

Observation of the $2\nu_2(l=2) \leftarrow 0$ overtone band of H_3^+

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The overtone band of $2\nu_2(l=2) \leftarrow 0$ of H_3^+ in the $2\ \mu\text{m}$ infrared region has been observed in absorption by using a difference frequency laser spectrometer. The LiIO_3 nonlinear optical system assembled by Bawendi and the bidirectional multiple path optical arrangement with velocity modulation have enabled us to observe 34 vibrational-rotation transitions from 5094 to $4557\ \text{cm}^{-1}$. Liquid- N_2 cooled plasmas were used for transitions involving low rotational levels, while gaseous- N_2 cooled plasmas were used for high rotational levels, up to $J, K = (9, 9)$. From the relative intensities of the transitions, rotational temperature has been estimated to be $\sim 270\ \text{K}$ for the former and $\sim 1300\ \text{K}$ for the latter. The $\Delta|k-l| = \pm 3$ selection rule of the overtone band allows us to determine the absolute energy level values by combining the frequencies of the overtone band with those of the fundamental and hot bands.

I. INTRODUCTION

The H_3^+ molecular ion is the simplest stable polyatomic system which plays important roles in quantum chemistry, ion chemical kinetics, plasma chemistry and physics, and astrophysics.^{1,2} Since the initial discovery of its infrared spectrum in 1980,³⁻⁵ a great many works have been done on its fully deuterated and partially deuterated species.^{4,6-15} Quite separate from these activities, Carrington, Buntenshaw, and Kennedy observed an enormous number of lines of H_3^+ and isotopic species near the dissociation limit.^{16,17}

Since H_3^+ is a very fundamental ion, extensive studies to characterize its vibration and rotation states have continued. After the extensive measurement and analysis of the ν_2 fundamental band,¹⁸ spectroscopy of high rotational levels¹⁹ and vibrationally hot bands²⁰ has been conducted using rotationally and vibrationally hot plasmas, respectively. In assigning the hot band transitions $2\nu_2(l=2) \leftarrow \nu_2$, $2\nu_2(l=0) \leftarrow \nu_2$, and $\nu_1 + \nu_2 \leftarrow \nu_1$, the first principle calculations by Miller and Tennyson^{21,22} based on the formalism of Tennyson and Sutcliffe²³ and using the potential surface of Meyer, Botschwina, and Burton²⁴ have played an essential role. The knowledge of the high vibration-rotation states thus obtained has led to the characterization of the remarkable overtone emission spectrum $2\nu_2(l=2) \rightarrow 0$ observed in Jupiter²⁵⁻²⁷ and in the laboratory.²⁸

In this paper, we report our observation of the $2\nu_2(l=2) \leftarrow 0$ overtone band in absorption. The purpose of this work is twofold. First, we attempt to provide accurate frequencies of the band for future astronomical observations. While the $4\ \mu\text{m}$ fundamental band of H_3^+ has been observed more strongly in Jupiter,²⁹ the $2\ \mu\text{m}$ overtone band might still be more useful as an astronomical probe because the frequency region for the latter is free from spectra of other species. Both bands will also be used to detect H_3^+ in other astronomical objects.^{5,30} Second, we attempt to determine the absolute energy level values for the vibration-rotation states of H_3^+ . This is possible because the $2\nu_2(l=2) \leftarrow 0$ band has the selection rule $\Delta(k-l) = \pm 3$ and thus allows us to determine energy differences between different K levels. The resulting experimentally obtained absolute energy

levels will be useful for the check and improvement of *ab initio* theory.

In order to observe the overtone band, it was necessary to extend the coverage of our difference frequency spectrometer from 2.5 to $2\ \mu\text{m}$. This was done by using a LiIO_3 crystal for the mixing element and angle tuning for phase matching rather than the conventional LiNbO_3 crystal and temperature tuning. This is the first case in which the LiIO_3 crystal assembled by Bawendi³¹ in our laboratory is used for high resolution spectroscopy in the $2\ \mu\text{m}$ region.

