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The Infrared Spectrum of H_3^+ and its Isotopomers

A Challenge to Theory and Experiment

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H_3^+ and its isotopomers are seen as a benchmark for the comparison of theory and experiment. The stages of an *ab initio* calculation (electronic structure, potential fitting and nuclear motion) are discussed and the sources of error highlighted by consideration of recent results. Fitting of the electronic structure data is seen to be an area needing more development. New results are presented for the low-lying rovibrational states of D_3^+. While rovibrational properties can be calculated in the low-energy region to within *ca.* 0.1% accuracy, the high-energy region is still largely unexplored. New developments in the calculation of excited rotational states ($J \leqslant 20$) are outlined and the possibility of quantum-mechanical calculations of vibrational levels in the near-dissociation region is discussed in the light of illustrative calculations.

1. Introduction

H_3^+ is the simplest stable polyatomic molecule and as such has posed a challenge to both theoreticians and experimentalists since its discovery by Thomson in 1912.[1] The first definitive spectrum of the molecule was, however, not recorded until 1980, when Oka[2] measured 15 rovibrational transitions in the ν_2 band.

As early as 1938 Hirschfelder[3] was able to establish on theoretical grounds that the equilibrium geometry of the molecule was an equilaterial triangle, but it was not until the pioneering work of Carney and Porter[4] after 1974 that sufficiently extensive electronic structure calculations were performed so that a potential-energy surface could be constructed on which reliable calculations of the rotation–vibration states of H_3^+ and its isotopomers could be made.[5]

The history of the study of these systems up to the early 1980s has been reviewed by Oka[6] and Porter,[7] but in spite of further work since then a number of intriguing problems still remain to be solved. Perhaps the most challenging of the problems to the theorist is the interpretation of the 27 000 transitions from states near the H_3^+ dissociation limit in a small (220 cm^{-1}) region of the predissociation infrared spectrum found by Carrington *et al.*[8] and Carrington and Kennedy.[9] These workers have observed similar spectra for H_2D^+, D_2H^+ and D_3^+. The complexity of this spectral region makes it very taxing for the usual variational approach to theoretical rovibrational spectra.[10]

H_3^+ is considered to be abundant in interstellar clouds and an important species in many reactions.[11,12] However, H_3^+ itself has yet to be observed in space because all its microwave transitions are nuclear-spin symmetry-forbidden. Nuclear-spin symmetry also contributes to the exothermicity of the deuterium fractionation reaction:

$$H_3^+ + D \rightleftharpoons H_2D^+ + H \qquad (1.1)$$

which is important in accounting for the observed excess of many deuterated species over that predicted from the natural abundance of D in the interstellar medium.

Following several laboratory studies[13-15] (whose assignments were much aided by the available theoretical predictions), the $1_{01} \leftarrow 1_{11}$ microwave transition of H_2D^+ has recently been tentatively observed in the cloud NGC 2264.[16]

The infrared spectroscopy of the mixed isotopomers, H_2D^+ and D_2H^+, has perhaps provoked the most interest because of its complexity. The symmetric-top species H_3^+ and D_3^+ have just two fundamental modes: a ν_1 stretching mode and a degenerate ν_2 bend. Excitation of the ν_1 band is infrared-forbidden but the ν_2 band of H_3^+ is now well characterised experimentally.[17] This band has also been observed for D_3^+,[18,19] although a full characterisation is still awaited. In the asymmetric-top species, ν_1 transitions are allowed and the degenerate band splits. Furthermore, strong Coriolis interactions between these ν_2 and ν_3 modes give their bands a complex structure, obscuring the vibrational parentage of many transitions. It is only recently that theory[20,21] and experiment[22] have combined to assign the ν_2/ν_3 levels observed by Shy *et al.* in 1981.[23]

The large rotational constants found in these hydrogenic species means that 'pure' rotational excitation can become similar in magnitude to vibrational excitations at relatively low values of the total angular momentum. For example, the $J = 15$ levels of the vibrational ground states of H_2D^+ span *ca.* 4 vibrational states. For states such as these the usual method of representing spectroscopic data in terms of a perturbation series of harmonic-oscillator and rigid-rotor functions may no longer be appropriate. Indeed, distortion and coupling constants obtained from the low-J states do not provide a good enough guide to give even tentative assignments of the high-J transitions.[24]

