Observation of Infrared Forbidden Transitions of H$_3^+$

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The $\nu_2 \rightarrow 0$ and $\nu_1 + \nu_2 \rightarrow \nu_2$ forbidden transitions of H$_3^+$ have been observed. The former is induced by the rovibrational Birss resonance between the $\nu_1$ and $\nu_2$ 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 $\nu_1$ and the $\nu_1 + \nu_2$ 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 $\nu_2 \rightarrow 0$ 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 in 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$_3^+$, $2\nu_2 (l = 2) \rightarrow \nu_2$, $2\nu_2 (l = 0) \rightarrow \nu_2$, and $\nu_1 + \nu_2 \leftrightarrow \nu_1$, in the 3.4–5.1 $\mu$m 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 overton band $2\nu_2 (l = 2) \rightarrow 0$ in the 1.9–2.3 $\mu$m region (5) and the second overton band $3\nu_2 (l = 1) \rightarrow 0$ in the 1.5 $\mu$m region (6), respectively. In assigning rovibrational transitions involving 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 $\mu$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 $\nu_2 \rightarrow 0$ fundamental for high rotational levels (14, 15), provided detailed energy level structure related to stacks of $\nu_2$ excitation. The first overton band $2\nu_2 (l = 2) \rightarrow 0$ 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 us to determine a value of $2\nu_2 (l = 2)$, $2\nu_2 (l = 0)$ on the absolute rovibronic energy levels, which are reported in this paper.

There have been a few values of $\nu_1$. The calculated values are close to 3178.348 cm$^{-1}$ (16). The paper on $\nu_1$ appears to be based on isolated systematic perturbations from Messmer, and Walther (17). We adopt the $\nu_1 = 3178.29 \pm 0.1$ cm$^{-1}$.

The studies of diatomic molecules provide a complete set of rovibrational energy levels. The study of the $\nu_1$ + $\nu_2 \rightarrow \nu_2$ and the $\nu_1 \rightarrow \nu_2$ transitions is based on the work 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 $\mu$m emission spectrum of H$_3^+$ observed in the auroral region of the Jovian ionosphere (12, 13).

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us to determine absolute rovibrational energy values for the ground state and the \( \nu_2 \), \( 2\nu_2(l = 2) \), \( 2\nu_2(l = 0) \), and \( 3\nu_2(l = 1) \) excited states. In order to obtain information on the absolute rovibrational energy levels of \( \nu_1 \) 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 \( \text{H}_2^+ \) which predicted the value of \( \nu_1 \). The calculated values up to 1980 are summarized in a review \( (16) \). Carney and Porter in their classic paper \( (17) \) gave the \( \nu_1 \) 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 \( \nu_1 \) 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 \textit{et al.} \( (15) \) isolated a systematic energy shift on a series of rotational levels of the \( \nu_2 \) state due to a perturbation from the \( \nu_1 \) state and estimated \( \nu_1 \) 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 \( \text{H}_3^+ \).

The studies of direct rovibrational forbidden transitions reported in the present paper provide absolute rovibrational energy level values of the \( \nu_1 \) and \( \nu_1 + \nu_2 \) states. The study of the \( \nu_1 \leftarrow 0 \) transition is based on the results of Majewski \textit{et al.} \( (15) \), where the perturbation between the \( \nu_1 \) and \( \nu_2 \) states is noted. The studies of the \( \nu_1 + \nu_2 \leftarrow \nu_2 \) and the \( \nu_1 \leftarrow \nu_2 \) 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 \( \text{H}_2^+ \) molecular ions in space relax radiatively.

## II. FORBIDDEN TRANSITIONS

The rovibrational states of \( \text{H}_2^+ \) 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 \( \nu_1 \) and \( \nu_2 \), the vibrational angular momentum quantum number \( I \), 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,

\[
\text{parity } + \leftrightarrow -,
\]

which leads to the rigorous rule

\[
\Delta k = \text{odd}.
\]

There exist very nearly rigorous rules

\[
\Delta J = 0, \pm 1 \quad \text{and} \quad \Delta I = 0.
\]

The latter of this rule signifies the stability of the \textit{ortho} \( (I = \frac{1}{2}) \) and the \textit{para} \( (I = \frac{1}{2}) \) spin modifications of \( \text{H}_2^+ \), and leads to the selection rule

\[
\Delta |k - I| = 3n \quad (n: \text{integer}).
\]