II. THEORY

The selection rules for the $2\nu_2 \leftarrow 0$ overtone band can be obtained from simple symmetry arguments. Let the quantum numbers be $v_2' = 2, J', k', l \leftarrow v_2 = 0, J, k$, where v_2 is the vibrational quantum number for the degenerate ν_2 vibrational mode, J is the quantum number for the rotational angular momentum, k (signed) is its projection along the C_3 axis, and l (signed) is the quantum number for the vibrational angular momentum. In the D_{3h} symmetry for H_3^+ , the space fixed dipole moment has the symmetry of A_1'' , which is invariant to the $C_3(123)$ operation and changes sign with the $\sigma_h(E^*)$ (parity) operation.³² Since the wave function $|J, k, l\rangle$ has the symmetry properties^{32,33}

$$C_3|J, k, l\rangle = \exp\left[\frac{2\pi i}{3}(k-l)\right]|J, k, l\rangle \quad (1)$$

and

$$\sigma_h|J, k, l\rangle = (-1)^k|J, k, l\rangle,$$

we have the selection rules

$$\Delta(k-l) = 3n \text{ and } \Delta k = 2n + 1.$$

We therefore see that for the overtone band $2\nu_2 \leftarrow 0$ with

$$l = \pm 2, \quad k' = k \mp 1,$$

are the only strongly allowed transitions. The weakly allowed $l = 0, k' = k \mp 3$ transitions are outside the scope of this paper. In general for the H_3^+ -type molecules, the $n\nu_2 \leftarrow 0$ overtone bands are strongest for

$$l = \pm 2, \quad k' = k \mp 1, \quad \text{if } n \text{ is even}$$

and

$$l = \pm 1, k' = k \pm 1, \text{ if } n \text{ is odd.}$$

The vibrational transition dipole moment μ_{eff} for the $2\nu_2 \leftarrow 0$ overtone band can be obtained from a perturbation (contact transformation) treatment³⁴ of the dipole operator

$$\mu_x \pm i\mu_y = \frac{\partial \mu}{\partial q_2} (q_{2x} \pm iq_{2y}) + \frac{1}{2} \frac{\partial^2 \mu}{\partial q_2^2} (q_{2x} \mp iq_{2y})^2 \quad (2)$$

and the anharmonic vibrational potential term

$$H' = \phi_{222} [(q_{2x} + iq_{2y})^3 + (q_{2x} - iq_{2y})^3]/12 \quad (3)$$

to be

$$\begin{aligned} (\mu_{\pm})_{\text{eff}} &= [(\mu_x \mp i\mu_y)/\sqrt{2}]_{\text{eff}} \\ &= \frac{1}{2\sqrt{2}} \left(\frac{\partial^2 \mu}{\partial q_2^2} + \frac{\phi_{222}}{3\nu_2} \frac{\partial \mu}{\partial q_2} \right) (q_{2x} \pm iq_{2y})^2, \end{aligned} \quad (4)$$

where q_{2x} and q_{2y} are the two components of the ν_2 dimensionless normal coordinate, $\phi_{222} = -1183 \text{ cm}^{-1}$ is the anharmonicity constant,³⁵ and $\nu_2 = 2521 \text{ cm}^{-1}$ is the vibrational frequency. The derivatives of the dipole have been calculated theoretically by Carney and Porter³⁶ in atomic units which are translated into $(\partial \mu / \partial q_2) = 0.237 \text{ D}$ and $(\partial^2 \mu / \partial q_2^2) = -0.106 \text{ D}$.³⁵ These values give for the $2\nu_2(2) \leftarrow 0$ band

$$\begin{aligned} \langle 2, \pm 2 | (\mu_{\pm})_{\text{eff}} | 0, 0 \rangle &= \frac{1}{2} \left(\frac{\partial^2 \mu}{\partial q_2^2} + \frac{\phi_{222}}{3\nu_2} \frac{\partial \mu}{\partial q_2} \right) \\ &= 0.0716 \text{ D.} \end{aligned} \quad (5)$$

