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The vibration–rotation spectrum and anharmonic potential of H_3^+

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Abstract

Some qualitative effects of anharmonicity on the spectra of H_3^+ and D_3^+ between low vibrational levels are described. Using large-basis vibration–rotation calculations with a Morse-based discrete variable representation for the vibrations and a symmetric-top basis for the rotations, new spectra of H_3^+ and D_3^+ have been assigned. This procedure was assisted by adjusting eight coefficients for H_3^+ and six coefficients for D_3^+ in the Meyer–Botschwina–Burton ab initio potential function, and eventually 621 new and old lines of H_3^+ to levels up to $3\nu_2$ and 529 new and old lines of D_3^+ to levels up to $2\nu_2$ have been fitted with standard deviations of 0.118 and 0.059 cm^{-1} , respectively. An attempt is made to compare five different potential energy functions for the H_3^+ system, two ab initio and three adjusted to fit spectra of H_3^+ or D_3^+ , by expanding them by the same procedure in the same variables. For extension of the present work to higher vibrational levels, more accurate boundary behaviour at linear configurations will be required, and some aspects of the use of hyperspherical coordinates are discussed.

1. Introduction: anharmonic effects in the low-energy spectrum of H_3^+

The equilibrium geometry of the H_3^+ molecular ion was first shown to be nonlinear in 1938 in the pioneering ab initio calculations of Hirschfelder [1]. However, the prediction of the equilateral triangular D_{3h} structure had to await the development of more powerful computational techniques in the 1960s [2–4]. This structure was first established experimentally by three groups using the Coulomb explosion method [5].

As H_3^+ has no permanent electric dipole moment, and the electronic spectrum is expected to be diffuse, apart from the extremely weak intersystem transition $^3\Sigma_u^+ (\text{D}_{\infty h}) \rightarrow ^1A'_1 (\text{D}_{3h})$, the allowed infrared fundamental $\nu_2(\text{e}')$ represented the most likely spectrum to be observed first. Calculation of this infrared band 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 $\omega_1 = 3471$ and $\omega_2 = 2814 \text{ cm}^{-1}$ [6] as the harmonic values of the fundamental vibrational frequencies. However, the effects of anharmonicity are large. This was shown in calculations by Carney and Porter, who first calculated an ab initio potential surface [6] and then solved for the vibration–rotation energy levels on this surface [7,8]. The first large effect of anharmonicity was in the calculated 1–0 vibrational intervals of $\nu_1 = 3185$ and $\nu_2 = 2516 \text{ cm}^{-1}$, 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 cm^{-1} by Oka [9] and of D_3^+ at 1835 cm^{-1} by Shy et al. [10]. Thus the anharmonic predictions greatly reduced the spectroscopic search problem.

The second large effect of anharmonicity is in the rotational structure of the ν_2 fundamental band. For such a perpendicular fundamental of an oblate sym-

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metric top, the K-structure spacing constant is $C_v - (C\xi_2)_v - B_v$ [11]. At equilibrium we have $B_e = 2C_e$, and the form of the (Q_{2a}, Q_{2b}) degenerate normal coordinates gives $(\xi_2)_e = -1$ [11]. Thus the equilibrium value of the K-structure spacing constant is zero. Perturbation calculations [12] give

$$C_v - (C\xi_2)_v - B_v = - \left(\frac{3B_e^2}{\omega_2} + \frac{B_e(k'_{222})^2}{12\omega_2^2} \right) (v_2 + 1), \quad (1)$$

where the cubic potential constant is defined as the third derivative

$$k'_{222} = \frac{1}{hc} \frac{\partial^3 V}{\partial q_{2a}^3}, \quad (2)$$

with respect to the dimensionless normal coordinate q_{2a} . Although the anharmonic term is not dominant, it plays an important role in determining the precise value of this spacing constant. More important, the fact that $C_v - (C\xi_2)_v - B_v$ is small means that the l -type doubling is resonant for all values of K . The l -doubling constant [12]

$$q_2 = 2 \left(\frac{B_e}{\omega_2} \right)^{3/2} k'_{222} \quad (3)$$

depends directly on the anharmonicity in this particular case. Its large value ($q_2 \approx 5 \text{ cm}^{-1}$) means that the structure of the fundamental band corresponds to the following approximate pattern: first each $P(J)$, $Q(J)$ and $R(J)$ transition is split into an upper and lower l -doubling component; then each l -doubling component has a closely-spaced K-structure. This is illustrated in Fig. 3 of Ref. [13]. The values of the constants, and particularly q_2 , predicted by Carney and Porter [8] made it comparatively easy to assign the rotational structure of the band when it was first observed by Oka [9]. However, the numbering of the closely-spaced K-structure became difficult when higher- J transitions were observed [13,14].

