_{11} \leftarrow 1_{10}$	2978.045	-1
$3_{30} \leftarrow 3_{31}$	2978.492	-2
$2_{21} \leftarrow 2_{20}$	2979.987	-9
$2_{20} \leftarrow 2_{21}$	2991.162	4
$1_{10} \leftarrow 1_{11}$	3003.276	11
$2_{11} \leftarrow 2_{12}$	3028.263	2
$1_{01} \leftarrow 0_{00}$	3038.177	-11
$2_{12} \leftarrow 1_{11}$	3068.845	-15
$2_{02} \leftarrow 1_{01}$	3077.611	-13
$2_{11} \leftarrow 1_{10}$	3094.671	4
$3_{13} \leftarrow 2_{12}$	3104.207	29
$3_{03} \leftarrow 2_{02}$	3109.645	26
$4_{14} \leftarrow 3_{13}$	3137.007	-27
$4_{04} \leftarrow 3_{03}$	3139.197	-9
$3_{12} \leftarrow 2_{11}$	3141.131	-6
$5_{15} \leftarrow 4_{14}$	3168.702	6
$4_{13} \leftarrow 3_{12}$	3178.973	1
Derived energy level separations in the ground state ^a		
$2_{12} - 1_{10}$	66.408	3
$3_{13} - 2_{11}$	78.129	-1
$2_{11} - 1_{11}$	115.906	-1
$2_{02} - 0_{00}$	131.654	2
$3_{12} - 2_{12}$	187.301	0
$3_{03} - 1_{01}$	205.714	-2
$4_{14} - 2_{12}$	265.111	3

^a See the text.

Because of possible complications in the upper-state energies due to (ν_1 , ν_3) Coriolis interactions, we gave the ground-state combination differences greater emphasis in the fit by including them as “data” that could be weighted separately. The observed transition wave numbers and these ground-state combination differences are listed in Table I. After several trial fits, we decided to give these ground-state differences ten times the weight of the directly observed lines. Because of the limited information, as described above, we decided to fix ΔK at the value obtained by fitting the *ab initio* rotational term values calculated by Tennyson and Sutcliffe¹³ to our effective Hamiltonian, and the same value was used for the upper state. Among the sextic centrifugal constants, only Φ_J , Φ_{JK} , and Φ_{KJ} were included as variable parameters. The Coriolis interaction between ν_1 and ν_3 was neglected, although it may have to be taken into account if more lines are observed in the future. The results of the fit are included in Table I, and the derived molecular constants are listed in Table II. The standard deviation of the fit was about 0.018 cm^{-1} , about ten times the experimental uncertainty.

IV. DISCUSSION

Table III compares the observed rotational constants with the *ab initio* values. The agreement is excellent. The agreement with the calculated band origins, 3000 cm^{-1} by Carney and Porter⁵ and 2999 cm^{-1} by Tennyson and Sutcliffe,¹³ is also very good.

The importance of H_2D^+ as an interstellar ion was discussed by Dalgarno *et al.*,⁴ who gave estimates of four K -type doubling frequencies. Carney⁶ calculated these frequencies with higher accuracy, and they can also be obtained from the term values of Tennyson and Sutcliffe.¹³ From the present analysis, the four ground-state K -type doubling frequencies (with standard deviations) $1_{10} - 1_{11}$, $2_{20} - 2_{21}$, $3_{30} - 3_{31}$, and $4_{40} - 4_{41}$ are calculated to be 372 383(106), 156 558(556), 45 402(744), and 10 999(737) MHz, respectively. Because of the lack of information in the least squares analysis described above, the accuracy of these calculated frequencies is not greatly improved over the *ab initio* estimates. The $1_{10} - 1_{11}$ prediction is the most reliable, but this line is unfortunately at the edge of a strong water absorption. Angerhofer,

TABLE II. Molecular constants of H_2D^+ (in cm^{-1}).

