Observation of Infrared Forbidden Transitions of H₃⁺

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The $v_1 \leftarrow 0$ and $v_1 + v_2 \leftarrow v_2$ forbidden transitions of H₃⁺ have been observed. The former is induced by the rovibrational Birss resonance between the v_1 and v_2 states and the latter by Fermi resonance. The observation leads us to the determination of absolute values of vibration-rotation energy levels related to the v_1 and the $v_1 + v_2$ states. The assignment of the spectrum was constantly helped by "first principles calculations" of Miller, Tennyson, and Sutcliffe. We give an interpretation of the spectrum also based on the traditional vibration-rotation formalism. © 1992 Academic Press, Inc.

I. INTRODUCTION

Since the initial observation of the infrared spectrum of the $v_2 \leftarrow 0$ fundamental band of H_3^+ in 1980 (1, 2), where the minimum detectable absorption coefficient was $\sim 4 \times 10^{-6}$ cm⁻¹, the sensitivity of molecular ion spectroscopy using frequency tunable laser infrared sources has increased by more than three orders of magnitude. This increase of sensitivity, together with the use of He dominated discharges for producing plasmas with high vibrational temperature, has enabled us to conduct an extensive spectroscopy of the three hot bands of H_3^+ , $2\nu_2$ $(l=2) \leftarrow \nu_2$, $2\nu_2$ $(l=0) \leftarrow \nu_2$, and $\nu_1 + \nu_2 \leftarrow \nu_1$, in the 3.4–5.1 µm region (3). In addition, the extension of the frequency coverage of the difference frequency laser system by the use of $LiIO_3(4)$, and the use of InGaAs communication diode lasers have led us to the observations of the first overtone band $2\nu_2$ (l = 2) $\leftarrow 0$ in the 1.9–2.3 μ m region (5) and the second overtone band $3\nu_2(l=1) \leftarrow 0$ in the 1.5 μ m region (6), respectively. In assigning rovibrational transitions involving such high vibrational states, we have constantly been helped by the first principle variational calculations of Miller, Tennyson, and Sutcliffe (7-9), which are based on the ab initio potential of Meyer, Botschwina, and Burton (10). Understanding of the rovibrational energy structure of the $2\nu_2(l=2)$ state obtained from these experimental and theoretical studies, and from the Fourier transform emission spectrum of Majewski et al. (11) was crucial in Watson's identification of the 2 μ m emission spectrum of H⁺₃ observed in the auroral region of the Jovian ionosphere (12, 13).

These observed results for high vibrational states, together with the extensive observation of the $\nu_2 \leftarrow 0$ fundamental for high rotational levels (14, 15), provided detailed energy level structure related to stacks of ν_2 excitation. The first overtone band $2\nu_2(l=2) \leftarrow 0$ obeys the selection rules $\Delta |k-l| = 3$, contrary to all other transitions for which $\Delta |k-l| = 0$. Combined with other transitions, it has allowed

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us to determine *absolute* rovibrational energy values for the ground state and the ν_2 , $2\nu_2(l=2)$, $2\nu_2(l=0)$, and $3\nu_2(l=1)$ excited states. In order to obtain information on the absolute rovibrational energy levels of ν_1 and $\nu_1 + \nu_2$, however, we need to observe transitions such as $\nu_1 \leftarrow 0$ and $\nu_1 + \nu_2 \leftarrow \nu_2$ which are infrared inactive. We report in this paper direct observation of such "forbidden" transitions.

