JOURNAL OF MOLECULAR SPECTROSCOPY 153, 718–725 (1992)

Bands of H_3^+ up to $4\nu_2$: Rovibrational Transitions from First Principles Calculations

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Band origins and Einstein A coefficients are presented for transitions linking all the vibrational levels of H_3^+ up to $4\nu_2(l = 4)$. The importance of these data for astrophysical modeling is discussed. For H_3^+, rovibrational wavefunctions and energy levels are obtained for J up to 16. These are used to synthesize sample rovibrational spectra with particular emphasis on the $\nu_1 + 2\nu_2(l = 2) \leftarrow 0$ and $4\nu_2(l = 2) \leftarrow 0$ bands, which would appear to be good candidates for laboratory observation.

1. INTRODUCTION

The spectrum of the H_3^+ molecular ion was first recorded in the laboratory in 1980 by Oka (*1*) in work which was greatly helped by the theoretical calculations of Carney and Porter (*2*). The spectrum of D_3^+ was recorded at the same time by Shy *et al.* (*3*). Following these pioneering studies a number of bands of the H_3^+ system have been observed including $\nu_2(l = 1) \leftarrow 0$ (*4, 5*), $2\nu_2(l = 2) \leftarrow 0$ (*6, 7*), $2\nu_2(l = 0) \leftarrow 0$ (*7*), $2\nu_2(l = 2) \leftarrow \nu_2(l = 1)$ (*8*), $2\nu_2(l = 0) \leftarrow \nu_2(l = 1)$ (*8*), $\nu_1 + \nu_2(l = 1) \leftarrow \nu_2(l = 1)$ (*8*) and $3\nu_2(l = 1) \leftarrow 0$ (*9*). In all cases theory played an important role in the assignment of the spectra.

H_3^+ is not only of interest because of its fundamental spectroscopic importance but also because of its perceived importance for astrophysics. Even before Oka's first laboratory spectrum, H_3^+ was used as an important constituent in models of the interstellar medium (*10*). However, the astrophysical study of H_3^+ was given great impetus by the observation of emissions from the $2\nu_2(l = 2) \rightarrow 0$ in the Jovian aurora (*11*). Subsequent studies have also observed emissions from $\nu_2(l = 1) \rightarrow 0$ (*12, 13*) and these are now being used to map Jupiter's auroral activity (*14, 15*). A further twist to the H_3^+ saga has been given by the assignment of $\nu_2(l = 1) \rightarrow 0$ emission features in the spectrum of supernova 1987A (*16*).

Both in the laboratory and in space H_3^+ is formed by the exothermic reaction

$$H_2 + H_2^+ \rightarrow H_3^+ + H, \tag{1}$$

which almost certainly results in the ion being formed hot. As H_3^+ spectroscopy is now the best available handle on the Jovian auroral ionosphere, studies of the vibrational distribution of H_3^+ in Jupiter and elsewhere are now being performed (see, for

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0022-2852/92 $5.00

example, Ref. (*17*)). These studies require detailed and accurate data on the lifetime of excited vibrational states of H_3^+. Furthermore, there is a distinct possibility that H_3^+ chemiluminescence may be observable in Jupiter and elsewhere. For such observations to be made, the higher vibrational bands of H_3^+ must first be characterized in the laboratory.

For a number of years now we have been involved in the first principle calculations of the rovibrational spectrum of H_3^+ (*18–22*). These computations used a very accurate potential energy surface calculated by Meyer *et al.* (MBB) (*23*) and, for the spectra, their associated dipole surfaces. These calculations have been instrumental in making many (*6–9, 11*) of the assignments discussed above. These calculations plus the observed laboratory and Jupiter spectra have recently been combined to give a compendium of H_3^+ transitions to aid astrophysical observations (*24*). Despite this work there are still many unassigned lines in the observed laboratory spectra of H_3^+ (*25, 26*).

In this work we extend our previous calculations to the vibrational bands of H_3^+ up to and including $4\nu_2(l = 4)$. Einstein A coefficients are calculated for vibrational transitions linking this and all lower states of H_3^+. These calculations suggest that the transitions $\nu_1 + 2\nu_2(l = 2) \leftarrow 0$ and $4\nu_2(l = 2) \leftarrow 0$ should be intense enough for laboratory observation. We therefore present rotational term values for these vibrationally excited states and sample rovibrational spectra at the relevant frequency regions.