The *ab initio* calculation of such high-lying rotational levels provides a challenge. This is because the size of a fully coupled rovibrational calculation is proportional to J, and such calculations rapidly become intractable as J is increased. Indeed, only calculations with $J \leqslant 4$ have been reported for H_3^+ systems, and even these have been made using truncated vibrational basis sets.[10,21,25,26]

In the present paper we consider in some detail the state of theoretical work on the various aspects of H_3^+ spectroscopy discussed above. The paper will be organised to consider the three stages involved in an *ab initio* calculation within the Born-Oppenheimer approximation: electronic potential calculation, representation of the electronic potential and rovibrational calculation. Since the errors involved in the first stage, although relatively large, are well documented elsewhere,[27] we will concern ourselves largely with the final two stages of such a calculation. We will also consider separately the status of nuclear motion calculations for states of low and high excitation as the latter area presents challenges which largely remain to be met.

2. The Theoretical Basis

When describing the vibration-rotation motion of a stable molecule it is the custom to assume that to a very high order of approximation it is possible to separate the electronic motion from the motion of the nuclei. This assumption is usually signalled by saying that the Born-Oppenheimer approximation is being made. This approximation is assumed in what follows, for there are no signs that it is inadequate for H_3^+, whose (unstable) excited electronic states are all well separated from the ground state.

In this approximation the nuclear motion occurs on a potential-energy surface that is obtained by solving, at least approximately, the clamped-nuclei electronic problem for a set of nuclear geometries. The resulting electronic energy is added to the nuclear repulsion energy to produce the potential-energy function. In principle a potential-energy function at the given level of approximation could be obtained as a continuous function of the internal coordinates specifying the nuclear geometries. In practice it is possible to obtain the potential only at a set of points. Indeed, as the electronic structure calculation is computationally the most expensive step, it is desirable to keep this set small. This at once raises difficulties. How should the set be chosen to give an adequate characterisation of the potential? How should the points be related to the presumed analytic potential?

For bound-state nuclear motion calculations, the choice of an adequate set of points is usually made by finding the minimum in the potential that corresponds to the stable molecule and distributing points around the minimum, largely by trial and error. The potential is often assumed to be of some predetermined analytic form with constants to be determined by the details of the potential calculation, usually by least-squares fitting.

As this fitting is usually complicated, the choice of suitable functions is often motivated by mathematical considerations, for example the use of sums of products of orthogonal polynomials. This can be combined with physical insight as, for example, in the Sorbie-Murrell scheme.[28]

Another difficulty that arises is that it is never possible to know, except in terms of the calculated points, precisely how good a given fit is. Therefore there is a measure of uncertainty about whether different results would have been obtained from a different set of points. There is also a concomitant uncertainty as to whether a deficiency in a calculated quantity should be attributed to defects in the actual electronic structure calculation or to defects in the fitting process, especially when the desire for a simple form for the potential leads to large standard deviations for the fit [see for example ref. (25)].

These uncertainties could be quantified to some extent by using the fitted function to estimate uncalculated values of the potential and comparing the estimate with actual calculations. This is rarely done [see ref. (29) for an exception], however, because of the computational expense involved. These matters are of some importance in H_3^+ because it is desirable not to degrade the high-accuracy electronic-structure calculations available by inappropriate fitting procedures.

Once a potential-energy surface has been obtained, then a choice of coordinates in which to formulate the nuclear motion problem must be made. Here again difficulties can arise, for there is no unique way of making this choice. Indeed, sometimes the fitting procedure is dictated in advance because of this choice.[5,25]

