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Hot Band Transition Frequencies and Line Strengths in H_3^+: First Principles Calculations

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Ro-vibrational transitions from lower states with one quantum of vibrational energy to upper states with two vibrational quanta, and from lower states with two vibrational quanta to upper states with three, have been calculated from first principles. The calculations make use of the accurate potential energy surface calculated for H_3^+ by Meyer, Botschwina, and Burton. The predicted frequencies for the (v=2 – v=1) transitions are reported in excellent agreement with new experimental data and the computed line strengths are consistent with the lines that have been observed. An estimate of the error in the (v=3 – v=2) transitions is made.

1. INTRODUCTION

The simple molecular ion H_3^+ continues to attract considerable experimental and theoretical interest, both as a result of earlier, challenging laboratory studies (*1*) and because of its importance as a protonating agent in interstellar chemical pathways (*2, 3*). The ν_2 fundamental infrared ro-vibrational spectrum is now extremely well characterized (*4, 5*) from accurate laboratory measurements.

During the past 2 years we have been using an ab initio electronic potential energy surface due to Meyer, Botschwina, and Burton (*6*) to compute ro-vibrational energy levels from first principles (*7*). Meyer *et al.* (hereafter MBB) also calculated a corresponding dipole surface (*6*). Transition frequencies for the ν_2 band calculated using the MBB potential energy surface are of near spectroscopic accuracy. For the sixty lines for which we compared experimental observations (*4, 5*) with our calculations, the transitions computed from MBB surface give a root mean square deviation of just 0.24 cm^{-1} (*8*). In addition, the line strengths computed from the MBB dipole surface reproduce the pattern of observed transitions (*8, 9*).

Among the experimentally measured ν_2 system were a number of lines which had, then, not been positively identified but were assumed to result from hot band transitions. Encouraged by the accuracy with which our calculations reproduced the ν_2 data, we published energy levels for overtone bands up to $2\nu_1$ and rotational states from J = 0 to 4 (*10*). Recently, Bawendi, Oka and Rehfuss (*11*) have been able to identify lines resulting from $2\nu_2$ (l = 2)–ν_2 and ($\nu_2 + \nu_1$)–ν_1 transitions, using the data contained in Ref. (*9*).

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In this paper, we present new, more accurate calculations of these hot band transitions, for which we now have data for angular momentum states up to $J = 12$, and for the yet to be identified $2\nu_2$ ($l = 0$)–ν_2 band. We have also calculated the corresponding line strengths. In addition, we have been able to compute accurate values of transition frequencies from lower states with two vibrational quanta to upper states with three. For these transitions however the range of angular momentum states is considerably reduced, and for some only upper state levels with $J' = 0$, 1, and 2 are available.

2. COMPUTATIONAL DETAILS

The computation of the ro-vibrational energy levels, transition frequencies, and line strengths were carried out using the TRIATOM program suite, which has been documented elsewhere (*9, 12*). The calculations were performed using the Cray XMP-48 at the Atlas Centre of the Rutherford Appleton Laboratories.

The TRIATOM suite has options to calculate levels using a number of different co-ordinate types. For these calculations, scattering co-ordinates were used with the body-fixed z-axis taken along the H–H_2 coordinate. In this representation of H_3^+, the wave functions are represented as products of basis functions carrying the rotational, radial, and bending co-ordinates. The radial co-ordinates were represented by the Morse oscillator-like functions used previously (*7*). The bending motion was carried by associated Legendre function, $\Theta_{jk}(\theta)$ (*13*), which are coupled to rotation matrices used to represent the overall rotational motion of the system (*9*).

For the rotationally excited levels, with $J > 0$, the TRIATOM suite uses a two-step method (*9, 12*) of calculating fully coupled ro-vibrational levels. In the first step, an intermediate basis set is generated, ignoring the effects of Coriolis coupling. At this point in the calculation, k, the projection of the angular momentum J along the molecule-fixed z-axis, is a good quantum number. For each J, k ($J = 0$–10, $k = 0$–J) block, 1700 basis functions selected on an energy ordering criterion (*12*) were used. This ensured that the levels were converged to 0.1 cm^{-1}. For calculations with $J > 0$, the lowest 800 non-Coriolis coupled eigenfunctions were computed.

In the second step, off-diagonal coupling between functions with $k'' = k$ to $k' = k \pm 1$ is included. The full secular matrix diagonalized in this step consisted of $(J + 1) \times 500$ basis functions derived from the first step calculations, again selected on an energy ordering criterion (*12*). This choice of basis sets ensured that the energy levels were again converged to at least 0.1 cm^{-1}—although most lower lying levels were much better converged than this. These basis sets were 60% larger than those used in the previous overtone level calculations (*10*).

For all angular momentum levels, no more than 80 lowest eigenstates were considered. For $J = 1$ this is sufficient to cover up to and including the entire $3\nu_1$ manifold. But for $J = 10$ this coverage only just extends into the $2\nu_2$ ($l = 0$) manifold. Nonetheless, we have computed enough energy levels to make predictions of several hundred frequencies and line strengths for significant hot band transitions, having either one or two vibrational quanta in the lower state, within a frequency range from 2000 to 3000 cm^{-1}.

3. RESULTS

Band origins for vibrational levels up to $v = 3$ are given in Table I. All the levels are converged to at least 0.1 cm^{-1}. The differences between the results given here and previously by us (*10*) arise because of the larger basis set used for the $J = 0$ calculation reported in this paper. Whitnell and Light (*14*) have recently published band origins for H_3^+ computed using the MBB potential and a discrete variable method in hyperspherical coordinates. While their results agree generally with those of Table I, their band origins are systematically between 0.5 and 1 cm^{-1} higher than ours or those calculated by MBB.

The labeling of the vibrational states in Table I is in accordance with Watson *et al.* (*4, 5*). States which include v_2 vibrational quanta of the ν_2 mode have an additional

TABLE I

Calculated Vibrational Band Origins for H_3^+ (cm^{-1})

Mode	v_2	$l_2 = 0$		± 1		± 2		± 3	
ν_2	1			2521.28	E				
ν_1	0	3178.35	A_1						
$2\nu_2$	2	4777.02	A_1			4997.42	E		
$\nu_2 + \nu_1$	1			5553.71	E				
$2\nu_1$	0	6262.06	A_1						
$3\nu_2$	3			7003.45	E			7282.55	A_1
								7492.66	A_2
$2\nu_2 + \nu_1$	2	7769.15	A_1			7868.77	E		
$\nu_2 + 2\nu_1$	1			8487.09	E				
$3\nu_1$	0	9251.62	A_1						