This value is comparable to the transition moment for fundamental bands of usual molecules and is much larger than that of overtone bands of usual molecules. This is due to the large-amplitude motion of protons in H₃⁺ which causes the unusually large mechanical (ϕ_{222}) and electrical ($\partial^2 \mu / \partial q_2^2$) anharmonicity. This unusually large transition moment for the overtone band makes the transition useful for both astronomical and laboratory observations. The value given in Eq. (5) is in approximate agreement with the value given by Carney and Porter³⁷ of 0.0667 D. In a recent paper, Miller, Tennyson, and Sutcliffe³⁸ calculated the transition moment of forbidden rotational transitions of H₃⁺ which include expressions similar to Eq. (5). The reasonable agreement between our value³⁵ ($5.2 \times 10^{-3} \text{ D}$) and their value ($5.9 \times 10^{-3} \text{ D}$) also gives a support to our treatment.

The Hönl-London formulae^{39,40} can be used to calculate the intensity dependence on rotational quantum numbers J and K in a straightforward manner (the formulas given in Ref. 40 should be divided by a factor of 4). The complication due to the large l -resonance present in the ν_2 state does not exist for the $2\nu_2$ state since the "accidentally" degenerate levels $l = 2, k + 2$ and $l = -2, k - 2$ are connected by a much smaller (by a factor of about 10^{-6}) vibration-rotation interaction term.

III. EXPERIMENTAL

We used a difference frequency laser system⁴¹ as the source of frequency tunable infrared radiation. A single fre-

quency single mode radiation at 488 or 476 nm from an argon ion laser is mixed with a frequency tunable red radiation from a ring dye laser in a nonlinear crystal.

In order to extend the frequency coverage into the $2 \mu\text{m}$ region, we used the LiIO₃ crystal system recently assembled by Bawendi³¹ based on the work of Volkov *et al.*⁴² Two LiIO₃ crystals (30 mm long, 12 mm wide, and 6 mm thick) are placed in the optical path of the collinearly combined Ar laser and dye laser beams in a symmetrical fashion to compensate for the effect of beam "walking." The crystal was cut such that the optical axis and the normal to the face of the crystal formed an angle of 22°. A 1° wedge was cut at one end of the crystal to prevent interference. The use of two crystals in a mirror image arrangement had the additional effect of increasing the effective path length by a factor of ~2. An optical arrangement similar to that of Volkov *et al.*⁴² was used to further increase the conversion efficiency. While the collinearly combined two radiations were focused in the crystal, the Ar laser radiation was passed through a cylindrical lens before it was combined in a polarizing cube to insure overlap of the two radiations throughout the crystals. More details can be found in Bawendi's thesis.³¹ In order to extend the infrared frequency to the $2 \mu\text{m}$ region, we needed to operate the dye laser to extreme red. We used a few dyes for this purpose R101, DCM, Kiton red, etc., but used Kiton red most of the time.

This arrangement enabled us to cover a wider range of 5300–1850 cm^{-1} than that by LiNbO₃ of 4500–2350 cm^{-1} . However, the power available from the LiIO₃ system is much less than that from the LiNbO₃ system, typically 1/40 to 1/100. This lower power resulted in lower sensitivity of the spectroscopy by a factor of perhaps 10 to 30. An additional difficulty of conducting spectroscopy in the $2 \mu\text{m}$ region was lack of suitable reference gases for frequency measurement. We mostly used N₂O isotope mixture and CO₂ for this purpose. Often the absorption was very weak and we used a multiple reflection sample cell for the reference gases.