There have been a great number of theoretical papers on H_3^+ which predicted the value of ν_1 . The calculated values up to 1980 are summarized in a review (16). Carney and Porter in their classic paper (17) gave the ν_1 value of 3185 cm⁻¹. More recent values are 3178.348 cm⁻¹ given by Miller and Tennyson (18) and 3178.68 cm⁻¹ given by Whitnell and Light (19) both based on the ab initio potential of Meyer, Botschwina, and Burton (10), who themselves gave the value of 3178.4 cm⁻¹. The first experimental paper on ν_1 appears to be that by Petty and Moran (20), who reported the value of 3350 cm⁻¹ based on their ion impact spectroscopy experiment. Majewski *et al.* (15) isolated a systematic energy shift on a series of rotational levels of the ν_2 state due to a perturbation from the ν_1 state and estimated ν_1 to be 3175 ± 0.7 cm⁻¹. Ketterle, Messmer, and Walther (21) reported the first direct spectroscopic determination of $\nu_1 = 3178.29 \pm 0.1$ cm⁻¹ from the limits of autoionizing Rydberg spectrum of H₃.

The studies of direct rovibrational forbidden transitions reported in the present paper provide absolute rovibrational energy level values of the v_1 and $v_1 + v_2$ states. The study of the $v_1 \leftarrow 0$ transition is based on the results of Majewski *et al.* (15), where the perturbation between the v_1 and v_2 states is noted. The studies of the v_1 $+ v_2 \leftarrow v_2$ and the $v_1 \leftarrow v_2$ transitions are based on the recent theoretical work by Miller, Tennyson, and Sutcliffe (22). In order to understand the origin of these forbidden transitions we present our analysis based on the traditional formulation of Watson (23). We also obtain an insight from these studies as to how H₃⁺ molecular ions in space relax radiatively.

II. FORBIDDEN TRANSITIONS

The rovibrational states of H_3^+ are specified by six quantum numbers—the rotational angular momentum quantum number J and its projection on the molecular axis k, the vibrational quantum numbers v_1 and v_2 , the vibrational angular momentum quantum number l, the total nuclear spin quantum number I. The parity is uniquely determined by $(-1)^k$. For an electric dipole induced single photon transition there exists the rigorous parity rule,

$$parity + \leftrightarrow -, \tag{1}$$

which leads to the rigorous rule

$$\Delta k = \text{odd.} \tag{2}$$

There exist very nearly rigorous rules

$$\Delta J = 0, \pm 1 \quad \text{and} \quad \Delta I = 0. \tag{3}$$

The latter of this rule signifies the stability of the ortho $(I = \frac{3}{2})$ and the para $(I = \frac{1}{2})$ spin modifications of H₃⁺, and leads to the selection rule

$$\Delta |k-l| = 3n \qquad (n: integer). \tag{4}$$

These selection rules are all obeyed. Following Watson, we use J and |k| to specify rotational levels of the ground state and the ν_1 state, and, for the other states involving

Observed Transitions in the $\nu_1 \leftarrow 0$ band of H_3^+ (in cm ⁻¹)				
$J', K' \leftarrow J, K$	J, G, U^{a}	Δv^{a}	v _{obs.}	v b calc.
7, 5 ← 6, 2	7, 2, 1	70.1	3282.308	3282.27
6, 5 ← 5, 2	6, 2, 1	79.9	3202.169	3202.15
7, 6 ← 6, 3	7, 3, 1	-21.9	3144.454	3144.33
5, 5 ← 4, 2	5, 2, 1	95.6	3120.199	3120.24
6, 6 ← 5, 3	6, 3, 1	-55.3	3066.561	3066.5
7, 7 ← 6, 4	7, 4, -1	36.6	3026.154	3025.96
6, 5 ← 6, 2	6, 2, 1	79.9	2709.479	2709.61
6, 6 ← 6, 3	6, 3, 1	-55.3	2569.726	2569.85
7,7 ← 7,4	7, 4, -1	36.6	2454.417	2453.39

TABLE	ΞI

^a Rotational levels in the ν_2 state which induce the transition through the Birss resonance and their energy separation from the observed level.

^b Wavenumbers were calculated from a table of energy values kindly provided by Miller and Tennyson.

 v_2 in which *l* is nonzero, we use *J*, Hougen's quantum number (24) G = |k - l|, and *U*. The last symbol *U* is to discriminate two rovibrational levels with the same *G* value according to the order of energy values.