TABLE II

Hot Band Transitions for H_3^+ from ν_2 to $2\nu_2(0)$

$J', K' - J'', G''_{U''}$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)^a$ (D^2)	$I_{Rel}(\omega)$ [b] 300K
$2,2-3,2_{-1}$	4941.353	2930.998	2010.355	0.739(-1)	0.156
$2,1-3,1_{-1}$	5022.056	3002.486	2019.570	0.203(-1)	0.031
$1,1-2,1_{+1}$	4841.240	2790.127	2051.113	0.333(-1)	0.141
$1,0-2,0_{-1}$	4868.973	2812.642	2056.331	0.573(-1)	0.218
$1,1-2,1_{-1}$	4841.240	2755.291	2085.949	0.335(-1)	0.171
$6,6-6,6_{+1}$	5703.358	3568.950	2134.408	0.522(-1)	0.006
$5,5-5,5_{+1}$	5458.853	3299.725	2159.129	0.502(-1)	0.006
$5,4-5,4_{+1}$	5689.112	3509.703	2179.409	0.612(-1)	0.009
$4,4-4,4_{+1}$	5250.219	3069.003	2181.216	0.474(-1)	0.056
$4,2-4,2_{+1}$	5542.504	3351.023	2191.481	0.210(-1)	0.006
$4,3-4,3_{+1}$	5432.735	3233.027	2199.708	0.509(-1)	0.028
$3,3-3,3_{+1}$	5077.489	2876.591	2200.898	0.441(-1)	0.133
$3,2-3,2_{+1}$	5209.308	2992.161	2217.147	0.400(-1)	0.070
$2,2-2,2_{+1}$	4941.353	2723.765	2217.588	0.385(-1)	0.243
$3,1-3,1_{+1}$	5280.799	3063.193	2217.607	0.110(-1)	0.014
$1,1-1,1_{+1}$	4841.240	2609.377	2231.863	0.310(-1)	0.339
$2,1-2,1_{+1}$	5022.056	2790.127	2231.929	0.228(-1)	0.105
$1,0-1,0_{-1}$	4868.973	2616.487	2252.486	0.578(-1)	0.618
$6,4-6,4_{-1}$	6139.144	3883.248	2255.896	0.191(+0)	0.005
$6,2-6,2_{-1}$	6392.663	4128.273	2264.391	0.386(+0)	0.003
$2,1-2,1_{-1}$	5022.056	2755.291	2266.765	0.702(-1)	0.389
$6,3-6,3_{-1}$	6299.228	4029.071	2270.157	0.326(+0)	0.004
$5,3-5,3_{-1}$	5828.522	3552.620	2275.902	0.218(+0)	0.027

[a] Powers of ten in brackets.

[b] Scaling factor $= 5.34 \times 10^{-6}$. This scaling factor relates the intensity of the strongest transition in this manifold to the strongest ν_2 fundamental transition, the $2,0_{-1} - 1,0$ line at 2725.71cm^{-1}, assuming all levels are populated according to a Boltzmann distribution at 300K.

TABLE II—*Continued*

$J', K' - J'', G''_{U''}$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)^a$ (D^2)	$I_{Rel}(\omega)$ [b] 300K
$5,2-5,2_{-1}$	5937.769	3659.563	2278.205	0.311(+0)	0.023
$3,2-3,2_{-1}$	5209.308	2930.998	2278.309	0.757(-1)	0.181
$3,1-3,1_{-1}$	5280.799	3002.486	2278.313	0.165(+0)	0.281
$3,0-3,0_{-1}$	5304.036	3025.528	2278.508	0.198(+0)	0.301
$5,0-5,0_{-1}$	6021.089	3742.346	2278.743	0.387(+0)	0.019
$5,1-5,1_{-1}$	6001.251	3721.811	2279.441	0.366(+0)	0.020
$4,2-4,2_{-1}$	5542.504	3259.663	2282.840	0.197(+0)	0.098
$4,1-4,1_{-1}$	5608.682	3325.518	2283.164	0.268(+0)	0.097
$4,3-4,3_{-1}$	5432.735	3144.790	2287.944	0.789(-1)	0.068
$5,4-5,4_{-1}$	5689.112	3395.911	2293.201	0.833(-1)	0.022
$6,5-6,5_{-1}$	5982.015	3684.325	2297.690	0.861(-1)	0.006
$1,1-0,1_{+1}$	4841.240	2521.282	2319.958	0.172(-1)	0.299
$2,2-1,2_{+1}$	4941.353	2548.041	2393.313	0.514(-1)	0.813
$2,1-1,1_{+1}$	5022.056	2609.377	2412.679	0.213(-1)	0.253
$3,3-2,3_{+1}$	5077.489	2614.135	2463.355	0.843(-1)	1.000
$3,2-2,2_{+1}$	5209.308	2723.765	2485.543	0.478(-1)	0.337
$3,1-2,1_{+1}$	5280.799	2790.127	2490.672	0.170(-1)	0.088
$3,0-2,0_{-1}$	5304.036	2812.642	2491.394	0.912(-2)	0.042
$3,1-2,1_{-1}$	5280.799	2755.291	2525.508	0.275(-2)	0.017
$4,4-3,4_{+1}$	5250.219	2719.308	2530.911	0.117(+0)	0.858
$4,1-3,1_{+1}$	5608.682	3063.193	2545.489	0.861(-2)	0.012
$4,2-3,2_{+1}$	5542.504	2992.161	2550.343	0.242(-1)	0.049
$4,3-3,3_{+1}$	5432.735	2876.591	2556.144	0.770(-1)	0.268
$5,2-4,2_{+1}$	5937.769	3351.023	2586.746	0.787(-2)	0.003
$5,5-4,5_{+1}$	5458.853	2863.711	2595.142	0.148(+0)	0.557
$5,3-4,3_{+1}$	5828.522	3233.027	2595.495	0.240(-1)	0.015
$4,1-3,1_{-1}$	5608.682	3002.486	2606.196	0.673(-2)	0.013
$4,2-3,2_{-1}$	5542.504	2930.998	2611.506	0.185(-1)	0.051
$5,4-4,4_{+1}$	5689.112	3069.003	2620.109	0.103(+0)	0.146
$6,6-5,6_{+1}$	5703.358	3047.090	2656.269	0.177(+0)	0.284

