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An introduction to the spectroscopy of H_3^+

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The infrared spectra of H_3^+ and D_3^+ were first observed almost simultaneously in 1980. Since then there has been extensive laboratory work on H_3^+ and its D-isotopomers. In addition, the spectrum of H_3^+ has been observed in emission from the atmospheres of the giant planets Jupiter, Saturn and Uranus, and probably from the supernova SN1987A, and recently in absorption in interstellar clouds. In this introductory paper, the assignment of the spectra and some of the characteristic features associated with the strong anharmonicity are discussed. As the convergence of the perturbation series is poor, the large centrifugal effects are best calculated in a variational type of approach, where the rotational energy in the Hamiltonian can be treated essentially exactly. *Ab initio* calculations have steadily improved over the years, and recent work has given completely theoretical vibration–rotation term values for the low vibrational states with an accuracy better than 0.1 cm^{-1} in almost all cases, adequate for most spectroscopic assignment purposes.

Keywords: H_3^+; spectroscopy; molecular vibrations and rotations

1. Introduction

The H_3^+ molecular ion was discovered by Thomson (1911) as a mass/charge $= 3m_p/e$ ray in what was, in today's language, the mass spectrum of a plasma produced by an electrical discharge through hydrogen gas. This observation was confirmed by Dempster (1916) using electron-beam excitation of hydrogen. The H_3^+ ion was not known in conventional chemistry, because it reacts rapidly as a protonating agent with most substrates. It is now recognized as the major positive ion in hydrogen plasmas under normal laboratory conditions. It also plays an important role in theories of interstellar chemistry, where the fast production reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H, \tag{1.1}$$

and the protonation reaction

$$H_3^+ + X \rightarrow HX^+ + H_2, \tag{1.2}$$

for a wide range of species X, initiate the series of ion–molecule reactions that produce larger ions and molecules (Herbst & Klemperer 1973; Watson 1973, 1976; Dalgarno & Black 1976). However, the static concentration of H_3^+ is relatively low unless the concentration of proton acceptors X is low.

In recent years, the presence of H_3^+ has become well established in the hydrogen-rich upper atmospheres of the planets Jupiter (Drossart *et al.* 1989; Trafton *et al.*

1989), Uranus (Trafton *et al*. 1993) and Saturn (Geballe *et al*. 1993). In the case of Jupiter, the spectroscopic detection was preceded by a mass-spectrometric measurement at about 54 Jupiter radii by the Voyager 2 spacecraft (Hamilton *et al*. 1980). Quite recently, the spectrum of H_3^+ was identified in dense (Geballe & Oka 1996) and diffuse (McCall *et al*. 1998) interstellar clouds, and there is a possible identification (Miller *et al*. 1992) in the supernova SN1987A. Some pure rotational lines of the polar isotopomer H_2D^+ are known in the laboratory (Bogey *et al*. 1984; Warner *et al*. 1984; Saito *et al*. 1985), and after a number of searches a positive astronomical detection has recently been claimed (Stark *et al*. 1999).

This brief summary is but an indication of the variety of fields for which a knowledge of the properties of H_3^+ is necessary. The purpose of this Discussion Meeting is to bring together experts from a number of these fields, in the hope that the exchange of ideas and information will lead to further advances in our knowledge of this basic molecular ion, and in our use of it to probe the physical conditions in different environments. To this end, this talk is intended as a general review of present knowledge of the spectrum of H_3^+.

Because of the size of this field—a search in *Chemical Abstracts* using the registry number of the main isotopomer produced 576 references since 1990—this article is necessarily selective. There have been a number of review articles of this field, the more extensive being by Oka (1983), McNab (1995) and Tennyson (1995). For lack of space, I will not discuss the infrared predissociation spectrum (Carrington *et al*. 1982, 1993; Carrington & Kennedy 1984), which is already a large subject in its own right. It is summarized in the reviews of McNab (1995) and Tennyson (1995).

2. Structure and potential energy of H_3^+

While H_3^+ is small enough that a simultaneous treatment of all five particles, three protons and two electrons, might be possible, all the calculations so far follow what is usually called the Born–Oppenheimer (BO) treatment, although it corresponds more to the spirit of Born (1951) and Born & Huang (1954) than to the original Born & Oppenheimer (1927) paper. In brief, the electronic Schrödinger equation is solved at various nuclear configurations, with the nuclear coordinates as parameters. The eigenvalues provide the potential energy surface for the zero-order Schrödinger equation for the motion of the nuclei, and then correction terms are introduced by perturbation theory. In this, the perturbation Hamiltonian contains the derivatives of the electronic wave functions with respect to the nuclear coordinates, which occur in the terms omitted in the zeroth-order approximation.

Nowadays, we are so used to the equilateral triangular structure for the equilibrium structure of H_3^+, at the minimum of the BO potential energy surface, that it comes as something of a surprise that in the first calculations of the electronic structure of H_3^+ Hirschfelder (1938) found a nonlinear C_{2v} equilibrium nuclear geometry. It was not until the advent of more powerful computers in the 1960s that several groups (Ellison *et al*. 1963; Christofferson *et al*. 1964; Conroy 1964*a*–*c*) obtained the equilateral D_{3h} structure that is accepted today. A recent highly accurate potential (Cencek *et al*. 1998; Jaquet *et al*. 1998) with adiabatic and relativistic corrections gives a minimum at $r_e = 1.650\,35a_0 = 0.8733$ Å. The first experimental confirmation of this shape came from one of the first applications of the Coulomb-explosion imaging technique (Gaillard *et al*. 1978), although the bond length was determined to be *ca.* 0.97(3) Å.

