

Observation of the Infrared Spectrum of H_3^+

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The infrared ν_2 band of H_3^+ has been observed. A direct infrared absorption method combining a liquid-nitrogen-cooled multiple-reflection discharge cell and a difference-frequency laser system has been used for the detection. Fifteen absorption lines have been measured in the region of 2950–2450 cm^{-1} and assigned. This is the first spectroscopic detection of this fundamental molecular ion in any spectral range.

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Since its discovery by Thomson,¹ the triatomic hydrogen molecular ion H_3^+ has been well known to mass spectroscopists. Because of the efficient exothermic reaction² $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$ and its large dissociation energy, H_3^+ is the most abundant ion in a hydrogen discharge. It is also the simplest polyatomic system, and is an important catalyst in interstellar ion chemistry.³ However, there has previously been no spectroscopic information on this fundamental ion. The recent major advances in our knowledge of this ion have been (a) the detailed *ab initio* calculation by Carney and Porter,⁴ (b) the confirmation of the equilateral-triangle structure by the novel method of foil-induced dissociation by Gaillard *et al.*,⁵ and (c) the observation of Rydberg-state emission spectra of neutral H_3 and D_3 by Herzberg.⁶ In this paper, I report the first observation of the spectrum of H_3^+ . The transitions observed are rovibrational transitions in the active degenerate ν_2 infrared-band.

A direct infrared absorption method combining a multiple-reflection discharge cell and a frequency-tunable infrared source was chosen as the detection method. The multiple-reflection discharge cell was 2 m long and was cooled with liquid nitrogen, as was done by Woods and his collaborators⁷ for their microwave detection of CO^+ , HCO^+ , and HNN^+ . For the tunable infrared source, a difference-frequency laser system developed by Pine⁸ was used. Mixing radiation from an Ar laser (ν_A) and that from a dye laser (ν_D) in a temperature-controlled LiNbO_3 crystal, we obtained an infrared radiation source with

the power of a few microwatts whose frequency ($\nu_A - \nu_D$) was tunable over the range of 4400–2400 cm^{-1} . The frequency of the infrared radiation was modulated by modulating the frequency of the Ar laser with an amplitude of ~ 400 MHz and a frequency of 2.5 kHz. The signal was processed (1f detection) through a phase-sensitive detector. The overall sensitivity for the search was $\sim 1.5 \times 10^{-2}$ and, with a path length of 32 m, the minimum detectable absorption coefficient was $\sim 4 \times 10^{-6} \text{ cm}^{-1}$. This sensitivity was checked by observing the weak $v=1 - v=0$ quadrupole spectrum⁹ of D_2 .

The direct absorption method is much less sensitive than the ingenious ion-beam laser-resonance method of Wing and his collaborators,¹⁰ who were successful in detecting the infrared spectra of HD^+ and HHe^+ , and the laser magnetic resonance method of Saykally and Evenson,¹¹ who detected HBr^+ . However, it makes it possible to cover a wide range of the infrared region and this coverage was essential in the detection of H_3^+ because the spectrum extends over a region of $\sim 500 \text{ cm}^{-1}$ and the estimated accuracy of the theoretical prediction¹² was $\sim 50 \text{ cm}^{-1}$.

The density of H_3^+ in the hydrogen discharge (current density $\sim 60 \text{ mA/cm}^2$, pressure ~ 1 Torr) is estimated to be $n \sim 3 \times 10^{10} / \text{cm}^3$ from the electron drift velocity¹³ ($v_d \sim 10^7 \text{ cm/sec}$) and the fraction of H_3^+ among other positive ions, $f \geq 0.75$, reported by Saporochenko.¹⁴ The translational and rotational temperature of H_3^+ is estimated to be not much higher than 200 K from the energy dissipation ($\sim 1 \text{ kW}$) and the thermal conductivity of the

flowing discharged gas. This classical estimate can be used based on the conclusion by Albritton *et al.*¹⁵ that H_3^+ survives many collisions with H_2 and is thermalized with the latter. Thus with use of the calculated transition dipole moment⁴ of 0.156 D, it was expected that the stronger lines of the H_3^+ spectrum would have absorption coefficients of $\sim 3 \times 10^{-5} \text{ cm}^{-1}$.

An example of an observed absorption line is shown in Fig. 1. This line, which was the first found in the search, corresponds to the $\nu_2 R_0(1)$ transition ($J=2, k=\pm 1, l=\pm 1$) \leftarrow ($J=1, k=0$) and is one of the two strongest transitions in the ν_2 fundamental, the other being the $\nu_2 Q_0(1)$ transition ($1, \pm 1, \pm 1$) \leftarrow ($1, 0$). These are the strongest because the lower level ($1, 0$) is occupied by about 30% of the total H_3^+ ions at the rotational temperature of ~ 200 K. This is because this level is the lowest for the ortho H_3^+ (with $I=\frac{3}{2}$); note that the statistical factor for ortho ($I=\frac{3}{2}$) and para ($I=\frac{1}{2}$) is 4 and 2, respectively, and that the lowest ortho level ($0, 0$) is not allowed by the Pauli principle (just as the corresponding level is not allowed for the lower inversion level of NH_3).