These selection rules are all obeyed. Following Watson, we use \( J \) and \( |k| \) to specify rotational levels of the ground state and the \( \nu_1 \) state, and, for the other states involving
TABLE I

Observed Transitions in the ν₁ ← 0 band of H₂⁺ (in cm⁻¹)

<table>
<thead>
<tr>
<th>J', K' ← J, K</th>
<th>J, G, U^a</th>
<th>Δυ^b</th>
<th>ν_{obs}</th>
<th>ν_{calc}^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>7, 5 ← 6, 2</td>
<td>7, 2, 1</td>
<td>70.1</td>
<td>3282.308</td>
<td>3282.27</td>
</tr>
<tr>
<td>6, 5 ← 5, 2</td>
<td>6, 2, 1</td>
<td>79.9</td>
<td>3202.169</td>
<td>3202.15</td>
</tr>
<tr>
<td>7, 6 ← 6, 3</td>
<td>7, 3, 1</td>
<td>-21.9</td>
<td>3144.454</td>
<td>3144.33</td>
</tr>
<tr>
<td>5, 5 ← 4, 2</td>
<td>5, 2, 1</td>
<td>95.6</td>
<td>3120.199</td>
<td>3120.24</td>
</tr>
<tr>
<td>6, 6 ← 5, 3</td>
<td>6, 3, 1</td>
<td>-55.3</td>
<td>3066.561</td>
<td>3066.5</td>
</tr>
<tr>
<td>7, 7 ← 6, 4</td>
<td>7, 4, 1</td>
<td>36.6</td>
<td>3026.154</td>
<td>3025.96</td>
</tr>
<tr>
<td>6, 5 ← 6, 2</td>
<td>6, 2, 1</td>
<td>79.9</td>
<td>2709.479</td>
<td>2709.61</td>
</tr>
<tr>
<td>6, 6 ← 6, 3</td>
<td>6, 3, 1</td>
<td>-55.3</td>
<td>2569.726</td>
<td>2569.85</td>
</tr>
<tr>
<td>7, 7 ← 7, 4</td>
<td>7, 4, 1</td>
<td>36.6</td>
<td>2454.417</td>
<td>2453.39</td>
</tr>
</tbody>
</table>

^a Rotational levels in the ν₂ state which induce the transition through the Birr 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.

ν₂ in which I is nonzero, we use J, Houg'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 ν₁ ← 0 and ν₁ + ν₂ ← ν₂ which are forbidden in the sense that they involve excitation of the totally symmetric vibration ν₁. It should be noted that there is a qualitative difference between these two transitions. The ν₁ ← 0 transition corresponds to symmetry A'₁ ← 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

\[ Δk = ±3. \] (5)

The ν₁ + ν₂ ← ν₂ transition \((E' ← E')\), 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

\[ Δk = ±1, \quad Δl = ±2. \] (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 H₂⁺ (28-31), but they are yet to be observed. Possible importance of such transitions for observing extragalactic H₂⁺ 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 interaction terms that enter our observed results.

A. The ν₁ ← 0 Transition

The rovibrational transition \(H_{22} = q, p\) represents a perturbation term fundamental band (15 cm⁻¹). The effect of this general treatment of the value of \(α₁₂\) and \(ν₁\) intensity borrowing in the vibrational energy is in that degeneracy occurs between the forbidden \(ν₁, J', K\),

\[ \langle ν₂, J', G = K, U|H_{2} = \frac{α_{12}}{V_2}[J'(J'+1)] \]

Observed spectral lines levels. For some of small (e.g., the 7, 7 ←
interaction terms that cause such effect for each forbidden transition and summarize our observed results.

A. The $\nu_1 \leftarrow 0$ Transition

The rovibrational transition $\nu_1, J', K + 3 \leftarrow J, K$ borrows intensity from the $\nu_2, l = 1, J', K + 1 \leftarrow J, K$ transition through the mixing term

$$H_{22}^{(2)} = -\frac{1}{2} \alpha_{12} \left[ \langle q_1 q_2, + p_1 p_2, \rangle J_2^2 + \langle q_1 q_2, - p_1 p_2, \rangle J_2^2 \right]$$