For high sensitivity detection of the spectrum, we used a 6 kHz ac discharge and velocity modulation.⁴³ The discharge tube (a liquid nitrogen cooled, multiple inlet-multiple outlet cell) and the gas mixture (He:H₂ ~ 7 Torr:0.5 Torr) were similar to those used for our study of hot bands.²⁰ For detecting transitions starting from high rotational levels ($J > 4$), we used the discharge cell with gaseous nitrogen as a coolant to increase the rotational temperature. For the most effective velocity modulation, noise subtraction, and multiple passing, the infrared beam was split into two beams with equal intensity which went through the cell unidirectionally four times in opposite directions and were detected by two matched detectors.

IV. OBSERVED SPECTRUM

In conducting the absorption spectroscopy of the $2\nu_2(l = 2) \leftarrow 0$ overtone band of H₃⁺, there was little search problem since for most vibration-rotation transitions the expected spectral positions were predicted with reasonable accuracy by (a) combining the frequency of the ν_2 fundamental band^{18,19} and those of the $2\nu_2(l = 2) \leftarrow \nu_2$ hot band given in the preceding paper,²⁰ and/or (b) the laboratory Fourier

TABLE I. Observed frequencies of the H₃⁺ 2ν₂(l = 2) ← 0 overtone band.

Transition <i>J, G, U</i> ← <i>J', k'</i>	Theoretical ^a (cm ⁻¹)	Jupiter ^b (cm ⁻¹)	FTIR ^c (cm ⁻¹)	This work (cm ⁻¹)	Absolute coefficient ^d (270 K) (cm ⁻¹)	Absolute coefficient ^d (1300 K) (cm ⁻¹)
2,3, + 2 ← 1,0	5093.729		5094.212	5094.218	7.28D-07	4.54D-08
3,4, + 2 ← 2,1	5061.407		5061.864	5061.882	1.81D-07	2.13D-08
4,2, + 2 ← 4,1	5054.087		5054.742			
4,5, + 2 ← 3,2	5032.028			5032.447	1.03D-07	2.72D-08
2,2, + 2 ← 2,1	5028.424			5029.071	1.36D-07	1.60D-08
1,2, + 2 ← 1,1	5022.899			5023.498	2.06D-07	1.16D-08
5,6, + 2 ← 4,3	5000.138	5000.527 ^h	5000.506	5000.499	8.34D-08	5.78D-08
5,3, - 2 ← 6,6	4973.813			4975.338	2.10D-08	6.08D-08
2,0, - 2 ← 3,3	4970.645	4971.537 ^h	4971.559	4971.561	3.59D-07	5.87D-08
2,4, + 2 ← 1,1	4967.871		4968.162 ^f	4968.272	4.11D-07	2.33D-08
6,7, + 2 ← 5,4	4966.504	4966.859 ^h	4966.862	4966.838	1.26D-08	2.75D-08
1,1, - 2 ← 2,2	4955.262		4955.988	4955.991	2.35D-07	2.07D-08
5,3, + 2 ← 5,0	4941.722		4942.862			
3,5, + 2 ← 2,2	4935.667	4935.946	4935.969 ^g	4936.000	3.92D-07	3.45D-08
7,8, + 2 ← 6,5	4931.277	4931.561	4931.604	4931.596	2.87D-09	2.35D-08
5,2, - 2 ← 6,5	4929.693		4930.981			
3,3, + 2 ← 3,0	4913.634	4914.247	4914.214 ^g	4914.248	1.73D-07	6.58D-08
3,0, - 2 ← 4,3	4907.827	4907.859	4907.869 ^f	4908.672	6.08D-08	4.22D-08
1,3, + 2 ← 1,0	4907.381	4907.859	4907.869 ^f	4907.871	7.28D-07	4.54D-08
4,6, + 2 ← 3,3	4900.138	4900.377	4900.393	4900.393	5.02D-07	8.22D-08