The general interest in H_3^+ stimulated further ab initio calculations, particularly one in 1984 by Meyer, Botschwina and Burton (MBB) [15]. Their potential surface has been used as a standard for the last few years, although a surface based on somewhat superior ab initio calculations was published by Lie and Frye (LF) in 1992 [16]. Calculations of the rotational levels of the two-quantum vibrational states by Miller and

Tennyson [17] based on the MBB potential were instrumental in assigning the lines of the $2\nu_2^0 - \nu_2^1$, $2\nu_2^2 - \nu_2^1$ and $\nu_1 + \nu_2^1 - \nu_1$ hot bands [18] and the $2\nu_2^2 - 0$ overtone band, which was first observed in emission both from the planet Jupiter [19] and in the laboratory [20]. In these spectra, two particular effects of anharmonicity were important, both predicted by Carney and Porter [6,7]: (i) the Einstein A coefficient for the harmonically forbidden band $2\nu_2^2 - 0$ is greater than for the allowed fundamental $\nu_2^1 - 0$; and (ii) the separation between the $2\nu_2^0(A'_1)$ and $2\nu_2^2(E')$ components of the $2\nu_2$ vibrational state, which vanishes in the harmonic approximation, is large (220.6 cm^{-1}). In the $2\nu_2$ state the l -doubling operator is off-diagonal between the $2\nu_2^0(A'_1)$ and $2\nu_2^2(E')$ components, and so its effects are less important than in the fundamental. Thus the $2\nu_2^2 - 0$ band looks much more like a classic oblate top perpendicular band, but with $\zeta'_{\text{eff}} \approx +2$.

A considerable amount of data has now accumulated on the various H and D isotopomers of H_3^+ , including all three fundamental bands of H_2D^+ and D_2H^+ , the pure rotational spectrum of H_2D^+ , and 621 and 529 lines of various bands of H_3^+ [21] and D_3^+ [22], respectively. In the most recent work [21,22], the MBB surface was fitted to the observed wavenumbers by adjusting the coefficients of a number of the lower-order terms. This procedure has the advantage over the effective-Hamiltonian methods used previously [13,14] that a large amount of data can be fitted with a comparatively small number of adjustable parameters. Also, one avoids the poor convergence of the perturbation expansions used in the effective-Hamiltonian approach.

The MBB potential surface [15] has been used as a basis for semiclassical calculations in attempts to understand the extensive near-dissociation spectrum of H_3^+ [23–25]. Associated with this endeavour are quantum calculations of all the bound $J=0$ levels of H_3^+ supported by the MBB surface [26–28]. Since the MBB ab initio calculations were aimed at the shape of the potential near its minimum, and extended to less than 65% of the dissociation energy, these calculations cannot really be expected to have much quantitative validity. Another complication is the existence of a crossing between the potential surfaces of the ground state $^1A'_1(D_{3h})$ surface and the lowest excited singlet state $^1E'(D_{3h})$. Most potential surfaces for the ground state do not have the correct conical shape at this

crossing, but a potential that takes it into account was published in the book by Murrell et al. [29]. The crossing occurs more than 9 eV above the minimum, and therefore at roughly double the lowest dissociation channel, but there might be significant vibronic effects on the ground state energies as a result of the interactions between the two states. These will show up as nuclear-mass-dependent corrections in the vibration–rotation Hamiltonian, and so might be detectable from a comparison of the different isotopomers. At present, the data of different isotopomers have generally been fitted separately, except for the work of Jensen [30], who did a simultaneous fit of all the isotopic data available at that time, but did not include non-Born–Oppenheimer terms in the Hamiltonian.

2. Comparison of potential surfaces for H_3^+

A variety of coordinate systems have been used in variational-type calculations for H_3^+ . In the present calculations the three bond lengths (r_1, r_2, r_3) are used, with a Morse-based discrete variable representation (DVR) for each of them [31]. After obtaining the approximate vibrational eigenfunctions, the matrix elements of the rotational terms in the Hamiltonian are calculated between the lowest 50 or so of them. Using D_{3h} -symmetrised products of these vibrational eigenfunctions with a complete set of symmetric-top rotational functions, the (truncated) matrix of the complete vibration–rotation Hamiltonian could be set up and diagonalised. The second step was the same as for the “supermatrix” approach [14], which used the matrix elements between the lowest few vibrational eigenfunctions calculated by Carney and Porter [8] and made an approximate extrapolation of them to higher vibrational levels.