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 $\nu_1, J', K + 3 \leftarrow J, K$, but such transitions are much weaker because of larger energy gaps between mixed levels. This perturbation term $H_{22}^{(2)}$ was isolated by Watson in his extensive analysis of the $\nu_2$ fundamental band (15) and the value of the constant $\alpha_{12}$ 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 $q^2 J^2 (33)$. A comparison of the value of $\alpha_{12}$ and $\nu_1 - \nu_2 = 656.9$ 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 $\nu_1, J', K + 3$ and $\nu_2, J', G = K, U$ and induces the forbidden $\nu_1, J', K + 3 \leftarrow J, K$ transition. The matrix element of $H_{22}^{(2)}$ is

$$\langle \nu_2, J', G = K, U | H_{22}^{(2)} | \nu_1, J', K + 3 \rangle$$

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

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%, $E_{rot} = 2002.46$ cm$^{-1}$). For others,
TABLE II

Observed Transitions in the $v_1 + v_2 \leftrightarrow v_2$ Band of H$_2^+$ (in cm$^{-1}$)

<table>
<thead>
<tr>
<th>$J'$, $G'$, $U'$ $\leftrightarrow$ $J$, $G$, $U$</th>
<th>$v_{\text{obs}}$</th>
<th>$v_{\text{calc}}$^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>4, 3, +1 $\leftrightarrow$ 3, 0, -1</td>
<td>3228.764</td>
<td>3228.49</td>
</tr>
<tr>
<td>2, 2, +1 $\leftrightarrow$ 1, 1, +1</td>
<td>3146.461</td>
<td>3146.08</td>
</tr>
<tr>
<td>4, 4, +1 $\leftrightarrow$ 3, 1, -1</td>
<td>3102.732</td>
<td>3102.74</td>
</tr>
<tr>
<td>3, 3, +1 $\leftrightarrow$ 2, 0, +1</td>
<td>3097.248</td>
<td>3096.97</td>
</tr>
<tr>
<td>1, 1, +1 $\leftrightarrow$ 1, 2, +1</td>
<td>3092.824</td>
<td>3091.96</td>
</tr>
<tr>
<td>2, 1, +1 $\leftrightarrow$ 2, 2, +1</td>
<td>3091.892</td>
<td>3091.41</td>
</tr>
<tr>
<td>1, 2, +1 $\leftrightarrow$ 0, 1, +1</td>
<td>3062.813</td>
<td>3062.48</td>
</tr>
<tr>
<td>2, 1, -1 $\leftrightarrow$ 3, 4, +1</td>
<td>3059.512</td>
<td>3058.90</td>
</tr>
<tr>
<td>4, 4, +1 $\leftrightarrow$ 3, 1, +1</td>
<td>3042.157</td>
<td>3042.03</td>
</tr>
<tr>
<td>2, 3, +1 $\leftrightarrow$ 1, 0, -1</td>
<td>3037.321</td>
<td>3037.15</td>
</tr>
<tr>
<td>3, 4, +1 $\leftrightarrow$ 2, 1, -1</td>
<td>3009.310</td>
<td>3009.43</td>
</tr>
<tr>
<td>0, 1, +1 $\leftrightarrow$ 1, 2, +1</td>
<td>3005.898</td>
<td>3005.67</td>
</tr>
<tr>
<td>5, 5, +1 $\leftrightarrow$ 4, 2, +1</td>
<td>2994.903</td>
<td>2994.99</td>
</tr>
<tr>
<td>4, 5, +1 $\leftrightarrow$ 3, 2, -1</td>
<td>2989.618</td>
<td>2989.82</td>
</tr>
<tr>
<td>5, 6, +1 $\leftrightarrow$ 4, 3, -1</td>
<td>2984.299^b</td>
<td>2984.79</td>
</tr>
<tr>
<td>1, 2, +1 $\leftrightarrow$ 1, 1, +1</td>
<td>2974.682</td>
<td>2974.43</td>
</tr>
<tr>
<td>3, 4, +1 $\leftrightarrow$ 2, 1, +1</td>
<td>2974.534</td>
<td>2974.55</td>
</tr>
<tr>
<td>5, 6, +1 $\leftrightarrow$ 4, 3, -1</td>
<td>2896.160</td>
<td>2896.55</td>
</tr>
<tr>
<td>3, 3, +1 $\leftrightarrow$ 3, 0, -1</td>
<td>2884.148</td>
<td>2884.12</td>
</tr>
<tr>
<td>2, 3, +1 $\leftrightarrow$ 2, 0, +1</td>
<td>2841.148</td>
<td>2841.04</td>
</tr>
<tr>
<td>5, 5, +1 $\leftrightarrow$ 5, 2, -1</td>
<td>2685.942</td>
<td>2686.47</td>
</tr>
</tbody>
</table>

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

^b Overlapped with stronger fundamental band transition.

vice versa (e.g., the 5, 5 $\leftrightarrow$ 4, 2 transition; mixing 13%, $E_{\text{rot}}$, = 768.47 cm$^{-1}$). The near-degenerate energy levels of the $v_2$ 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 $v_1 + v_2 \leftrightarrow v_2$ 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 $2v_2(l = 2) \leftrightarrow v_2$. 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.