8,9, + 2 ← 7,6	4895.237	4895.498	4895.520	4895.518	1.09D-09	3.78D-08
2,1, - 2 ← 3,2	4876.231	4876.912	4876.985 ^g	4876.938	6.56D-08	1.73D-08
5,7, + 2 ← 4,4	4861.606	4861.839 ^h	4861.849	4861.790	1.20D-07	4.30D-08
9,10, + 2 ← 8,7	4858.897		4859.209	4859.212 ^e	8.20D-11	1.41D-08
1,2, + 2 ← 2,1	4849.725			4850.264	8.16D-08	9.61D-09
5,4, + 2 ← 5,1	4839.030		4839.508			
10,11, + 2 ← 9,8	4823.076		4823.348	4823.315 ^e	1.40D-11	1.00D-08
6,8, + 2 ← 5,5	4820.503	4820.542	4820.616	4820.598	4.34D-08	4.09D-08
4,4, + 2 ← 4,1	4818.456		4818.901			
4,0, - 2 ← 5,3	4815.465	4816.415	4816.361	4816.353	6.83D-09	2.81D-08
5,0, - 2 ← 6,3	4813.846		4814.521			
3,1, + 2 ← 4,2	4804.609		4805.287			
3,4, + 2 ← 3,1	4804.080	4804.463	4804.406 ^f			
2,4, + 2 ← 2,1	4794.697	4795.018		4795.066 ^e	9.09D-08	1.07D-08
11,12, + 2 ← 10,9	4788.666		4788.544 ^f			
7,9, + 2 ← 6,6	4777.123	4777.215	4777.228	4777.226	2.49D-08	7.19D-08
2,2, + 2 ← 3,1	4771.097		4771.641			
12,13, + 2 ← 11,10	4756.442		4756.345			
4,1, + 2 ← 5,2	4744.124		4744.797			
6,5, + 2 ← 6,2	4735.264		4735.941			
8,10, + 2 ← 7,7	4732.158	4732.050	4732.053	4732.060 ^e	2.73D-09	2.95D-08
5,5, + 2 ← 5,2	4711.921	4712.334 ^h	4712.309			
3,2, + 2 ← 4,1	4699.645		4700.139			
4,5, + 2 ← 4,2	4691.684		4691.962			
9,11, + 2 ← 8,8	4685.694	4685.582	4685.558	4685.564	5.47D-10	2.29D-08
3,5, + 2 ← 3,2	4677.032	4677.268	4677.285	4677.273	3.44D-08	9.07D-09
2,3, + 2 ← 3,0	4663.949	4664.274	4664.303	4664.306	4.95D-08	1.88D-08
7,6, + 2 ← 7,3	4641.550		4641.987			
10,12, + 2 ← 9,9	4638.688	4638.361	4638.338	4638.331	1.37D-10	3.34D-08
4,2, + 2 ← 5,1	4637.488		4637.992 ^g			
6,6, + 2 ← 6,3	4606.887		4607.205			
5,2, + 2 ← 6,1	4586.619		4587.373			
5,6, + 2 ← 5,3	4578.502		4578.742	4578.735	3.96D-09	1.66D-08
4,6, + 2 ← 4,3	4556.883	4557.057		4557.020	2.08D-08	1.44D-08
4,3, + 2 ← 5,0	4539.484		4539.759			

^a Miller and Tennyson, Ref. 21.^b Reference 26.^c Reference 28.^d Calculated with assumed ion density = 3 × 10¹⁰ cm⁻³.^e Large uncertainty, ± 0.02 cm⁻¹.^f Apparently coincident with the H₂ line in the FTIR spectrum.^g The shoulder on an H₂ line in the FTIR spectrum.^h Corresponding to lines detected in the uncalibrated spectrum in Jupiter spectrum, but with large uncertainties in the calibration procedure.

transform, infrared (FTIR) emission spectrum by Majewski *et al.*²⁸ and the Jupiter emission spectrum by Drossart *et al.*,²⁶ and/or (c) the first principle calculation of Miller and Tennyson.^{21,22} Unlike the case of hot bands,²⁰ the $2\nu_2(l=2) \leftarrow 0$ overtone band is isolated and there was no ambiguity in assignment as long as the signal was observed with reasonable signal to noise ratio.