In this paper we loosely use the word "forbidden" to mean vibrational transitions such as $\nu_1 \leftarrow 0$ and $\nu_1 + \nu_2 \leftarrow \nu_2$ which are forbidden in the sense that they involve excitation of the totally symmetric vibration ν_1 . It should be noted that there is a qualitative difference between these two transitions. The $\nu_1 \leftarrow 0$ transition corresponds to symmetry $A'_1 \leftarrow A'_1$ and cannot be caused by vibrational interaction alone. Thus, an interaction between vibration and rotation has to be invoked to cause such transitions. For both levels of this transition the *l* quantum number is zero and, in order to satisfy the rules (2) and (4), we have the selection rule

$$\Delta k = \pm 3. \tag{5}$$

The $\nu_1 + \nu_2 \leftarrow \nu_2$ transition $(E' \leftarrow E')$, on the other hand, is allowed from symmetry and thus vibrational interaction (Fermi interaction) is sufficient to cause such transitions. We find that for such transitions, the selection rules are

$$\Delta k = \pm 1, \qquad \Delta l = \pm 2. \tag{6}$$

These situations are parallel to those of forbidden *rotational* transitions (25); for the ground vibrational state, centrifugal distortion is needed to cause such transitions, while the mechanical and electrical anharmonicity are sufficient to cause them in a degenerate vibrational state. The general theory of such transitions by Watson (26) and Mizushima and Venkateswarlu (27) has been applied to H_3^+ (28–31), but they are yet to be observed. Possible importance of such transitions for observing extragalactic H_3^+ has been noted (32).

III. INTENSITY BORROWING AND OBSERVED SPECTRUM

The forbidden transitions become allowed as results of perturbation mixing and intensity borrowing from allowed transitions. Here we examine the vibration-rotation



FIG. 1. Typical examples of observed forbidden transitions.

interaction terms that cause such effect for each forbidden transition and summarize our observed results.

A. The $v_1 \leftarrow 0$ Transition

The rovibrational transition ν_1 , J', $K + 3 \leftarrow J$, K borrows intensity from the ν_2 , $l = 1, J', K + 1 \leftarrow J$, K transition through the mixing term

$$H'_{22} = -\frac{1}{2}\alpha_{12}[(q_1q_{2+} + p_1p_{2+})J^2_+ + (q_1q_{2-} + p_1p_{2-})J^2_-], \qquad (7)$$

where q and p represent dimensionless normal coordinates and momenta conjugate to them, respectively, and the subscripts \pm signify vibrational and rotational ladder operators. This term also causes the forbidden transitions v_1 , J', $K - 3 \leftarrow J$, K, but such transitions are much weaker because of larger energy gaps between mixed levels. This perturbation term H'_{22} was isolated by Watson in his extensive analysis of the v_2 fundamental band (15) and the value of the constant α_{12} was determined to be 1.377 cm⁻¹. The effect of this term was called "Birss resonance" after F. W. Birss, who gave a general treatment of the perturbation term of the form q^2J^2 (33). A comparison of the value of α_{12} and $v_1 - v_2 = 656.9$ cm⁻¹ suggests that a significant mixing and hence intensity borrowing results only for high J, K levels where the large difference in vibrational energy is compensated by that in rotational energy. Such "accidental" degeneracy occurs between the states v_1 , J', K + 3 and v_2 , J', G = K, U and induces the forbidden v_1 , J', $K + 3 \leftarrow J$, K transition. The matrix element of H'_{22} is

$$\langle \nu_2, J', G = K, U | H'_{22} | \nu_1, J', K + 3 \rangle$$

= $-\frac{\alpha_{12}}{\sqrt{2}} [J'(J'+1) - (K+1)(K+2)]^{1/2} [J'(J'+1) - (K+2)(K+3)]^{1/2}.$ (8)