The most widely used approach to coordinate choice for the nuclear-motion problem for stable molecules stems from the work of Eckart.[30] In this approach it is assumed that the minimum of the potential-energy surface defines an equilibrium nuclear geometry and that the internal coordinates can be expressed as sums of displacements from that equilibrium. The hamiltonian for non-linear molecules based on this approach is

$$\hat{H}=\sum_{\alpha,\beta}\mu_{\alpha\beta}(\Pi_\alpha-\pi_a)(\Pi_\beta-\pi_\beta)-\frac{\hbar^2}{2}\sum_{k=1}^{3N-6}\frac{\partial^2}{\partial Q_k^2}-\frac{\hbar^2}{8}\sum_\alpha\mu_{\alpha\alpha}+V(\boldsymbol{Q}) \tag{2.1}$$

and was first given in this definitive form by Watson,[31] to whom we refer for a detailed explanation of the terms. The coordinates Q_k used in this Hamiltonian are usually chosen to be normal coordinates. The Π_α are the angular momentum operators for the system and π_α are Coriolis coupling operators. The matrix $\boldsymbol{\mu}$ is closely related to the inverse of the moment-of-inertia tensor for the problem.

For small displacements from the equilibrium geometry, the Q_k are small so that the π_α are negligible and the inertia tensor is well approximated by its value at equilibrium. Furthermore, since the potential has a minimum at the equilibrium geometry, $V(\boldsymbol{Q})$ can be expanded in a Taylor series about its minimum. To second order this gives

$$V(\boldsymbol{Q})=V(\boldsymbol{0})+\tfrac{1}{2}\sum_{k,l}^{3N-6}F_{kl}Q_kQ_l \tag{2.2}$$

where $\mathbf{F}$ is the matrix of force constants. Thus for sufficiently small vibrations eqn (2.1) can be well approximated as the sum of rigid-rotor plus simple harmonic-oscillator

Hamiltonians. This is the basis of much of the qualitative experimental interpretation of the low-lying levels of H_3^+. Solutions of this approximate Hamiltonian take the form

$$^J\Psi_n = \Phi_n(\boldsymbol{Q}) \sum_{k=-J}^{J} C_k^J |Jk\rangle \tag{2.3}$$

where Φ_n is a product of harmonic-oscillator functions and the $|Jk\rangle$ are symmetric-top eigenfunctions.

Of course, a simple function like eqn (2.3) is not sufficient to yield quantitative results of spectroscopic accuracy even if it is regarded as a trial function for the full variational Hamiltonian eqn (2.1). It does, however, suggest the form that a single basis function might take in a linear variation calculation. It is along these lines that the early calculations of Carney and Porter[5] were conducted and developed.[32-34] Much recent work on $J=0$ states has used this approach too.[24,35,36]

There is no doubt that this approach is capable of yielding highly accurate results for the low-lying vibrational states of H_3^+ and its isotopomers, as is evinced in the literature cited, but there are some difficulties with it in the description of higher vibration-rotation states. Just those states, in fact, that it seems likely are needed to account for the results of Carrington *et al.*

It is easy to see what may go wrong when the form of eqn (2.1) is examined. For large-amplitude vibrations the Q_k can become large and lead to a triatomic system becoming almost linear. In this case the instantaneous inertia tensor contains a zero diagonal element and $\boldsymbol{\mu}$ becomes singular. Furthermore, the Coriolis terms will become large for these large-amplitude motions.

In some recent work on H_3^+,[10,21,26,37] an approach different from the classical Eckart one has been adopted. This approach allows for large-amplitude internal motions and vibration-rotation couplings by considering the system as an atom interacting with a diatom.

It thus has a strong similarity to scattering calculations. In these coordinates the diatomic bond length is conventionally denoted by r, the distance of the atom from the diatomic centre-of-mass by R, and the angle between $\boldsymbol{r}$ and $\boldsymbol{R}$ by θ. Writing a suitable set of angular basis functions

$$\theta_{jk}(\theta)|Jk\rangle \tag{2.4}$$

where θ_{jk} is an associated Legendre polynomial, one can derive an effective radial Hamiltonian[38,39]

$$\hat{H} = \hat{K}_{\mathrm{V}} + \hat{K}_{\mathrm{VR}} + \delta_{kk'} V_{jj'k}(R, r) \tag{2.5}$$

where the vibration kinetic operator is

$$\hat{K}_{\mathrm{V}} = \hbar^2 \delta_{kk'} \delta_{jj'} \left[-\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R - \frac{1}{2\mu_{\mathrm{d}} r} \frac{\partial^2}{\partial r^2} r + j(j+1)\left(\frac{1}{2\mu R^2} + \frac{1}{2\mu_{\mathrm{d}} r^2} \right) \right] \tag{2.6}$$