Altogether, 34 vibration-rotation transitions have been measured and assigned; they are listed in Table I. We also list the frequencies of the Jupiter spectrum, the FTIR emission spectrum, and the theoretical calculation. Compared with the FTIR emission spectrum reported by Majewski *et al.*, our observation is more complete for transitions with low rotational quantum numbers, but less complete for those involving high rotational levels, reflecting the high temperature of Majewski's hollow cathode discharge. Unlike the FTIR emission spectrum which is sometimes overshadowed by much stronger H_2 emission lines, our spectrum is almost completely free from other lines and leads us to firmer assignments of transitions. The uncertainty of the measured frequencies is estimated to be $\sim 0.005 \text{ cm}^{-1}$, except for a few lines which are marked in Table I.

The rotational temperatures and the ion concentrations in the plasmas were estimated from the observed relative and absolute intensities, respectively. For the liquid nitrogen cooled discharges used for detecting transitions involving low rotational levels, we obtained the rotational temperature of $\sim 270 \text{ K}$, while for the gaseous N_2 cooled discharges used for detecting transitions involving high rotational levels, $\sim 1300 \text{ K}$. The temperatures have large uncertainties partly because of inaccuracy of intensity measurements of weak lines separated by many cm^{-1} and partly because the rotational states are not in thermal equilibrium in discharges. Using the theoretically estimated transition dipole moment of 0.0716 D discussed earlier in this paper, we obtained the H_3^+ number density to be $\sim 3 \times 10^{10} \text{ cm}^{-3}$ in the discharge. Note that this value is an average over the ac discharge whose duty cycle is considerably less than 1. At the peak current the concentration must be higher. Calculated absorption coefficients based on these temperatures and ion density are listed in Table I.

One example of the observed spectral line for each of the two plasma conditions is shown in Fig. 1. The strongest observed line in the liquid nitrogen cooled plasma corresponding to the $1,3, +2 \leftarrow 1,0$ transitions at 4907.871 cm^{-1} is shown in Fig. 1(a). Figure 1(b) shows the observed transition with the highest J,K value corresponding to the $10,12, +2 \leftarrow 9,9$ transition at 4638.331 cm^{-1} , observed in the gaseous N_2 cooled discharge. From the calculated absorption coefficients and the observed signal to noise ratios, we estimate the sensitivity of the spectroscopy to be $\Delta I/I \sim 10^{-5}$ which is considerably lower than that of 5×10^{-7} in the $3\text{--}4 \mu\text{m}$ region, where LiNbO_3 is used as the nonlinear optical element. This is due to the lower power (by a factor of 40–100) generated from the LiIO_3 mixing discussed earlier. The power is so low that in some cases the detector noise was the major noise source.

Computer generated stick diagrams based on the calculated intensities of the overtone bands are shown in Fig. 2 for