Observed spectral lines are listed in Table I. They all start from relatively high rotational levels. For some of them the mixing is large but the rotational Boltzmann factor is small (e.g., the 7, 7 \leftarrow 7, 4 transition; mixing 38%, $E_{\rm rot.} = 2002.46 \text{ cm}^{-1}$). For others,

TAB	LE II	
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$J', G', U' \leftarrow J, G, U$	v _{obs} .	v a calc.
4, 3, $+1 \leftarrow 3, 0, -1$	3228.764	3228.49
2, 2, +1 ← 1, 1, +1	3146.461	3146.08
4, 4, +1 ← 3, 1, -1	3102.732	3102.74
3, 3, $+1 \leftarrow 2, 0, +1$	3097.248	3096.97
$1, 1, +1 \leftarrow 1, 2, +1$	3092.824	3091.96
2, 1, +1 \leftarrow 2, 2, +1	3091.892	3091.41
1, 2, +1 ← 0, 1, +1	3062.813	3062.48
2, 1, $-1 \leftarrow 3$, 4, +1	3059.512	3058.90
4, 4, $+1 \leftarrow 3, 1, +1$	3042.157	3042.03
2, 3, $+1 \leftarrow 1, 0, -1$	3037.321	3037.15
3, 4, $+1 \leftarrow 2, 1, -1$	3009.310	3009.43
$0, 1, +1 \leftarrow 1, 2, +1$	3005.898	3005.67
5, 5, +1 ← 4, 2, +1	2994.903	2994.99
4, 5, +1 ← 3, 2, -1	2989.618	2989.82
5, 6, $+1 \leftarrow 4, 3, -1$	2984.259 ^b	2984.79
$1, 2, +1 \leftarrow 1, 1, +1$	2974.682	2974.43
$3, 4, +1 \leftarrow 2, 1, +1$	2974.534	2974.55
5, 6, $+1 \leftarrow 4, 3, +1$	2896.160	2896.55
3, 3, +1 ← 3, 0, −1	2884.148	2884.12
2, 3, $+1 \leftarrow 2, 0, +1$	2841.148	2841.04
5, 5, +1 ← 5, 2, -1	2685.942	2686.47

Observed Transitions in the $v_1 + v_2 \leftarrow v_2$ Band of H⁺₃ (in cm⁻¹)

^a Calculated wavenumbers are from Miller, Tennyson, and Sutcliffe (21).

^h Overlapped with stronger fundamental band transition.

vice versa (e.g., the 5, 5 \leftarrow 4, 2 transition; mixing 13%, $E_{\text{rot.}} = 768.47 \text{ cm}^{-1}$). The near-degenerate energy levels of the ν_2 state which give largest mixings are given in the second column of Table I together with the energy separation. Note the remarkable accuracy of the prediction by Miller, Tennyson, and Sutcliffe (22). An example of the observed lines is shown in Fig. 1.

B. The $v_1 + v_2 \leftarrow v_2$ Transitions

This transition has been predicted by Carney and Porter (17) to have the transition dipole moment which is about six times smaller than that of the allowed hot band transition $2\nu_2(l=2) \leftarrow \nu_2$. The intensities of spectral lines are expected to be 40 times smaller than those of the hot band which in turn is 50 times smaller than those of the fundamental band due to the vibrational Boltzmann factor (3). In spite of this serious reduction of intensity, quite a few lines have been observed.