The MBB potential energy function is an expansion in the form [15]

$$V(r_1, r_2, r_3) = \sum_{nmk} V_{nmk} S_a^n S_e^{2m+3k} \cos(3k\phi), \quad (4)$$

in terms of symmetrised Morse coordinates,

$$\begin{aligned} S_a &= (\tilde{R}_1 + \tilde{R}_2 + \tilde{R}_3) / \sqrt{3}, \\ S_x &= (2\tilde{R}_1 - \tilde{R}_2 - \tilde{R}_3) / \sqrt{6} = S_e \cos \phi, \\ S_y &= (\tilde{R}_2 - \tilde{R}_3) / \sqrt{2} = S_e \sin \phi, \end{aligned} \quad (5)$$

where \tilde{R}_i is

$$\tilde{R}_i = \{1 - \exp[-\beta(r_i/r_a - 1)]\} / \beta. \quad (6)$$

The potential contains a linear term in S_a , and so the parameter r_a is not the true equilibrium bond length, although the notation r_e for it is the usual one in the literature. Values of the coefficients V_{nmk} were obtained by Meyer, Botschwina and Burton [15] by fitting their ab initio calculations, and they also proposed a semiempirical adjustment of the coefficient of S_e^2 to fit the observed ν_2 of H_3^+ .

Comparison between the calculated and observed vibration–rotation spectra showed systematic differences, and some of the MBB potential constants were adjusted to optimise the fit. In the end, 8 coefficients were adjusted for H_3^+ and 6 for D_3^+ , where the data only extend to the two-quantum vibrational levels. The parameters of the MBB ab initio potential [15] and the H_3^+ [21] and D_3^+ [22] adjusted potentials are shown in Table 1. Any significant differences between the H_3^+ and D_3^+ potentials indicate possible non-Born–Oppenheimer effects. However, the latter affect the effective masses of the nuclei [32] as well as the effective potential, and so have not been properly included here. Nevertheless, the non-Born–Oppenheimer terms should have an approximate m^{-1} dependence on the atomic mass, and so the D_3^+ potential should be about midway between the H_3^+ potential and the Born–Oppenheimer potential.

A comparison with the coefficients in the Lie–Frye [16] and Dinelli–Miller–Tennyson (DNT) [33] potentials is not straightforward, because they use different Morse parameters r_a and β and a different weighting of the ab initio points. In particular, Lie and Frye fitted a sixth-degree function in the Morse variables, and then froze the coefficients of these terms and adjusted the seventh-degree coefficients separately. This is probably a good way of minimising the size of the seventh-degree coefficients, but differs from the procedure of MBB [15], who fitted all degrees up to seven simultaneously. A further complication is the fact that there appear to be two typographical errors in Table 1 of Ref. [16]. Dinelli et al. [33] adjusted 11 coefficients in the LF potential to fit the vibration–rotation term values of H_3^+ .

To make a comparison, it was decided to fit the MBB potential (with their semiempirical correction to the S_e^2 term) and the H_3^+ and D_3^+ adjusted potentials by

Table 1

Coefficients ^a of MBB ab initio and adjusted potentials of H₃⁺ and D₃⁺

<i>n</i>	<i>2m</i>	<i>3k</i>	ab initio ^b	H ₃ ⁺ ^{c,e}	D ₃ ⁺ ^{d,e}
1	0	0	130	131.6(5.0)	139.0(4.9)
2	0	0	204603	204371.7(8.0)	204457.7(8.1)
0	2	0	266219	266521.3(8.8)	266441.1(8.3)
3	0	0	−49832	−49206.6(26.0)	
1	2	0	−241851	−240541.7(50.0)	−239477.0(27.3)
0	0	3	−6490	−5802.1(18.2)	5703.7(10.1)
4	0	0	25002		
2	2	0	131115		
1	0	3	88684	90959.9(91.9)	
0	4	0	44851	45247.9(58.2)	44455.6(54.0)
5	0	0	−2115		
3	2	0	−50919		
2	0	3	−28688		
1	4	0	−11820		
0	2	3	−3185		
6	0	0	4346		
4	2	0	50424		
3	0	3	57028		
2	4	0	120688		
1	2	3	73273		
0	6	0	15068		
0	0	6	−339		
7	0	0	−277		
5	2	0	887		
4	0	3	9333		
3	4	0	23840		
2	2	3	104361		
1	6	0	37493		
1	0	6	−3238		
0	4	3	7605		

^a Units: μE_h . The parameters in the Morse variables \tilde{R}_n , Eq. (6), are $r_n = 1.6504 a_0$, $\beta = 1.3$.^b The coefficients of the ab initio 87 CGTO ($N=7$) potential of Meyer, Botschwina and Burton [15] are quoted. In the usual MBB potential the 020 coefficient is adjusted to 266725 to fit the observed ν_2 of H₃⁺.^c Ref. [20]. Eight coefficients were adjusted to fit 621 lines of H₃⁺ with equal weights. The standard deviation of the fit was 0.118 cm^{−1}.^d Ref. [21]. Six coefficients were adjusted to fit 529 lines of D₃⁺, most with unit weight. The standard deviation for a line of unit weight was 0.059 cm^{−1}.^e The standard deviations of the coefficients are given in parentheses.

calculating their values at the LF points and using the same weighting and fitting procedure as them. This gives the parameters in Table 2. The uncertainties given there are purely those from this fitting procedure. The ab initio data of Frye et al. [34] were also fitted to find the uncertainties in the LF coefficients. The DMT uncertainties are from the original paper [33].