2. CALCULATIONS

Calculations were performed in scattering coordinates using the TRIATOM program suite (*27*). Vibrational wavefunctions were obtained using the 1700 lowest-basis functions from a previously optimized basis set (*22*). Test calculations showed that this basis is sufficient to converge the vibrational levels to better than 0.1 cm^{-1} up to and including $4\nu_2(l = 4)$. Vibrational band intensities and hence Einstein A coefficients were obtained using the rotationless vibrational wavefunctions and the recently proposed method of Le Sueur *et al.* (*28*).

TABLE I

H_3^+ Band Origins in cm^{-1}. Observed Band Origins (and References) Are Given for Comparison

	(ν_1, ν_2^{ℓ})	This work	Observed
A_1	$(0,0^0)$	0.00	
E	$(0,1^1)$	2521.28	2521.31 (4)
A_1	$(1,0^0)$	3178.35	3178.3 (29)
A_1	$(0,2^0)$	4777.02	
E	$(0,2^2)$	4997.42	
E	$(1,1^1)$	5553.71	
A_1	$(2,0^0)$	6261.99	
E	$(0,3^1)$	7003.45	
A_1	$(0,3^3)$	7282.50	
A_2	$(0,3^3)$	7492.60	
A_1	$(1,2^0)$	7769.13	
E	$(1,2^2)$	7868.66	
E	$(2,1^1)$	8486.97	
A_1	$(0,4^0)$	8996.63	
E	$(0,4^2)$	9107.60	
A_1	$(3,0^0)$	9251.54	
E	$(0,4^4)$	9650.57	

TABLE II

$A_1 \leftrightarrow E$ Einstein A Coefficients in s^{-1} (Powers of Ten in Parentheses)

	$(0,1^1)$	$(0,2^2)$	$(1,1^1)$	$(0,3^1)$	$(1,2^2)$	$(2,1^1)$	$(0,4^2)$	$(0,4^4)$
$(0,0^0)$	257.6	289.2	0.695	31.3	28.7	3.00	13.5	0.569
$(1,0^0)$	0.846	0.422	254.7	0.922	238.9	0.022	4.19	12.7
$(0,2^0)$	139.2	0.047	1.14	171.0	40.2	1.04	504.2	245.1
$(2,0^0)$	0.242	0.056	2.31	4(-4)	1.09	246.9	0.047	0.655
$(0,3^3)$	242.4	232.6	0.491	0.057	0.766	0.441	42.9	276.4
$(1,2^0)$	74.1	108.5	179.3	1.27	6(-4)	2.20	1.88	32.6
$(0,4^0)$	65.9	273.2	1.75	136.9	0.482	0.002	0.005	0.270
$(3,0^0)$	0.481	0.838	1.44	0.016	0.011	4.80	2(-8)	6(-5)

Rotationally excited levels were obtained, as before (*22*), using a two-step variational procedure (*27*). Our previous calculations have studied levels of H_3^+ rotational angular momentum, J, up to 12 and vibrational states up to and including $3\nu_2(l = 3)$. Care is needed in extending these limits. It is well known that H_3^+ can sample linear geometries at energies about 11 000 cm^{-1} above its vibrational ground state (*23*). As the vibrational basis functions that were used for the present study are not well adapted to studying these linear geometries, in this work we have confined ourselves to studying rovibrational levels below linear geometries.

For the two-step calculations we retained 800 solutions from each of the $J + 1$ first step problems of dimension 1700. From these the lowest $600 \times (J + 1)$ solutions were used to solve the full rovibrational problem. Test calculations with $J = 5$ showed that this procedure gave a convergence error of 0.2 cm^{-1} for the worst level and that nearly all the 283 levels with $J = 5$ that were computed by us were converged to better than 0.02 cm^{-1}. For $J = 12$, tests showed that nearly all the rotational levels converged within 0.1 cm^{-1}, while a few higher levels converged to only about 0.5 cm^{-1}. In all these cases we would expect that this error is less than that introduced by inaccuracies in the potential.

3. RESULTS AND DISCUSSION

Table I presents our calculated band origins for levels up to $4\nu_2(l = 4)$. Their wavenumbers are in good agreement with previous, less accurate, discrete variable (DVR) calculations (*30*) from which the assignments are also taken. Actually, the assignment of the higher vibrational states becomes increasingly difficult as H_3^+ begins to probe linear geometries. This is not only because the density of states increases but also because the description of the vibrations in terms of normal modes becomes increasingly dubious. The assignment of the level at 9650.57 cm^{-1} to $4\nu_2(l = 4)$ is particularly tenuous.