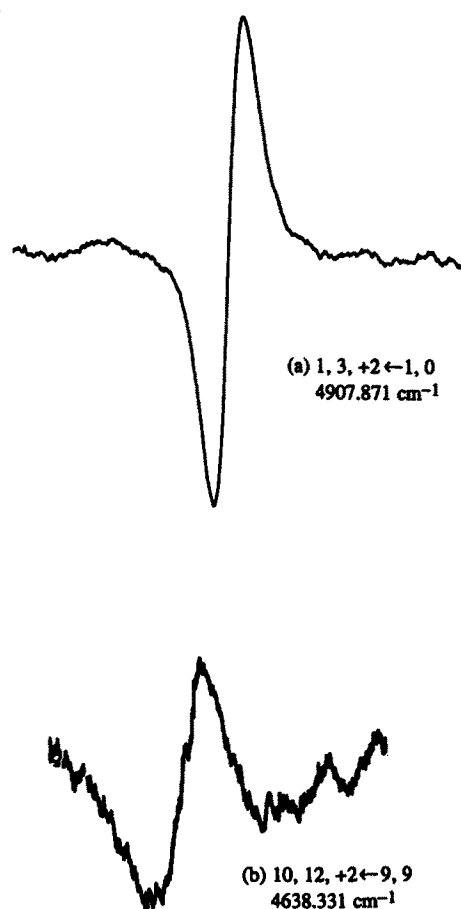


FIG. 1. Two examples of observed spectral lines. (a) The strongest $(J,G,U) = (1,3,+2) \leftarrow (1,0)$ transition at 4907.871 cm^{-1} observed by using a liquid- N_2 cooled discharge ($\text{He}:\text{H}_2 \sim 7 \text{ Torr}:0.5 \text{ Torr}$). (b) The $(J,G,U) = (10,12,+2) \leftarrow (9,9)$ transition at 4638.331 cm^{-1} involving a highest rotational level observed by using a gaseous- N_2 cooled discharge. The time constant of detection was 3 s.

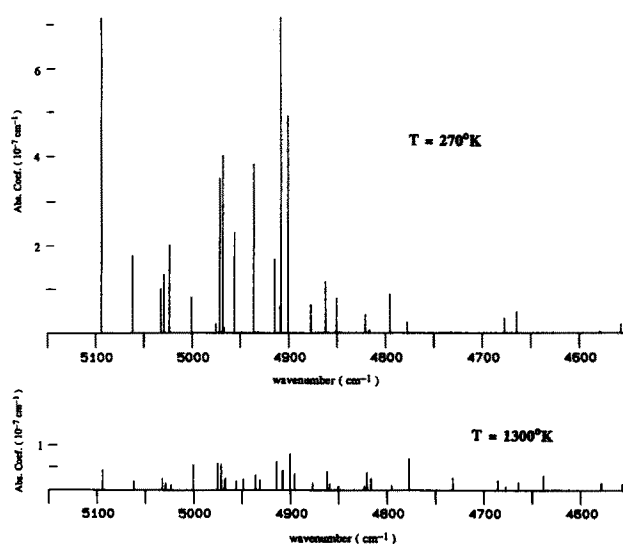


FIG. 2. Computer generated stick diagrams of the observed overtone transitions for the rotational temperature of 270 K (above) and 1300 K (below). The lower temperature gave strong lines, but higher temperature was necessary to observe many high J,K lines.

TABLE II. Absolute vibration-rotation term values in the ground ν_2 , $2\nu_2(l=2)$, and $2\nu_2(l=0)$ states of H_3^+ (units are in cm^{-1}).