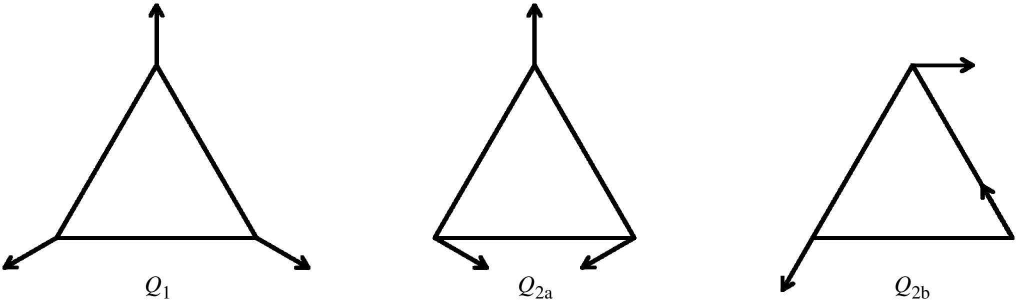

Figure 1. The structure and normal modes of H_3^+.

The vibrational frequencies of H_3^+ are of particular interest, especially the infrared-active mode ν_2. Calculation of this infrared frequency requires an accurate knowledge of the shape of the potential energy surface in the vicinity of the minimum. A number of *ab initio* calculations converged on $\omega_1 = 3471\ \mathrm{cm}^{-1}$ and $\omega_2 = 2814\ \mathrm{cm}^{-1}$ (Carney & Porter 1974) as the harmonic values of the fundamental vibrational frequencies. However, the effects of anharmonicity are large. This was shown in the calculations by Carney & Porter, who first calculated an *ab initio* potential surface (Carney & Porter 1974) and then solved for the vibration–rotation energy levels on this surface (Carney & Porter 1976, 1980). The first large effect of anharmonicity was in the calculated 1–0 vibrational intervals of $\nu_1 = 3185\ \mathrm{cm}^{-1}$ and $\nu_2 = 2516\ \mathrm{cm}^{-1}$, well shifted from their harmonic values. These predictions played a crucial role in the first experimental observation of the ν_2 bands of H_3^+ at $2521\ \mathrm{cm}^{-1}$ by Oka (1980) and of D_3^+ at $1835\ \mathrm{cm}^{-1}$ by Shy *et al.* (1980). Thus, the anharmonic predictions greatly reduced the spectroscopic search problem.

A number of BO potentials of improving quality have been published since Carney & Porter (1974). Among these, Meyer *et al.* (1986) calculated an *ab initio* potential, which they then adjusted to fit the observed value of ν_2 (Oka 1980). This adjusted Meyer–Botschwina–Burton (MBB) potential has been used by other authors in calculations of the energy levels of H_3^+. The most accurate potential at present, with 'sub-micro-Hartree accuracy', is that of Cencek *et al.* (1998), who also calculated the non-BO adiabatic and relativistic correction functions. Very recently, a slightly less accurate global potential surface has been calculated for a wide range of geometries (Aguado *et al.* 2000); this should be valuable for calculations of dissociative processes.

3. Vibration–rotation basis functions

For small displacements, the levels of the breathing mode $Q_1(a')$ are described by the vibrational quantum number v_1. On the other hand, the degenerate mode $Q_2(e')$ has two components, Q_{2a}, which is the typical 'bending' mode of a triatomic molecule and preserves C_{2v} symmetry, and Q_{2b}, which is the 'antisymmetric stretching' mode of a triatomic and leaves only C_s symmetry (figure 1). It seems slightly surprising that these have the same frequency, and in fact this is only true in the harmonic approximation. Figure 2, which is a contour diagram of the potential energy for $Q_1 = 0$, shows the harmonic behaviour as near-circles for small displacements, but the effects of trigonal symmetry are already marked at the level of the $5000\ \mathrm{cm}^{-1}$

