

# Spectral lines and distribution of $\text{H}_3^+$ in high rotational levels

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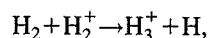
Infrared spectrum of the  $\nu_2$  fundamental band of  $\text{H}_3^+$  in high rotational levels has been studied. Three motives for this study were (i) to provide laboratory data for the observation of astronomical objects in which a large abundance of  $\text{H}_3^+$  exists at high temperature, (ii) to study kinetic energy distribution of  $\text{H}_3^+$  in plasmas and to determine its rotational and translational temperatures, and (iii) to provide information on high rovibrational states for the variational calculations on the intramolecular dynamic of  $\text{H}_3^+$ . In order to increase the kinetic temperature, water-cooled plasmas with helium dominated gas mixtures with  $\text{He}/\text{H}_2 \sim 5/0.6$  torr were used. The observed rotational level in the ground state with the highest rotational quantum numbers was  $J=K=15$  which has the rotational energy of  $5091.6 \text{ cm}^{-1}$ . It was found from the observed relative intensities of the rovibrational transitions and linewidths that  $\text{H}_3^+$  in the plasmas were in approximate thermal equilibrium with both rotational and translational temperature of  $\sim 1000 \text{ K}$ . On the contrary, an analysis of the relative intensities of the  $\text{H}_3^+$  spectral lines observed in our previous study of carbocation spectroscopy showed nonthermal rotational distribution. A semiquantitative discussion is given on the observed results.

## I. INTRODUCTION

Recent discoveries of the  $\text{H}_3^+$  infrared emission in Jupiter ionospheres in the  $2 \mu\text{m } 2\nu_2$  overtone band<sup>1,2</sup> and in the  $4 \mu\text{m } \nu_2$  fundamental band<sup>3-5</sup> have demonstrated that the  $\text{H}_3^+$  ions, which exist abundantly in polar regions of Jupiter, are in approximate thermal equilibrium corresponding to a high temperature of  $\sim 1100 \text{ K}$ . The highest emitting states so far identified are the  $2\nu_2$ ,  $l=2$ ,  $(J,G,U)=10, 12, +2$  level for the  $2\nu_2$  overtone emission band<sup>1</sup> and the  $\nu_1+\nu_2$ ,  $l=1$ ,  $(J,G,U)=7, 6, -1$  level for the  $\nu_1+\nu_2-\nu_1$  hot band<sup>6</sup> that are  $6669$  and  $6985 \text{ cm}^{-1}$  above the lowest state, respectively. Obviously these levels at energies of  $\sim 10\,000 \text{ K}$  are well populated. [Here  $l$  is the vibrational angular momentum quantum number,  $J$  and  $k$  are the rotational quantum number and its projection along the molecular axis, respectively,  $G=|k-l|$ , and  $U$  represents the higher (+) or lower (-)  $l$  resonance level.] The high translational temperature of  $1150 \text{ K}$  was also reported from the observed linewidths of the Jovian emission lines.<sup>7</sup> Observations of the  $\text{H}_3^+$  emission from Uranus<sup>8</sup> and Saturn<sup>9</sup> also showed similar high temperatures of their ionospheres. Moreover, the claim<sup>10</sup> of the detection of the  $\text{H}_3^+$  emission in supernova 1987A introduced the possibility that there are other astronomical objects in which  $\text{H}_3^+$  is populated in even higher rovibrational states.<sup>11</sup> (Miller *et al.*<sup>10</sup> used the temperature of  $2050 \text{ K}$  in their simulation of the observed spectrum.) The first motive to study  $\text{H}_3^+$  in high rotational levels arose from the fact that the laboratory spectrum, which was once thought to be fairly complete,<sup>12</sup> was insufficient for further astronomical observations.

The second motive for this work came from a preliminary observation in our plasmas for carbocation spectroscopy. While the distribution of  $\text{H}_3^+$  over rotational levels seemed approximately thermal, some transitions starting from high rotational levels seemed anomalously strong.

Since  $\text{H}_3^+$  is produced initially in hot rovibrational states due to the highly exothermic reaction ( $1.7 \text{ eV}$ )



and rotational relaxation for high energy levels may be slow, such an anomaly may be expected. At the back of our minds was the anomalously high population in  $J=K$  "metastable states" of interstellar  $\text{NH}_3$ .<sup>13</sup> Such an anomaly in the high rotational levels of diatomic molecules during the relaxation process has also been reported by Ding and Polanyi.<sup>14</sup> Since a plasma is not an equilibrium state (with a high electron temperature of a few electron volts and much lower molecular temperatures), a nonthermal rotational distribution is, in principle, possible. However, in plasmas with relatively high pressure ( $\sim 0.5$ – $10$  torr) such as those used for our molecular ion spectroscopy and in molecular lasers, it has, in general, been observed that the rotational distribution of molecules is thermal and that rotational and translational temperatures are approximately equal. The extremely high rotational levels of  $\text{H}_3^+$  allows us to explore this theme for molecular ions. We measured the rotational temperature from relative intensities of spectral lines and the translational temperature from their line widths.