The principal conclusion from Table 2 is the usual one, that there are large uncertainties in many of the coefficients, and they are often strongly correlated so that comparisons of individual coefficients may not be very meaningful. While there is general agreement

between the MBB and LF potentials for the coefficients up to quartic, the higher-degree coefficients bear little resemblance to each other, even allowing for the large uncertainties.

The different behaviour of the higher-degree contributions will tend to produce differences between the potentials obtained by adjusting either the MBB or the LF potential. Thus the H₃⁺ and D₃⁺ coefficients from the present work are in better agreement with each other than with the DMT potential. In particular, both the present fits favour large values (2814 or 2910 μE_h) for the 003 coefficient in the LF representation, whereas

Table 2
Coefficients of potentials expanded in LF variables ^a

V^b	MBB	H_3^+	D_3^+	LF ^c	DMT ^d
100	−90(12)	−88	−80	−15(7)	−45(1)
200	204667(67)	204434	204521	204613(41)	204091(2)
020	266819(28)	266614	266533	266482(17)	266648(2)
300	−40884(248)	−40268	−40890	−40228(151)	−39558(14)
120	−224006(950)	−222756	−220677	−215816(579)	−211590(18)
003	2132(134)	2814	2910	2111(81)	2241(8)
400	24935(698)	24974	24935	24946(425)	
220	186972(6036)	187255	187378	147173(3681)	134320(65)
103	93661(1098)	96075	93865	93087(670)	90019(208)
040	45305(306)	45760	45016	45547(187)	43919(14)
500	−117(945)	−106	−119	109(576)	
320	−86370(7536)	−86346	−86230	−53083(4596)	
203	−11850(3980)	−11416	−11707	6097(2428)	
140	89552(4956)	89979	89719	55216(3023)	
023	2124(766)	2222	2134	5751(467)	
600	3479(1844)	3479	3473	4422(1125)	
420	15008(7932)	14977	15026	57593(4838)	
303	34589(5799)	34778	34663	73538(3537)	88933(2550)
240	−100788(24393)	−100882	−100780	36870(14877)	
123	114315(6906)	114564	114416	88511(4212)	
060	12361(998)	12391	12364	15090(609)	19430(21)
006	−2433(282)	−2431	−2433	−841(172)	
700	−5(140)	−5	−5	8(83)	
520	45872(24212)	45983	45920	−27444(14465)	
403	5946(5909)	5961	5954	−11406(3530)	
340	−28447(13625)	−28516	−28478	17652(8140)	
223	493(2988)	494	493	2645(1785)	
160	3574(1586)	3583	3578	−2407(947)	
106	−170(684)	−171	−170	−29(408)	
043	−290(185)	−290	−290	115(111)	

^a Units: μE_h . The parameters in the Morse variables \tilde{R}_e , Eq. (6), are $r_a = 1.6499 a_0$, $\beta = 1.375$. The standard deviations of the MBB, LF and DMT potentials are given in parentheses; those for the H_3^+ and D_3^+ were essentially identical to those for the MBB potential. The MBB and LF errors are for fitting the potential with the LF procedure, whereas those for DMT are from adjusting 11 coefficients to fit the term values of H_3^+ .

^b The three numbers are n , $2m$ and $3k$ for the potential terms in Eq. (4).

^c The standard deviations were obtained by repeating the fit of Ref. [16]. From this fit the 060 and 006 coefficients appear to have been interchanged in Ref. [16], and also the sign of the coefficient with numerical value 841 seems to be incorrect.

^d The interchange of 060 and 006 was corrected by DMT, but the sign of 006 was not changed. Allowing this coefficient to adjust gives a positive value (B.M. Dinelli, private communication).

the MBB, LF and DMT potentials have lower values (2132, 2111 and 2241 μE_h). This coefficient is closely associated with the constant k'_{222} , and from the arguments in Section 1, it should be well determined and relatively uncorrelated. It will therefore be interesting to explore the reason for this difference.