In the traditional f $J'$, $k \pm 1$, $l = \mp 1$ - transitions through F

(a) from the 2v

(b) from the 3v

The value of $k_{122}$ was determined the value of distortion correction values are determined $k_{122}$, which clearly $c$ reported values of $q_0^2$ that are neglected in.
TABLE III
Experimentally Determined Absolute Energy Level Values (in cm\(^{-1}\))

<table>
<thead>
<tr>
<th>J, K state</th>
<th>(E)</th>
<th>J, G, U state</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7, 5</td>
<td>4962.092</td>
<td>4, 2, 1</td>
<td>6363.419</td>
</tr>
<tr>
<td>7, 6</td>
<td>4721.781</td>
<td>5, 5, 1</td>
<td>6346.282</td>
</tr>
<tr>
<td>7, 7</td>
<td>4456.877</td>
<td>4, 2, -1</td>
<td>6276.372</td>
</tr>
<tr>
<td>6, 5</td>
<td>4389.267</td>
<td>4, 3, 1</td>
<td>6254.703</td>
</tr>
<tr>
<td>6, 6</td>
<td>4147.052</td>
<td>4, 3, -1</td>
<td>6158.269</td>
</tr>
<tr>
<td>5, 5</td>
<td>3888.670</td>
<td>5, 6, 1</td>
<td>6129.537</td>
</tr>
<tr>
<td>4, 3</td>
<td>3820.803</td>
<td>4, 4, 1</td>
<td>6105.633</td>
</tr>
<tr>
<td>4, 4</td>
<td>3667.139</td>
<td>3, 2, 1</td>
<td>6015.948</td>
</tr>
<tr>
<td>3, 2</td>
<td>3595.742</td>
<td>3, 2, -1</td>
<td>5949.445</td>
</tr>
<tr>
<td>3, 3</td>
<td>3485.311</td>
<td>4, 5, 1</td>
<td>5920.987</td>
</tr>
<tr>
<td>2, 2</td>
<td>3343.150</td>
<td>3, 3, 1</td>
<td>5910.107</td>
</tr>
<tr>
<td>1, 1</td>
<td>3240.751</td>
<td>2, 1, 1</td>
<td>5815.859</td>
</tr>
</tbody>
</table>

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,

\[
\langle \nu_1 + \nu_2, l = \mp 1 | \frac{1}{4} k_{1222} q_1 (q_1^2 + q_2^2 + 3) | 2\nu_2, l = \pm 2 \rangle = \frac{1}{4} k_{1222};
\]  

(9)

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

\[
\langle \nu_1 + \nu_2, l = \mp 1 | \frac{1}{4} k_{1222} q_1 q_2 | 3\nu_2, l = \mp 1 \rangle = \frac{1}{4} k_{1222};
\]  

(10)

The value of \(k_{1222}\) was obtained to be 1290 cm\(^{-1}\) as shown below. We attempted to determine the value of \(k_{1222}\) from the reported values of \(q_4^2\) and \(q_5^2\) (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 \(q_4^2\) and \(q_5^2\) are contaminated by the effect of other high order terms that are neglected in the perturbation treatment (34). If we use the theoretical intensity
TABLE IV
Newly Observed Transitions in the \( \nu_2 \leftarrow 0 \) Band (in cm\(^{-1}\))