## II. EXPERIMENT

The  $\text{H}_3^+$  spectral lines were observed using a difference frequency laser system which has been described in earlier papers.<sup>15,16</sup> Radiation from an argon ion laser and a tunable ring dye laser are combined in a temperature-controlled  $\text{LiNbO}_3$  crystal to generate tunable infrared radiation. A small part of the infrared radiation is reflected and used for the spectroscopy of reference gases, while the main beam is sent to the discharge cell. The one-meter long, water-cooled glass cell is the latest in our family of cells, with 9 pumping ports and 18 pairs of inlets that are constricted at the points where they touch the wall of the cell to produce jetlike

TABLE I. Frequencies  $\nu$  and lower energy levels  $E''$  of the  $\nu_2$  fundamental transitions of H<sub>3</sub><sup>+</sup> used in the analysis.

| $J'$ | $G'$ | $U$ | $J''$ | $K''$ | $\nu$ (cm <sup>-1</sup> ) | $E''$ (cm <sup>-1</sup> ) |
|------|------|-----|-------|-------|---------------------------|---------------------------|
| 2    | 1    | -1  | 1     | 1     | 2691.445                  | 64.124                    |
| 2    | 0    | -1  | 1     | 0     | 2725.896                  | 86.961                    |
| 2    | 1    | +1  | 1     | 1     | 2726.224                  | 64.124                    |
| 3    | 2    | -1  | 2     | 2     | 2762.067                  | 169.298                   |
| 3    | 1    | -1  | 2     | 1     | 2765.542                  | 237.354                   |
| 3    | 2    | +1  | 2     | 2     | 2823.135                  | 169.298                   |
| 3    | 1    | +1  | 2     | 1     | 2826.113                  | 237.354                   |
| 4    | 3    | -1  | 3     | 3     | 2829.921                  | 315.346                   |
| 4    | 2    | -1  | 3     | 2     | 2832.194                  | 428.015                   |
| 5    | 4    | -1  | 4     | 4     | 2894.487                  | 502.029                   |
| 5    | 3    | -1  | 4     | 3     | 2894.614                  | 658.707                   |
| 4    | 3    | +1  | 3     | 3     | 2918.022                  | 315.346                   |
| 4    | 2    | +1  | 3     | 2     | 2923.356                  | 428.015                   |
| 6    | 4    | -1  | 5     | 4     | 2955.155                  | 928.956                   |
| 6    | 5    | -1  | 5     | 5     | 2956.075                  | 729.000                   |
| 5    | 4    | +1  | 4     | 4     | 3008.109                  | 502.029                   |
| 7    | 5    | -1  | 6     | 5     | 3011.510                  | 1238.425                  |
| 7    | 6    | -1  | 6     | 6     | 3014.357                  | 995.854                   |
| 5    | 3    | +1  | 4     | 3     | 3015.240                  | 658.707                   |
| 8    | 6    | -1  | 7     | 6     | 3064.354                  | 1586.554                  |
| 8    | 7    | -1  | 7     | 7     | 3069.170                  | 1302.110                  |
| 6    | 5    | +1  | 5     | 5     | 3096.409                  | 729.000                   |
| 6    | 4    | +1  | 5     | 4     | 3106.801                  | 928.956                   |
| 9    | 7    | -1  | 8     | 7     | 3113.525                  | 1972.750                  |
| 9    | 8    | -1  | 8     | 8     | 3120.312                  | 1647.218                  |
| 10   | 8    | -1  | 9     | 8     | 3159.008                  | 2396.349                  |
| 10   | 9    | -1  | 9     | 9     | 3167.590                  | 2030.558                  |
| 7    | 6    | +1  | 6     | 6     | 3182.035                  | 995.854                   |
| 7    | 5    | +1  | 6     | 5     | 3193.227                  | 1238.425                  |
| 11   | 9    | -1  | 10    | 9     | 3200.716                  | 2856.630                  |
| 11   | 10   | -1  | 10    | 10    | 3210.794                  | 2451.451                  |
| 12   | 10   | -1  | 11    | 10    | 3238.616                  | 3352.813                  |
| 12   | 11   | -1  | 11    | 11    | 3249.698                  | 2909.160                  |
| 8    | 7    | +1  | 7     | 7     | 3265.128                  | 1302.110                  |
| 15   | 12   | -1  | 14    | 12    | 3270.564 <sup>a</sup>     | 5502.880                  |
| 13   | 11   | -1  | 12    | 11    | 3272.704                  | 3884.065                  |
| 8    | 6    | +1  | 7     | 6     | 3276.193                  | 1586.554                  |
| 13   | 12   | -1  | 12    | 12    | 3284.080                  | 3402.890                  |
| 8    | 4    | +1  | 7     | 4     | 3302.420 <sup>a</sup>     | 2002.410                  |
| 14   | 12   | -1  | 13    | 12    | 3303.084 <sup>a</sup>     | 4449.507                  |
| 8    | 1    | +1  | 7     | 1     | 3305.924 <sup>a</sup>     | 2300.796                  |
| 8    | 0    | +1  | 7     | 0     | 3308.668 <sup>a</sup>     | 2320.332                  |
| 14   | 13   | -1  | 13    | 13    | 3313.747 <sup>a</sup>     | 3931.800                  |
| 8    | 3    | +1  | 7     | 3     | 3321.005 <sup>a</sup>     | 2142.048                  |
| 15   | 13   | -1  | 14    | 13    | 3329.932 <sup>a</sup>     | 5048.217                  |
| 15   | 14   | -1  | 14    | 14    | 3338.529 <sup>a</sup>     | 4495.000                  |
| 9    | 8    | +1  | 8     | 8     | 3345.703 <sup>a</sup>     | 1647.218                  |
| 9    | 7    | +1  | 8     | 7     | 3355.508 <sup>a</sup>     | 1972.750                  |
| 9    | 2    | +1  | 8     | 2     | 3356.742 <sup>a</sup>     | 2868.792                  |
| 16   | 15   | -1  | 15    | 15    | 3358.368 <sup>a</sup>     | 5091.560                  |
| 9    | 6    | +1  | 8     | 6     | 3368.102 <sup>a</sup>     | 2242.142                  |
| 9    | 5    | +1  | 8     | 5     | 3380.008 <sup>a</sup>     | 2462.812                  |
| 9    | 1    | +1  | 8     | 1     | 3381.395 <sup>a</sup>     | 2925.329                  |
| 9    | 4    | +1  | 8     | 4     | 3392.544 <sup>a</sup>     | 2639.072                  |
| 9    | 3    | +1  | 8     | 3     | 3399.506 <sup>a</sup>     | 2775.593                  |
| 10   | 2    | +1  | 9     | 2     | 3411.853 <sup>a</sup>     | 3555.336                  |
| 10   | 9    | +1  | 9     | 9     | 3423.809 <sup>a</sup>     | 2030.558                  |
| 10   | 8    | +1  | 9     | 8     | 3431.299 <sup>a</sup>     | 2396.349                  |
| 9    | 2    | +1  | 8     | 2     | 3441.407 <sup>a</sup>     | 2868.792                  |
| 10   | 7    | +1  | 9     | 7     | 3443.146 <sup>a</sup>     | 2702.008                  |
| 10   | 1    | +1  | 9     | 1     | 3445.694 <sup>a</sup>     | 3609.493                  |
| 10   | 0    | +1  | 9     | 0     | 3452.854 <sup>a</sup>     | 3627.484                  |
| 10   | 6    | +1  | 9     | 6     | 3455.000 <sup>a</sup>     | 2957.223                  |
| 10   | 5    | +1  | 9     | 5     | 3461.305 <sup>a</sup>     | 3167.250                  |
| 10   | 4    | +1  | 9     | 4     | 3476.178 <sup>a</sup>     | 3335.468                  |