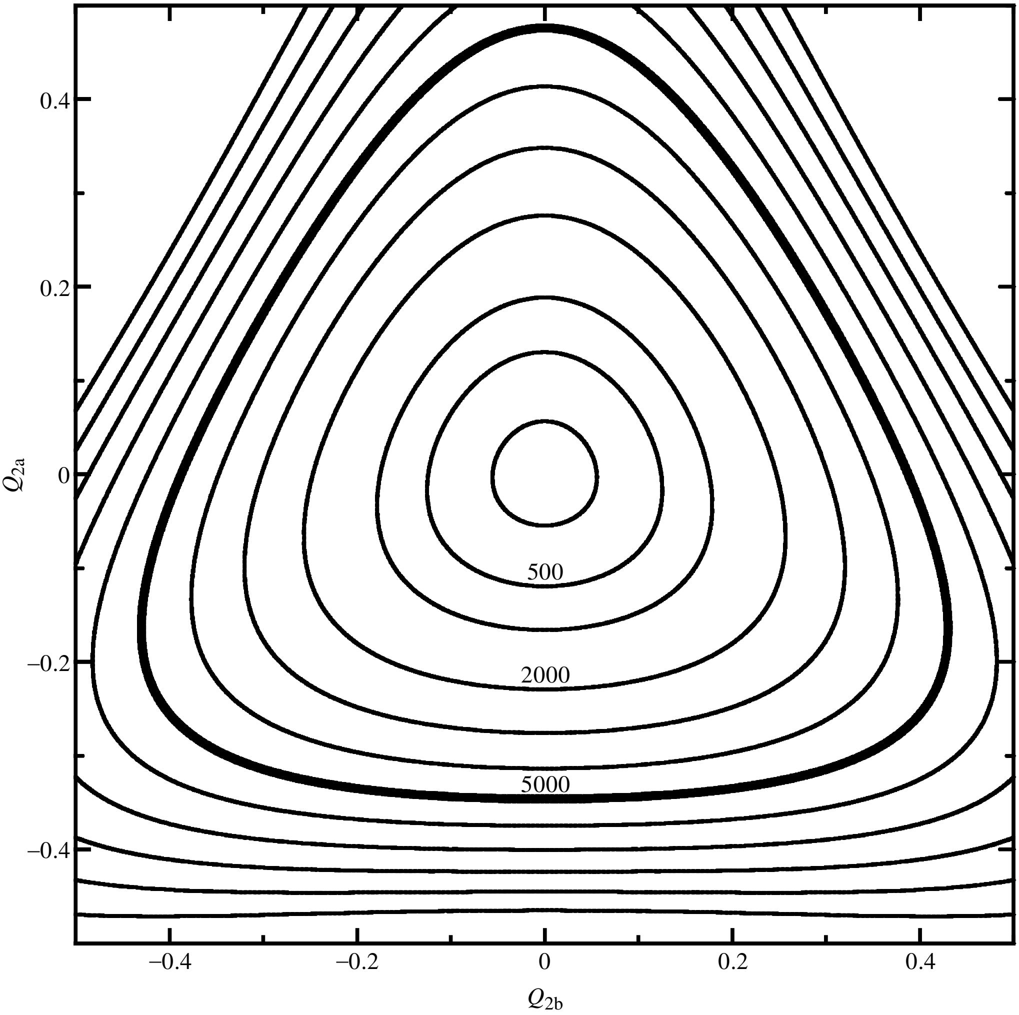

Figure 2. Contours of the H_3^+ potential energy surface of Meyer *et al.* (1986) for $Q_1 = 0$. The contours are in units of cm^{-1}; the bold contour is near the energy in the Q_2 modes for $v_2 = 1$.

contour, which is near the energy of the fundamental level $v_2 = 1$. The vibrational states of ν_2 can be described in terms of the component quantum numbers (v_{2a}, v_{2b}), but in general it is more convenient to use the polar quantum numbers (v_2, l_2), where $v_2 = 0, 1, 2, \ldots$, and $l_2 = -v_2, -v_2 + 2, \ldots, v_2 - 2, v_2$, giving $v_2 + 1$ components for given v_2. The quantum number l_2 measures the angular momentum about the figure axis generated by the degenerate vibration.

H_3^+ is a symmetric top, and so a convenient rotational basis is provided by the symmetric top eigenfunctions $|m, J, k\rangle$; here I will omit the space-fixed quantum number m, which does not contribute to the energy of the molecule in field-free situations, and only provides a statistical weight factor of $(2J + 1)$. The vibration–rotation basis can then be written:

$$|v_1, v_2, l_2, J, k\rangle = |v_1\rangle|v_2, l_2\rangle|J, k\rangle. \tag{3.1}$$

Before considering the approximate energies, it is useful to consider the symmetries of these functions. For this purpose it is convenient to introduce the quantum number g of Hougen (1962), but with the opposite sign to Hougen. For this point group we have $g = k - l_2$.

The permutation-inversion group (Bunker & Jensen 1998) equivalent to $D_{3\mathrm{h}}$ is generated by the operations $(123)^*$ and (23), equivalent to the point-group operations S_3 and C_2, respectively. These have the following effects on the basis functions (Watson 1984):

$$(123)^*|v_1, v_2, l_2, J, k\rangle = (-1)^{v_2}\mathrm{e}^{-g\pi\mathrm{i}/3}|v_1, v_2, l_2, J, k\rangle, \tag{3.2}$$

$$(23)|v_1, v_2, l_2, J, k\rangle = (-1)^J|v_1, v_2, -l_2, J, -k\rangle. \tag{3.3}$$

The latter can be used to symmetrize the functions with respect to (23). The function

$$|v_1, v_2, l_2, J, k, s\rangle = \frac{1}{[2(1 + s\delta_{l_2 0}\delta_{k0})]^{1/2}}\{|v_1, v_2, l_2, J, k\rangle + (-1)^J s|v_1, v_2, -l_2, J, -k\rangle\}, \tag{3.4}$$

where $s = \pm 1$, belongs to the eigenvalue s of (23). (The function with $s = -(-1)^J$ does not exist for $l_2 = k = 0$.) The operation (23) commutes with the Hamiltonian H and with the space-fixed components of the electric dipole moment operator M, and so the eigenvalue of (23) is preserved. This gives the selection rule $s \leftrightarrow s$ for both transitions and perturbations.

The operation $(123)^*$ is, in general, more informative. If we consider matrix elements of H or M in the unsymmetrized basis set, and take account of the fact that H is symmetric and M is antisymmetric to $(123)^*$, we obtain the selection rules:

$$\text{perturbations}: \ \Delta g + 3\Delta v_2 \equiv 0 \pmod 6, \tag{3.5}$$

$$\text{electric dipole transitions}: \ \Delta g + 3\Delta v_2 \equiv 3 \pmod 6. \tag{3.6}$$

In either case, Δg is a multiple of 3, a selection rule that follows from considering the operation (123) alone.