and the vibration-rotation kinetic energy operator is

$$\hat{K}_{\mathrm{VR}} = \delta_{jj'} \frac{\hbar^2}{2\mu_1 v_1^2} \{ \delta_{kk'} [J(J+1) - 2k^2] - \delta_{k',k+1} C_{Jk}^+ C_{jk}^+ - \delta_{k',k-1} C_{Jk}^- C_{jk}^- \} \tag{2.7}$$

where

$$C_{lk}^{\pm} = [l(l+1) - k(k \pm 1)]^{1/2}. \tag{2.8}$$

μ_{d} and μ are the reduced mass of the diatomic and the complex. For a coordinate system with z along $\boldsymbol{R}$

$$\mu_1 = \mu \quad \text{and } v_1 = R \tag{2.9}$$

while if z is embedded along $\boldsymbol{r}$

$$\mu_1 = \mu_d \quad \text{and} \quad v_1 = r. \tag{2.10}$$

In the above, $V_{jj'k}$ is the electronic potential integrated over the angular coordinate. The use of this Hamiltonian for vibration-rotation calculations, especially for triatomics, has just been reviewed,[40] and we note the form of the Hamiltonian has recently been generalised to one encompassing any triatomic coordinate system composed of two lengths and an angle.[41]

The Hamiltonian will not cease to be defined for a linear geometry and makes no assumption about equilibrium structure. Furthermore, the vibrational and rotational motions of the molecule are coupled in a sensible and physically appealing way. There is every reason to suppose, therefore, that a Hamiltonian of this kind can offer an adequate description of triatomic systems in highly excited rotations and vibrations, and in the following sections some example of its use will be given.

3. Low-lying Vibration–Rotation States

There are now many theoretical predictions of the infrared spectrum of H_3^+ and to a lesser extent its isotopomers. However, the majority of these have concentrated on the lowest few vibrational states calculated with $J = 0$. Table 1 gives a summary of results. These results are classified according to the electronic structure calculation, fitting procedure and vibrational calculation. Comparison is instructive.

The first point is that, despite the use of large basis sets and the inclusion of all allowed configurations in the calculation, the best electronic energy is still between 150 and 200 cm^{-1} higher than the absolute energy of the minimum obtained by Mentch and Anderson using a random-walk calculation.[51] This problem is well known and means that any *ab initio* electronic potential calculation must concentrate on obtaining accurate relative energies or shapes of the surface. Systematic procedures are beginning to be used for this, and we refer the reader to the work of Meyer *et al.*[36] for an instructive example.

Looking at the results of the vibrational calculation, a striking feature is the good measure of agreement between the calculations and experiment, with all the predicted transition frequencies lying within 1% of the observed ones. By this measure the least accurate surfaces are the augmented surface of Carney[34] and the surface of Schinke *et al.*[42] which are, respectively, too stiff and too weak in the bending coordinates. Neither of these surfaces is the worst in a strictly variational sense.

Vibrational calculations on the same surface show a very good measure of agreement, at least for the fundamental transitions. Because of this we have not included calculations[52,53] that essentially reproduced our results[10] for the surface of Schinke *et al.*[42] Note, however, that the calculations of Spirko and coworkers[25,45] seem to be exceptions to this agreement. In their calculations, deviations of up to 20 cm^{-1} are observed from the results of other workers using supposedly equivalent potentials. It is not possible to say definitely whether this lack of agreement arises from differences in their potential fits or intrinsically from their choice of internal coordinates. Although in their work they use a conventional Eckart approach to the problem, they use an explicit set of curvilinear symmetry coordinates in terms of which the elements of $\boldsymbol{\mu}$ are expressible only as power series which in practice are truncated at quartic terms.