v ₁ state		$v_1 + v_2$ state		
J, K	E	J, G, U	E	
7, 5	4962.092	4, 2, 1	6363.419	
7.6	4721.781	5, 5, 1	6346.282	
7, 7	4456.877	4, 2, -1	6276.372	
6, 5	4389.267	4, 3, 1	6254.703	
6, 6	4147.052	4, 3, -1	6158.269	
5, 5	3888.670	5, 6, 1	6129.537	
4, 3	3820.803	4, 4, 1	6105.633	
4, 4	3667.139	3, 2, 1	6015.948	
3, 2	3595.742	3, 2, -1	5949.445	
3, 3	3485.311	4, 5, 1	5920.987	
2, 2	3343.150	3, 3, 1	5910.107	
1, 1	3240.751	2, 1, 1	5815.859	
		2, 1, -1	5779.004	
		3, 4, 1	5764.880	
		2, 2, 1	5756.010	
		2, 3, 1	5654.009	
		1, 1, 1	5640.500	
		1, 2, 1	5584.227	
		0, 1, 1	5554.069	

TABLE III

Experimentally Determined Absolute Energy Level Values (in cm⁻¹)

In the traditional formalism of the vibration-rotation interaction (23), the $\nu_1 + \nu_2$, J', $k \pm 1$, $l = \mp 1 \leftarrow \nu_2$, J, k, $l = \pm 1$ transitions borrow intensity from allowed transitions through Fermi resonances. The two major ones are

(a) from the $2\nu_2(l=2) \leftarrow \nu_2$ transition through the mixing,

$$\langle \nu_1 + \nu_2, l = \mp 1 | \frac{1}{12} k_{1222} q_1 (q_{2+}^3 + q_{2-}^3) | 2\nu_2, l = \pm 2 \rangle = \frac{1}{4} k_{1222};$$
 (9)

(b) from the $3\nu_2(l=1) \leftarrow \nu_2$ transition through the mixing,

$$\langle \nu_1 + \nu_2, l = \pm 1 | \frac{1}{2} k_{122} q_1 q_{2+} q_{2-} | 3\nu_2, l = \pm 1 \rangle = \frac{1}{2} k_{122}.$$
 (10)

The value of k_{122} was obtained to be 1290 cm⁻¹ as shown below. We attempted to determine the value of k_{1222} from the reported values of q_2^J and q_2^K (15), the centrifugal distortion correction to the *l*-doubling constant, and cubic potential constants whose values are determined as discussed below. This gave an abnormally large value of k_{1222} , which clearly contradicted the experimentally observed intensities. Perhaps the reported values of q_2^J and q_2^K are contaminated by the effect of other high order terms that are neglected in the perturbation treatment (34). If we use the theoretical intensity

Newly Observed Transitions in the $\nu_2 \leftarrow 0$ Band (in cm⁻¹)

$J', G', U' \leftarrow J, K$	v _{obs.}	V _{calc.}
8, 2, 1 ← 7, 2	3290.752	3290.47
8, 5, 1 ← 7, 5	3289.100	3288.89
13, 12, -1 ← 12, 12	3284.087	
8, 6, 1 ← 7, 6	3276.193	3275.90
8, 7, 1 ← 7, 7	3265.135	3264.75
12, 11, -1 ← 11, 11	3249.699	3248.86
12, 10, -1 ← 11, 10	3238.616	3237.48
13, 11, 1 ← 12, 11	3272.711	
7, 1, 1 ← 6, 1	3220.810	3220.62
7, 3, 1 ← 6, 3	3216.352	3216.21
11, 10, -1 ← 10, 10	3210.787	3209.92
12, 9, -1 ← 11, 9	3209.068	3207.94
7, 4, 1 ← 6, 4	3205.293	3205.07
10. 8, -1 ← 9, 8	3159.009	3158.05
$11, 9, -1 \leftarrow 10, 9$	3200.717	3199.66
10, 7, -1 ← 9, 7	3140.637	3139.62
10, 6, -1 ← 9, 6	3130.210	3129.27
6, 1, 1 ← 5, 1	3129.803	3129.62
6, 2, 1 ← 5, 2	3122.247	3122.04
9, 5, -1 ← 8, 5	3102.361	3100.96
9, 6, -1 ← 8, 6	3099.901	3099.00
8, 5, -1 ← 7, 5	3056.250	3055.50
8, 3, -1 ← 7, 3	3029.063	3028.12
8, 4, -1 ← 7, 4	3025.934	3025.05
7, 3, -1 ← 6, 3	2985.494	2986.67
6, 1, -1 ← 5, 1	2938.491	2937.79
8, 6, 1 ← 8, 6	2620.589	2620.49
6, 4, 1 ← 6, 4	2605.060	2604.96
7, 3, -1 ← 7, 3	2420.728	2420.07
7, 0, -1 ← 7, 0	2418.899	2418.19