In general, the strongest vibration–rotation transitions have the smallest value(s) of Δg given by this selection rule. Thus, in the fundamental $\nu_2 - 0$, with $\Delta v_2 = 1$, the strongest transitions have $\Delta g = 0$, while the first overtone $2\nu_2 - 0$ has $\Delta v_2 = 2$ and $\Delta g = \pm 3$. Pure rotational transitions (Watson 1971) and the fundamental $\nu_1 - 0$ are forbidden to a first approximation, but become weakly allowed through vibration–rotation interactions and also obey the selection rule $\Delta g = \pm 3$.

4. Approximate energy levels and spectra

The textbook term values of a symmetric top molecule, allowing for vibrational angular momentum and ignoring centrifugal terms, are (Herzberg 1991)

$$E(v_1, v_2, l_2, J, k)/hc = T_{\mathrm{vib}}(v_1, v_2, l_2) + B_v[J(J+1) - k^2] + C_v k^2 - 2(C\zeta_2)_v l_2 k, \tag{4.1}$$

where

$$T_{\mathrm{vib}}(v_1, v_2, l_2) \approx \omega_1(v_1 + \tfrac{1}{2}) + \omega_2(v_2 + 1),$$

$$B_v = (\hbar^2/2hcI_x)_{\mathrm{eff}} \quad \text{and} \quad C_v = (\hbar^2/2hcI_z)_{\mathrm{eff}}$$

are the effective rotational constants, and $(\zeta_2)_v$ is the effective value of the coefficient describing the coupling of the two components of Q_2 by Coriolis forces about the figure axis. At equilibrium, $(\zeta_2)_{\mathrm{e}}$ has the simple value -1. For actual levels, a perturbation treatment (Watson 1984) gives the approximate formula

$$(\zeta_2)_v = -1 + \frac{k'^2_{222}}{6\omega_2^2}(v_2 + 1), \tag{4.2}$$

where the cubic potential coefficient k'_{222} is the lowest-order parameter describing the deviation from circular contours in figure 2. The value of k'_{222} is about $k'_{222} = 6k_{222} \approx -1200\ \mathrm{cm}^{-1}$ (Carney *et al.* 1986). As a result, $(\zeta_2)_v$ for the ν_2 fundamental is about -0.948. The difference from -1 may seem small, but it is multiplied by $2C_v \approx 39.14\ \mathrm{cm}^{-1}$, together with the quantum numbers $l_2 k$.

Equation (4.1) with appropriate values for the 0 and ν_2 levels (including centrifugal distortion) and the selection rules $\Delta J = 1$, $\Delta k = \Delta l_2 = \pm 1$, $\Delta g = 0$ gives the calculated central region of the ν_2 fundamental shown in figure 3*a*. This consists of widely spaced J-structure and more narrowly spaced K-structure. The approximate K-structure spacing constant (Herzberg 1991) is $2[C_v - (C\zeta_2)_v - B_v]$. This would be 0 for the equilibrium values of the constants, but actually has a value of *ca.* $-12.1\ \mathrm{cm}^{-1}$ because of vibrational effects. However, the structure calculated according to this theory bears little relation to that observed (McKellar & Watson 1998), as shown in figure 3*c*.

The missing element here is l-type doubling and resonance (Oka 1967). In the general symmetric top molecule, this is an effect that has harmonic, Coriolis and anharmonic contributions (like the α vibration–rotation terms, of which it can be regarded as a particular case), but for the equilateral X_3 type of molecule, only the anharmonic term exists. The parameter describing the l-type doubling and resonance is $(q_2)_v$, and its equilibrium value is (Watson 1984)

$$(q_2)_{\mathrm{e}} = 2\left(\frac{B_{\mathrm{e}}}{\omega_2}\right)^{3/2} k'_{222}, \tag{4.3}$$

involving the same cubic potential constant k'_{222} as above.

The matrix elements of this interaction obey the selection rules $\Delta k = \Delta l_2 = \pm 2$, and so they connect levels with the same value of g. For each g in a vibrational level (v_1, v_2), we can set up a sub-matrix of dimension $(v_2 + 1)$ for the different values of l_2. The matrix elements are

$$\begin{aligned}\langle v_1, v_2, l_2 \pm 2, J, k \pm 2 | H_{\mathrm{eff}}/hc | v_1, v_2, l_2, J, k\rangle \\ = \tfrac{1}{4}[(q_2)_v + \text{higher-order terms}][(v_2+1)^2 - (l_2 \pm 1)^2]^{1/2} \\ \times [J(J+1) - k(k \pm 1)]^{1/2}[J(J+1) - (k \pm 1)(k \pm 2)]^{1/2}.\end{aligned} \tag{4.4}$$

Ab initio values of these matrix elements calculated by Carney & Porter (1980) were valuable in the initial assignment of the ν_2 fundamental (Oka 1980).