TABLE III

$A_2 \leftrightarrow E$ Einstein A Coefficients in s^{-1} (Powers of Ten in Parentheses)

	$(0,1^1)$	$(0,2^2)$	$(1,1^1)$	$(0,3^1)$	$(1,2^2)$	$(2,1^1)$	$(0,4^2)$	$(0,4^4)$
$(0,3^3)$	476.5	468.2	0.893	0.016	0.283	5(-4)	0.627	213.1

TABLE IV

$E \leftrightarrow E$ Einstein A Coefficients in s^{-1} (Powers of Ten in Parentheses)

	$(0,1^1)$	$(0,2^2)$	$(1,1^1)$	$(0,3^1)$	$(1,2^2)$	$(2,1^1)$	$(0,4^2)$
$(0,2^2)$	256.0						
$(1,1^1)$	16.5	0.509					
$(0,3^1)$	133.1	35.1	0.487				
$(1,2^2)$	0.116	2.80	236.5	0.722			
$(2,1^1)$	3.00	0.984	25.6	0.065	1.47		
$(0,4^2)$	35.5	12.4	8.38	135.8	0.025	0.011	
$(0,4^4)$	0.778	340.0	27.0	96.7	2.80	0.251	0.321

For comparison Table I also gives the available experimental band origins. Perhaps surprisingly, although a number of overtone and combination levels have been experimentally characterized (*6–9*), only the band origins of the fundamentals are known experimentally. For these levels the agreement between theory and experiment is excellent, although it should be borne in mind that the MBB surface we use was adapted to reproduce the observed value of the ν_2 fundamental (*23*). Previous studies have suggested that our $2\nu_2$ levels are about 0.4 cm^{-1} too low (*6*) and the $3\nu_2(l = 1)$ about 2.5 cm^{-1} too low (*9*); we would therefore expect to have underestimated the $4\nu_2$ levels by about 5 cm^{-1}.

Tables II–IV present Einstein A coefficients for all possible transitions between vibrational bands up to $4\nu_2(l = 4)$. As H_3^+ has a dipole of E symmetry, transitions between A states are symmetry forbidden. The tables therefore present results for $A_1 \leftrightarrow E$, $A_2 \leftrightarrow E$, and $E \leftrightarrow E$ transitions, respectively. The assignments correspond to the levels given in Table I, from which estimates of transition wavenumbers may be obtained.

The first row in Table II gives Einstein A coefficients for allowed transitions to the vibration ground state and is thus appropriate for deciding which bands may be observable in the laboratory. It is notable that the now well characterized (*24*) transitions $\nu_2(l = 1) \leftarrow 0$ and $2\nu_2(l = 2) \leftarrow 0$ have very large Einstein A coefficients. However, the $3\nu_2(l = 1) \leftarrow 0$ band, whose A coefficient is an order of magnitude less, has also been observed (*9*). In fact, our calculations predict that the nearby $\nu_1 + 2\nu_2(l = 2) \leftarrow 0$ band should have a very similar intensity. This band appears to be a good candidate for observation.

At higher wavenumbers, our calculations suggest that the $4\nu_2(l = 2) \leftarrow 0$ band is likely to be 20 times more intense than $4\nu_2(l = 4) \leftarrow 0$, although in practice the rotational levels of these bands are likely to be strongly mixed. This band is also a good candidate for experimental observation, especially with the advent of new powerful lasers in this region.

Tables II–IV show that the various transitions listed display large fluctuations in intensity. One might expect, from harmonic-type considerations, that these transitions would obey the $\Delta l = 1$ selection rule. In fact, transitions with $\Delta l = 0$, 1, or 2 all appear to be of similar intensity, but transitions involving larger changes in l are much less favored. Similarly, the harmonic oscillator model would suggest the selection rule $\Delta\nu_1 = 0$; however, as noted previously (*22*), symmetry-allowed transitions involving excitation of the symmetric stretch, such as $\nu_1 + \nu_2(l = 1) - \nu_2(l = 1)$, are actually found to have observable intensities (25).