	$\nu_1 = 1$ state	Ground state
ν_0	2992.488(16) ^a	
A	41.523(73)	43.362(72)
B	29.364(22)	29.143(12)
C	16.394(14)	16.610 5(81)
Δ_J	0.014 7(10)	0.011 75(89)
Δ_{JK}	-0.016 2(68)	-0.008 3(53)
Δ_K	[0.031 86] ^b	[0.031 86] ^b
δ_J	0.003 47(30)	0.003 84(18)
δ_K	0.0361(72)	0.020 1(41)
$\Phi_J \times 10^4$	1.92(23)	1.67(24)
$\Phi_{JK} \times 10^4$	-11.9(70)	-12.9(61)
$\Phi_{KJ} \times 10^4$	-7.1(17)	-5.1(13)

^a One standard error to the last digits of the constants.

^b Fixed. See the text.

TABLE III. Comparison of major molecular constants.

	Observed ^a	Calculated
ν_0	2992.488(16)	3000 ^b 2999 ^c
A_0	43.362(72)	43.54 ^b
B_0	29.143(12)	29.13 ^b
C_0	16.610 5(81)	16.71 ^b
A_1	41.523(73)	41.40 ^d
B_1	29.364(22)	28.98 ^d
C_1	16.394(14)	16.17 ^d

^aThis work.^bReference 6.^cReference 13.^dReference 12.

Churchwell, and Porter searched for the $4_{40}-4_{41}$ line in circumstellar and interstellar sources in the range 10 027–10 055 MHz, without success.¹⁴ This frequency range is possibly too low. An unidentified interstellar line observed at Nobeyama Radio Observatory,¹⁵ U45.379 is close to our calculated $3_{30}-3_{31}$ frequency.

Finally it may be useful to discuss the dependence of the signal intensity on the mixing ratio of H_2 and D_2 . Figure 2 shows the intensity dependence of H_3^+ , H_2D^+ , and HD_2^+ , on the mixing ratio between D_2 and H_2 , when the total pressure is kept at 500 mTorr. The isotope exchange reactions



are exothermic on account of the differences in zero-point energies. From the zero-point energies of H_3^+ and its isotopic species calculated by Carney,⁶ together with the zero-point energies of H_2 , HD, and D_2 ,¹⁶ the exothermicities of reactions (1)–(5) are 39, 165, 72, 230, and 104 cm^{-1} , respectively. In addition, one must take account of the fact that the lowest populated level of H_3^+ has a rotational energy of 64.1 cm^{-1} as a result of spin statistics.¹⁷ Our experiment was made with a liquid nitrogen cooled cell, and the translational and rotational temperatures were found to be about 200 K. The exothermicity of these reactions is therefore of the same

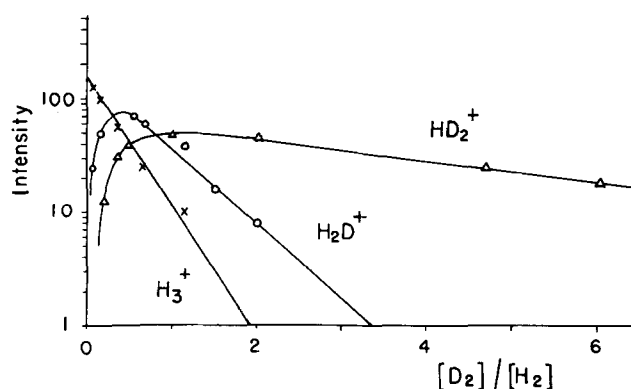


FIG. 2. The dependence of the signal intensities on the mixing ratio $[\text{D}_2]/[\text{H}_2]$. The relative intensity among the three species H_3^+ , H_2D^+ , and HD_2^+ is arbitrary.

order as the temperature, and the reverse reactions are not negligible. However, the general tendency shown in Fig. 2 indicates that the isotopic exchange reactions favor the more deuterated species by the reaction chains (1)–(5). Spectroscopically, this dependence of the intensity of each isotopic species on the mixing ratio is of great help in identifying the lines of the species.

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