given by Miller *et al.* (22), we obtain the reasonable value of $k_{1222} = 267 \text{ cm}^{-1}$. We see that the mixing (a) contributes about 40% and the mixing (b) 60% to the induced transition dipole moment.

Observed transitions are listed in Table II. An example of the spectral lines is shown in Fig. 1.

C. The $v_1 \leftarrow v_2$ Transitions

The band origin of the difference transition $\nu_1 \leftarrow \nu_2$ occurs at ~660 cm⁻¹. While this band has not been observed, we discuss it here for completeness. The first principles calculation by Carney and Porter (17) and that by Miller *et al.* (22) predicted that the transition dipole moment is approximately one-third of that for the fundamental band. Thus this transition is expected to be weaker than the fundamental band by a factor of 500, and is perhaps detectable using diode laser spectroscopy.

In the traditional formalism of the vibration-rotation interaction, the $\nu_1 \leftarrow \nu_2$ transition borrows intensities from a variety of Fermi resonances. Three major ones are

(a) from the $2\nu_2(l=0) \leftarrow \nu_2$ band through the mixing

$$\langle 2\nu_2, l=0|\frac{1}{2}k_{122}q_1q_{2+}q_{2-}|\nu_1\rangle = \frac{\sqrt{2}}{4}k_{122};$$
 (11)

(b) from the $\nu_1 + \nu_2 \leftarrow \nu_1$ band through the mixing,

$$\langle \nu_1 + \nu_2, l = \pm 1 | \frac{1}{6} k_{111} q_1^3 | \nu_2, l = \pm 1 \rangle = \frac{1}{4\sqrt{2}} k_{111};$$
 (12)

(c) from the $v_2 \leftarrow 0$ band through the mixing,

$$\langle \nu_1 | \frac{1}{6} k_{111} q_1^3 | 0 \rangle = \frac{1}{4\sqrt{2}} k_{111}.$$
 (13)

Using $k_{111} = 1820 \text{ cm}^{-1}$ as determined below, we see these mechanisms contribute transition moments of 0.037, 0.025, and 0.022 Debye, respectively.

D. Anharmonicity Constants

The anharmonicity constants used in the above calculations were determined using Watson's formulation of the vibration-rotation interaction of the X_3 -type molecule (23) and experimental vibration-rotation constants and band origins. The constants were defined by the potential

$$V = \frac{1}{2} \sum_{k} \nu_{k} q_{k}^{2} + \frac{1}{3!} \sum_{lmn} k_{lmn} q_{l} q_{m} q_{n} + \frac{1}{4!} \sum_{lmnr} k_{lmnr} q_{l} q_{m} q_{n} q_{r} + \cdots, \quad (14)$$

where q's are dimensionless normal coordinates q_1 or q_2 . Three cubic constants k_{111} , k_{122} , and k_{222} , and four quartic constants k_{1111} , k_{1122} , k_{1222} , and k_{2222} are nonvanishing. The cubic constants k_{111} and k_{122} were determined from the variation of rotational constants upon vibrational excitation. If we used the *B* constants, we obtained

 $k_{111} = 1770 \text{ cm}^{-1}$ and $k_{122} = 1030 \text{ cm}^{-1}$,

while if we used the C constants, we obtained

$$k_{111} = 1820 \text{ cm}^{-1}$$
 and $k_{122} = 1290 \text{ cm}^{-1}$

The discrepancy between the two sets of constants results from neglect of higherorder terms both in theory and in the analysis and indicates the limit of accuracy of these constants. Because of the small mass of proton and the relatively small curvature