The difference between the true r_e for H_3^+ determined from the present fit, 1.65009(1) a_0 and from the DMT fit, 1.65000(1) a_0 , is small but seems significant, in view of the fact that much of the same experimental

data forms the basis of both fits. One difference between them is the fact that the present H_3^+ potential was fitted to the wavenumbers of the lines, whereas the DMT potential was fitted to term values of the levels. The latter procedure requires calculated values for some of the lowest term values. For self-consistency, these values should be calculated from the fitted potential, but this may not have been done in the work of DMT [33].

3. Near-linear behaviour

Part of the reason for using the (r_1, r_2, r_3) coordinates and the Morse basis was the fact that the MBB potential is expanded in Morse coordinates. However, the constraints on the ranges of (r_1, r_2, r_3) cause difficulties. One type of constraint familiar from diatomic molecules is the condition $r_i \geq 0$, $i = 1-3$, whereas the range assumed in the Morse basis is $[-\infty, \infty]$. This is more a difficulty in principle than in practice, because typical Morse wavefunctions have extremely small amplitudes for $r_i < 0$. However, the other type of constraint, the three triangle conditions

$$r_i \leq r_j + r_k, \quad i \neq j \neq k, \quad (7)$$

are much more serious. The equality here occurs for linear configurations. The lowest saddle point at linear geometries is about 12500 cm^{-1} above the zero-point level for H_3^+ , and so becomes important in the $5 \nu_2$ vibrational state, but has an influence on lower states as well.

For vibrational levels near and above the barrier to linearity it becomes important to ensure that the wavefunctions have the correct behaviour at linear geometries. So far I have used an ad hoc solution of introducing a high (10^6 cm^{-1}) artificial potential for unphysical geometries. This has the effect of giving the wavefunction small amplitudes for these geometries. However, it requires that the vibrational wavefunctions essentially vanish at the linear configurations, and this is not correct boundary behaviour for the $J=0$ functions.

To discuss this problem in more detail, it is convenient to introduce Δ , the area of the nuclear triangle,

$$\Delta = \frac{1}{4} [(r_1 + r_2 + r_3)(-r_1 + r_2 + r_3) \times (r_1 - r_2 + r_3)(r_1 + r_2 - r_3)]^{1/2}. \quad (8)$$

Naturally, Δ becomes zero for linear configurations, and then it is imaginary for unphysical configurations. We also need the alternative well-known formula

$$\Delta = \frac{1}{2} r_2 r_3 \sin \omega, \quad (9)$$

where ω is the angle measuring the deviation from linearity of r_2 and r_3 . Now for the bending vibration of a linear molecule the wavefunction near linearity behaves as

$$\psi \sim \omega^{|l|}, \quad (10)$$

where the volume element $\sin \omega d\omega$ is assumed. The volume element $dr_1 dr_2 dr_3$ used in the Morse calculations is

$$dr_1 dr_2 dr_3 = \frac{r_2 r_3}{r_2 + r_3} dr_2 dr_3 \sin \omega d\omega. \quad (11)$$

Thus the two volume elements are equivalent as far as ω is concerned. Using the fact that $\omega \sim \Delta$ near linear configurations, we can put the near-linear behaviour of the wavefunction in the symmetrical form $\psi \sim \Delta^{|l|}$, which should apply for the three different types of near-linear geometries. The exponent $|l|$ is an integer. Near linear geometries the molecule is an asymmetric top, with a -axis as the near-linear axis. Thus we can replace the notation l by that for the asymmetric-top quantum number K_a , as has been done by Carter and Meyer [35], giving

$$\psi \sim \Delta^{K_a}. \quad (12)$$

The component K_a of the angular momentum cannot be greater than the magnitude J , giving $K_a \leq J$.

It can be seen that for $J=0$ we have $K_a=0$, and therefore Eq. (12) gives no restriction on the behaviour of the wavefunction at the boundary. This is already well known for conventional linear molecules, where the restrictions on the wavefunctions for Σ (i.e. $K_a=0$) vibrational states is that they should be even functions of ω that do not vanish for $\omega=0$. (Even functions that do vanish are Δ , Γ , ... states.) Thus my artificial potential wall, which essentially gives $\psi=0$ on the boundary, does not achieve the correct boundary conditions for $J=0$. Before this wall was introduced, the matrix elements of the coefficients of the rotational terms containing Δ^{-2} factors tended to blow up for vibrational levels near or above the linear barrier. When ψ is made to vanish as $\Delta \rightarrow 0$, this difficulty is avoided, but this procedure will obviously not give correct results for $K_a=0$ states near or above the linear saddle point. This boundary condition represents a kind of compromise in order to use a single boundary condition for all rotational levels, whereas in fact the vibrational wavefunction should have different boundary behaviour for different rotational levels.