However this may be, their stated aim is to use their method as a means of inverting the now extensive empirical data on H_3^+ and its isotopomers. We would comment that there is a danger in doing this with an approximate procedure as the resulting potential will reflect the approximations and may not be like the true potential. A dramatic example of this pitfall was encountered recently in work on acetylene.[54,55]

Table 1. Comparison of *ab initio* calculations for the band origins of H_3^+ and isotopomers, in cm^{-1}. All electronic structure calculations and full CI calculations except Burton *et al*,[43] who used a PNO-CI(D) procedure. See text for discussion of the fitting procedures.

electronic calculation	basis	$-E_{min}/E_h$ [a]	fit		vibrational calculation	H_3^+		H_2D^+			D_2H^+			D_3^+	
			coordinates	order[b]		ν_1	ν_2	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3	ν_1	ν_2
ref. (4)	24 FSGO[c]	1.335 19	SPF[4]	5th	ref. (5)	3185	2516	3000	2203	2328	2742	1961	2072	2307	1826
	augmented[34]	?	SPF[34]	5th	ref. (34)	3220	2546								1848
			Morse[25]	4th	ref. (25)	3191	2546							2310	1835
ref. (42)	42 CGTO[d]	1.340 23	damped displacement[42]	6th	ref. (10)	3191	2494	3000	2184	2310					
ref. (43)	81 CGTO[d]	1.341 88	SPF[+43]	6th	ref. (43)	3189	2509								
					ref. (26)	3188	2508	3000	2196	2321	2743	1958	2067		
			SPF[44]	6th	ref. (44)	3176	2519								
					ref. (26)	3175	2518	2989	2203	2331	2733	1965	2075	2297[e]	1831[e]
			Morse[45]	4th	ref. (45)			2984	2200	2325	2728	1959	2073		
ref. (46)	63 CGTO[d]	1.342 78	Morse[36]	7th	ref. (36)	3186	2521	2999	2206	2334	2742	1968	2078		
			SPF[47]	6th	ref. (47)	3180	2522	2994	2207	2336	2739	1969	2080	2303	1835
			Morse[44]	6th	ref. (44)	3185	2522							2306	1835
ref. (36)	87 CGTO[d]	1.343 09	Morse[36]	7th	ref. (36)	3178	2519	2993	2204	2333	2737	1966	2077	2301	1833
observed							2521[17]	2992[48]	2206[22]	2335[22]	2737[49]	1968[50]	2078[50]		1835[18]

[a] 1 $E_h = 2.194\,75 \times 10^5\ cm^{-1}$. [b] The order of a fit is the highest power used. Not all terms of a particular order are necessarily retained. [c] FSGO = floating spherical Gaussian type orbitals. [d] CGTO = contracted Gaussian type orbitals. [e] This work, see table 2.

Table 2. Vibrational band origins, in cm^{-1}, for D_3^+ calculated using the BVDH potential of Martire and Burton.[44] (*a*) Simple product basis, (*b*) perturbation selected basis.[a]

quantum numbers				(*a*) $m \leqslant 7$, $n \leqslant 9$, $j \leqslant 19$		(*b*) $N = 800$	
ν_1	ν_2	l	symmetry	j even	j odd	j even	j odd
0	1	1	E'	1831.07	1831.07	1831.07	1831.07
1	0	0	E'	2297.49		2297.49	
0	2	0	A_1'	3523.24		3523.23	
0	2	2	E'	3647.43	3647.40	3647.40	3647.40
1	1	1	E'	4052.65	4052.60	4052.61	4052.60
2	0	0	A_1'	4549.89		4549.88	
3	0	1	E'	5208.17	5206.71	5207.17	5206.71
3	0	3	A_1'	5400.25		5399.28	
3	0	3	A_2'		5470.59		5468.39
1	2	0	A_1'	5704.28		5703.90	
1	2	2	E'	5791.20	5788.69		5788.71
zero-point energy				3102.23		3102.23	

[a] For both bases $r_e = 1.78a_0$, $\omega_e = 0.009E_h$ and $D_e = 0.12$ E_h for the r coordinate and $R_e = 1.48$ a_0, $\omega_e = 0.009$ E_h and $D_e = 0.20$ E_h for the R coordinate.[59]

Table 1 shows a number of cases where different fitting procedures have been used to represent the same grid of electronic potential points. As discussed in the previous section, there are a number of difficulties in this process. Burton *et al.*[43] tested the effect of three coordinate representations, those due to Dunham,[56] Simons, Parr and Finlan (SPF)[57] and Ogilvie,[58] before favouring fits based on an expansion in SPF coordinates. Schinke *et al.*[42] used exponential damping functions and displacement coordinates, which are related to the Dunham coordinates by a constant. Other workers have transformed to Morse coordinates as their variables in a series expansion. We note that none of these fitting procedures is orthogonal and thus coefficients for fits differing only in the order of the expansion are not strictly comparable.