If we apply this to the fundamental level, we get a 2×2 matrix corresponding to $l_2 = -1$ and $+1$:

$$\boldsymbol{H}_{\mathrm{eff}} = \begin{bmatrix} H_{-1,-1} & H_{-1,1} \\ H_{1,-1} & H_{1,1} \end{bmatrix}, \tag{4.5}$$

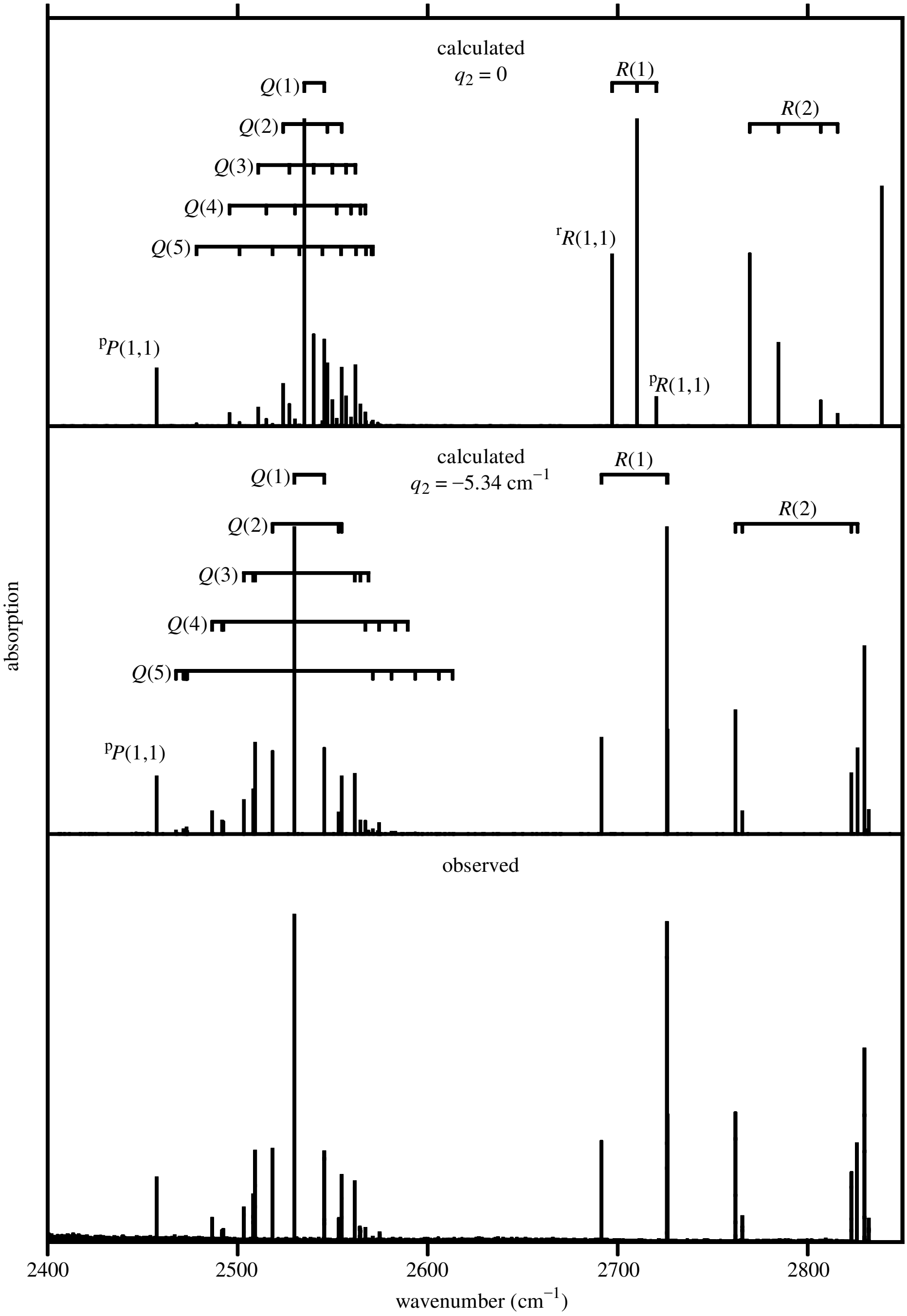

Figure 3. Calculated and observed spectra of the fundamental ν_2 band of H_3^+, showing the effect of l-type doubling and resonance. (*b*) Spectrum calculated with values of the parameters fitted to the observed spectrum, while in (*a*), the same parameter values are used, except that q_2 and the higher-order l-type doubling parameters are set equal to zero. (*c*) Observed spectrum of McKellar & Watson (1998).

and the energy levels are

$$E_{\mathrm{vr}}(v_1, v_2, J, g, U) = T_{\mathrm{vib}} + B_v J(J+1) + (C_v - B_v)(g^2+1) - 2(C\zeta_2)_v + \tfrac{1}{2}U\varDelta, \tag{4.6}$$

where $U = \pm 1$ and

$$\begin{aligned}\varDelta &= [(H_{1,1} - H_{-1,-1})^2 + 4H_{-1,1}H_{1,-1}]^{1/2} \\ &= \{16g^2[C_v - B_v - (C\zeta_2)_v]^2 \\ &\qquad + (q_2)_v^2[J(J+1) - g(g-1)][J(J+1) - g(g+1)]\}^{1/2}.\end{aligned} \tag{4.7}$$

For H_3^+, $C_v - B_v - (C\zeta_2)_v = -6.061\ \mathrm{cm}^{-1}$, $(q_2)_v = -5.340\ \mathrm{cm}^{-1}$. Because of the J quantum-number dependence, the $(q_2)_v$ term is usually dominant for low g.

Figure 3*b* shows a spectrum calculated with the inclusion of l-doubling and resonance, with parameters fitted to the observed spectrum. This now agrees well with the observed spectrum shown in figure 3*c*. Because the l-doubling is large and connects nearly degenerate levels, each J-transition is mainly split into a lower ($U = -1$) and an upper ($U = +1$) component, and then the spacing of the different transitions with $g' = k''$ within each component is small. This narrow spacing of the k structure made it difficult to give definite k numberings in the early assignments.