TABLE I. (Continued.)

| $J'$ | $G'$ | $U$ | $J''$ | $K''$ | $\nu$ (cm <sup>-1</sup> ) | $E''$ (cm <sup>-1</sup> ) |
|------|------|-----|-------|-------|---------------------------|---------------------------|
| 10   | 3    | +1  | 9     | 3     | 3497.963 <sup>a</sup>     | 3460.973                  |
| 11   | 10   | +1  | 10    | 10    | 3499.418 <sup>a</sup>     | 2451.451                  |
| 11   | 9    | +1  | 10    | 9     | 3503.339 <sup>a</sup>     | 2857.341                  |
| 11   | 8    | +1  | 10    | 8     | 3513.532 <sup>a</sup>     | 3196.800                  |
| 11   | 6    | +1  | 10    | 6     | 3531.276 <sup>a</sup>     | 3726.462                  |
| 11   | 5    | +1  | 10    | 5     | 3546.570 <sup>a</sup>     | 3926.069                  |
| 11   | 3    | +1  | 10    | 3     | 3551.563 <sup>a</sup>     | 4215.125                  |
| 12   | 11   | +1  | 11    | 11    | 3571.293 <sup>a</sup>     | 3352.813                  |
| 12   | 10   | +1  | 11    | 10    | 3572.428 <sup>a</sup>     | 2909.160                  |
| 12   | 9    | +1  | 11    | 9     | 3579.291 <sup>a</sup>     | 3725.504                  |

<sup>a</sup>Previously unobserved.

streams. Use of this plasma tube with He-dominated gas mixtures was expected to produce the highest rotational temperatures. Before reaching the discharge cell, the infrared radiation was split into two beams of equal intensity which were propagated in opposite directions through the cell four times in a cyclic multiple-path arrangement<sup>16</sup> to increase the path length. After traversing the plasma tube, the two beams were sent to two matched InSb detectors, and the two signals were combined in opposite phase so that the amplitude noise due to the argon ion and dye lasers is subtracted. The plasma was generated by a.c. voltage and the velocity-modulated signal was processed by a lock-in amplifier.<sup>17</sup> The first derivative ion signals together with the reference signals were simultaneously recorded on a chart recorder and a computer. Before the systematic scanning was initiated, we optimized the discharge conditions and chemistry to maximize the H<sub>3</sub><sup>+</sup> spectral lines. The optimum stable plasma conditions were 0.6 torr of H<sub>2</sub> and 5 torr of He in a 6 kHz a.c. discharge with an rms current of 200 mA.

### III. OBSERVED HIGH ROTATIONAL LEVELS

For this study, we measured 75 rovibrational transitions of the  $\nu_2$  fundamental band of H<sub>3</sub><sup>+</sup> in the region 3579–2691 cm<sup>-1</sup>. Their assignments and frequencies are listed in Table I together with the rotational energy in the ground state  $E''$ . About half of them are new transitions corresponding to R-branch lines with high rotational quantum numbers  $J$ ,  $K$ . Other transitions were measured for the purpose of determining temperature under the same conditions. The wave numbers of the transitions were calibrated by reference spectra of NH<sub>3</sub>,<sup>18</sup> C<sub>2</sub>H<sub>4</sub>,<sup>19</sup> H<sub>2</sub>CO,<sup>19</sup> and D<sub>2</sub>O.<sup>20</sup>

Being a well-bound light molecular species, H<sub>3</sub><sup>+</sup> is the polyatomic molecule with the largest rotational constants. If the traditional polynomial formalism of a symmetric rotor is used for the analysis, we obtain the rotational constants<sup>21</sup>  $B_0=43.56$  cm<sup>-1</sup> and  $C_0=20.71$  cm<sup>-1</sup>, and the centrifugal distortion constants  $D_J=0.047$  cm<sup>-1</sup>,  $D_{JK}=0.099$  cm<sup>-1</sup>, and  $D_K=0.040$  cm<sup>-1</sup>. Clearly the polynomial diverges with high  $J$ ,  $K$  values. (For the  $J=K=15$  level reported in this paper the centrifugal distortion "correction"  $-D_{JK}J(J+1)K^2$  exceeds 5000 cm<sup>-1</sup>.) For a while the Pade approximation<sup>22</sup> was used to cope with this problem.<sup>23,24</sup> However, as the laboratory measurements were extended to higher rovibrational states,<sup>16,25–29</sup> the variational calculations