TABLE II—*Continued*

$J', K' - J'', G''_{l''}$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)^a$ (D^2)	$I_{Rel}(\omega)^b$ 300K
$5,1 - 4,1_{-1}$	6001.251	3325.518	2675.734	0.834(-2)	0.004
$5,2 - 4,2_{-1}$	5937.769	3259.663	2678.105	0.297(-1)	0.017
$6,5 - 5,5_{+1}$	5982.015	3299.725	2682.290	0.129(+0)	0.062
$5,3 - 4,3_{-1}$	5828.522	3144.790	2683.731	0.549(-1)	0.055
$6,2 - 5,2_{-1}$	6392.663	3659.563	2733.100	0.299(-1)	0.003
$7,6 - 6,6_{+1}$	6310.101	3568.950	2741.151	0.154(+0)	0.021
$6,4 - 5,4_{-1}$	6139.144	3395.911	2743.233	0.124(+0)	0.038
$6,3 - 5,3_{-1}$	6299.228	3552.620	2746.608	0.757(-1)	0.011
$7,5 - 6,5_{-1}$	6448.892	3684.325	2764.567	0.140(+0)	0.011
$8,8 - 7,8_{+1}$	6298.772	3529.762	2769.010	0.229(+0)	0.038
$7,4 - 6,4_{-1}$	6671.363	3883.248	2788.114	0.113(+0)	0.003
$8,7 - 7,7_{+1}$	6673.502	3876.409	2797.093	0.179(+0)	0.006
$6,2 - 5,4_{-1}$	6392.663	3395.911	2996.752	0.188(-1)	0.006

vibrational angular momentum quantum number, l_2, with values given by $l_2 = -v_2$, $(-v_2 + 2), \ldots, (v_2 - 2), v_2$. Vibrational band origins with $l_2 = 0$ belong to A_1 symmetry. Those with l_2 exactly divisible by three, e.g., $l_2 = \pm 3, \pm 6$, etc., form A_1/A_2 nondegenerate pairs. All other band origins form doubly degenerate E-modes. In the tables, and in the above text $l = |l_2|$.

Hot band transitions for lower states with one quantum of vibrational energy are given in Tables II–IV, and for lower states with two quanta of vibrational energy in Tables V–X. As well as the transition frequency, values for the initial and final energies, E'' and E', respectively, are given relative to the $J = 0$ vibrational ground state of H_3^+. There are thousands of possible transitions and we have used intensity criteria in order to reduce the data presented here to manageable proportions. Absolute intensities were calculated assuming a Boltzmann distribution and a temperature of 300 K from the computed line strengths.

Tables II–IV include all those lines which have at least 0.1% of the intensity of the strongest transition from a lower state with one quantum of vibrational energy. Tables V–X use the same criterion with respect to the strongest transition from a lower state with two quanta of vibrational energy.

Levels in these tables are also labeled according to the conventions of Refs. (*4*) and (*5*). For vibrational manifolds with $l_2 = 0$, states with angular momentum J are also labeled with K, the projection of the total angular momentum along the body-fixed c-axis (out of plane axis). For the other manifolds, states are labeled with $G = K + l_2$ and subscripted with l_2 (=u) itself. Although they belong to states of different vibrational symmetry, the ro-vibrational lines of $3\nu_2$ ($l_2 = +3$), (A_1 band origin), and $3\nu_2$ ($l_2 = -3$), (A_2 band origin), have all been put under the one heading of $3\nu_2$ ($l = 3$).

Assignment of the ro-vibrational levels has been made on the basis both of energy ordering and on the line strength of the transitions. Thus an initial assignment of the low-v, low-J levels can be used as a starting point from which the assignment of higher levels can be inferred using selection rules as a criterion. The additional information provided by the line strength data is especially important for these overtone levels, since overlap of the various vibrational manifolds begins for rotational states as low as $J = 2$.

On the basis of line strength information we have made one alteration to the assignments given in Ref. (*10*). The level originally assigned to $4,6_{+2}$ of $2\nu_2$ ($l = 2$) is now assigned to 4,4 of $2\nu_2$ ($l = 0$), and vice versa.

Table II contains energy levels, frequencies and line strengths for the $2\nu_2$ ($l = 0$)–ν_2 band. Unfortunately, there was an error in labeling the term values for the $l_2 = 0$ states in Reference (*10*) which has impeded the assignment of this band. This paper contains the correct values of the energy levels of $2\nu_2$ ($l = 0$).

Table III gives transitions belonging to the $2\nu_2$ ($l = 2$)–ν_2 manifold. The computed frequencies compare very well with the experimental data of Bawendi *et al.* (*11*). For the 48 transitions these workers have measured, the computed frequencies give a root-mean-square deviation of 0.63 cm^{-1} from the experimental ones. The ($\nu_2 + \nu_1$)–ν_1 transitions are given in Table IV. For this manifold, Bawendi *et al.* have measured 14 transitions and our results give a root-mean-square deviation of 0.61 cm^{-1} from theirs.

All the transitions that Bawendi *et al.* have identified are reproduced using our intensity criteria, with the exception of the $4,3_{+1}$–4,3 line in ($\nu_2 + \nu_1$)–ν_1, which we compute to have a frequency of 2433.421 cm^{-1}. For both manifolds our computed results are consistently lower than the experimental frequencies, indicating that the MBB potential energy surface is slightly too soft in this region.

The hot band transitions contained in Tables II–IV are very much as would be expected from selection rules, showing the normal $\Delta G/K = 0$ behavior. This is not, however, the case for the (v=3 – v=2) transitions. The existence of transitions from $2\nu_2$ ($l = 0$) to $3\nu_2$ ($l = 3$), given in Table VII, breaks the expected $\Delta l = 1$ rule, although—with one exception—the line strengths associated with this mode are generally small. The exception, the $3,5_{+3}$–2,1 line at 2573.756 cm^{-1}, is considered to be due to intensity stealing, the upper level mixing with the $3,1_{-1}$ level of $3\nu_2$ ($l = 1$).

In addition, there are many examples of $\Delta G/K = 6$ behavior, for example the $3,5_{+3}$–$3,1_{-2}$ and $1,4_{+3}$–$2,2_{+2}$ lines in $3\nu_2$ ($l = 3$)–$2\nu_2$ ($l = 2$), which occur at 2022.978 cm^{-1} and 2060.229 cm^{-1}, respectively. (Here transitions from $G = 1$–5 or 2–4 are considered as transitions from $G = -1$ to $G = +5$ or $G = -2$ to $G = +4$, etc.)

