

Near-infrared spectroscopy of H_3^+ above the barrier to linearity

BY JENNIFER L. GOTTFRIED*

Department of Chemistry, University of Chicago, Chicago, IL 60637, USA

Since the Royal Society Discussion Meeting on H_3^+ in 2000, the laboratory spectroscopy of H_3^+ has entered a new regime. For the first time, transitions of H_3^+ above the barrier to linearity have been observed. A highly sensitive near-infrared spectrometer based on a titanium:sapphire laser and incorporating a dual-beam, double-modulation technique with bidirectional optical multi-passing has been developed in order to detect these transitions, which are more than 4600 times weaker than the fundamental band. We discuss our recent work on the $2\nu_1 + 2\nu_2 \leftarrow 0$, $3\nu_1 + \nu_2 \leftarrow 0$, $\nu_1 + 4\nu_2 \leftarrow 0$, $\nu_1 + 4\nu_2' \leftarrow 0$ and $2\nu_1 + 3\nu_2 \leftarrow 0$ combination bands and the $5\nu_2 \leftarrow 0$, $5\nu_2' \leftarrow 0$, $5\nu_2'' \leftarrow 0$ and $6\nu_2 \leftarrow 0$ overtone bands. Experimentally determined energy levels provide a critical test of *ab initio* calculations in this challenging energy regime (greater than $10\,000\text{ cm}^{-1}$). By comparing the experimental energy levels and theoretical energy levels from *ab initio* calculations in which the adiabatic and relativistic corrections are incorporated, the extent of higher-order effects such as non-adiabatic and radiative corrections is revealed.

Keywords: H_3^+ ; near-infrared spectroscopy; barrier to linearity

1. Introduction

Despite a deceptively simple structure consisting of only three protons and two electrons, the spectrum of H_3^+ is beautifully complex. With the detection of the infrared spectrum by Oka (1980), the potential of this unique molecular ion was finally unlocked nearly 70 years after its initial detection by Thomson (1911). Because H_3^+ is easy to produce in hydrogen discharges, an enormous number of experiments, both spectroscopic and kinetic in nature, have been performed. Its importance to theoreticians and astronomers has also resulted in extensive literature, as demonstrated in this issue.

The laboratory spectroscopy of H_3^+ provides the direct determination of accurate transition frequencies. The ground-state (X^1A_1') equilibrium geometry of H_3^+ is an equilateral triangle. The only available spectroscopic data on H_3^+ corresponds to vibrational excitations, so the search for the H_3^+ spectrum has concentrated primarily on the infrared region. H_3^+ has two vibrational modes: the totally symmetric A_1' mode ν_1 and the doubly degenerate E' mode ν_2 . Only the ν_2 mode is infrared active. More than 900 transitions of H_3^+ from the fundamental, forbidden, overtone and combination bands have been observed. These frequencies provide valuable

*jennifer.gottfried@arl.army.mil

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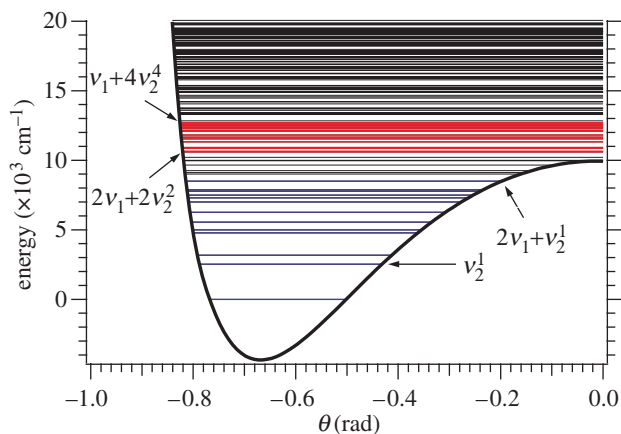


Figure 1. One-dimensional cut of the potential energy surface of Röhse *et al.* (1994) along with calculated rotationless ($J=0$) energy levels. This slice of the potential surface was created by varying two equal H–H bond lengths of the H_3^+ molecule to minimize the energy for each value of the angle θ , which measures the deviation from linearity (where $\theta=0$ is the top of the barrier to linearity). Prior to the work described in this paper, $2\nu_1 + \nu_2^1$ was the highest energy level observed. The lowest level observed above the barrier to linearity to date is $2\nu_1 + 2\nu_2^2$; $\nu_1 + 4\nu_2^4$ is the highest.

information about the structure and dynamics of H_3^+ , enable the astronomical detection of H_3^+ in extraterrestrial environments and provide data for the refinement of theoretical potential energy surfaces and variational calculations. A recent review by Lindsay & McCall (2001) compiled and evaluated the 17 laboratory spectroscopic studies of transitions of H_3^+ below the barrier to linearity.