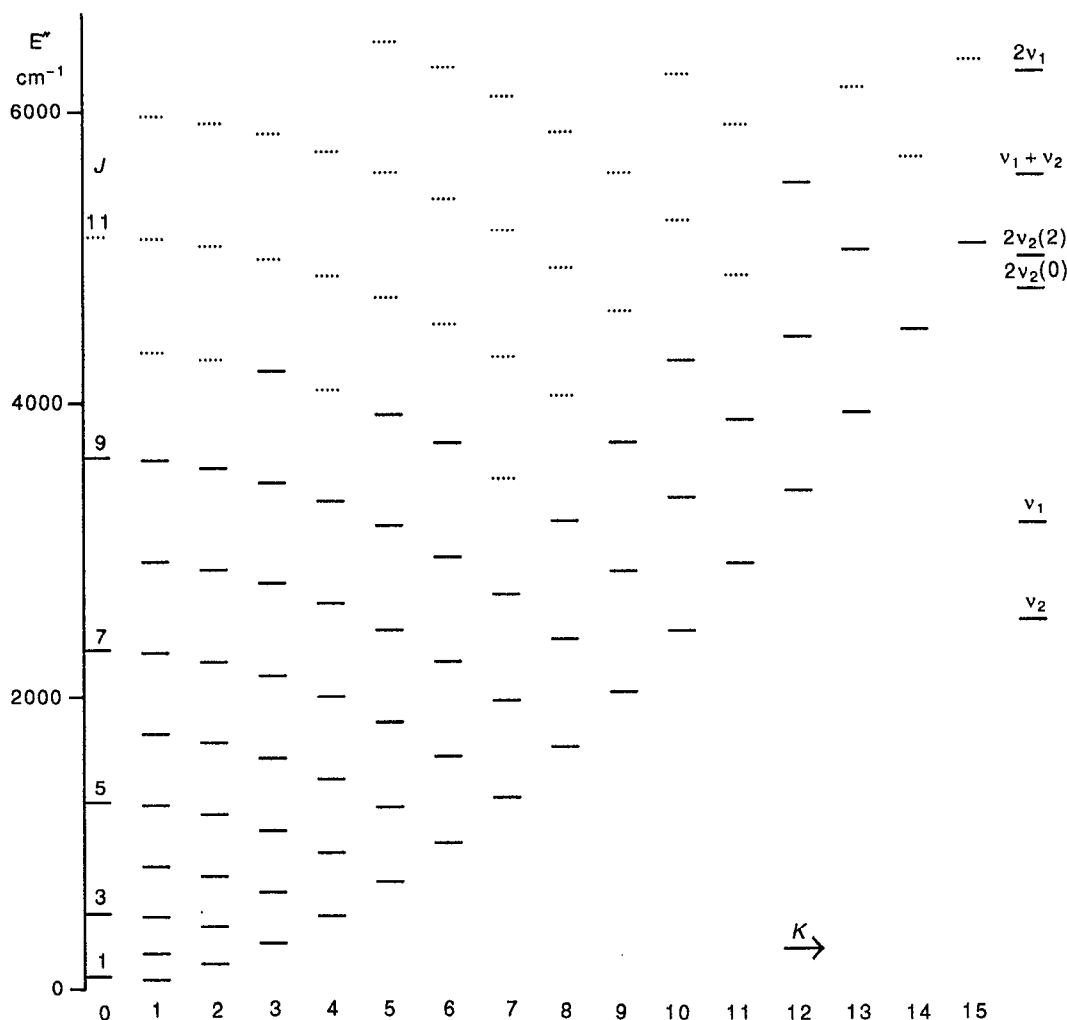


FIG. 1. Rotational energy levels of H<sub>3</sub><sup>+</sup> in the ground vibrational state. Solid lines show the rotational levels from which a transition has been observed. Note that some such levels are higher than the second excited vibrational state shown on the right reflecting the high rotational temperature (1000 K) in the plasma.

by Miller, Tennyson, and Sutcliffe<sup>30-36</sup> have become indispensable for the analysis of the H<sub>3</sub><sup>+</sup> spectrum. In those calculations the rovibrational eigenvalue problems of H<sub>3</sub><sup>+</sup> is solved by brute force computation of the three-proton dynamics in an *ab initio* potential<sup>37,38</sup> (modified to fit  $\nu_2$ ) using a supercomputer.<sup>39</sup> More recently, Jensen,<sup>40</sup> Watson,<sup>41</sup> and Dinelli, Miller, and Tennyson<sup>42</sup> developed programs in which the *ab initio* potential is modified by a least squares procedure to fit the observed spectral lines. The results of such calculations are amazingly accurate and fit to the observed transitions to within a fraction of a cm<sup>-1</sup>. The assignment and analysis of the high  $J, K$  transitions listed in Table I were assisted by a computer output kindly provided to us by J. K. G. Watson. The variational calculation will be needed more and more for other molecules whose spectra defy the traditional method of analysis, such as the quasilinear molecular ions NH<sub>2</sub><sup>+</sup> (Ref. 43) and CH<sub>2</sub><sup>+</sup> (Ref. 44), and molecular ions like C<sub>2</sub>H<sub>3</sub><sup>+</sup> (Ref. 45) and CH<sub>3</sub><sup>+</sup> (Ref. 46) in which the protons are tunneling between their equilibrium positions. Since the analysis of H<sub>3</sub><sup>+</sup> is the simplest of these, it provides the pilot case for such intramolecular dynamics calculations. This pro-

vides the third motive to experimentally reach high rovibrational states.