Some of these "unexpected" lines are also clearly due to intensity stealing from nearby "allowed" transitions. In addition, there is considerable difficulty in unambig-

TABLE III

Hot Band Transitions for H_3^+ from ν_2 to $2\nu_2(2)$

$J', G'_{U'} - J'', G''_{U''}$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)$[a] (D^2)	$I_{Rel}(\omega)$[b] 300K
$6,6_{+2} - 7,6_{+1}$	6183.721	4177.240	2006.481	0.515(+0)	0.001
$6,7_{+2} - 7,7_{+1}$	5895.176	3876.409	2018.767	0.636(+0)	0.007
$6,8_{+2} - 7,8_{+1}$	5549.281	3529.762	2019.518	0.753(+0)	0.047
$5,4_{+2} - 6,4_{+1}$	6088.940	4035.215	2053.725	0.309(+0)	0.002
$4,1_{+2} - 5,1_{+1}$	5930.849	3862.944	2067.905	0.129(+0)	0.002
$5,5_{+2} - 6,5_{+1}$	5898.647	3824.873	2073.774	0.402(+0)	0.006
$5,6_{+2} - 6,6_{+1}$	5658.641	3568.950	2089.691	0.518(+0)	0.027
$5,7_{+2} - 6,7_{+1}$	5363.481	3269.207	2094.274	0.631(+0)	0.140
$4,2_{+2} - 5,2_{+1}$	5887.398	3792.568	2094.830	0.155(+0)	0.003
$3,0_{-2} - 4,0_{-1}$	5566.330	3446.685	2119.645	0.740(-1)	0.007
$4,3_{+2} - 5,3_{+1}$	5810.346	3673.497	2136.849	0.217(+0)	0.007
$4,4_{+2} - 5,4_{+1}$	5651.768	3509.703	2142.064	0.296(+0)	0.021
$3,1_{+2} - 4,1_{+1}$	5572.834	3422.758	2150.077	0.767(-1)	0.008
$4,0_{-2} - 5,0_{-1}$	5895.604	3742.346	2153.258	0.655(-1)	0.002
$3,1_{-2} - 4,1_{-1}$	5485.152	3325.518	2159.634	0.132(-1)	0.010
$4,5_{+2} - 5,5_{+1}$	5459.909	3299.725	2160.185	0.403(+0)	0.080
$4,6_{+2} - 5,6_{+1}$	5215.387	3047.090	2168.297	0.511(+0)	0.343
$3,2_{+2} - 4,2_{+1}$	5532.956	3351.023	2181.933	0.123(+0)	0.019
$3,3_{+2} - 4,3_{+1}$	5430.347	3233.027	2197.320	0.194(+0)	0.054
$4,2_{+2} - 5,2_{-1}$	5887.398	3659.563	2227.835	0.384(-1)	0.001
$3,4_{+2} - 4,4_{+1}$	5298.686	3069.003	2229.683	0.290(+0)	0.181
$2,1_{-2} - 3,1_{+1}$	5304.112	3063.193	2240.920	0.451(-1)	0.029
$3,5_{+2} - 4,5_{+1}$	5104.913	2863.711	2241.202	0.393(+0)	0.657
$3,1_{+2} - 4,1_{-1}$	5572.834	3325.518	2247.317	0.233(-1)	0.004
$4,4_{+2} - 5,4_{-1}$	5651.768	3395.911	2255.856	0.205(-1)	0.003
$4,3_{+2} - 5,3_{-1}$	5810.346	3552.620	2257.726	0.411(-1)	0.003
$2,0_{-2} - 3,0_{-1}$	5285.893	3025.528	2260.365	0.171(-1)	0.013

[a] Powers of ten in brackets.

[b] Scaling factor = 1.04×10^{-5}.

TABLE III—*Continued*

$J',G'_{U'} - J'',G''_{U''}$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)^a$ (D^2)	$I_{Rel}(\omega)^b$ 300K
$3,2_{+2} - 4,2_{-1}$	5532.956	3259.663	2273.293	0.259(-1)	0.007
$2,2_{+2} - 3,2_{+1}$	5265.703	2992.161	2273.543	0.101(+0)	0.093
$3,3_{+2} - 4,3_{-1}$	5430.347	3144.790	2285.556	0.145(-1)	0.006
$5,3_{-2} - 5,3_{+1}$	5969.366	3673.497	2295.869	0.443(-1)	0.002
$2,1_{-2} - 3,1_{-1}$	5304.112	3002.486	2301.626	0.140(-1)	0.012
$2,3_{+2} - 3,3_{+1}$	5180.662	2876.591	2304.071	0.184(+0)	0.296
$2,4_{+2} - 3,4_{+1}$	5031.976	2719.308	2312.668	0.277(+0)	0.956
$1,1_{-2} - 2,1_{+1}$	5124.508	2790.127	2334.380	0.235(-1)	0.058
$2,2_{+2} - 3,2_{-1}$	5265.703	2930.998	2334.705	0.102(-1)	0.013
$1,2_{+2} - 2,2_{+1}$	5087.004	2723.765	2363.239	0.802(-1)	0.277
$4,2_{-2} - 4,2_{+1}$	5714.864	3351.023	2363.841	0.405(-1)	0.007
$1,1_{-2} - 2,1_{-1}$	5124.508	2755.291	2369.217	0.365(-2)	0.011
$5,2_{-2} - 5,2_{+1}$	6167.744	3792.568	2375.176	0.104(+0)	0.002
$1,3_{+2} - 2,3_{+1}$	4994.314	2614.135	2380.179	0.163(+0)	0.961
$3,1_{-2} - 3,1_{+1}$	5485.152	3063.193	2421.959	0.396(-1)	0.027
$4,1_{-2} - 4,1_{+1}$	5845.422	3422.758	2422.664	0.108(+0)	0.013
$4,0_{-2} - 4,0_{-1}$	5895.604	3446.685	2448.920	0.197(+0)	0.022
$0,2_{+2} - 1,2_{+1}$	4997.423	2548.041	2449.382	0.538(-1)	0.446
$4,2_{-2} - 4,2_{-1}$	5714.864	3259.663	2455.200	0.111(-1)	0.003
$2,0_{-2} - 2,0_{-1}$	5285.893	2812.642	2473.251	0.828(-1)	0.195
$3,1_{-2} - 3,1_{-1}$	5485.152	3002.486	2482.665	0.255(-1)	0.024
$4,1_{+2} - 4,1_{+1}$	5930.849	3422.758	2508.092	0.840(-1)	0.011
$3,1_{+2} - 3,1_{+1}$	5572.834	3063.193	2509.642	0.103(+0)	0.074
$2,1_{-2} - 2,1_{+1}$	5304.112	2790.127	2513.985	0.100(+0)	0.268
$1,1_{-2} - 1,1_{+1}$	5124.508	2609.377	2515.130	0.754(-1)	0.479
$4,1_{-2} - 4,1_{-1}$	5845.422	3325.518	2519.904	0.149(-1)	0.003
$5,2_{+2} - 5,2_{+1}$	6326.970	3792.568	2534.401	0.126(+0)	0.003
$4,2_{+2} - 4,2_{+1}$	5887.398	3351.023	2536.375	0.140(+0)	0.025
$1,2_{+2} - 1,2_{+1}$	5087.004	2548.041	2538.963	0.808(-1)	0.696
$5,3_{+2} - 5,3_{+1}$	6212.584	3673.497	2539.087	0.133(+0)	0.005