A way of avoiding this problem is to use the Pekeris coordinates [36]

$$R_i = \frac{1}{2}(r_j + r_k - r_i), \quad i \neq j \neq k. \quad (13)$$

These cover the range $0 \leq R_i \leq \infty$ independently. Calculations of vibrational energies using these coordinates have been described recently by Wei and Carrington [37]. Unfortunately, they are rather awkward coordinates near dissociation.

It seems appropriate at this point to comment on calculations of “all the (bound) vibrational states” of H_3^+ . “Vibrational states” are actually defined differently for nonlinear and linear molecules. For nonlinear molecules they are defined as the $J=0$ states. However, taking a triatomic molecule as an example, for linear molecules they are usually defined as all $(v_1, v_2^{1/2}, v_3)$ states. As $J \geq |l_2|$, a calculation of all $J=0$ states would miss such vibrational states as the bending fundamental of a linear molecule, which has $v_2 = |l_2| = 1$. One reason for raising this point is that part of the motivation for calculating “all the vibrational states” was to find the quantum equivalents of the semiclassical “horse-shoe orbits”. These can be described as large-amplitude bending motions through the linear configuration, so in other language they would be described as quasi-linear states. However, the different boundary behaviour for different values of K_a can produce significant differences in the levels and wavefunctions. Thus a calculation restricted to $J=0$ might miss some essential aspect of the whole picture.

4. Hyperspherical coordinates

The most promising coordinates for treating the boundary conditions correctly seem to be hyperspherical coordinates [38]. These have been applied to H_3^+ by Whitnell and Light [39], Bartlett and Howard [40] and Carter and Meyer [35,41]. Although hyperspherical coordinates are usually used with instantaneous principal axes of inertia, this is not necessary. As with any other set of internal coordinates, once the values of the internal coordinates are specified, it is always possible to orient the molecular axes to satisfy any given rotational condition. Here I introduce the hyperspherical coordinates relative to Eckart axes, and then rotate to principal axes. The latter have the advantage that the kinetic energy operator does not contain ϕ , and so the eigenfunctions of the kinetic energy can be chosen to be eigenfunctions of p_ϕ or p_ϕ^2 .

In Ref. [31] are given the expressions for the bond lengths r_i in terms of the conventional normal coordi-

nates Q_1 , Q_{2a} and Q_{2b} . From these and the definitions of the hyperspherical coordinates [38–41] it is relatively easy to show that the normal coordinates are given by

$$\begin{aligned} m^{-1/2} Q_1 &= \rho \cos \theta - r_e, \\ m^{-1/2} Q_{2a} &= \rho \sin \theta \cos \phi, \\ m^{-1/2} Q_{2b} &= \rho \sin \theta \sin \phi, \end{aligned} \quad (14)$$

where ρ , θ , ϕ are the present hyperspherical coordinates, with the ranges

$$0 \leq \rho \leq \infty, \quad 0 \leq \theta \leq \frac{1}{4}\pi, \quad 0 \leq \phi < 2\pi. \quad (15)$$

They are chosen here to give a nice representation of the normal coordinates, and are related to ρ , Θ , Φ of Carter and Meyer [35] by

$$\rho = \rho, \quad \Theta = \pi - 4\theta, \quad \Phi = \phi. \quad (16)$$

The area of the triangle is

$$\Delta = \frac{1}{4}\sqrt{3} \rho^2 \cos 2\theta, \quad (17)$$

and thus the linear geometries correspond to $\theta = \frac{1}{4}\pi$.

Relative to Eckart axes (x^E, y^E, z^E) it is found from Eq. (14) above and Eqs. (4) of Ref. [31] that the coordinates of nucleus i are

$$\begin{aligned} x_i^E &= \frac{\rho}{\sqrt{3}} [\cos \theta \cos \epsilon_i - \sin \theta \cos(\phi + \epsilon_i)], \\ y_i^E &= \frac{\rho}{\sqrt{3}} [\cos \theta \sin \epsilon_i + \sin \theta \sin(\phi + \epsilon_i)], \\ z_i^E &= 0, \end{aligned} \quad (18)$$

where $\epsilon_i = 2\pi(i-1)/3$. From these coordinates we can calculate the instantaneous inertia tensor, and find that the principal axes of inertia are rotated relative to the Eckart axes by an angle $\frac{1}{2}(\pi - \phi)$ about the z -axis. The Eckart-axes hyperspherical coordinates are single-valued, whereas the principal-axes hyperspherical coordinates are double-valued because of this half-angle rotation between them. If γ^E is the value of the third Euler angle for the Eckart axes, then for principal axes the third Euler angle is

$$\gamma = \gamma^E + \frac{1}{2}\pi - \frac{1}{2}\phi. \quad (19)$$

Thus the angular factor $\exp[i(l_2\phi + k_c\gamma^E)]$ in the usual symmetric-top vibration-rotation basis becomes $\exp[i[(l_2 + \frac{1}{2}k_c)\phi + k_c(\gamma - \frac{1}{2}\pi)]]$, and so the quantum

number associated with ϕ in the principal axis system is

$$\lambda = l_2 + \frac{1}{2}k_c. \quad (20)$$

Carter and Meyer [35] use the symbol M for $|\lambda|$, which can be either integer or half-integer.