The rotational energy levels of H<sub>3</sub><sup>+</sup> in the ground vibrational state are shown in Fig. 1. The highest rotational level from which a spectral line is observed is  $J=14, K=12$  which is 5502.9 cm<sup>-1</sup> above the lowest rotational level. The level with the highest rotational quantum numbers is  $J=K=15$  which has the rotational energy of 5091.6 cm<sup>-1</sup>. They are clearly above the  $2\nu_2$  vibrational energy (4997 cm<sup>-1</sup> for  $l=2$  and 4777 cm<sup>-1</sup> for  $l=0$ ) and are perhaps the highest ground state rotational levels from which absorption lines are observed for any molecule. The observed spectral line is shown in Fig. 2.

While these rotational energies and many others in this paper far exceed that of  $J=K=9$ , which at 2030.56 cm<sup>-1</sup> is the highest so far reported in astronomical observations, past experience on H<sub>2</sub> quadrupole emission suggests that nature will eventually surpass laboratory capabilities. The highest observed rotational level of H<sub>2</sub> in the laboratory<sup>47</sup> is  $J=7$  (at 3187.5 cm<sup>-1</sup>) while it is  $J=17$  (at 15 042 cm<sup>-1</sup> ~ 1.9 eV) in the Orion Molecular Cloud.<sup>48</sup>

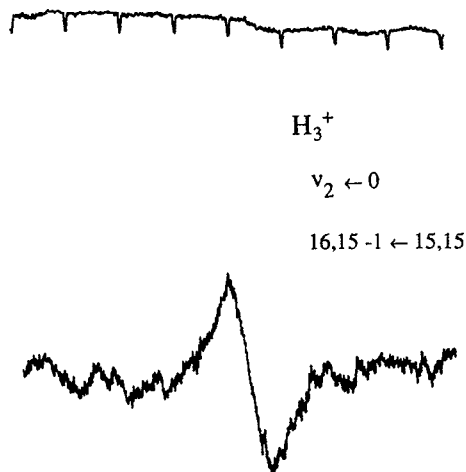


FIG. 2. An example of an H<sub>3</sub><sup>+</sup>  $\nu_2$  fundamental transition starting from a high rotational level. The transition is  $(J, G, U) = 16, 15, -1 \leftarrow 15, 15$ ; the lower level is 5091.6 cm<sup>-1</sup> above the lowest rotational level. The fraction of H<sub>3</sub><sup>+</sup> populating the level at 1000 K is  $3.3 \times 10^{-4}$ . Velocity modulation with unidirectional multipass arrangement with a time constant of 3 s was used for the recording.

#### IV. MEASUREMENT OF TEMPERATURE

##### A. Rotational temperature

The rotational temperature  $T_r$  was determined from the relative intensities of spectral lines using the Boltzmann distribution formula

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} \exp[-(E_i - E_j)/kT_r], \quad (1)$$

where  $n_i$  represents the molecular population in the  $i$ th rotational level in the ground vibrational state,  $E_i$  its energy, and  $g_i$  its degeneracy,  $g_i(2J+1)$ . The nuclear spin statistical weight  $g_I$  is 4 for ortho ( $I = \frac{3}{2}$ ) H<sub>3</sub><sup>+</sup> in  $K = 3n$  levels and is 2 for para ( $I = \frac{1}{2}$ ) H<sub>3</sub><sup>+</sup> in  $K = 3n \pm 1$ . The population  $n_i$  is related to the spectral intensity  $\Delta I_{if}/I_0$  through Beer's Law

$$\frac{I_{if}(\nu)}{I_0} = 1 - \frac{\Delta I_{if}(\nu)}{I_0} = \exp[-\gamma_{if}(\nu)l] \quad (2)$$

and the expression of the absorption coefficient  $\gamma_{if}$  (Ref. 49)

$$\gamma_{if}(\nu) = \frac{8\pi^3\nu}{3hc} n_i |\mu_{if}|^2 [1 - \exp(-h\nu/kT_v)] \Phi(\nu, T_t), \quad (3)$$

where  $l$  is the path length,  $\mu_{if}$  is the transition dipole moment, and  $T_v$  and  $T_t$  are the vibrational and translational temperatures, respectively. The normalized line shape function  $\Phi(\nu, T_t)$  can be expressed, for a Doppler-broadened spectral line, as a Gaussian

$$\Phi(\nu, T_t) = (1/\sqrt{\pi}\Delta\nu) \exp\left[-\left(\frac{\nu - \nu_0}{\Delta\nu}\right)^2\right], \quad (4)$$

where

$$\Delta\nu = \frac{\nu}{c} \left(\frac{2kT_t}{m}\right)^{1/2}. \quad (5)$$

The peak height of the line shape function is  $(\sqrt{\pi}\Delta\nu)^{-1}$  and the half-width at half-maximum is given by  $\sqrt{\ln 2}\Delta\nu$ . Since  $\exp(-h\nu/kT_v) \ll 1$ , the expression in the brackets of Eq. (3) is nearly equal for all transitions. Therefore for  $\gamma_{if}l \ll 1$ , the population  $n_i$  and the peak absorption  $\Delta I_{if}/I_0$  are related by a simple formula

$$\frac{\Delta I_{if}}{I_0} = \gamma_{if}l = Cn_i |\mu_{if}|^2, \quad (6)$$

where  $\Delta I_{if}$  and  $\gamma_{if}$  are their peak values and  $C$  is a constant common to all transitions. The observed values of  $\Delta I_{if}/I_0$  and theoretical values of  $\mu_{if}$  provided by Watson<sup>41</sup> allowed us to calculate  $Cn_i$ .