Our present calculations represent a systematic attempt to improve the H_3^+ rovi-

TABLE V

Rotational Term Values, $F(J, G, U = \pm 1)$, in cm^{-1}, for the $3\nu_2(l = 1)$ Band of H_3^+ (K is Given by $G - U$)

J	G	s		$U=-1$	$U=+1$
1	0	+1	A_2''	76.7	
1	0	−1	A_1''	103.9	
1	1		E′		96.9
1	2		E″		40.8
2	0	−1	A_2''	322.0	
2	0	+1	A_1''	243.0	
2	1		E′	201.8	295.2
2	2		E″		229.5
2	3	+1	A_1'		113.5
2	3	−1	A_2'		116.6
3	0	+1	A_2''	491.7[a]	
3	0	−1	A_1''	635.0[a]	
3	1		E′	453.3	590.8
3	2		E″	355.5	519.4
3	3	+1	A_2'		387.8
3	3	−1	A_1'		401.1
3	4		E″		223.8

[a]assignment only tentative

brational transitions database that we have built up over a number of years (*18–22*). The improvement is in both the scope of the calculations, covering higher vibrational and rotational levels, and also in the accuracy of the results. Incidentally, it should be noted that as our calculations are variational (i.e., converge on the exact answer for a given potential from above) and the MBB potential slightly underestimates the observed transition wavenumbers, improvement in our calculations sometimes leads to an apparent worsening of agreement with experiment.

The main problem confronting us with these calculations is the volume of data generated. The most useful data are undoubtedly transition frequencies and associated transition dipoles. However, we are now computing so many of these that we no longer even obtain computer print outs of them! This means that any publication has to be very selective as to which results are presented. In this work we focus on the transitions identified above as being good candidates for laboratory observation.

Tables V and VI give rotational term values up to $J = 3$ for the vibrational states $3\nu_2(l = 1)$, $\nu_1 + 2\nu_2(l = 2)$ and $4\nu_2(l = 2)$. Although they are spin-forbidden, we have included A_1 states for completeness, since they are often useful in fitting molecular constants. For higher rotational levels the manifolds of the nearby vibrational band overlap and assignments become nearly impossible. Even for $J \leqslant 3$, assignments are difficult, and in making them we were extensively guided by the intensity of transitions from lower rovibrational levels. The quantum numbers, G, U, s, used to assign the levels are due to Watson (*31*), to which the reader is referred to for a full explanation. We have included a table of $3\nu_2(l = 1)$ term values because, although spectra involving this band have been observed (*9*), only 4 lines have been assigned and we have not previously published term values for this state.

TABLE VI

Rotational Term Values, $F(J, G, U = \pm 2)$, in cm^{-1}, for the $\nu_1 + 2\nu_2(l = 2)$ and $4\nu_2(l = 2)$ Bands of H_3^+ (K Is Given by $G - U$)

J	G	U	s		$(1,2^2)$	$(0,4^2)$
1	1	−2		E″	119.0	98.5
1	2	2		E′	88.5	108.9
1	3	2	+1	A_2''	2.5	25.3
1	3	2	−1	A_1''	7.2	57.1
2	0	−2	+1	A_1'	276.1	279.5[a]
2	0	−2	−1	A_2'	271.2	216.3
2	1	−2		E″	297.6	331.3
2	2	2		E′	265.4	300.3
2	3	2	−1	A_2''	187.2	292.7
2	3	2	+1	A_1''	173.9	208.1
2	4	2		E′	94.8	105.3
3	0	−2	−1	A_1'	535.0	536.5
3	0	−2	+1	A_2'	554.7	659.4
3	1	−2		E″	564.9	455.9
3	1	−2		E″	464.2	310.7
3	2	2		E′	530.1	409.5
3	3	2	+1	A_2''	431.7	493.1
3	3	2	−1	A_1''	455.6	632.0[a]
3	4	2		E′	306.9	663.7
3	5	2		E″	147.8	670.4

[a] assignment only tentative

As stated previously, the vibrational band intensities of $\nu_1 + 2\nu_2(l = 2) \leftarrow 0$ and $4\nu_2(l = 2) \leftarrow 0$ suggest that these bands are good candidates for laboratory observation. Figures 1 and 2 present sample absorption spectra for these bands synthesized using a 200-K Boltzmann distribution typical of many of the cold hydrogen plasmas used to produce H_3^+. These spectra, like other bands of H_3^+, are irregular in appearance, but both show features considerably stronger than the ones already observed in the $3\nu_2(l = 1) \leftarrow 0$ band (*9*).