Since the 2000 Discussion Meeting, an additional 37 transitions of H_3^+ have been recorded. For the first time, transitions to levels above the barrier to linearity have been observed. The detection of these extremely weak transitions, which are more than 4600 times weaker than the fundamental ν_2 band (McCall 2001), required the development of a highly sensitive near-infrared spectrometer using a double-modulation technique. The following sections describe the difficulties encountered when studying transitions of H_3^+ above the barrier to linearity, present our results and compare the results to theoretical predictions. Future prospects for the rovibrational spectroscopy of H_3^+ above the barrier to linearity are also discussed.

2. Complications above the barrier to linearity

Rovibrational energy levels with the same good quantum numbers can mix with one another; the strength of the mixing is inversely proportional to the energy separation between the two levels. This mixing becomes particularly severe in H_3^+ above the barrier to linearity as the density of energy levels increases substantially (figure 1). The concept of quantum monodromy is used to describe systems such as H_3^+ that may reach linear structures with cylindrically symmetrical potential energy barriers. Quantum monodromy ‘implies the absence of any smoothly valid set of quantum numbers for the entire spectrum’ (Child *et al.* 1999).

For H_3^+ , the quantum number ℓ is associated with the ν_2 mode. It represents the angular momentum associated with the vibrational mode and can take on the values $\ell = -\nu_2, -\nu_2 + 2, \dots, \nu_2 - 2, \nu_2$ where ν_2 is the number of quanta of excitation of the ν_2 mode. The number of quanta of excitation of the ν_1 mode is given by ν_1 . The quantum number $g \equiv k - \ell$ (Hougen 1962) represents the part of the projection of the total angular momentum J that is due to rotation. $G = |g|$ is a good quantum number at low energies. Mixed states above the barrier to linearity (as well as highly mixed states below the barrier) can no longer be described by integral values of ν_1 , ν_2 , ℓ and G .

J. K. G. Watson (2002, personal communication) calculated expectation values for ν_1 , ν_2 , ℓ and G up to approximately $23\,000\text{ cm}^{-1}$ ($J \leq 20$). Figure 2 illustrates the failure of traditional quantum numbers above the barrier to linearity using Watson's expectation values. As discussed by Lindsay & McCall (2001), the breakdown of ν_1 , ν_2 , ℓ and G (represented by non-integer values of the quantum numbers) becomes markedly apparent near the barrier to linearity. However, figure 2 also demonstrates that at low J , the approximate quantum numbers remain reasonably good even above the barrier to linearity. This becomes very important when trying to assign quantum numbers to transitions of H_3^+ above the barrier to linearity.

Although the calculated expectation values are approximate and only intended to be used to form a qualitative picture of the nature of the energy levels, they provide the only available indication of the degree of mixing for a particular energy level, and the Oka group has found them to be extremely helpful for the assignment of approximate quantum numbers to levels both below (Lindsay & McCall 2001) and above (Gottfried *et al.* 2003) the barrier to linearity. However, at higher values of J , the mixing of the energy levels becomes so severe that there is no longer any point in labelling the energy levels using approximate quantum numbers. The levels will then have to be labelled using only the good quantum numbers J , I and \pm and the energy-ordering index n .

3. Laboratory spectroscopy of H_3^+

In order to achieve near-shot-noise-limited sensitivity our near-infrared spectrometer (based on a Coherent 899 titanium:sapphire ring laser) incorporates velocity modulation, phase modulation with heterodyne detection, bidirectional optical multi-passing and dual-beam subtraction. The H_3^+ ions were produced in a pure H_2 discharge with a current of approximately 500 mA at 20 kHz in an 18 mm diameter liquid-nitrogen-cooled cell, designed to probe the positive column region of the plasma. As described in previous H_3^+ experiments (McCall 2000), many of the H_3^+ lines were obscured by the presence of hydrogen Rydberg (H_2^*) transitions. The addition of 10 torr of He was sufficient to remove most of the interfering H_2^* lines. The experimental setup has been described in detail elsewhere (Gottfried *et al.* 2003; Gottfried 2005). A total of 37 transitions of H_3^+ above the barrier to linearity have been observed to date. The original 22 transitions (Gottfried *et al.* 2003) were obtained during a survey of the mid-wavelength optics set of the laser ($11\,000\text{--}12\,500\text{ cm}^{-1}$). Subsequent surveys of the short wavelength optics set ($12\,000\text{--}13\,800\text{ cm}^{-1}$) and a combination long

wavelength/mid-wavelength (10 650–11 500 cm^{-1}) optics set are underway at Chicago (C. F. Neese 2005, personal communication; Morong *et al.* 2006) and have thus far yielded an additional 15 transitions. Table 1 lists the observed transitions and assignments.