The logarithmic values of  $Cn_i/g_i$

$$\begin{aligned} \ln[Cn_i/g_i] &= \ln[\Delta I_{if}/I_0 g_I(2J+1) |\mu_{if}|^2] \\ &= \ln[\Delta I_{if}/I_0 g_I S_{ij}] \end{aligned} \quad (7)$$

are plotted in Fig. 3 with respect to the rotational energy of the ground state  $E''$ . The least squares fit gives a linear relation demonstrating the thermal rotational distribution of Eq. (1) corresponding to the rotational temperature of  $T_r = 1002 \pm 35$  K, obtained from the negative reciprocal of the slope.

##### B. Translational temperature

The translational temperature  $T_t$  of H<sub>3</sub><sup>+</sup> was determined from the observed linewidth and the line shape function  $\Phi(\nu, T_t)$  given in Eq. (4). Since velocity modulation and the phase sensitive detection give the first derivative line shape, it is most convenient to measure the separation between the maximum and minimum of the derivative shape that can be located accurately. The frequency for the extrema  $\nu_x$  can be determined from  $d^2[\Phi(\nu, T_t)]/d\nu^2 = 0$  to be

$$|\nu_x - \nu_0| = \delta\nu = \Delta\nu/\sqrt{2}. \quad (8)$$

The translational temperature then is determined from the measured  $2\delta\nu$  and Eq. (5) to be

$$T_t = \left(\frac{\delta\nu}{\nu_0}\right)^2 \frac{mc^2}{k}. \quad (9)$$

A complication arises from modulation broadening of the spectral lines due to the velocity modulation. Such effect has been considered by Gudeman *et al.*,<sup>17</sup> Solka *et al.*,<sup>50</sup> and Farley.<sup>51</sup> Modulation broadening was treated for sinusoidal and square wave modulation. We adopt the latter for its simplicity. While the a.c. voltage from the last stage step-up transformer is sinusoidal, the saturation behavior of the electric field and the threshold of ion current make this assumption somewhat justified. With this assumption, the derivative shape is calculated from<sup>50,51</sup>

$$\Phi(\nu) = \phi(\nu + m) - \phi(\nu - m), \quad (10)$$

where  $m$  is the amplitude of velocity modulation and  $T_t$  is omitted for brevity. The extrema of this functions are determined from  $\delta\Phi(\nu)/\delta\nu = 0$  and satisfy

$$\frac{X+M}{X-M} = \exp[4MX], \quad (11)$$

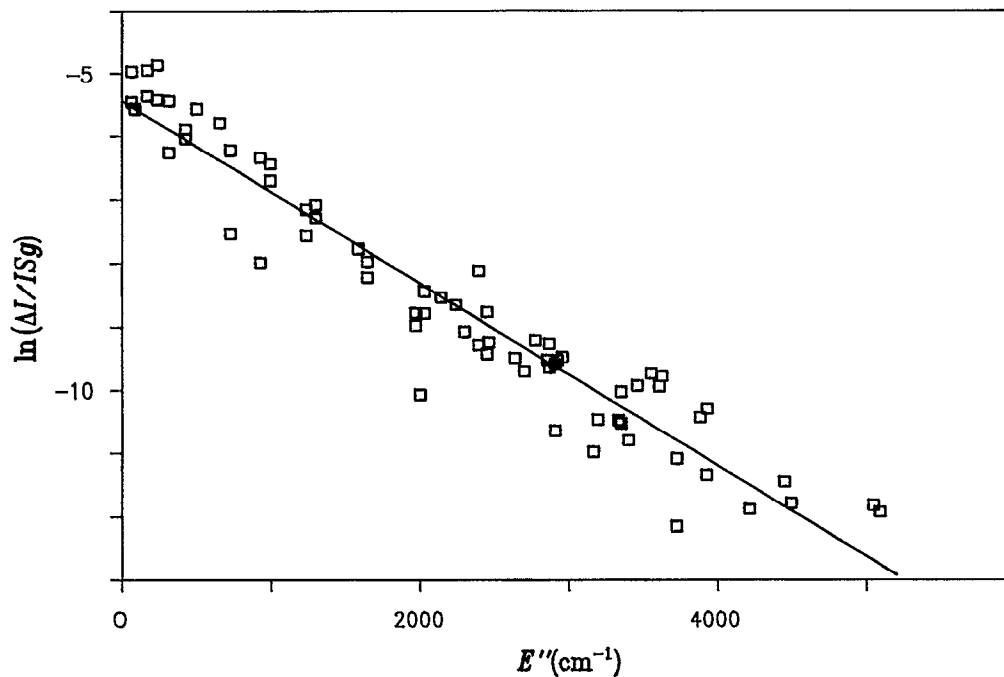


FIG. 3. Observed  $\ln[\Delta I/ISg]$  [see Eq. (7)] vs  $E''$ . The linear relation demonstrates the approximately thermal distribution of  $H_3^+$  in the water-cooled plasmas using gas mixtures with  $He/H_2=5/0.6$  torr. The slope gives  $-(kT_r)^{-1}$  from which the rotational temperature of  $H_3^+$  was determined to be  $T_r=1002 \pm 35$  K.

where  $X \equiv |v_x - v_0|/\Delta v$  and  $M \equiv m/\Delta v$ .