TABLE III—*Continued*

$J',G'_{U'} - J'',G''_{U''}$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)^a$ (D^2)	$I_{Rel}(\omega)^b$ 300K
$3,2_{+2} - 3,2_{+1}$	5532.956	2992.161	2540.796	0.142(+0)	0.146
$3,0_{-2} - 3,0_{-1}$	5566.330	3025.528	2540.802	0.768(-1)	0.067
$2,2_{+2} - 2,2_{+1}$	5265.703	2723.765	2541.938	0.126(+0)	0.466
$2,1_{-1} - 2,1_{-1}$	5304.112	2755.291	2548.821	0.154(-1)	0.049
$3,3_{+2} - 3,3_{+1}$	5430.347	2876.591	2553.756	0.142(+0)	0.255
$2,3_{+2} - 2,3_{+1}$	5180.662	2614.135	2566.527	0.927(-1)	0.588
$3,1_{+2} - 3,1_{-1}$	5572.834	3002.486	2570.348	0.357(-1)	0.035
$4,3_{+2} - 4,3_{+1}$	5810.346	3233.027	2577.319	0.169(+0)	0.055
$5,4_{+2} - 5,4_{+1}$	6088.940	3509.703	2579.237	0.167(+0)	0.015
$3,4_{+2} - 3,4_{+1}$	5298.686	2719.308	2579.378	0.981(-1)	0.377
$4,4_{+2} - 4,4_{+1}$	5651.768	3069.003	2582.764	0.154(+0)	0.111
$6,5_{+2} - 6,5_{+1}$	6414.529	3824.873	2589.656	0.150(+0)	0.003
$4,5_{+2} - 4,5_{+1}$	5459.909	2863.711	2596.198	0.103(+0)	0.199
$5,5_{+2} - 5,5_{+1}$	5898.647	3299.725	2598.922	0.159(+0)	0.038
$3,2_{+2} - 3,2_{-1}$	5532.956	2930.998	2601.958	0.137(-1)	0.019
$1,1_{-2} - 0,1_{+1}$	5124.508	2521.282	2603.226	0.548(-1)	0.550
$4,1_{+2} - 4,1_{-1}$	5930.849	3325.518	2605.331	0.472(-1)	0.010
$5,6_{+2} - 5,6_{+1}$	5658.641	3047.090	2611.551	0.106(+0)	0.086
$6,6_{+2} - 6,6_{+1}$	6183.721	3568.950	2614.771	0.164(+0)	0.011
$6,7_{+2} - 6,7_{+1}$	5895.176	3269.207	2625.969	0.109(+0)	0.031
$4,2_{+2} - 4,2_{-1}$	5887.398	3259.663	2627.735	0.280(-1)	0.008
$7,7_{+2} - 7,7_{+1}$	6504.257	3876.409	2627.848	0.165(+0)	0.003
$7,8_{+2} - 7,8_{+1}$	6169.328	3529.762	2639.566	0.112(+0)	0.009
$5,0_{-2} - 5,0_{-1}$	6390.680	3742.346	2648.335	0.511(-1)	0.001
$8,9_{+2} - 8,9_{+1}$	6481.318	3828.412	2652.907	0.115(+0)	0.002
$5,3_{+2} - 5,3_{-1}$	6212.584	3552.620	2659.964	0.253(-1)	0.002
$4,3_{+2} - 4,3_{-1}$	5810.346	3144.790	2665.556	0.130(-1)	0.007
$2,0_{-2} - 1,0_{-1}$	5285.893	2616.487	2669.406	0.153(+0)	1.000
$5,4_{+2} - 5,4_{-1}$	6088.940	3395.911	2693.029	0.106(-1)	0.002

TABLE III—*Continued*

$J', G'_{U'} - J'', G''_{U''}$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)^a$ (D^2)	$I_{Rel}(\omega)$ [b] 300K
$2,1_{-2} - 1,1_{+1}$	5304.112	2609.377	2694.735	0.892(-1)	0.607
$3,1_{-2} - 2,1_{+1}$	5485.152	2790.127	2695.024	0.413(-1)	0.012
$2,2_{+2} - 1,2_{+1}$	5265.703	2548.041	2717.663	0.334(-1)	0.308
$4,2_{-2} - 3,2_{+1}$	5714.864	2992.161	2722.703	0.504(-1)	0.055
$3,1_{-2} - 2,1_{-1}$	5485.152	2755.291	2729.861	0.204(+0)	0.700
$5,3_{-2} - 4,3_{+1}$	5969.366	3233.027	2736.339	0.539(-1)	0.019
$6,4_{-2} - 5,4_{+1}$	6249.022	3509.703	2739.318	0.593(-1)	0.005
$3,0_{-2} - 2,0_{-1}$	5566.330	2812.642	2753.687	0.208(+0)	0.546
$4,1_{-2} - 3,1_{+1}$	5845.422	3063.193	2782.229	0.626(-1)	0.050
$3,1_{+2} - 2,1_{+1}$	5572.834	2790.127	2782.707	0.122(+0)	0.359
$4,2_{-2} - 3,2_{-1}$	5714.864	2930.998	2783.866	0.240(+0)	0.362
$3,2_{+2} - 2,2_{+1}$	5532.956	2723.765	2809.191	0.746(-1)	0.306
$3,3_{+2} - 2,3_{+1}$	5430.347	2614.135	2816.212	0.286(-1)	0.199
$5,2_{-2} - 4,2_{+1}$	6167.744	3351.023	2816.721	0.814(-1)	0.017
$3,1_{+2} - 2,1_{-1}$	5572.834	2755.291	2817.543	0.116(-1)	0.041
$5,3_{-2} - 4,3_{-1}$	5969.366	3144.790	2824.576	0.185(+0)	0.101
$6,3_{-2} - 5,3_{+1}$	6514.192	3673.497	2840.694	0.796(-1)	0.003
$4,1_{-2} - 3,1_{-1}$	5845.422	3002.486	2842.936	0.199(+0)	0.217
$6,4_{-2} - 5,4_{-1}$	6249.022	3395.911	2853.110	0.412(-1)	0.007
$4,1_{+2} - 3,1_{+1}$	5930.849	3063.193	2867.657	0.177(+0)	0.146
$4,0_{-2} - 3,0_{-1}$	5895.604	3025.528	2870.076	0.201(+0)	0.197
$6,4_{+2} - 5,4_{+1}$	6403.157	3509.703	2893.454	0.645(-1)	0.006
$4,2_{+2} - 3,2_{+1}$	5887.398	2992.161	2895.238	0.116(+0)	0.135
$5,2_{-2} - 4,2_{-1}$	6167.744	3259.663	2908.081	0.214(+0)	0.070
$4,1_{+2} - 3,1_{-1}$	5930.849	3002.486	2928.363	0.170(-1)	0.019
$4,4_{+2} - 3,4_{+1}$	5651.768	2719.308	2932.459	0.279(-1)	0.122
$4,3_{+2} - 3,3_{+1}$	5810.346	2876.591	2933.755	0.725(-1)	0.150
$5,0_{-2} - 4,0_{-1}$	6390.680	3446.685	2943.996	0.313(+0)	0.042
$4,2_{+2} - 3,2_{-1}$	5887.398	2930.998	2956.400	0.976(-2)	0.016
$6,3_{-2} - 5,3_{-1}$	6514.192	3552.620	2961.572	0.130(+0)	0.011
$6,3_{+2} - 5,3_{+1}$	6638.729	3673.497	2965.232	0.624(-1)	0.003
$5,2_{+2} - 4,2_{+1}$	6326.970	3351.023	2975.947	0.136(+0)	0.029
$5,3_{+2} - 4,3_{+1}$	6212.584	3233.027	2979.557	0.138(+0)	0.052