5. Variational types of calculations

While the effective-Hamiltonian approach described in § 4 is fairly successful up to about $J \approx 5$, it rapidly gets into difficulties at higher J. The reason is the difficulty of dealing with the large centrifugal distortion effects, and the usual power series in the components of $\boldsymbol{J}$ (Papoušek & Aliev 1982) does not converge adequately. This is a common problem in the spectra of light molecules, another well-known example being the water molecule. The difficulty arises from the fact that the basic molecular Hamiltonian contains only terms up to quadratic in the angular momentum, and so an expansion of degree 8, for example, increases far too rapidly for high values of J and k. One way of reducing this difficulty is to use a Padé formulation of the centrifugal terms (Polyansky 1985; Majewski *et al.* 1987), the numerator and denominator being polynomials with the degree of the numerator two greater than that of the denominator. However, this approach can suffer from numerical difficulties if the denominator becomes accidentally small for some levels.

In these circumstances, variational approaches come into their own. The rotational kinetic energy is an exactly known operator, and so it can, in principle, be calculated exactly for any value of $\boldsymbol{J}$. The accuracy of the calculations is, therefore, almost independent of the quantum number J, with only a slight degradation because higher-J levels explore larger and possibly lesser-known regions of the potential surface.

The potentialities of the variational approach were demonstrated by Miller & Tennyson (1987), who calculated the rotational levels of the zero-point and fundamental vibrational states and represented them in terms of molecular constants, for all the H and D isotopomers. Their calculated wavenumbers of individual lines (Miller & Tennyson 1988) compared with observed lines show a scatter of $0.154\ \mathrm{cm}^{-1}$ about an average shift of $0.187\ \mathrm{cm}^{-1}$ for ν_2 of H_3^+. (The shift occurs partly because Miller & Tennyson (1987) used a different choice of effective atomic mass from that used in the original adjustment of the MBB potential.) These scatter and shift parameters have no strong dependence on J, and so the calculated data can be used for further assignments, unless the lines happen to be very close together.

The assignments of bands involving levels with two or more vibrational quanta have depended heavily on these variational calculations. The emission spectrum of H_3^+ from Jupiter (Drossart *et al.* 1989) was identified by comparison with a laboratory spectrum (Majewski *et al.* 1989), but line assignments were difficult because the high rotational temperature (*ca.* 1100 K) meant that some of the strong lines had quite high values of J, up to $J' = 10$ in the Jupiter spectrum and $J' = 12$ in the laboratory spectrum. However, the calculations of Miller & Tennyson (Drossart *et al.* 1989; Majewski *et al.* 1989) gave unambiguous assignments in most cases, with a scatter of 0.398 cm^{-1} about a shift of 0.306 cm^{-1} for the laboratory $2\nu_2 - 0$ data.

Based on this success, a variational type of program using a Morse-base discrete variable representation was written (Watson 1994) and used to assign many of the lines of H_3^+ (Majewski *et al.* 1994) and D_3^+ (Amano *et al.* 1994) observed by various techniques in Ottawa. For this purpose, several of the coefficients of the MBB potential were adjusted to improve the fit, giving a semi-empirical potential. A similar approach was used by Dinelli *et al.* (1994) with a different initial potential.

The assignment of the spectrum of D_3^+ (Amano *et al.* 1994) paralleled that of H_3^+. In this case, the narrow separation of some of the K structure made some of the assignments particularly difficult, but the variational type of approach left little doubt about most of the assignments.

With improvements in the *ab initio* potentials, it is now largely unnecessary to make empirical adjustments. The recent calculations of Polyansky & Tennyson (1999), based entirely on the *ab initio* data of Cencek *et al.* (1998), give calculated transition wavenumbers for H_3^+ and its D isotopomers that are almost all within 0.1 cm^{-1} of the laboratory wavenumbers; this is much less than the typical spacing of the lines in these spectra.

6. Calculations using hyperspherical coordinates

The spectra of H_3^+ obtained by the Oka group in Chicago have been gradually climbing up the ladder of vibrational states (McCall, this issue). At *ca.* 10 000 cm^{-1} above the zero-point level, or just above $4\nu_2$, is the barrier to linearity, and it is important to use wave functions that behave correctly in the vicinity of the barrier. This is most easily accomplished by using hyperspherical coordinates (Johnson 1983). These have been applied to H_3^+ vibration–rotation calculations by a number of authors (Whitnell & Light 1989; Bartlett & Howard 1990; Carter & Meyer 1994; Wolniewicz & Hinze 1994). Further calculations extending to higher values of J, with calculated intensities, will probably be required to assist the experimental search.

The hyperspherical coordinates consist of the Euler angles $\alpha\beta\gamma$ and internal coordinates $\rho\theta\phi$. The latter are closely related to the normal coordinates $Q_1Q_{2\mathrm{a}}Q_{2\mathrm{b}}$ (Watson 1995):

$$\left.\begin{aligned}\rho\cos\theta &= r_\mathrm{e} + m^{-1/2}Q_1,\\ \rho\sin\theta\cos\phi &= m^{-1/2}Q_{2\mathrm{a}},\\ \rho\sin\theta\sin\phi &= m^{-1/2}Q_{2\mathrm{b}},\end{aligned}\right\}$$

where m is the chosen atomic mass. The vibration–rotation Hamiltonian in these coordinates is

$$H = \frac{\hbar^2}{2m}\left\{-\frac{\partial^2}{\partial\rho^2} + \frac{15}{4\rho^2} + \frac{\boldsymbol{L}^2}{\rho^2}\right\} + V(\rho,\theta,\phi), \tag{6.1}$$

where $\boldsymbol{L}^2$ is the square of the grand angular momentum (Johnson 1983):

$$\boldsymbol{L}^2 = -\frac{1}{\sin 4\theta}\frac{\partial}{\partial\theta}\sin 4\theta\frac{\partial}{\partial\theta} + \frac{(p_\phi + \frac{1}{2}J_c)^2}{\cos^2\theta} + \frac{(p_\phi - \frac{1}{2}J_c)^2}{\sin^2\theta} + \frac{J_a^2}{\sin^2(\theta - \frac{1}{4}\pi)} + \frac{J_b^2}{\cos^2(\theta - \frac{1}{4}\pi)}. \tag{6.2}$$