Relative to principal axes, the nuclear coordinates are found to be

$$\begin{aligned} x_i &= \sqrt{\frac{2}{3}} \rho \cos(\theta - \frac{1}{4}\pi) \sin(\frac{1}{2}\phi + \epsilon_i), \\ y_i &= \sqrt{\frac{2}{3}} \rho \sin(\theta - \frac{1}{4}\pi) \cos(\frac{1}{2}\phi + \epsilon_i), \\ z_i &= 0, \end{aligned} \quad (21)$$

where the x axis is the axis of least moment of inertia. It is seen from Eqs. (21) that it is necessary for the coordinate ϕ to increase by 4π to achieve the same configuration relative to the molecule-fixed axes. However the same configuration relative to space-fixed axes is achieved by the changes

$$\phi \rightarrow \phi + 2\pi, \quad \gamma \rightarrow \gamma + \pi. \quad (22)$$

The most convenient way of handling this situation is to allow ϕ to have the range $0 \leq \phi < 4\pi$, but to exclude wavefunctions that are not invariant to the transformation given in Eq. (22).

In the principal axis system the Hamiltonian is

$$\begin{aligned} H = & \frac{\hbar^2}{2m} \left(-\frac{\partial^2}{\partial \rho^2} + \frac{15}{4\rho^2} - \frac{1}{\rho^2 \sin 4\theta} \frac{\partial}{\partial \theta} \sin 4\theta \frac{\partial}{\partial \theta} \right. \\ & + \frac{4}{\rho^2 \sin^2 2\theta} p_\phi^2 - \frac{4 \cos 2\theta}{\rho^2 \sin^2 2\theta} p_\phi J_z + \frac{1}{\rho^2 \sin^2 2\theta} J_z^2 \\ & + \frac{2(1 + \sin 2\theta)}{\rho^2 \cos^2 2\theta} J_x^2 + \frac{2(1 - \sin 2\theta)}{\rho^2 \cos^2 2\theta} J_y^2 \Big) \\ & + V(\rho, \theta, \phi), \end{aligned} \quad (23)$$

where the vibrational volume element is taken as

$$d\tau = \sin 4\theta d\rho d\theta d\phi. \quad (24)$$

In Eq. (23) J_x , J_y and J_z are the (dimensionless) components of the total angular momentum. As the kinetic energy does not contain ϕ , eigenfunctions of the kinetic energy can be chosen to be eigenfunctions of p_ϕ , with eigenvalues λ as discussed above.

Basis functions. In a product basis, Morse functions or other oscillator functions are a suitable choice for the ρ coordinate. For the ϕ coordinate the functions $(2\pi)^{-1/2} \exp(i\lambda\phi)$ are obviously a suitable basis.

Thus the most interesting factor is the θ factor. It seems that a good choice of the θ factor should reproduce the correct behaviour at the singularities of the kinetic energy operator in Eq. (23), as the potential energy operator is non-singular. The terms of interest here are those in $(\sin 2\theta)^{-2}$ and $(\cos 2\theta)^{-2}$, and it is useful to compare the θ and $\partial/\partial\theta$ dependence of the kinetic energy with that of the differential equation for the rotational functions $d_{m,n}^j(\beta)$ [42] with $\beta=4\theta$, which can be written

$$\begin{aligned} & \left(-\frac{1}{\sin 4\theta} \frac{\partial}{\partial \theta} \sin 4\theta \frac{\partial}{\partial \theta} \right. \\ & \quad \left. + \frac{4(m-n)^2}{\sin^2 2\theta} + \frac{4(m+n)^2}{\cos^2 2\theta} \right) d_{m,n}^j(4\theta) \\ & = 16j(j+1) d_{m,n}^j(4\theta). \end{aligned} \quad (25)$$