The transitions are labelled following the convention described in Lindsay & McCall (2001). The vibrational states involved in a transition are labelled according to the notation

$$v_1\nu_1 + v_2\nu_2^{|k|}. \quad (3.1)$$

The rotational transitions are given by the branch symbol

$$^{[n|t|\pm 6|\pm 9|\dots]} \{P|Q|R\} (J, G)_{[u|l]}^{[u|l]}, \quad (3.2)$$

where $\{P|Q|R\}$ represents $\Delta J = \{-1|0|+1\}$, (J, G) are the values of J and G in the lower state, $[u|l]$ discriminates between the two levels of an ℓ -resonance pair for the lower state of the transition (subscript) or the upper state (superscript) with u for the upper energy level of the pair or l for the lower energy level, and the superscripted n or t is used for transitions where $\Delta G = \mp 3$. For $\Delta g = \pm 3$ transitions, which wrap around zero (e.g. $g' = \pm 2 \leftarrow g'' = \mp 1$) and formally look like $\Delta G = +1$, n is used. For highly mixed levels where g changes by more than 3, the numerical value of ΔG is used ($\pm 6, \pm 9, \dots$).

The complexity of the observed spectrum owing to the large number of vibrational states above the barrier to linearity is readily apparent in figure 3. For each band observed, the strongest transition based on the Einstein A coefficients of Neale *et al.* (1996) is labelled. Both the rotational and vibrational band assignments were made based on the calculated intensities of Neale *et al.* (1996), the expectation values of J. K. G. Watson (2002, personal communication), and the assignments of Schiffels *et al.* (2003b) and Alijah (2003, personal communication).

Using the new transition frequencies and the experimentally observed ground-state energy levels (Lindsay & McCall 2001), experimental upper-state energy levels were determined. The determination of accurate experimental energy levels enables the evaluation of accurate *ab initio* calculations in the challenging regime above the barrier to linearity.

4. Comparison with theoretical calculations

The energy regime near and above the barrier to linearity is particularly difficult theoretically—until recently, few of the rovibrational calculations performed in this range included the correct boundary conditions for linear geometries. The variational treatment, which is essential in calculating high rovibrational energy levels of H_3^+ , encounters a difficulty near the top of the barrier to linearity at an energy of approximately 10 000 cm^{-1} above the zero-point level. This is because the kinetic Hamiltonian, which is inversely proportional to the moment of inertia, contains a singularity when large-amplitude vibrational motion distorts the molecule into a linear configuration. Theoretical calculations of the rovibrational spectrum of H_3^+ above the barrier to linearity use different techniques to circumvent this difficulty, with varying degrees of accuracy (table 2). For a detailed comparison of the theoretical methods, see Gottfried *et al.* (2003).

Table 1. Observed transitions of H_3^+ above the barrier to linearity. Intensities were calculated at 300 K from the Einstein A coefficients of Neale *et al.* (1996) and normalized to the $R(1, 0) 5\nu_2^1$ line. The uncertainty in the last decimal place of the frequency is listed in parentheses. The listed transitions are from Nee05 (C. F. Neese 2005, personal communication; Morong *et al.* 2006) and Got03 (Gottfried *et al.* 2003). Three of the band assignments from Nee05 could not be determined.