TABLE IV

Hot Band Transitions for H_3^+ from ν_1 to $\nu_2 + \nu_1$

$J', G'_{U'} - J'', K''$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)$[a] (D^2)	$I_{Rel}(\omega)$ [b] 300K
$4,5_{+1} - 5,5$	5920.834	3888.463	2032.371	0.257(+0)	0.112
$3,3_{+1} - 4,3$	5909.649	3820.625	2089.024	0.163(+0)	0.101
$3,4_{+1} - 4,4$	5764.679	3667.003	2097.676	0.216(+0)	0.281
$2,0_{-1} - 3,0$	5834.642	3682.614	2152.028	0.615(-1)	0.075
$2,1_{+1} - 3,1$	5815.188	3660.983	2154.205	0.717(-1)	0.098
$2,2_{+1} - 3,2$	5755.490	3595.663	2159.827	0.103(+0)	0.194
$2,3_{+1} - 3,3$	5653.682	3485.273	2168.409	0.156(+0)	0.499
$1,1_{+1} - 2,1$	5639.999	3409.833	2230.166	0.458(-1)	0.217
$1,2_{+1} - 2,2$	5583.811	3343.175	2240.637	0.926(-1)	0.604
$0,1_{+1} - 1,1$	5553.712	3240.819	2312.893	0.305(-1)	0.336
$4,3_{-1} - 4,3$	6157.342	3820.625	2336.717	0.868(-1)	0.061
$4,2_{-1} - 4,2$	6275.437	3927.953	2347.485	0.184(+0)	0.076
$4,1_{-1} - 4,1$	6341.605	3991.586	2350.019	0.244(+0)	0.075
$3,2_{-1} - 3,2$	5948.615	3595.663	2352.952	0.902(-1)	0.185
$3,1_{-1} - 3,1$	6022.981	3660.983	2361.998	0.175(+0)	0.262
$3,0_{-1} - 3,0$	6046.732	3682.614	2364.118	0.207(+0)	0.281
$2,1_{-1} - 2,1$	5778.263	3409.833	2368.430	0.907(-1)	0.456
$1,0_{-1} - 1,0$	5644.114	3263.187	2380.927	0.900(-1)	0.919
$1,1_{+1} - 1,1$	5639.999	3240.819	2399.179	0.456(-1)	0.523
$2,1_{+1} - 2,1$	5815.188	3409.833	2405.355	0.342(-1)	0.175
$2,2_{+1} - 2,2$	5755.490	3343.175	2412.316	0.513(-1)	0.362
$3,2_{+1} - 3,2$	6015.313	3595.663	2419.650	0.497(-1)	0.105
$3,3_{+1} - 3,3$	5909.649	3485.273	2424.376	0.546(-1)	0.195
$4,4_{+1} - 4,4$	6105.255	3667.003	2438.252	0.572(-1)	0.086
$2,1_{-1} - 1,1$	5778.263	3240.819	2537.444	0.574(-1)	0.695
$2,0_{-1} - 1,0$	5834.642	3263.187	2571.455	0.906(-1)	1.000
$2,1_{+1} - 1,1$	5815.188	3240.819	2574.369	0.471(-1)	0.579
$3,2_{-1} - 2,2$	5948.615	3343.175	2605.441	0.115(+0)	0.873
$3,1_{-1} - 2,1$	6022.981	3409.833	2613.148	0.318(-1)	0.176
$3,1_{+1} - 2,1$	6080.220	3409.833	2670.387	0.986(-1)	0.558
$4,3_{-1} - 3,3$	6157.342	3485.273	2672.069	0.170(+0)	0.670
$3,2_{+1} - 2,2$	6015.313	3343.175	2672.138	0.426(-1)	0.333
$4,2_{-1} - 3,2$	6275.437	3595.663	2679.775	0.769(-1)	0.179
$4,2_{+1} - 3,2$	6362.564	3595.663	2766.901	0.102(+0)	0.245
$4,3_{+1} - 3,3$	6254.046	3485.273	2768.773	0.405(-1)	0.165
$4,0_{-1} - 3,0$	6452.726	3682.614	2770.112	0.153(+0)	0.243

[a] Powers of ten in brackets.

[b] Scaling factor = 2.66×10^{-7}.

TABLE V

Hot Band Transitions for H_3^+ from $2\nu_2(0)$ to $3\nu_2(1)$

$J', G'_{U'} - J'', K''$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)$[a] (D^2)	$I_{Rel}(\omega)$ [b] 300K
$2,1_{+1} - 3,1$	7299.534	5280.799	2018.735	0.618(-1)	0.058
$2,0_{-1} - 3,0$	7326.850	5304.036	2022.814	0.465(-1)	0.039
$2,2_{+1} - 3,2$	7233.902	5209.308	2024.594	0.120(+0)	0.159
$2,3_{+1} - 3,3$	7121.694	5077.489	2044.205	0.200(+0)	0.504
$1,1_{+1} - 2,1$	7103.618	5022.056	2081.562	0.521(-1)	0.174
$1,2_{+1} - 2,2$	7046.035	4941.353	2104.682	0.116(+0)	0.580
$0,1_{+1} - 1,1$	7003.453	4841.240	2162.212	0.374(-1)	0.310
$3,1_{-1} - 3,1$	7460.696	5280.799	2179.897	0.250(+0)	0.254
$2,1_{-1} - 2,1$	7206.861	5022.056	2184.805	0.120(+0)	0.423
$1,0_{-1} - 1,0$	7082.243	4868.973	2213.270	0.112(+0)	0.834
$1,1_{+1} - 1,1$	7103.618	4841.240	2262.378	0.618(-1)	0.535
$2,1_{+1} - 2,1$	7299.534	5022.056	2277.478	0.421(-1)	0.154
$2,2_{+1} - 2,2$	7233.902	4941.353	2292.548	0.751(-1)	0.408
$3,3_{+1} - 3,3$	7392.981	5077.489	2315.492	0.856(-1)	0.244
$2,1_{-1} - 1,1$	7206.861	4841.240	2365.621	0.656(-1)	0.594
$3,1_{-1} - 2,1$	7460.696	5022.056	2438.640	0.336(-1)	0.132
$2,0_{-1} - 1,0$	7326.850	4868.973	2457.877	0.121(+0)	1.000
$2,1_{+1} - 1,1$	7299.534	4841.240	2458.294	0.667(-1)	0.628

[a] Powers of ten in brackets.