\[
\begin{array}{cccc}
J', G', U' \leftarrow J, K & v_{\text{obs}} & v_{\text{calc}} \\
8, 2, 1 \leftarrow 7, 2 & 3290.752 & 3290.47 \\
8, 5, 1 \leftarrow 7, 5 & 3289.100 & 3288.89 \\
13, 12, -1 \leftarrow 12, 12 & 3284.087 & - \\
8, 6, 1 \leftarrow 7, 6 & 3276.193 & 3275.90 \\
8, 7, 1 \leftarrow 7, 7 & 3265.135 & 3264.75 \\
12, 11, -1 \leftarrow 11, 11 & 3249.699 & 3248.86 \\
12, 10, -1 \leftarrow 11, 10 & 3238.616 & 3237.48 \\
13, 11, 1 \leftarrow 12, 11 & 3272.711 & - \\
7, 1, 1 \leftarrow 6, 1 & 3220.810 & 3220.62 \\
7, 3, 1 \leftarrow 6, 3 & 3216.352 & 3216.21 \\
11, 10, -1 \leftarrow 10, 10 & 3210.787 & 3209.92 \\
12, 9, -1 \leftarrow 11, 9 & 3209.068 & 3207.94 \\
7, 4, 1 \leftarrow 6, 4 & 3205.293 & 3205.07 \\
10, 8, -1 \leftarrow 9, 8 & 3159.099 & 3158.05 \\
11, 9, -1 \leftarrow 10, 9 & 3200.717 & 3199.66 \\
10, 7, -1 \leftarrow 9, 7 & 3140.637 & 3139.62 \\
10, 6, -1 \leftarrow 9, 6 & 3130.210 & 3129.27 \\
6, 1, 1 \leftarrow 5, 1 & 3129.803 & 3129.62 \\
6, 2, 1 \leftarrow 5, 2 & 3122.247 & 3122.04 \\
9, 5, -1 \leftarrow 8, 5 & 3102.361 & 3100.96 \\
9, 6, -1 \leftarrow 8, 6 & 3099.901 & 3099.00 \\
8, 5, -1 \leftarrow 7, 5 & 3056.250 & 3055.50 \\
8, 3, -1 \leftarrow 7, 3 & 3029.063 & 3028.12 \\
8, 4, -1 \leftarrow 7, 4 & 3025.934 & 3025.05 \\
7, 3, -1 \leftarrow 6, 3 & 2985.494 & 2986.67 \\
6, 1, -1 \leftarrow 5, 1 & 2938.491 & 2937.79 \\
8, 6, 1 \leftarrow 8, 6 & 2620.589 & 2620.49 \\
6, 4, 1 \leftarrow 6, 4 & 2605.060 & 2604.96 \\
7, 3, -1 \leftarrow 7, 3 & 2420.728 & 2420.07 \\
7, 0, -1 \leftarrow 7, 0 & 2418.899 & 2418.19 \\
\end{array}
\]

C. The \( \nu_1 \leftarrow \nu_2 \) Transition

The band origin of this band has not been calculated by Carney and the transition dipole moment. Thus this transition factor of 500, and is per

In the traditional form, the transition borrows intensities

(a) from the \( 2\nu_2 \leftarrow \)

\( <^{2}_{s} > \)

(b) from the \( \nu_1 + \)

\( <^{1}_{s} > \)

(c) from the \( \nu_2 \leftarrow \)

Using \( k_{111} = 1820 \text{ cm}^{-1} \)

D. Anharmonicity Correction

The anharmonicity of Watson's formulation (23) and experimental were defined by the potential

\[
V = \frac{1}{2} \sum q_i^2
\]

where \( q_i \)'s are dimensionless \( k_{122}, \) and \( k_{222}, \) and four

The cubic constants \( k_1 \) constants upon vibration

while if we used the \( k_{111} \)

The discrepancy between these constants, but in these constants, because
C. The $\nu_1 \rightarrow \nu_2$ Transitions

The band origin of the difference transition $\nu_1 \rightarrow \nu_2$ occurs at $\approx 660 \text{ cm}^{-1}$. 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 $\nu_1 \rightarrow \nu_2$ 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

$$\langle 2\nu_2, l = 0 | \frac{1}{2} k_{122}q_1q_2 + q_2 | \nu_1 \rangle = \frac{\sqrt{2}}{4} k_{122}, \quad (11)$$

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

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

(c) from the $\nu_2 \leftarrow 0$ band through the mixing,

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

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 $X_2$-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

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

while if we used the $C$ constants, we obtained

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

The discrepancy between the two sets of constants results from neglect of higher-order 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
TABLE V
Newly Observed Transitions in the $2v_3 (l = 2) \leftrightarrow v_2$ Band (in cm$^{-1}$)