band	assignment	rel. int.	observed (cm^{-1})	reference
$2\nu_1 + 2\nu_2^2 \leftarrow 0$	${}^tR(2, 1)$	0.175	10 725.941(10)	Nee05
$5\nu_2^1 \leftarrow 0$	$P(3, 3)$	0.719	10 730.111(10)	Nee05
$2\nu_1 + 2\nu_2^2 \leftarrow 0$	${}^tR(1, 0)$	0.739	10 752.151(10)	Nee05
$5\nu_2^1 \leftarrow 0$	$P(2, 2)$	0.362	10 752.368(10)	Nee05
$2\nu_1 + 2\nu_2^2 \leftarrow 0$	${}^nQ(2, 2)$	0.096	10 766.110(20)	Nee05
$5\nu_2^1 \leftarrow 0$	$P(2, 1)$	0.143	10 766.320(15)	Nee05
$5\nu_2^1 \leftarrow 0$	$Q(3, 2)^l$	0.117	10 779.137(10)	Nee05
$5\nu_2^3 \leftarrow 0$	${}^{+6}Q(2, 1)$	0.292	10 789.844(10)	Nee05
$2\nu_1 + 2\nu_2^2 \leftarrow 0$	${}^nR(2, 2)^u$	0.374	11 019.358(10)	Got03
$5\nu_2^1 \leftarrow 0$	$R(1, 1)^l$	0.238	11 044.149(10)	Got03
$5\nu_2^1 \leftarrow 0$	$R(3, 3)^l$	0.683	11 053.680(10)	Got03
$3\nu_1 + \nu_2^1 \leftarrow 0$	$P(3, 3)$	0.164	11 111.791(10)	Got03
$5\nu_2^1 \leftarrow 0$	$R(1, 0)$	1.000	11 228.613(10)	Got03
$5\nu_2^1 \leftarrow 0$	$R(1, 1)^u$	0.258	11 244.366(10)	Got03
$5\nu_2^1 \leftarrow 0$	$R(2, 1)^l$	0.131	11 246.712(10)	Got03
$5\nu_2^1 \leftarrow 0$	$R(2, 2)^u$	0.191	11 304.484(10)	Got03
$3\nu_1 + \nu_2^1 \leftarrow 0$	$Q(1, 0)$	0.181	11 318.084(10)	Got03
$5\nu_2^1 \leftarrow 0$	$R(2, 1)^u$	0.167	11 496.796(10)	Got03
$3\nu_1 + \nu_2^1 \leftarrow 0$	$R(1, 0)$	0.123	11 503.620(10)	Got03
$5\nu_2^5 \leftarrow 0$	$P(3, 3)$	0.165	11 571.880(10)	Got03
$5\nu_2^1 \leftarrow 0$	$R(3, 3)^u$	0.276	11 576.156(10)	Got03
$5\nu_2^5 \leftarrow 0$	${}^{+6}Q(1, 0)$	0.297	11 606.160(10)	Got03
$5\nu_2^5 \leftarrow 0$	${}^{+6}R(2, 2)$	0.121	11 694.790(10)	Got03
$5\nu_2^5 \leftarrow 0$	${}^{+6}R(1, 1)$	0.142	11 707.265(10)	Got03
$5\nu_2^5 \leftarrow 0$	${}^{+6}R(1, 0)$	0.366	11 854.463(10)	Got03
$2\nu_1 + 3\nu_2^1 \leftarrow 0$	$P(2, 2)$	0.120	12 222.027(10)	Got03
$\nu_1 + 4\nu_2^2 \leftarrow 0$	${}^tR(1, 0)$	0.121	12 246.362(20)	Got03
$2\nu_1 + 3\nu_2^1 \leftarrow 0$	$P(3, 3)$	0.166	12 246.550(20)	Got03
$2\nu_1 + 3\nu_2^1 \leftarrow 0$	$Q(1, 0)$	0.322	12 253.670(10)	Got03
$6\nu_2^2 \leftarrow 0$	${}^tQ(1, 0)$	0.228	12 419.121(10)	Got03
$6\nu_2^2 \leftarrow 0$	${}^nP(3, 3)$	0.133	12 502.606(10)	Nee05
$\nu_1 + 4\nu_2^2 \leftarrow 0$	${}^nR(3, 3)$	0.245	12 658.335(10)	Nee05
$\nu_1 + 4\nu_2^4 \leftarrow 0$	${}^tR(1, 0)$	0.157	12 897.888(10)	Nee05
$6\nu_2^2 \leftarrow 0$	${}^tR(1, 0)$	0.263	13 056.013(10)	Nee05
—	$Q(1, 0)$	0.171	13 597.367(10)	Nee05
—	$R(3, 3)$	0.117	13 606.093(10)	Nee05
—	$Q(1, 0)$	0.193	13 676.446(10)	Nee05