[b] Scaling factor $= 1.54 \times 10^{-10}$

uously assigning energy levels, particularly for the $v = 3$ levels, and this difficulty increases as J increases.

In the absence of experimental data, it is not possible to be sure of the accuracy of the (v=3 – v=2) frequencies. We are confident that the levels are converged to within 0.1 cm^{-1}. If the trend of the MBB potential, which is to underestimate slightly the vibrational band origins, continues, we estimate that the transition frequencies we have given for (v=3 – v=2) lines to be about 1 cm^{-1} too low.

TABLE VI

Hot Band Transitions for H_3^+ from $2\nu_2(2)$ to $3\nu_2(1)$

$J', G'_{U'} - J'', G''_{U''}$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)$[a] (D^2)	$I_{Rel}(\omega)$[b] 300K
$2,0_{-1} - 2,0_{-2}$	7326.850	5285.893	2040.957	0.224(-1)	0.146
$1,2_{+1} - 0,2_{+2}$	7046.035	4997.423	2048.613	0.117(-1)	0.307
$2,3_{+1} - 1,3_{+2}$	7121.694	4994.314	2127.381	0.360(-1)	1.000
$2,2_{+1} - 1,2_{+2}$	7233.902	5087.004	2146.898	0.131(-1)	0.234
$2,1_{+1} - 1,1_{-2}$	7299.534	5124.508	2175.026	0.158(-2)	0.024
$2,1_{+1} - 3,5_{+2}$	7299.534	5104.913	2194.621	0.132(-1)	0.222
$2,2_{+1} - 2,4_{+2}$	7233.902	5031.976	2201.926	0.426(-3)	0.010
$3,3_{+1} - 2,3_{+2}$	7392.981	5180.662	2212.320	0.274(-1)	0.323
$3,1_{-1} - 3,5_{+2}$	7460.696	5104.913	2355.784	0.110(-2)	0.020

[a] Powers of ten in brackets.

[b] Scaling factor $= 2.17 \times 10^{-11}$.

TABLE VII

Hot Band Transitions for H_3^+ from $2\nu_2(0)$ to $3\nu_2(\pm 3)$

$J', G'_{U'} - J'', K''$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)$[a] (D^2)	$I_{Rel}(\omega)$[b] 300K
$2,5_{+3} - 3,1$	7369.035	5280.799	2088.236	0.230(-2)	0.005
$2,4_{+3} - 3,2$	7514.590	5209.308	2305.283	0.121(-2)	0.004
$3,5_{+3} - 3,1$	7595.812	5280.799	2315.013	0.105(-1)	0.024
$2,5_{+3} - 2,1$	7369.035	5022.056	2346.979	0.375(-2)	0.031
$2,5_{+3} - 1,1$	7369.035	4841.240	2527.795	0.161(-2)	0.034
$2,4_{+3} - 2,2$	7514.590	4941.353	2573.237	0.316(-3)	0.004
$3,5_{+3} - 2,1$	7595.812	5022.056	2573.756	0.112(+0)	1.000
$2,3_{+3} - 3,3$	7758.420	5077.489	2680.930	0.928(-3)	0.007

[a] Powers of ten in brackets.

[b] Scaling factor $= 7.15 \times 10^{-11}$.

TABLE VIII

Hot Band Transitions for H_3^+ from $2\nu_2(2)$ to $3\nu_2(\pm 3)$

$J', G'_{U'} - J'', G''_{U''}$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)^a$ (D^2)	$I_{Rel}(\omega)$ [b] 300K
$3,5_{+3} - 3,1_{-2}$	7595.812	5572.834	2022.978	0.408(-1)	0.011
$,4_{+3} - 2,2_{+2}$	7325.932	5265.703	2060.229	0.619(-2)	0.007
$2,1_{-1} - 3,5_{+2}$	7206.861	5104.913	2101.948	0.763(-3)	0.002
$3,5_{+3} - 3,1_{-2}$	7595.812	5485.152	2110.660	0.121(-1)	0.032
$2,1_{-3} - 3,1_{+2}$	7703.435	5572.834	2130.600	0.179(-1)	0.005
$3,5_{+3} - 4,5_{+2}$	7595.812	5459.909	2135.903	0.779(-1)	0.038
$1,3_{+3} - 2,3_{+2}$	7381.569	5180.662	2200.907	0.918(-1)	0.176
$2,4_{+3} - 3,4_{+2}$	7514.590	5298.686	2215.904	0.192(+0)	0.210
$2,2_{-3} - 3,2_{+2}$	7751.643	5532.956	2218.686	0.568(-1)	0.020
$1,4_{+3} - 1,2_{+2}$	7325.932	5087.004	2238.929	0.138(-1)	0.042
$2,5_{+3} - 1,1_{-2}$	7369.035	5124.508	2244.527	0.107(-1)	0.027
$2,4_{+3} - 2,2_{+2}$	7514.590	5265.703	2248.887	0.156(-1)	0.020
$2,5_{+3} - 3,5_{+2}$	7369.035	5104.913	2264.122	0.353(+0)	1.000
$1,4_{+3} - 2,4_{+2}$	7325.932	5031.976	2293.956	0.173(+0)	0.704
$1,2_{-3} - 2,2_{+2}$	7571.941	5265.703	2306.238	0.275(-1)	0.037
$2,3_{+3} - 3,3_{+2}$	7758.420	5430.347	2328.073	0.194(+0)	0.119
$1,4_{+3} - 0,2_{+2}$	7325.932	4997.423	2328.510	0.105(-1)	0.051
$1,3_{+3} - 1,3_{+2}$	7381.569	4994.314	2387.255	0.950(-1)	0.482
$2,1_{-3} - 2,1_{-2}$	7703.435	5304.112	2399.322	0.806(-1)	0.093
$2,4_{+3} - 1,2_{+2}$	7514.590	5087.004	2427.587	0.170(-1)	0.056
$2,2_{-3} - 3,4_{+2}$	7751.643	5298.686	2452.957	0.923(-1)	0.011
$2,4_{+3} - 2,4_{+2}$	7514.590	5031.976	2482.614	0.104(+0)	0.457
$1,2_{-3} - 1,2_{+2}$	7571.941	5087.004	2484.937	0.879(-1)	0.298
$2,2_{-3} - 2,2_{+2}$	7751.643	5265.703	2485.940	0.144(+0)	0.207
$3,5_{+3} - 3,5_{+2}$	7595.812	5104.913	2490.899	0.295(-1)	0.092
$0,3_{+3} - 1,3_{+2}$	7492.660	4994.314	2498.346	0.963(-1)	0.512
$1,2_{-3} - 2,4_{+2}$	7571.941	5031.976	2539.965	0.843(-1)	0.380
$1,2_{-3} - 0,2_{+2}$	7571.941	4997.423	2574.518	0.610(-1)	0.328
$2,3_{+3} - 2,3_{+2}$	7758.420	5180.662	2577.758	0.234(+0)	0.524
$2,1_{-3} - 1,1_{-2}$	7703.435	5124.508	2578.927	0.166(+0)	0.487
$2,1_{-3} - 3,5_{+2}$	7703.435	5104.913	2598.522	0.805(-1)	0.261
$2,2_{-3} - 1,2_{+2}$	7751.643	5087.004	2664.639	0.992(-1)	0.360
$2,2_{-3} - 2,4_{+2}$	7751.643	5031.976	2719.667	0.397(-1)	0.192
$2,3_{+3} - 1,3_{+2}$	7758.420	4994.314	2764.106	0.540(-1)	0.316