Here, p_ϕ is $-\mathrm{i}\partial/\partial\phi$, and J_a, J_b, J_c are the components of the total angular momentum (in units of $\hbar$) with the principal axes taken so that $I_a \leqslant I_b \leqslant I_c$. The vibrational volume element is taken as $\mathrm{d}\tau = \sin 4\theta\,\mathrm{d}\rho\mathrm{d}\theta\mathrm{d}\phi$, and the coordinates have the ranges $0 \leqslant \rho \leqslant \infty$, $0 \leqslant \theta \leqslant \pi/4$, $0 \leqslant \phi \leqslant 4\pi$.

The eigenvalues of $\boldsymbol{L}^2$ are $L(L+4)$, where $L = 0, 1, 2, \ldots$. (Frequently, K is used rather than L, but it is desirable to find a different symbol.) Also, $\boldsymbol{L}^2$ commutes with $\boldsymbol{J}^2$, with any space-fixed component of $\boldsymbol{J}$, and with p_ϕ, giving the quantum numbers J, m, and ν, respectively. Because of the range of ϕ, the dependence on ν is $\exp(\mathrm{i}\nu\phi/2)$. There is an additional quantum label, which can be taken as K_a, the quantum number of J_a. Because J_a^2 rather than J_a occurs in $\boldsymbol{L}^2$, it is sufficient to take K_a as non-negative. Then the eigenfunctions of $\boldsymbol{L}^2$, which are the hyperspherical harmonics (Avery 1989) in this coordinate system, can be written (Wolniewicz 1989)

$$\Psi^{LJ}_{\nu m K_a} = N\mathrm{e}^{\mathrm{i}\nu\phi/2}\sum_i \langle\alpha\beta\gamma|mJk_i\rangle(1+C)^{\lambda_i/2}(1-C)^{\mu_i/2}\sum_{n=0}^{n_{\max}(i)} c_{in}C^{K_a+n}. \tag{6.3}$$

Here, N is a normalization factor, C is $\cos 2\theta$, and $\langle\alpha\beta\gamma|mJk_i\rangle$ is a normalized Wigner rotation matrix element (Brink & Satchler 1993)

$$\langle\alpha\beta\gamma|mJk_i\rangle = [(2J+1)/4\pi^2]^{1/2}\mathcal{D}^J_{mk_i}(\alpha\beta\gamma)^*. \tag{6.4}$$

The quantum numbers L, ν and k_i differ by even integers, so that we can take the i sum such that $k_i = \nu - 2i$ and $\nu - J \leqslant 2i \leqslant \nu + J$. The indices $\lambda_i = \frac{1}{2}|\nu + k_i|$ and $\mu_i = \frac{1}{2}|\nu - k_i|$ are both integers, and the n-sum is a polynomial with $n_{\max}(i) = (L - \lambda_i - \mu_i)/2 - K_a$. The singularity of (6.2) for $\theta \sim \pi/4$, that is $C \sim 0$, means that Ψ should be an eigenfunction of J_a^2 at this geometry; this is achieved by constraining the coefficients for $n = 0$ to be the Wigner rotation functions (Brink & Satchler 1993)

$$c_{i0} = d^J_{k_i,K_a}(\pi/2) \equiv \Delta^J_{k_i,K_a}. \tag{6.5}$$

Equation (6.3) is substituted in the eigenvalue equation for Ψ, and a recursion relation is obtained, which is solved for the coefficients c_{in}. This procedure is applied for descending values of K_a, starting at $K_a = J$, and at each step the solution (if there is one) is Schmidt-orthogonalized to the solutions with higher values of K_a and the same values of $LJ\nu m$. The whole algorithm and the numbers of solutions with different values of the quantum numbers have been described by Wolniewicz (1989). It is interesting that it is possible to give expressions for the coefficients c_{in} for ranges of values of the quantum numbers, but there does not seem to be an explicit general formula for these coefficients (excluding artificial 'formulae' that list all the particular cases).

Applications of these hyperspherical harmonics as angular bases in calculations for H_3^+ and its D isotopomers have been given by Wolniewicz and colleagues (Wolniewicz & Hinze 1994; Alijah *et al.* 1995*a*, *b*; Alijah & Beuger 1996).