 $J', G', U' \leftarrow J, G, U$ Vobs ٧ $7, 6, 2 \leftarrow 6, 6, 1$ 3214.601 3214.04 $6, 3, 2 \leftarrow 5, 3, -1$ 3085.609 3086.11 $5, 2, 2 \leftarrow 4, 2, -1$ 3067.732^b 3067.31 $5, 4, 2 \leftarrow 4, 4, 1$ 3020.490 3019.94 $6, 4, 2 \leftarrow 5, 4, -1$ 3006.993^b 3007.25 $5, 3, 2 \leftarrow 4, 3, 1$ 2979.658 2979.56 $5, 2, 2 \leftarrow 4, 2, 1$ 2976.566^b 2975.95 $6, 3, 2 \leftarrow 5, 3, 1$ 2964.984^b 2965.23 $6, 3, -2 \leftarrow 5, 3, -1$ 2962.822 2961.57 $4, 2, 2 \leftarrow 3, 2, -1$ 2956.947^b 2956.40 5, 2, $-2 \leftarrow 4, 2, -1$ 2909.239^b 2908.08 $6, 4, 2 \leftarrow 5, 4, 1$ 2893.370^b 2893.45 $6, 3, 2 \leftarrow 6, 3, 1$ 2436.653 2436.96

Newly Observed Transitions in the $2\nu_2(l=2) \leftarrow \nu_2$ Band (in cm⁻¹)

^a Predicted wavenumbers are from Miller and Tennyson (18).

^b Assignment confirmed by combination difference within 0.01 cm⁻¹.

of the vibrational potential at equilibrium, the convergence of the perturbation treatment is not fast in H_3^+ . The value of k_{222} was calculated from the observed *l*-doubling constant to be 1180 cm⁻¹.

Three quartic potential constants were determined from the anharmonicity of vibrational energy levels, $x_{11} = -47.2 \text{ cm}^{-1}$, $x_{12} = -148.4 \text{ cm}^{-1}$, and $x_{22} = 327 \text{ cm}^{-1}$ to be $k_{1111} = 890 \text{ cm}^{-1}$, $k_{1122} = 330 \text{ cm}^{-1}$, and $k_{2222} = 130 \text{ cm}^{-1}$. The remaining quartic constant k_{1222} should in principle be determinable from the observed values of q_2^J and q_2^K , but this was not done, as was mentioned earlier.

IV. EXPERIMENTAL DETAILS

The observation of forbidden transitions was made by using our difference frequency spectrometer in a manner similar to that reported earlier (3). Tunable visible single mode radiation from a ring dye laser and single mode radiation from an Ar ion laser are passed through a temperature controlled LiNbO₃ crystal to generate frequency tunable infrared radiation, the method initially developed by Pine (35). The H⁺₃ molecular ions were generated by ac glow discharges using mixtures of 600 mTorr H₂ and 6 Torr He in a liquid-nitrogen-cooled multiple-inlet multiple-outlet discharge cell. The velocity modulation method initiated by Gudeman and Saykally (36) and the unidirectional multiple passing were used for high-sensitivity detection. The infrared beam was split into two beams of equal power before entering the White cell mirror setup. The two beams went through the discharge cell unidirectionally four times in opposite directions and were detected by two matched infrared detectors. The outputs from the two detectors were combined in a set of transformers in opposite phase to subtract noise and to double the velocity modulated signal.