The observed line disappeared when a small trace of air was introduced into the discharge. Also when the flow of hydrogen was stopped, this line did not increase in intensity. From these observations it was concluded that this line was due to a pure hydrogen compound. In order to confirm that this line was due to an ionic species, an attempt was made to resolve the two symmet-

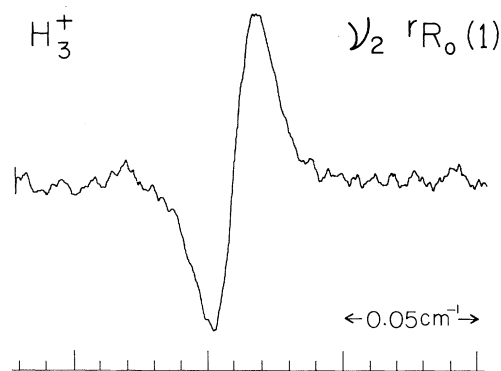


FIG. 1. The observed $\nu_2 R_0(1)$ transition ($J=2, k=\pm 1, l=\pm 1$) \leftarrow ($J=1, k=0$) of H_3^+ at 2725.885 cm^{-1} . Discharge current, 140 mA; pressure, 0.5 Torr; the time constant for detection, 400 msec.

rical Doppler components. Such splitting is expected from the drift velocity of H_3^+ in the dc discharge and the multiply reflected infrared radiation. This attempt was unsuccessful because the present discharge cell did not allow the discharge condition to be achieved for a large drift velocity; that is, a high discharge electric field and a low pressure. Thus the identification of the H_3^+ ion had to be based on the observed spectral pattern.

A continuous scan of the spectrum was done between 2800 – 2460 cm^{-1} . Ten lines were observed and they formed a pattern expected for H_3^+ ; that is, the two prominent lines mentioned earlier

TABLE I. The observed spectral lines of the ν_2 band of H_3^+ .

Transitions (J, k, l) \leftarrow (J, k)	Observed frequencies (cm^{-1})	obs. - calc. (cm^{-1})	Intensity ^a (10^{-5} cm^{-1})
$R(3) [(4, \pm 4, \pm 1) - (4, \pm 2, \mp 1)]_I \leftarrow (3, \pm 3)$	2918.013	0.126	0.4
$R(3) [(4, \pm 4, \pm 1) - (4, \pm 2, \mp 1)]_{II} \leftarrow (3, \pm 3)$	2829.911	-0.053	1.0
$R(2) [(3, \pm 2, \pm 1) - (3, 0, \mp 1)]_I \leftarrow (2, \pm 1)$	2826.022	-0.010	0.6
$R(2) [(3, \pm 3, \pm 1) - (3, \pm 1, \mp 1)]_I \leftarrow (2, \pm 2)$	2823.125	-0.320	0.5
$R(2) [(3, \pm 3, \pm 1) - (3, \pm 1, \mp 1)]_{II} \leftarrow (2, \pm 2)$	2762.057	0.099	1.0
$R(1) [(2, \pm 2, \pm 1) - (2, 0, \mp 1)]_I \leftarrow (1, \pm 1)$	2726.208	0.001	1.1
$R(1) (2, \pm 1, \pm 1) \leftarrow (1, 0)$	2725.885	0.161	3.0
$R(1) [(2, \pm 2, \pm 1) - (2, 0, \mp 1)]_{II} \leftarrow (1, \pm 1)$	2691.430	0.039	1.0
$Q (3, \pm 2, \mp 1) \leftarrow (3, \pm 3)$	2561.486	-0.052	0.3
$Q (2, \pm 1, \mp 1) \leftarrow (2, \pm 2)$	2554.655	0.172	0.5
$Q (1, 0, \mp 1) \leftarrow (1, \pm 1)$	2545.412	0.024	0.9
$Q (1, \pm 1, \pm 1) \leftarrow (1, 0)$	2529.711	-0.164	3.0
$Q [(2, \pm 2, \pm 1) - (2, 0, \mp 1)]_{II} \leftarrow (2, \pm 1)$	2518.198	-0.041	0.6
$Q (3, \pm 1, \pm 1) \leftarrow (3, 0)$	2509.063	0.020	0.3
$P(1) (0, 0, \mp 1) \leftarrow (1, \pm 1)$	2457.277	-0.001	0.6

^aCalculated values.

are each accompanied by the expected number of weaker lines and there is a wide region between them without any lines. A computer program¹⁶ for calculating the spectrum of H_3^+ was run by Watson with use of rotational constants which were recently communicated to him by Carney and Porter¹⁷ and the result agreed well with the observed pattern except for one line which was later ascribed to the hydrogen-atom Brackett α line. Subsequently six more lines were observed close to their predicted positions. The observed lines are summarized in Table I and the calculated pattern is shown in Fig. 2. The frequencies of the lines were measured using the reference gases of various isotopes of N_2O (Ref. 18) and H_2CO (Ref. 19). The accuracy of measurement is 0.005 cm^{-1} .