The value of modulation depth  $M$

$$M = \frac{v_m}{c} \cdot \frac{\nu}{\Delta \nu} \quad (12)$$

can be estimated from ion migration velocity<sup>52,53</sup>

$$v_{im} = \frac{760}{p} \cdot \frac{T}{273} K_0 E, \quad (13)$$

where  $T$ (K),  $p$ (torr),  $E$ (v/cm), and  $K_0$ (cm<sup>2</sup>/Vs) are temperature, pressure, the electric field, and the reduced mobility, respectively. The value of  $K_0$  can be estimated from the Chapman-Enskog formula<sup>54,55</sup> to be

$$K_0 = \frac{3}{16N} \left( \frac{3}{2\pi\mu\alpha} \right)^{1/2} = 12.5/\sqrt{\mu\alpha}, \quad (14)$$

where  $\alpha$  is the polarizability of He,  $\mu$  is the reduced mass of  $H_3^+$  and He, and  $N$  is Avogadro's number. In order to use the last expression in Eq. (14),  $\alpha$  of He in  $\text{\AA}^3$  (0.205) and  $\mu$  in a.m.u. (1.73) should be used to obtain  $K_0$  in cm<sup>2</sup>/Vs (21.0). Using our experimental conditions  $p=5.6$  torr,  $T=1000$  K, and  $E=10$  V/cm, we obtain  $v_m=1.0 \times 10^5$  cm/s which gives  $M=0.44$ . For this value, Eq. (11) gives  $X=0.756$ . Therefore the fractional increase of the linewidth is  $X/(1/\sqrt{2})=1.07$ , i.e., 7%. This has been corrected for from the observed linewidth. The translational temperature obtained from the measured linewidths was  $T_t=1020 \pm 100$  K, which agrees with the rotational temperature.

## V. H<sub>3</sub><sup>+</sup> IN PLASMAS FOR CARBOCATION SPECTROSCOPY

As mentioned in Sec. I, the possibility of nonthermal rotational distribution of  $H_3^+$  was initially suggested in our extensive carbocation spectroscopy<sup>15,44,45,56</sup> in which liquid-N<sub>2</sub> cooled plasmas with He-dominated gas mixtures containing a small amount of hydrocarbon were used. The observed values of  $\ln[\Delta I/ISg]$  vs  $E''$  are plotted in Fig. 4 for a series of experiments using a gas mixture of  $He/H_2/CH_4=7/0.1/0.12$  torr. For this set of data, the observed points do not line up on a straight line and it is impossible to determine the rotational temperature uniquely. If we use observed values for low rotational levels ( $E'' < 2000$  cm<sup>-1</sup>), a least squares fitting gives the straight line shown in Fig. 4 and gives the rotational temperature  $T_r=771 \pm 67$  K. The average of the observed linewidths gave the translational temperature  $T_t=590 \pm 50$  K after the modulation broadening was corrected for. It is noted in Fig. 4 that the observed points corresponding to higher rotational energy lie considerably higher than the straight line indicating that these levels are more populated than expected from the thermal equilibrium corresponding to the straight line.

## VI. SUMMARY AND DISCUSSION

The experimental results and analysis given in Secs. IV and V show that the rotational distribution of  $H_3^+$  in water-cooled plasmas with the mixture  $He/H_2=5/0.6$  torr is Boltzmannian corresponding to a temperature of 1000 K. The agreement of the rotational and translational temperatures shows the kinetic equilibrium. The temperature is compa-

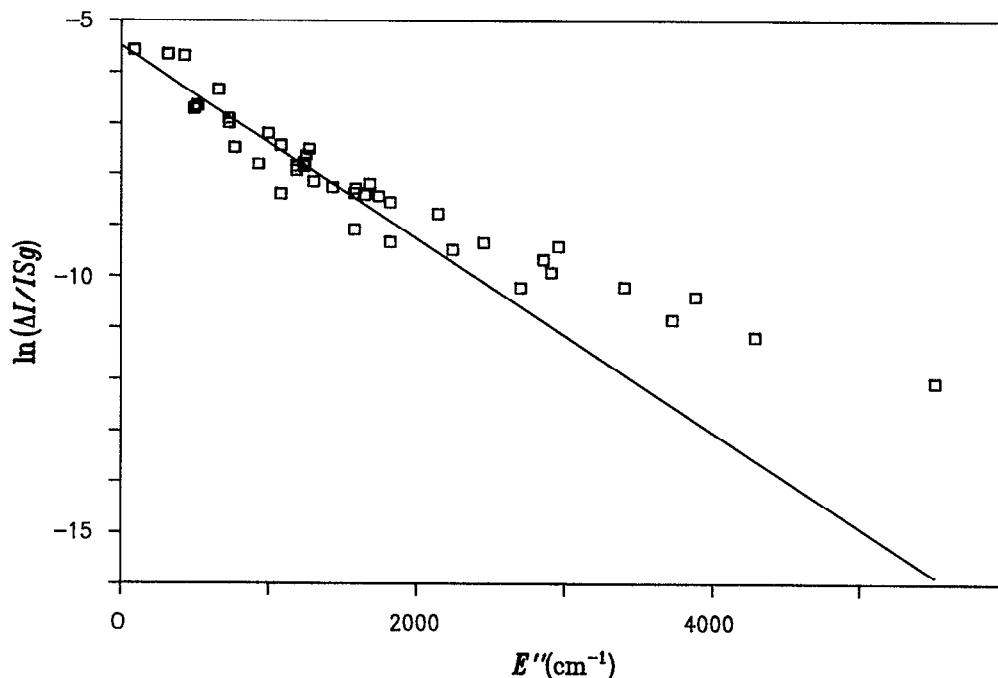


FIG. 4. Observed  $\ln[\Delta I/ISg]$  vs  $E''$  for  $H_3^+$  spectral lines in carbocation spectroscopy. Gas mixtures with  $He/H_2/CH_4=7/0.1/0.12$  torr were used in liquid- $N_2$  cooled plasmas.  $H_3^+$  ions with high values of  $E''$  are populated more than expected from the temperature of  $771 \pm 67$  K determined from the straight line fit to low  $E''$  data.

rable to the vibrational temperature of  $H_3^+$  in liquid- $N_2$  cooled plasmas which ranged from 700–1500 K.<sup>16</sup> It is higher than the rotational temperature in liquid- $N_2$  cooled pure- $H_2$  plasmas which may be as low as 200 K.<sup>56,23</sup> The kinetic temperature in the plasmas used in the present study is high for three reasons: (a) The high ionization potential of He keeps the electron temperature high;<sup>57</sup> (b) water-cooling was used instead of liquid- $N_2$  cooling; (c) the plasma tube is designed such that fresh chemical reactions occur in many points of the optical path.