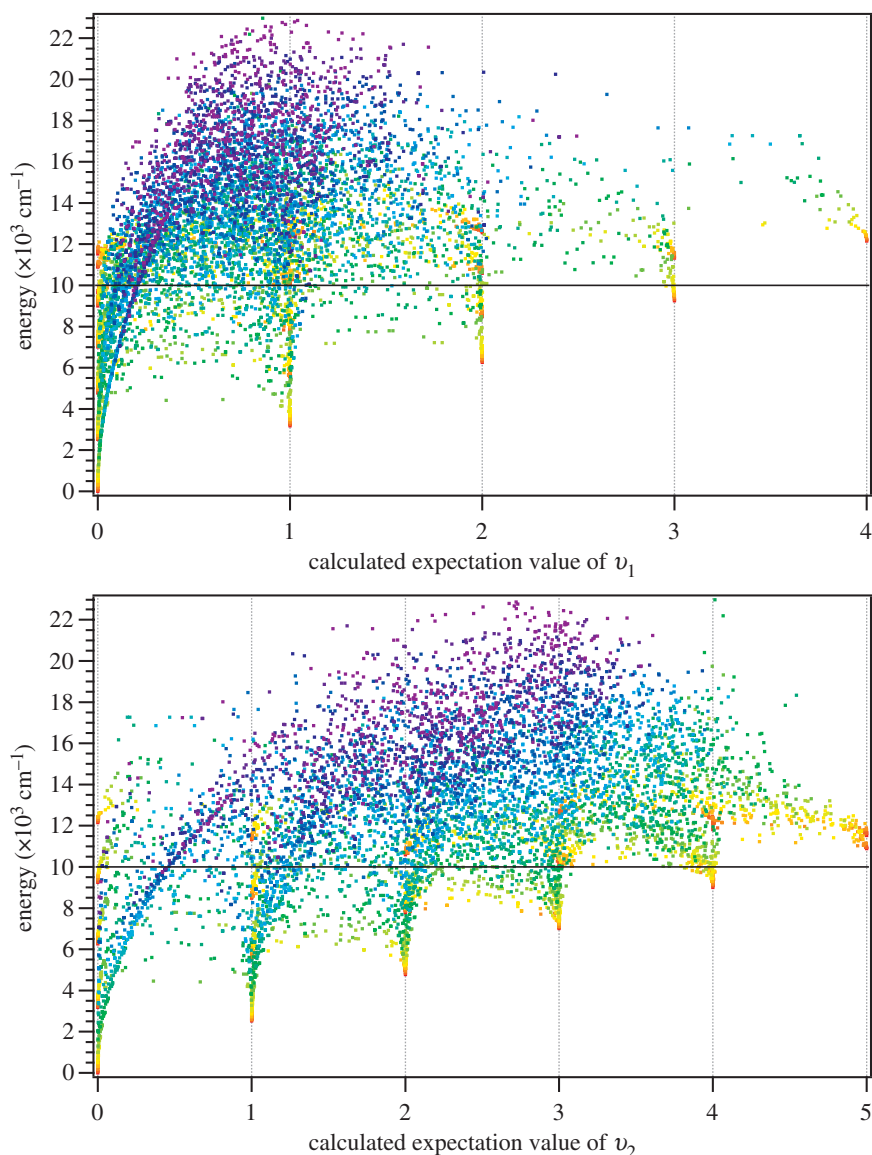


Figure 2. Rovibrational energy levels of H_3^+ versus calculated expectation values of approximately good quantum numbers (obtained from J. K. G. Watson). Below the barrier to linearity (approx. $10\,000\text{ cm}^{-1}$), the quantum numbers v_1 , v_2 , ℓ and G are identifiable, though they deviate from integral values. Near the barrier, however, the mixing of the rovibrational levels increases and the quantum numbers are chaotic. The rovibrational energy levels are colour-coded by the good quantum number J : $J=0-2$ (red/orange), $J=3-5$ (yellow), $J=6-10$ (green), $J=11-15$ (aqua) and $J=16-20$ (purple). Even above the barrier to linearity, the low J levels are reasonably well behaved.

The most efficient way to treat the large-amplitude motion of H_3^+ is to use hyperspherical coordinates (ρ, θ, ϕ) . The basis set of hyperspherical harmonics not only allows rigorous treatment of singularities in the kinetic Hamiltonian, but also retains the D_{3h} permutation-inversion symmetry of the system, so that

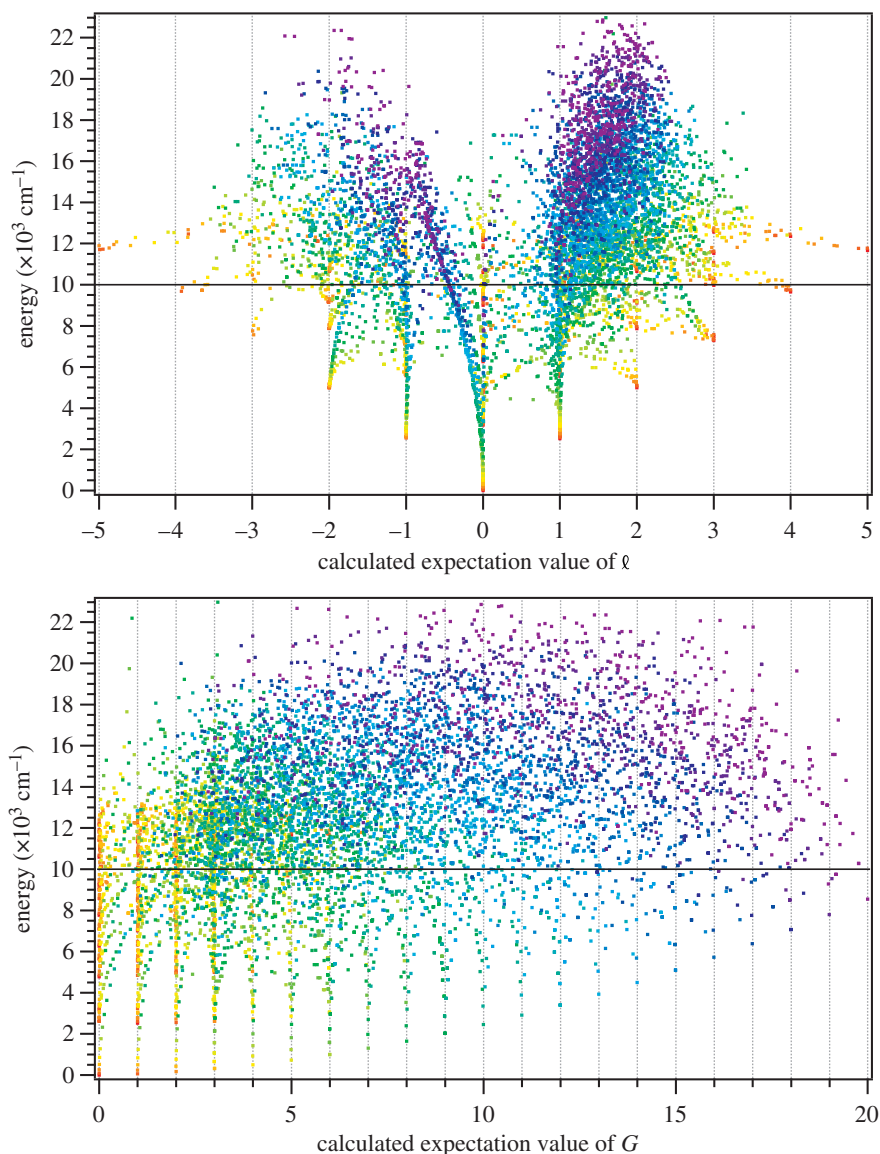


Figure 2. (Continued.)

full advantage of the symmetry properties of the molecule may be taken. AHW (Alijah *et al.* 1995) applied this formalism to H_3^+ using both the MBB (Meyer *et al.* 1986) and RKJK (Röhse *et al.* 1994) surfaces.