To relate these hyperspherical harmonics to the wave functions in § 3, it is necessary to change first to Eckart axes by putting (Watson 1995)

$$\gamma = \gamma^{\mathrm{E}} + \tfrac{1}{2}\pi - \tfrac{1}{2}\phi, \tag{6.6}$$

where γ^{E} is the value of γ for the Eckart axes. Also, i can be replaced by l_2, and $\nu - k_i = 2l_2$, $\mu_i = |l_2|$. Thus, the hyperspherical harmonic can be written

$$\begin{aligned}\Psi^{LJ}_{\nu m K_a} = N i^{\nu} \sum_{l_2 \geqslant (\nu-J)/2}^{\leqslant (\nu+J)/2} (-1)^{l_2} \langle \alpha\beta\gamma^{\mathrm{E}} | mJk = \nu - 2l_2 \rangle \\ \times 2^{(|\nu+l_2|+|l_2|)/2} \cos^{|\nu+l_2|}\theta \sin^{|l_2|}\theta \mathrm{e}^{\mathrm{i}l_2\phi} \sum_{n=0}^{n_{\max}(l_2)} c_{l_2 n} C^{K_a+n}.\end{aligned} \tag{6.7}$$

From this it can be shown that the $(\theta\phi)$ dependence of the Eckart-frame hyperspherical harmonics can be written entirely in terms of the spherical harmonics $Y^{l}_{l_2}(\theta\phi)$ for $l = L, L-2, L-4, \ldots$, but care must be taken because the volume element $\mathrm{d}\omega = \sin 4\theta \, \mathrm{d}\theta \mathrm{d}\phi$ and range of coordinates $0 \leqslant \theta \leqslant \pi/4$, $0 \leqslant \phi \leqslant 2\pi$, are different from those normally assumed.

It is seen that Ψ is a linear combination of functions with the same value of $\nu = k + 2l_2 = g + 3l_2$. Analogous to equations (3.2) and (3.3), we have

$$(123)^* \Psi^{LJ}_{\nu m K_a} = \mathrm{e}^{-\nu\pi\mathrm{i}/3} \Psi^{LJ}_{\nu m K_a}, \tag{6.8}$$

$$(23) \Psi^{LJ}_{\nu m K_a} = (-1)^{J} \Psi^{LJ}_{-\nu m K_a}, \tag{6.9}$$

for a suitable choice of the relative phases of $\Psi^{LJ}_{\nu m K_a}$ and $\Psi^{LJ}_{-\nu m K_a}$. The symmetry quantum number M used by Watson (1994) is the solution of $M = \pm\nu$ (mod 6) in the range $0 \leqslant M \leqslant 3$. Equation (6.8) means that the potential energy, for example, has matrix elements with $\Delta\nu \equiv 0$ (mod 6).

A full calculation for H_3^+ with J up to 4, using hyperspherical harmonics as the angular basis, is described by Wolniewicz & Hinze (1994). Obviously, it will be desirable to extend this calculation to higher J and calculate transition intensities, in order to assist with the search for transitions to or from levels near the linear barrier.

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Discussion

F. Scappini (*Instituto di Spettroscopia Molecolare, Bologna, Italy*). You have not mentioned the forbidden rotation spectrum of H_3^+. How accurately can the rotation transition frequencies be calculated? This spectrum is, in fact, of possible astrophysical interest.

J. K. G. Watson. I agree that this forbidden rotational spectrum (Watson 1971) might be observable in emission from astrophysical sources, because the populations in the upper levels may build up.

Some time ago (Watson 1993) I calculated the two lowest-frequency pure rotational transitions of H_3^+ as $(J, K) = (4, 4)$–(3,1) and (7,6)–(6,3), at 217.925(18) and 277.551(34) GHz, respectively, but cautioned that the uncertainties (from propagation of errors) may be underestimated. The tabulation of Dinelli *et al.* (1997) gives similar frequencies, 217.859 and 277.443 GHz. Both of these pairs of values are calculated from potentials adjusted to fit the observed spectrum. A term-value fit of the observed spectrum (Watson 1994) gave 217.680 and 277.760 GHz, but the above calculated frequencies are probably more accurate. The fully *ab initio* calculation of Polyansky & Tennyson (1999) gives 215.533 GHz for the first frequency, but does not extend high enough in J for the second frequency; the discrepancy of about 2 GHz is of the same order of magnitude as for their other calculated frequencies. The values from the fitted potentials possibly give the best estimates at present, and the discrepancy between them gives some idea of the uncertainties involved.

J. B. A. MITCHELL (*PALMS, Université de Rennes, France*). You showed the beautiful clear spectrum of H_3^+ in Jupiter. Could you comment on why it was so difficult to find the spectrum in the laboratory.

J. K. G. WATSON. The question refers to the beautifully clean spectrum of the ν_2 fundamental of H_3^+ from Jupiter (Maillard *et al*. 1990), which was shown during my talk, but is not mentioned in the main body of this paper.

The difficulty with the laboratory spectrum was that the technique was being developed during this search. I believe that Oka's (1980) spectrum was the first observed infrared absorption spectrum of a polyatomic molecular ion. He was using a tunable difference-frequency laser source, and there was quite a serious search problem. Shortly after Oka observed H_3^+, it was found that the sensitivity could be greatly increased by modulating the discharge current, which produces a modulation of the ion concentration; this is much more effective than the frequency modulation used by Oka. The infrared Fourier transform spectrum (Nakanaga *et al*. 1990; McKellar & Watson 1998) might have been observed at that time, but of course its eventual observation depended on knowledge of the best conditions derived from the earlier work.

The Jupiter spectrum is an emission spectrum. While the emission spectrum is known in the laboratory (Majewski *et al*. 1987, 1989, 1994), it is heavily contaminated by the many-line spectrum between excited states of H_2; Majewski *et al*. used the pressure dependence of the intensities to discriminate between the H_2 and H_3^+ lines. The Jupiter spectrum is supposed to be due to thermal emission, and the temperature is not high enough to produce these excited states of H_2.

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