The observed thermal distribution of  $H_3^+$  in a He/ $H_2$  mixture demonstrates that  $H_3^+$  relax rapidly during their short lifetimes. Since  $H_3^+$  survives collisions with He and  $H_2$ , its lifetime is limited either by recombination with electrons or by ambipolar diffusion and destruction at the wall of the plasma tube. The rate of the former process is estimated to be  $\sim 2 \times 10^4$  s<sup>-1</sup> from the recombination rate constant ( $1.8 \times 10^{-7}$  cm<sup>3</sup> s<sup>-1</sup>) (Ref. 58) and the electron density ( $\sim 10^{11}$  cm<sup>-3</sup>) (Ref. 55) and is less than that of the latter. The lifetime of  $H_3^+$  limited by the ambipolar diffusion is estimated to be on the order of 10  $\mu$ s using Eq. (13) with  $K_0=21.0$  cm<sup>2</sup>/Vs, the 6 mm radius of the plasma tube, and the assumed ambipolar diffusion field of  $\sim 5$  V/cm, a half of the axial field.<sup>59,60</sup>

During the lifetime of 10  $\mu$ s,  $H_3^+$  collide with He and  $H_2$  many times and thermalize. For the longest range Langevin potential  $V=\alpha e^2/2r^4$ , the collision cross sections may be calculated to be 21 and 42 Å<sup>2</sup>, respectively, for  $H_3^+$ -He and  $H_3^+$ - $H_2$  collisions using the formula<sup>61,52,55</sup>

$$\sigma = \pi e(4\alpha/3kT)^{1/2} \quad (15)$$

and the polarizability of He ( $0.205$  Å<sup>5</sup>) and  $H_2$  ( $0.790$  Å<sup>3</sup>) at  $T=1000$  K. We thus estimate that  $H_3^+$  undergo  $\sim 250$  and  $\sim 60$  collisions with He and  $H_2$ , respectively, during its lifetime. Since it takes only several collisions to thermalize translational motion,<sup>62</sup>  $H_3^+$  stay thermal for most of their lifetimes. The rotational relaxation, however, is less efficient since the Langevin interaction, being independent of the angular orientation of  $H_3^+$ , is ineffective.<sup>63</sup> Other orientation dependent interactions such as the charge induced dipole-quadrupole interaction between  $H_3^+$  and He and the  $1/R^5$  quadrupole-quadrupole interaction between  $H_3^+$  and  $H_2$  are much smaller. The major cooling mechanism for the rovibrational states of  $H_3^+$  must be the ion-neutral exchange reactions



(16b)

where the tilde marks the initial constituent atom of  $H_2$ . The first reaction is a proton hop reaction while the second is a hydrogen exchange reaction. The deuterium analog of these reactions have been studied extensively since they lead to the efficient deuterium fractionation in interstellar space.<sup>64</sup> Many rate constants ranging from  $1.30 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup> to  $2.6 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> have been reported,<sup>65</sup> and the reactions are still under intense study.<sup>66</sup> Even if we use the lowest reported rate constant of  $2.6 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>, we note that  $H_3^+$  undergo the reaction 15 times during their lifetimes. The efficient thermalization of the rovibrational states of  $H_3^+$  must

be due to these reactions. This is particularly true in plasmas in planetary ionospheres where H<sub>2</sub> is the dominant collision partner.

The situation of H<sub>3</sub><sup>+</sup> in hydrocarbon plasmas is quite different. The lifetime of H<sub>3</sub><sup>+</sup> in this case is limited more by the proton hopping to the hydrocarbon rather than by ambipolar diffusion. For example, in our plasmas using a gas mixture of He/H<sub>2</sub>/CH<sub>4</sub>=7/0.1/0.12 torr, the lifetime of H<sub>3</sub><sup>+</sup> is estimated to be ~300 ns using the proton hop rate constant<sup>65</sup> of  $1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . Our results shown in Fig. 4 indicate that H<sub>3</sub><sup>+</sup> in low rotational levels thermalize during this time but those in high rotational levels lag behind in much the same way discussed by Ding and Polanyi.<sup>14</sup> For example, the energy difference between  $J=14, K=12$  and  $J=13, K=12$  levels is more than  $1000 \text{ cm}^{-1}$ , which is a large energy to impart to a collision partner.<sup>67</sup>

These crude order of magnitude estimates are complicated by the fact that H<sub>3</sub><sup>+</sup> are under acceleration in the plasmas and that the plasma conditions, such as ion density, temperature, ambipolar diffusion field, etc., are highly inhomogeneous. Nevertheless, we believe it explains semi-quantitatively the different rotational distributions of H<sub>3</sub><sup>+</sup> in the He/H<sub>2</sub> and He/H<sub>2</sub>/CH<sub>4</sub> plasmas.

*Note added in proof.* Regarding our remark in this paper that the high  $J, K$  levels of H<sub>3</sub><sup>+</sup> "are perhaps the highest ground state rotational levels from which absorptions are observed," Dr. I. R. McNab has drawn attention to the molecular beam spectroscopy at HD<sup>+</sup> by Carrington *et al.* [A. Carrington, C. A. Leach, A. J. Marr, R. E. Moss, C. H. Pyne, R. A. Kennedy, and I. R. McNab, *Chem. Phys.* **116**, 145 (1992).] Their  $v=1, N=45 \leftarrow v=0, N=44$  transition starting from the ground state rotational energy level of  $22\,803 \text{ cm}^{-1}$  clearly vitiate the remark. A qualifying phrase "observed in bulk gas" should have been added to the remark.

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