More recently, SAH (Schiffels *et al.* 2003*a,b*; Alijah 2003, personal communication) applied their formalism using hyperspherical coordinates to the most accurate *ab initio* potential energy surface available, CRJK (Cencek *et al.* 1998). They calculated energy levels both below 9000 cm^{-1} (Schiffels *et al.* 2003*a*) and from 9000 to $13\,000 \text{ cm}^{-1}$ (Schiffels *et al.* 2003*b*), which was later extended to $13\,500 \text{ cm}^{-1}$ (Alijah 2003, personal communication). The SAH result is rigorously *ab initio* without any adjustment of the potential energy

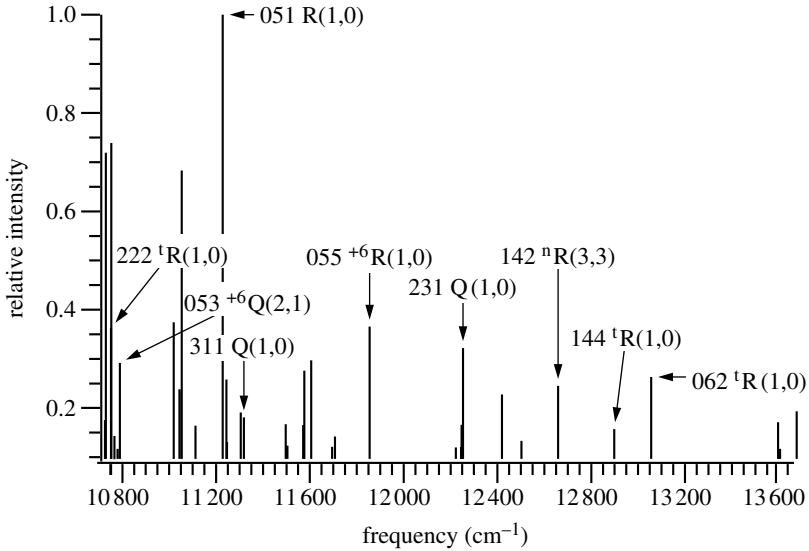


Figure 3. The observed spectrum of H_3^+ above the barrier to linearity. The relative intensities were calculated using the Einstein A coefficients of Neale *et al.* (1996) at 300 K. The strongest transition observed for each band is labelled using the notation $v_1'v_2'\ell' \Delta^G \Delta J(J'', G'')$.

surface. By comparing their calculated energy levels below 9000 cm^{-1} to the available experimental data compiled by Lindsay & McCall (2001), SAH discovered a systematic deviation on the order of a fraction of a cm^{-1} , which can be expressed as

$$\Delta E = E_{\text{obs}} - E_{\text{calc}} = -b_1 E_{\text{calc}}^0 - \bar{a}_1 J(J+1) - \bar{a}_2 G^2, \quad (4.1)$$

where E_{calc}^0 is the calculated band origin and $b_1 = 1.0123 \times 10^{-4} \text{ cm}^{-1}$, $\bar{a}_1 = 2.0436 \times 10^{-3} \text{ cm}^{-1}$ and $\bar{a}_2 = -1.3600 \times 10^{-3} \text{ cm}^{-1}$ are empirical constants. Since the adiabatic and relativistic corrections are already included in the CRJK potential, SAH ascribe ΔE to the largest of the remaining corrections—the non-adiabatic effect. This leaves the quantum electrodynamic radiative effect as the only remaining sizeable correction. In the calculations of J. K. G. Watson (2002, personal communication) and NMT (Neale *et al.* 1996), who also give energy levels beyond the barrier to linearity, the non-adiabatic and radiative corrections were effectively incorporated when they adjusted the potential surface to fit experimental data.