The rotational structure of H_3^+ in the ground state is that of a simple planar symmetric-top rotor ($B \sim 2C$). In the ν_2 state, because of $\zeta = -1$ and $B \sim 2C$, the levels with the same J and $k-l$ are nearly degenerate. Because of this and the selection rule $\Delta(k-l) = 0$, this perpendicular band has a structure similar to a simple parallel band. The situation is complicated because of a large mixing term²⁰

$$H_l = q(q_+^2 J_+^2 + q_-^2 J_-^2)/4 \quad (1)$$

where J_{\pm} and q_{\pm} are the rotational and the vibrational ladder operators and q is the l -doubling constant. This term shifts levels with $(J, k = \pm 1, l = \pm 1)$ by $q_J(J+1)/2$ and mixes (l -resonance) levels with (J, k, l) and $(J, k \pm 2, l \pm 2)$. Thus the two nearly degenerate levels with the same $k-l$ are completely mixed and form an l -resonance dyad. These dyads are specified in Table I as I and II in the order of frequency.

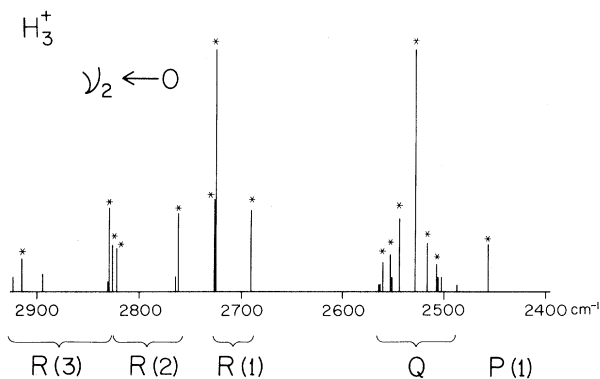


FIG. 2. The spectral pattern for the ν_2 band of H_3^+ calculated by Watson for the rotational temperature of 200 K. Observed transitions are marked with asterisks.

A least-squares fitting to the observed spectrum was made by Watson and the results are as follows:

$$\nu_2 = 2521.564 \pm 0.135 \text{ cm}^{-1},$$

$$B(\nu_2) = 44.051 \pm 0.045 \text{ cm}^{-1},$$

$$C(\nu_2) = 19.689 \pm 0.038 \text{ cm}^{-1},$$

$$\langle \zeta C \rangle (\nu_2) = -18.527 \pm 0.050 \text{ cm}^{-1},$$

$$q = -5.380 \pm 0.074 \text{ cm}^{-1},$$

$$B_0 = 43.568 \pm 0.048 \text{ cm}^{-1},$$

$$C_0 = 20.708 \pm 0.048 \text{ cm}^{-1},$$

$$D_J(\nu_2) = D_{0J} = 0.047 \pm 0.007 \text{ cm}^{-1},$$

$$D_{JK}(\nu_2) = D_{0JK} = -0.099 \pm 0.018 \text{ cm}^{-1},$$

$$D_K(\nu_2) = D_{0K} = 0.040 \pm 0.003 \text{ cm}^{-1},$$

$$q_J = 0.018 \pm 0.005 \text{ cm}^{-1},$$

where the last four constants are centrifugal corrections to rotation and l resonance. In order to separate B_0 and C_0 , a calculated value of the inertial defect²¹ $\Delta = 3h/4\pi^2 c \nu_2$ was used. Also the relations $\eta_{2J} = 2D_{JK}$, $\eta_{2K} = 4D_K$ derived for this molecule from Aliev and Watson's general formula²² were employed. The quoted uncertainties are the standard deviations. The values given above are subject to slight changes as we measure more lines and introduce more terms for fitting.

It is noted that the predicted values by Carney and Porter^{4,17} of $\nu_2 = 2516.08 \text{ cm}^{-1}$, $B(\nu_2) = 43.843 \text{ cm}^{-1}$, $C(\nu_2) = 19.735 \text{ cm}^{-1}$, $\langle \zeta C \rangle (\nu_2) = -18.516 \text{ cm}^{-1}$, $B_0 = 43.223 \text{ cm}^{-1}$, $C_0 = 20.565 \text{ cm}^{-1}$, and $|q| = 4.846 \text{ cm}^{-1}$ agree excellently within the observed values, showing the reliability of *ab initio* calculations for molecules of this size.

The result of this observation seems to open the following paths for future research in various fields: (1) systematic ion-molecule infrared spectroscopy in discharge, (2) *in situ* monitoring of H_3^+ in chemical reactions and in ion migration-velocity measurement, (3) detection of H_3^+ in space.

During the four years of this project, the assembling, adjustment, and operation of the apparatus and the search for the spectrum was greatly helped by the enthusiastic and able technical assistance of A. Karabonik. Also, I have constantly profited from discussions with A. E. Douglas, G. Herzberg, A. R. W. McKellar, and J. K. G. Watson. A. R. W. McKellar designed the multiple-reflection mirror system and the liquid-ni-

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