Near $\theta=0$ the singular terms in Eqs. (23) and (25) behave like $(2p_\phi - J_z)^2/\sin^2 2\theta$ and $4(m-n)^2/\sin^2 2\theta$, respectively. Thus if we replace p_ϕ and J_z by their quantum numbers λ and J_z , we get

$$(\lambda - \frac{1}{2}k_c)^2 = l_2^2 = (m-n)^2. \quad (26)$$

Near $\theta=\frac{1}{4}\pi$ we can replace $\sin 2\theta$ in Eq. (23) by 1, and we find that the singular terms become $4J_x^2/\cos^2 2\theta$. The numerator here is the square of the component of the total angular momentum along the principal axis, and so its eigenvalue is K_a^2 . Thus to match Eqs. (23) and (25) near this singularity we require

$$K_a^2 = (m+n)^2. \quad (27)$$

Solving these equations with one choice of sign gives

$$m = \frac{1}{2}(K_a + l_2), \quad n = \frac{1}{2}(K_a - l_2). \quad (28)$$

As K_a and l_2 are both integers, m and n are either both integers or both half-integers. The quantum number j in the functions $d_{m,n}^j(4\theta)$ differs from m and n by integers, and so has the same integral or half-integral character as they have.

This suggests that a suitable basis for the vibration-rotation wavefunctions would be

$$\Psi = \psi_v^{\text{Morse}}(\rho) d_{m,n}^j(4\theta) e^{i\lambda\phi} [D_{M,k_c}^j(\alpha, \beta, \gamma)]^*, \quad (29)$$

but this has seven independent quantum numbers and only six degrees of freedom. Carter and Meyer [35] have solved this problem by using the fact that the

$d_{m,n}^j$ functions with higher m and n can be written as linear combinations of functions with lower values of m and n . Thus they use only the four basis functions $d_{m,n}^j(\theta)$ with $(m, n) = (0, 0), (1, 0), (1/2, 1/2)$ and $(1/2, -1/2)$, and let the diagonalisation of the Hamiltonian choose the correct linear combinations for higher (m, n) .

Another possibility under study in the present work is to solve the rotational Hamiltonian

$$H_{\text{rot}} = \cos^2 2\theta [4p_\phi^2 - 4 \cos 2\theta p_\phi J_z + J_z^2] + 2 \sin^2 2\theta [(1 + \sin 2\theta) J_x^2 + (1 - \sin 2\theta) J_y^2], \quad (30)$$

which is the numerator of the singular terms from Eq. (23), or to use a simplified version of this rotational Hamiltonian with the same behaviour near $\theta=0$ and $\theta=\frac{1}{4}\pi$. This can be solved like an asymmetric-top Hamiltonian for each value of θ . Thus, for given J and λ , we get a series of $(2J+1)$ eigenfunctions as functions of θ , which can be labelled by $\tau = -J, -J+, \dots, J$ like asymmetric-top functions. Their behaviour at $\theta=0$ and $\frac{1}{4}\pi$ gives the values of K_a and $|l_2|$, and so we can choose the appropriate $d_{m,n}^j(4\theta)$ factors to go with them. If we call the latter $d_{\tau}^j(4\theta)$, we can write the basis in the form

$$\Psi = \psi_{\nu}^{\text{Morse}}(\rho) d_{\tau}^j(4\theta) e^{i\lambda\phi} [D_{M,\tau}^J(\alpha, \beta, \gamma, \theta)]^*, \quad (31)$$

with six quantum numbers. To use this basis we need the first and second derivatives of $[D_{M,\tau}^J(\alpha, \beta, \gamma, \theta)]^*$ with respect to θ , and this is a reason for using a simplified version of Eq. (30). So far I have tried fitting the eigenfunctions from the full Eq. (30) to Fourier series in θ , but they are rather complicated functions and require a large number of terms. Thus a simplified version of Eq. (30), such as

$$H_{\text{rot}} = \cos^2 2\theta (2p_\phi - J_z)^2 + 4 \sin^2 2\theta J_x^2, \quad (32)$$

might be preferable.

5. Summary

In the present article, I have compared some of the available potentials of H_3^+ , both ab initio and semiempirical, near the minimum. So far, spectra in the low-

energy region have been observed up to $3\nu_2$ of H_3^+ , about 12000 cm^{-1} above the minimum. I hope to use hyperspherical coordinates to calculate vibration-rotation energy levels near and above the linear barrier. This has already been done for low J by Carter and Meyer [35]. Another step in the analysis of the low-energy spectrum will be to try to detect non-Born–Oppenheimer effects by combining the data for different isotopes. This procedure is already well known for diatomic molecules [43]. The polyatomic equivalent is to find a suitable effective nuclear Hamiltonian, including the mass correction terms that can be fitted to the observed isotope effects. A Hamiltonian of this type was derived by Bunker and Moss [32].

Further information on aspects of the general spectroscopy of H_3^+ can be found in a recent comprehensive review by McNab [44], which covers both the low-energy and the near-dissociation vibration–rotation spectra.

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