SAH (Schiffels *et al.* 2003a) found that energy levels calculated by applying an empirical correction formula similar in form to equation (4.1), but using coefficients based on a least-squares fit to individual experimental band origins agreed with approximately 500 laboratory-determined energy levels below 9000 to within 0.1 cm^{-1} , with only a few exceptions. Based on the success of this approach, SAH (Schiffels *et al.* 2003b) gave predictions for energy levels between 9000 and $13\,500 \text{ cm}^{-1}$. While the experimental agreement with the corrected transition frequencies of SAH is rather good compared to the other calculations above the barrier to linearity (within 1 cm^{-1} , see table 2), figure 4 shows that the scatter in the deviation of the corrected energy levels (using the extrapolation formula (4.1)) from the experimental values increases significantly (by an order or magnitude) above the barrier to linearity. The scatter in the corrected energy

Table 2. Comparison among theoretical and observed transition frequencies. The theoretically predicted transitions are from the calculations of AHW (Alijah *et al.* 1995), NMT (Neale *et al.* 1996), SAH (Schiffels *et al.* 2003*b*), and Jaq03 (Jaquet 2003) using the potential energy surfaces of RKJK (Röhse *et al.* 1994), DPT (Dinelli *et al.* 1995), CRJK (Cencek *et al.* 1998) and Jaq02 (Jaquet 2002). Also included are the empirically corrected energies from SAH, which provide the most accurate transition frequencies.

observed (cm^{-1})	calc.-obs. (cm^{-1})				
	AHW (RKJK)	NMT (DPT)	SAH (CRJK)	SAH (corrected)	Jaq03 (Jaq02)
10 725.941	2.604	1.264	0.548	-0.52	-0.837
10 730.111	-0.647	-0.012	1.142	0.06	0.814
10 752.151	2.517	1.266	0.504	-0.57	-0.875
10 752.368	-1.051	-0.098	1.058	-0.03	6.455
10 766.110	—	1.359	0.403	-0.68	-0.911
10 766.320	-0.819	0.009	1.069	-0.02	—
10 779.137	—	1.164	0.555	-0.54	0.178
10 789.844	-0.952	-0.179	0.981	-0.09	-0.340
11 019.358	—	0.198	0.925	-0.17	2.089
11 044.149	-0.563	0.172	0.998	-0.12	2.313
11 053.680	—	0.202	0.926	-0.19	6.063
11 111.791	3.282	1.594	0.704	-0.43	—
11 228.613	-0.182	0.230	1.062	-0.04	-0.595
11 244.366	-0.001	0.213	1.107	-0.01	—
11 246.712	-0.053	0.355	0.996	-0.12	—
11 304.484	—	0.291	1.011	-0.09	0.975
11 318.084	3.286	1.627	0.612	-0.53	-0.800
11 496.796	—	0.450	1.213	0.10	-0.700
11 503.620	3.433	1.605	0.640	-0.51	—
11 571.880	0.097	0.885	0.822	-0.34	-0.090
11 576.156	—	0.577	1.148	0.03	-0.711
11 606.160	0.106	0.898	0.830	-0.30	0.283
11694.790	—	1.002	1.225	0.12	—
11 707.265	1.111	1.007	1.025	-0.14	—
11 854.463	0.851	1.262	1.008	-0.13	-0.709
12 222.027	-1.983	-0.154	0.499	-0.74	—
12 246.362	0.946	0.847	0.390	-0.82	—
12 246.550	0.670	0.825	0.523	-0.71	—
12 253.670	-1.335	0.399	0.374	-0.87	—
12 419.121	-0.966	0.191	0.552	-0.70	—
12 502.606	—	0.444	0.995	-0.27	—
12 658.335	—	0.591	0.476	-0.77	—
12 897.888	2.018	2.190	0.407	-0.87	—
13 056.013	—	0.618	0.481	-0.78	—
13 597.367	—	0.618	—	—	—
13 606.093	—	0.748	—	—	—
13 676.446	—	-2.210	—	—	—
average error:	0.538	0.607	0.800	-0.35	0.700
std. deviation:	1.614	0.744	0.280	0.32	2.249

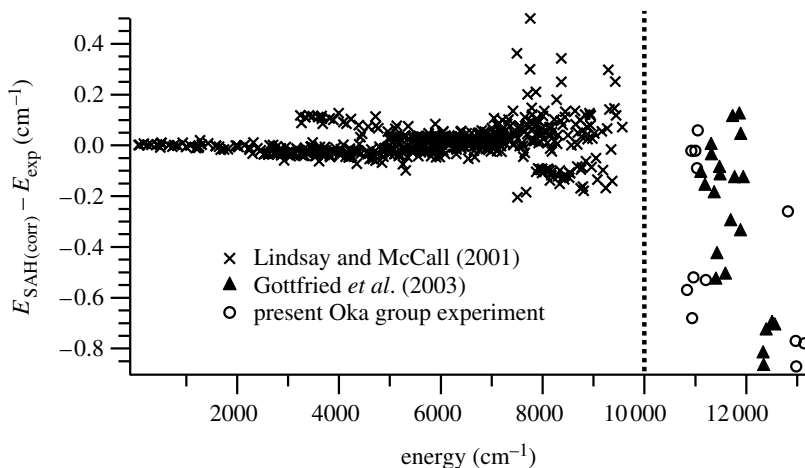


Figure 4. Comparison between the corrected energy levels of SAH (Schiffels *et al.* 2003*a,b*; Alijah 2003, personal communication) and all experimental energy levels of H_3^+ . The dashed line is drawn at the barrier to linearity. The scatter in the deviation of the corrected energy levels from the experimental values increases significantly above the barrier to linearity.

levels above the barrier to linearity suggests that none of these band origins are reproduced very accurately by the extrapolation correction formula and more experimental band origins are needed to improve the predictive power of equation (4.1).