TA	BL	E	VI

Cilussigin		Discharge (1910)	<i>it zakely of 113)</i>	(mem)
3293.783	3206.893	3097.985	3038.913	2979.325
3292.515	3203.517	3096.661	3035.457	2977.488
3288.439	3203.095	3093.664	3033.304	2976.080
3285.763	3194.792	3067.730	3028.539	2975.656
3284.087	3182.593	3065.775	3024.429	2966.864
3277.424	3180.420	3065.574	3023.674	2965.791
3270.564	3180.242	3063.922	3022.416	2964.985
3269.491	3179.108	3063.273	3022.332	2958.899
3266.011	3161.895	3063.078	3021.856	2958.735
3259.832	3140.637	3061.287	3003.250	2953.405
3249.788	3137.808	3060.506	3002.750	2950.605
3247.890	3137.325	3059.381	3002.355	2941.187
3247.685	3128.912	3053.562	3000.105	2934.357
3240.382	3121.475	3053.347	2998.339	2928.470
3238.658	3121.210	3052.071	2995.601	2924.414
3236.265	3120.826	3051.406	2993.467	2918.157
3220.176	3118.509	3050.542	2990.585	2915.872
3219.107	3103.866	3046.038	2984.082	
3209.068	3101.391	3042.578	2979.507	
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Unassigned Lines in Our Discharge (Most Likely of H₃⁺) (in cm⁻¹)

The spectral lines were searched in the region where they were predicted. These results were augmented by a high sensitivity, continuous scan for carbo-ion spectros-copy between 3300 and 2900 cm⁻¹, which also included many H_3^+ lines. This continuous scan complements the earlier scan by Bawendi and Rehfuss between 2900 and 2400 cm⁻¹ (3).

V. ABSOLUTE ENERGY LEVELS

The observed spectral lines of the forbidden $v_1 \leftarrow 0$ and $v_1 + v_2 \leftarrow v_2$ bands have enabled us to determine the absolute energy level values of many vibration-rotation levels in the v_1 and the $v_1 + v_2$ states. They are listed in Table III. The $v_1 \leftarrow 0$ transitions and the $v_1 + v_2 \leftarrow v_2$ transitions provided complementary information; they respectively provided direct information on high J, K levels and low J, K levels. Then our previous observation of the difference $v_1 + v_2 \leftarrow v_1$ band supplied extra information. It seems that if we had an extra sensitivity factor of 10, we could have determined these levels nearly completely.

VI. OTHER TRANSITIONS

In the process of detecting and assigning the weak forbidden transitions, we observed a great many new H_3^+ spectral lines belonging to allowed transitions. Newly assigned

spectral lines of the $v_2 \leftarrow 0$ fundamental band and the $2v_2(l=2) \leftarrow v_2$ hot band are listed in Tables IV and V. For the fundamental band, we now reach J = 12 and K =12 rotational level in the ground state, which is 3402 cm⁻¹ above the lowest level. We note that such J = K levels are metastable in laboratory plasmas, as in interstellar molecular clouds, and have anomalously large population. The observed J = 13, G = 12, $U = -1 \leftarrow J = K = 12$ transition has a signal-to-noise ratio of at least 20 in a plasma which was not optimized to H_3^+ , indicating that we should be able to reach much higher transitions in the shorter wavelength region. A similar effect has been noted in the spectrum of CH₃⁺. It is very likely that these high rotational lines play an important role in the future as an astronomical probe for high temperature ionized regions.

These new assignments still leave many observed lines unassigned. They are listed in Table VI. From their appearance and their responses to plasma conditions, we believe most of them are due to H_3^+ . Altogether over 600 H_3^+ spectral lines have been observed. Together with the great many lines near the dissociation limit reported by Carrington, Buttenshaw, Kennedy, and others (*36*), the richness of the spectrum of this most fundamental polyatomic species is simply amazing.

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Note added in proof. It has been pointed out by Watson (34) that the $\nu_1 + \nu_2 \leftarrow \nu_2$ transition borrows intensity also from the $\nu_2 \leftarrow \nu_2$ and the $\nu_1 + \nu_2 \leftarrow \nu_1 + \nu_2$ forbidden rotational transitions. Inclusion of this effect may reduce the value of k_{1222} given in this paper.

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