[a] Powers of ten in brackets.

[b] Scaling factor = 1.34×10^{-10}.

TABLE IX

Hot Band Transitions for H_3^+ from $\nu_2 + \nu_1$ to $2\nu_2(0) + \nu_1$

$J', K' - J'', G''_{U''}$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)$[a] (D^2)	$I_{Rel}(\omega)$[b] 300K
$1,0 - 2,0_{-1}$	7859.324	5834.642	2024.682	0.762(-1)	0.360
$1,1 - 2,1_{+1}$	7841.529	5815.188	2026.341	0.365(-1)	0.189
$1,1 - 2,1_{-1}$	7841.529	5778.263	2063.266	0.511(-1)	0.323
$2,1 - 2,1_{+1}$	8014.243	5815.188	2199.055	0.438(-1)	0.246
$1,1 - 1,1_{+1}$	7841.529	5639.999	2201.530	0.394(-1)	0.515
$1,0 - 1,0_{-1}$	7859.324	5644.114	2215.211	0.773(-1)	1.000
$2,1 - 2,1_{-1}$	8014.243	5778.263	2235.980	0.871(-1)	0.596
$1,1 - 0,1_{+1}$	7841.529	5553.712	2287.817	0.220(-1)	0.451
$2,1 - 1,1_{+1}$	8014.243	5639.999	2374.245	0.218(-1)	0.307

[a] Powers of ten in brackets.

[b] Scaling factor = 2.15×10^{-12}.

4. CONCLUSIONS

The recent experimental results of Bawendi *et al.* (*11*) show that the MBB potential energy surface is clearly valid for (v=2 – v=1) hot band transitions. Watson (*15*) has also been able to assign some overone transitions, using the results contained in Ref. (*10*). We feel it is therefore justified to extend it to look at higher hot bands.

Our results show that, as well as the expected transitions, there are some interesting effects which are not strictly in accordance with normal selection rules. Nonetheless, we believe they do correspond to physically observable phenomena. A detailed study of a number of "forbidden" bands in H_3^+ is currently in preparation.

Work is also in progress to measure and assign (v=3 – v=2) lines in the spectrum of H_3^+ (*16*). Comparison of the predictions in this paper with the experimental results should be extremely fruitful, not only because these transitions are themselves interesting, but because they will give an insight into the true nature of the H_3^+ potential energy surface as the molecule moves away from its equilibrium geometry.

Such information is extremely important if progress is to be made on one of the most exciting challenges to theoretical chemists—explaining the complex and intriguing predissociation spectrum of H_3^+, measured in 1982 by Carrington and coworkers (*1*).

Finally, the transitions presented here are only a small subset of the possible transitions between levels of H_3^+ with three or less vibrational quanta, selected on the basis

TABLE X

Hot Band Transitions for H_3^+ from $\nu_2 + \nu_1$ to $2\nu_2(2) + \nu_1$

$J', G'_{U'} - J'', G''_{U''}$	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f-i)^a$ (D^2)	$I_{Rel}(\omega)$ [b] 300K
$2,1_{-2} - 3,1_{+1}$	8170.369	6080.220	2090.149	0.632(-1)	0.042
$2,3_{+2} - 3,3_{+1}$	8058.213	5909.649	2148.563	0.208(+0)	0.322
$2,4_{+2} - 3,4_{+1}$	7916.363	5764.679	2151.684	0.304(+0)	0.943
$1,1_{-2} - 2,1_{+1}$	7991.681	5815.188	2176.493	0.283(-1)	0.070
$1,2_{+2} - 2,2_{+1}$	7963.841	5755.490	2208.350	0.917(-1)	0.305
$1,3_{+2} - 2,3_{+1}$	7874.402	5653.682	2220.720	0.183(+0)	1.000
$0,2_{+2} - 1,2_{+1}$	7868.771	5583.811	2284.960	0.608(-1)	0.476
$1,1_{-2} - 1,1_{+1}$	7991.681	5639.999	2351.683	0.857(-1)	0.530
$2,1_{-2} - 2,1_{+1}$	8170.369	5815.188	2355.181	0.112(+0)	0.297
$1,2_{+2} - 1,2_{+1}$	7963.841	5583.811	2380.029	0.918(-1)	0.751
$2,3_{+2} - 2,3_{+1}$	8058.213	5653.682	2404.531	0.104(+0)	0.612
$1,1_{-2} - 0,1_{+1}$	7991.681	5553.712	2437.969	0.619(-1)	0.599
$2,1_{-2} - 1,1_{+1}$	8170.369	5639.999	2530.370	0.107(+0)	0.710

[a] Powers of ten in brackets.

Scaling factor = 4.89×10^{-12}.

of intensity criteria and within a fixed frequency range. There are some notable absences arising from this procedure, including the lack of $(\nu_2 + 2\nu_1)-2\nu_1$ lines, all of which were too weak to be included as a result of the adverse Boltzmann weighting.

We do, however, have considerably more data than has been presented here, including the $(\nu_2 + 2\nu_1)-2\nu_1$ band, and the authors would be glad to provide data on other spectral regions of interest upon request.

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