Jaq03 (Jaquet 2003) used Jacobi coordinates with a potential energy surface based on the CRJK surface, Jaq02 (Jaquet 2002). In these calculations, he corrected for the non-adiabatic effects using mass-dependent simulations. Numerical problems for energies near the barrier to linearity caused by the choice of coordinate system and basis set are the most probable sources of the large errors in the Jaq03 calculations. Jaq03 reports that new calculations with the DVR3DRJ program suite reproduce the hyperspherical coordinates results of SAH exactly (using the same potential energy surface as SAH). New calculations using the DVR3DRJ program on the Jaq02 surface are presently underway (Jaquet 2003). Although Jaq03 also calculated transition intensities (at 300 K), the predicted intensities do not agree very well with our observed intensities.

5. Future prospects

The most accurate intensities available for transitions above the barrier to linearity are by NMT. As a result of the extremely weak nature of these transitions and the irregularity of the rovibrational spectrum (see figure 3), the search for additional H_3^+ lines is dependent upon the theoretical calculations. Based on the calculated intensities of NMT and the sensitivity of our spectrometer, we expect to observe an additional 90 or so transitions of H_3^+ above the barrier to linearity (Gottfried 2005). Although technical problems with the laser system (resulting from the absorption of strong water lines in the region) make closing the gap in experimental data between the $2\nu_1 + \nu_2^1$ and $2\nu_1 + 2\nu_2^2$ levels difficult, we hope to obtain more information about this very challenging regime. The availability of experimental data in this region

should enable the refinement of theoretical calculations above the barrier. The acquisition of additional H_3^+ transitions extending into the range of the visible dye laser ($6\nu_2^4 \leftarrow 0$, $7\nu_2^1 \leftarrow 0$, etc.) will require a significant improvement in the experimental sensitivity.

The lack of assigned spectroscopic data in the intermediate energy regime from 10 000 to 35 000 cm^{-1} (until recently) means that the potential is not strongly constrained (Tennyson *et al.* 2000). Consequently, none of the potential energy surfaces near the H_3^+ dissociation limit (approx. 35 000 cm^{-1}) are considered reliable, and experimental data on higher-energy levels are needed to improve them. An improved potential energy surface might finally enable the analysis of the near-dissociation spectrum, which has remained completely unassigned since its initial discovery by Carrington *et al.* (1982) more than 20 years ago.

Finally, we note that completely first principle *ab initio* theory for H_3^+ has reached the point of spectroscopic accuracy, leaving only the non-adiabatic and quantum electrodynamic correction to be calculated. This is analogous to the status of first principle calculations for molecular hydrogen by Kolos & Wolniewicz (1975)—so it has taken about 30 years for the *ab initio* theory to progress from a two-particle problem to a three-particle problem.

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Discussion

E. HERBST (*Department of Physics and Department of Astronomy, The Ohio State University, Columbus, USA*). How were the vibrational levels that are shown on the potential diagram obtained (figure 1)?

J. L. GOTTFRIED. This is explained in the caption to the figure. The calculated rotationless energy levels kindly provided by J. K. G. Watson (2002, personal communication) were used.

A. ALIJAH (*Departamento de Química, Universidade de Coimbra, Portugal*). This comment refers to the performance of our correction formula at approximately $13\,000\text{ cm}^{-1}$ or higher. Because the corrections are derived by extrapolation from the low energy region, we might use your new experimental data in the $13\,000\text{ cm}^{-1}$ range to adjust our parameters and make predictions for higher energies.

B. J. MCCALL (*Department of Chemistry and Department of Astronomy, University of Illinois at Urbana-Champaign, Urbana, USA*). This may be a question for Jonathan Tennyson. In the context of future work on even higher vibrationally

excited states, do you have any idea how the intensity of the $n\nu_2 \leftarrow 0$ overtone bands scale with n for $n > 5$?

J. TENNYSON (*Department of Physics and Astronomy, University College London, UK*). This problem was studied by Le Sueur *et al.* (1993) who calculated the vibrational band intensity for transitions to every vibrational state of H_3^+ starting from the ground vibrational state. They found that while, of course, the intensity dropped for the higher bending states, transitions of the type $n\nu_2 \leftarrow 0$ remain much stronger than all other transitions all the way to dissociation. Specific numbers can be found in their paper. Le Sueur *et al.*'s findings were supported by Munro *et al.* (2005) who repeated these calculations using the more reliable PPKT2 potential. It should be noted in this context that Le Sueur *et al.* also found that low-energy ν_2 bending modes and the high-energy so-called horseshoe states formed a single set of states in the quantum mechanical calculations, in contrast to classical studies which associate these motions with different families of periodic orbits (Depolavieja *et al.* 1994).

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