<table>
<thead>
<tr>
<th>$J', G', U' \leftrightarrow J, G, U$</th>
<th>$v_{obs}$</th>
<th>$v_{calc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7, 6, 2 $\leftrightarrow$ 6, 6, 1</td>
<td>3214.601</td>
<td>3214.04</td>
</tr>
<tr>
<td>6, 3, 2 $\leftrightarrow$ 5, 3, -1</td>
<td>3085.609</td>
<td>3086.11</td>
</tr>
<tr>
<td>5, 2, 2 $\leftrightarrow$ 4, 2, -1</td>
<td>3067.732$^b$</td>
<td>3067.31</td>
</tr>
<tr>
<td>5, 2, 2 $\leftrightarrow$ 4, 4, 1</td>
<td>3020.490</td>
<td>3019.94</td>
</tr>
<tr>
<td>6, 4, 2 $\leftrightarrow$ 5, 4, -1</td>
<td>3006.993$^b$</td>
<td>3007.25</td>
</tr>
<tr>
<td>5, 3, 2 $\leftrightarrow$ 4, 3, 1</td>
<td>2979.658</td>
<td>2979.56</td>
</tr>
<tr>
<td>5, 2, 2 $\leftrightarrow$ 4, 2, 1</td>
<td>2976.566$^b$</td>
<td>2975.95</td>
</tr>
<tr>
<td>6, 3, 2 $\leftrightarrow$ 5, 3, 1</td>
<td>2964.984$^b$</td>
<td>2965.23</td>
</tr>
<tr>
<td>6, 3, 2 $\leftrightarrow$ 5, 3, -1</td>
<td>2962.822</td>
<td>2961.57</td>
</tr>
<tr>
<td>4, 2, 2 $\leftrightarrow$ 3, 2, -1</td>
<td>2956.947$^b$</td>
<td>2956.40</td>
</tr>
<tr>
<td>5, 2, 2 $\leftrightarrow$ 4, 2, -1</td>
<td>2909.239$^b$</td>
<td>2908.08</td>
</tr>
<tr>
<td>6, 4, 2 $\leftrightarrow$ 5, 4, 1</td>
<td>2893.370$^b$</td>
<td>2893.45</td>
</tr>
<tr>
<td>6, 3, 2 $\leftrightarrow$ 6, 3, 1</td>
<td>2436.653</td>
<td>2436.96</td>
</tr>
</tbody>
</table>

$^a$ Predicted wavenumbers are from Miller and Tennyson (78).

$^b$ 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 $I$-doubling constant to be 1180 cm$^{-1}$.

Three quartic potential constants were determined from the anharmonicity of vibrational energy levels, $x_{11} = -47.2$ cm$^{-1}$, $x_{12} = -148.4$ cm$^{-1}$, and $x_{22} = 327$ cm$^{-1}$ to be $k_{1111} = 890$ cm$^{-1}$, $k_{1122} = 330$ cm$^{-1}$, and $k_{2222} = 130$ cm$^{-1}$. The remaining quartic constant $k_{1122}$ should in principle be determinable from the observed values of $q_2^2$ and $q_3^2$, 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 LiNbO$_3$ 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 H$_2$ 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.
TABLE VI

| Unassigned Lines in Our Discharge (Most Likely of H$_3^+$) (in cm$^{-1}$) |
|----------------|----------------|----------------|----------------|----------------|
| 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       |               |

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 spectroscopy 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 $\nu_1 \leftrightarrow 0$ and $\nu_1 + \nu_2 \leftrightarrow \nu_2$ bands have enabled us to determine the absolute energy levels of many vibration–rotation levels in the $\nu_1$ and the $\nu_1 + \nu_2$ states. They are listed in Table III. The $\nu_1 \leftrightarrow 0$ transitions and the $\nu_1 + \nu_2 \leftrightarrow \nu_2$ 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 $\nu_1 + \nu_2 \leftrightarrow \nu_1$ 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$_2^+$, 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 CH$_3$. 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$_2^+$. Altogether over 600 H$_2^+$ spectral lines have been observed. Together with the great many lines near the dissociation limit reported by Carrington, Buttenschow, Kennedy, and others (36), the richness of the spectrum of this most fundamental polyatomic species is simply amazing.

ACKNOWLEDGMENTS

We are deeply indebted to S. Miller and J. Tennyson for sending their theoretical results prior to publication and helpful discussions. This work was supported by NSF PHY 90-22647. M. R. acknowledges the financial support of the Swiss National Science Foundation.

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Note added in proof. It has been pointed out by Watson (34) that the $v_1 + v_2 \leftarrow v_2$ transition borrows intensity also from the $v_2 \leftarrow v_2$ and the $v_1 + v_2 \leftarrow v_1 + v_2$ forbidden rotational transitions. Inclusion of this effect may reduce the value of $k_{122}$ given in this paper.

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FORBIDDEN TRANSITIONS OF H⁺

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