4. CONCLUSIONS

We have considered rotationally excited states of the lowest 17 vibrational levels of H_3^+. We have calculated Einstein A coefficients for all the symmetry-allowed vibrational transitions between these states and have shown that a number of bands, in particular $\nu_1 + 2\nu_2(l = 2) \leftarrow 0$ and $4\nu_2(l = 2) \leftarrow 0$, are good candidates for laboratory observation. We have presented detailed results for these bands.

These calculations represent a further improvement and extension of a series of calculations that were performed on the H_3^+ system (*18–22*). The vibrational levels up to $4\nu_2(l = 4)$ considered here are all below the barrier to linearity of H_3^+. However, higher-lying vibrational levels, and most of the rotational states not considered in this work, are significantly influenced by the linear saddle points (*30*). These states cannot be represented satisfactorily by the basis functions used in this paper. Further spectroscopic calculations on H_3^+ will therefore have to adopt an approach specifically

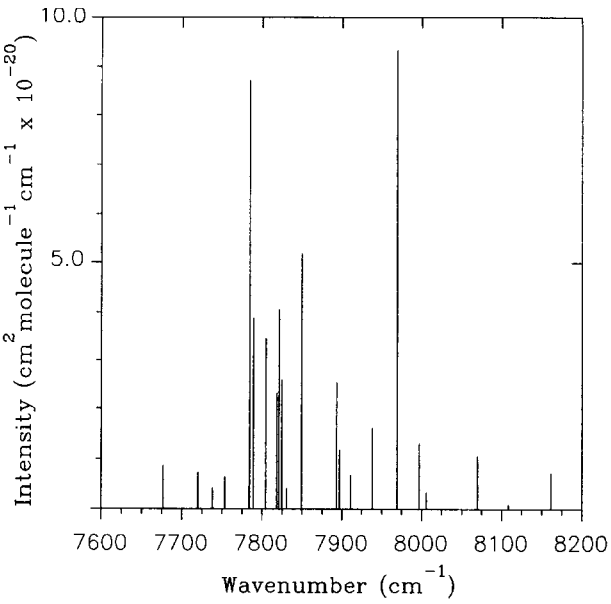

FIG. 1. Simulated infrared absorption spectrum of H_3^+ at 200 K in the region of the $\nu_1 + 2\nu_2(l = 2) \leftarrow 0$ band.

designed to cope with linear geometries and the rapid increase in the density of states above linearity.

In the course of this work we have built up a very extensive list of transition frequencies and intensities, a portion of which has been published (*24*) and a less-complete version of which has been used to compute detailed thermodynamic data for H_3^+ (*32*).

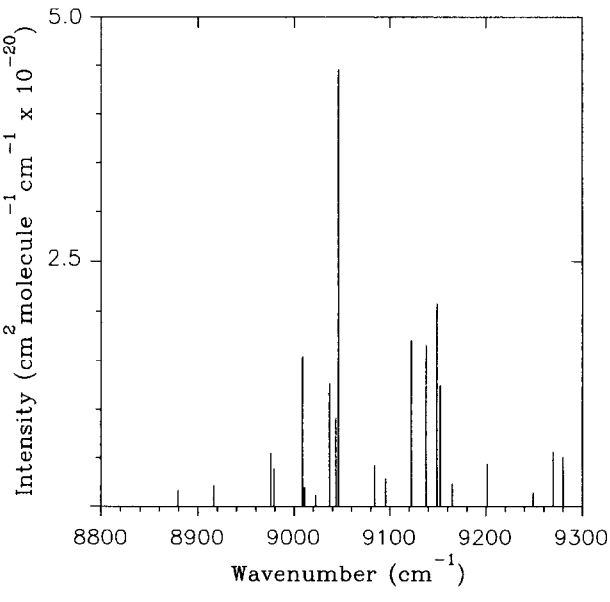

FIG. 2. Simulated infrared absorption spectrum of H_3^+ at 200 K in the region of the $4\nu_2(l = 2) \leftarrow 0$ band.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the inspiration that the work of Professor Takeshi Oka has been to us and to thank him for his constant encouragement. We thank NATO for supporting our collaboration with Professor Oka, and the Science and Engineering Research Council for support under various grants.

RECEIVED: January 9, 1992

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