J	G	Ground State	ν_2 state		$2\nu_2(l=2)$ state		$2\nu_2(l=0)$ state
			$U = -1$	$U = +1$	$U = -2$	$U = +2$	
0	0	0.000					
1	0	86.963	2616.687				
2	0	...		2812.861	5286.916		
3	0	516.881	3025.956			5567.390	5305.589
4	0	...		3447.044	5896.843		
5	0	1271.264 ^b	3743.178 ^b			6391.876	
6	0	...		4399.320 ^b			
0	1			2521.415			
1	1	64.125		2609.544		5125.296	
2	1	237.359	2755.568	2790.346		5304.962	5023.466
3	1	494.771	3002.904	3063.473	5486.456	5573.763	5282.322
4	1	833.577	3326.115	3423.120	5846.795	5931.878	
5	1	1250.305	3722.629	3863.390			
6	1	1740.868	4188.769				
0	2					4998.056	
1	2			2548.171		5087.623	
2	2	169.302		2723.967		5266.432	4942.727
3	2	428.021	2931.369	2992.434		5533.732	5210.811
4	2	768.471	3260.219	3351.381	5716.491	5888.312	5544.211
5	2	1187.101	3660.338	3793.022	6169.453	6327.945	
6	2	1679.784	4129.312				
7	2		4664.032	4892.164 ^b			
1	3					4994.834	
2	3			2614.282		5181.184	
3	3	315.352		2876.846		5431.125	5078.934
4	3	658.717	3145.275	3233.377		5811.004	5434.330
5	3	1080.490	3553.327	3673.955	5971.230	6213.700	5830.434
6	3	1577.327	4030.040	4202.294			
7	3	2142.094 ^b	4563.977 ^b				
2	4					5032.397	
3	4			2719.493		5299.241	
4	4	502.042		3069.327		5652.482	5251.746
5	4	928.976	3396.530	3510.157		6089.829	5690.841
6	4	1430.722	3884.132	4035.782	6250.723		
7	4	2002.461	4420.233				
3	5					5105.292	
4	5			2863.942 ^b		5460.465	
5	5	729.020		3300.143		5899.408	
6	5	1238.459	3685.093	3825.434		6415.749	5983.893
7	5	1818.148	4249.966	4431.688			
8	5	2462.888 ^b	4874.399 ^b				
4	6					5215.740	
5	6			3047.388		5659.223	
6	6	995.875		3569.465		6184.533	5705.040
7	6	1586.586	4010.230	4177.908		6784.062	
8	6	2242.188 ^b	4650.933 ^b				
5	7					5363.832	
6	7			3269.594 ^b		5895.814	
7	7	1302.144 ^b		3877.038 ^b			
8	7		4371.303 ^b				
9	7	1972.774 ^b	5086.303 ^b				
6	8					5549.618	
7	8			3530.249 ^c		6170.055	
8	8	1647.277 ^c		4222.653 ^c			
9	8	2396.493 ^c	4767.587				
7	9					5773.101	
8	9			3829.012		6482.105	
9	9	2030.616		4605.728			
8	10					6034.190 ^{b,d}	
9	10					6831.986 ^{b,d}	
9	11					6332.841 ^c	
10	11					7219.808 ^{c,d}	
10	12					6668.947	

^a Symmetry forbidden.^b Based on FTIR data (Ref. 19).^c Based on theoretical calculation (Ref. 21).^d Large uncertainty.

the two temperatures. The higher temperature makes the spectral lines much weaker, but allows us to observe many additional high J, K transitions.

V. ABSOLUTE ENERGY LEVEL VALUES

The $\Delta G = \Delta|k - l| = \pm 3$ selection rule for the $2\nu_2(l=2) \leftarrow 0$ overtone band discussed in Sec. II allows us to determine the separations between the ground state rotational levels with the same J quantum number, but with k differing by ± 3 . This is done by comparing the frequencies of the overtone transitions

$$(2\nu_2, l=2, J', G=k+3) \leftarrow (0, J, k)$$

with those of the ladder of the hot band and the fundamental band

$$(2\nu_2, l=2, J', G=k+3) \leftarrow (\nu_2, l=1, J'', G=k+3) \leftarrow (0, J, k+3).$$

Thus we can determine the separations between rotational levels of *ortho* ($I=3/2$) H₃⁺ levels and those between *para* ($I=1/2$) H₃⁺ levels experimentally. Although separations between *ortho* and *para* levels cannot be determined experimentally, the separation between the lowest *ortho* level ($J=1, K=0$) and the lowest *para* level ($J=1, K=1$) can be calculated quite accurately and lead us to the absolute rotational energy level values in the ground state. This in turn allows us to calculate absolute energy values for most levels for the ground $\nu_2, 2\nu_2(l=0)$, and $2\nu_2(l=2)$ states.

The experimental absolute energy levels thus determined are listed in Table II. The U label is according to Watson.⁴⁴ We estimate the accuracy of the absolute energy level values to be $\leq 0.01 \text{ cm}^{-1}$, assuming correct assignment.

In determining some levels, it was necessary to use FTIR¹⁹ or theoretical results.^{21,22} They are indicated in Table II. For them the uncertainty is larger.

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