A disturbing feature of table 1 is that results obtained with different fits to the same electronic data do not agree. Thus, for example, the agreement between theory and experiment for calculations based on the surface of Dykstra and Swope is good, reproducing all the experimental band origins to within 3 cm^{-1} according to Carney *et al.*,[47] but their results disagree by up to 6 cm^{-1} with those of Meyer *et al.*,[36] who used an alternative fit to the same surface!

A way of demonstrating the accuracy of the final, vibrational step of the calculation is by showing that the variational procedure used for the calculation is converged. Table 2 compares the lowest 12 states of D_3^+ calculated using the scattering Hamiltonian discussed above, as implemented in program ATOMDIAT[59] generalised for an arbitrary potential function.[60] The energy levels recorded on the left were computed using all possible products of the truncated set of one-dimensional functions. Thus 8 ($m \leqslant 7$) and 10 ($n \leqslant 9$) Morse oscillator-like functions[38] were used for the r and R coordinates, respectively, and Legendre polynomials with $j \leqslant 19$ were used to carry the angular functions. The energy levels recorded on the right were calculated using basis functions selected using a first-order perturbation-theory selection technique, whereby the functions with the N lowest diagonal elements are used to build a basis. The agreement for the lowest levels is excellent, suggesting a high degree of convergence. For the higher levels the selected basis generally gives better results.

A knowledge of the rotational structure of the molecule is probably more helpful than the band origins in assigning complicated asymmetric-top spectra, such as those encountered in the ν_2 and ν_3 bands of H_2D^+ and D_2H^+. However, few of the theoretical

Table 3. Rotational levels for the lowest three vibrational states of D_3^+ calculated using the BDVH potential of Matire and Burton.[44] [a]

		A_1' state					E' state									
J	k^b	j^+	K		(0, 0)	(1, 0)	G	U	s	j^c		(0, 1)	s	j^c		(0, 1)
1	1^f	o	0	A_1'	43.496	42.74	1	+1		o	E_y'	43.82		e	E_x'	43.82
	0^e	e	1	E''	32.244	31.67	2	+1		e	E_x'	12.68		o	E_y'	12.69
	1^e	o	1		32.241	31.66	0	−1	+1	o	A_2''	49.58	−1	e	A_1''	53.29
2	2^f	e	1	E''	110.072	116.99	0	−1	+1	e	A_1''	133.33	−1	o	A_2''	144.29
	1^f	o	1		119.069	116.99	2	+1		o	E_y''	100.21		e	E_x''	100.26
	0^e	e	2	E'	85.418	83.87	3	+1	+1	e	A_1'	45.70	−1	o	A_2'	45.62
	1^e	o	2		85.413	83.86	1	−1		o	E_y'	121.04		e	E_y'	121.07
	2^e	e	0	A_1'	130.258	128.00	1	+1		e	E_x'	133.21		o	E_x'	133.17
3	3^f	o	0	A_2'	259.807	255.31	1	+1		o	E_y'	268.36		e	E_x'	268.39
	2^f	e	2	E'	215.379	211.59	1	−1		e	E_x'	246.95		o	E_y'	246.95
	1^f	o	2		215.372	211.58	3	+1	−1	o	A_2'	176.77	+1	e	A_1'	177.01
	0^e	e	3	A_1''	159.481	156.57	4	+1		e	E_x''	99.12		o	E_y''	98.89
	1^e	o	3	A_2''	159.466	156.54	2	−1		o	E_y''	212.07		e	E_x''	212.11
	2^e	e	1	E''	248.725	244.40	2	+1		e	E_x''	233.64		o	E_y''	233.58
	3^e	o	1		248.722	244.40	0	−1		o	A_2''	258.34	+1	e	A_1''	280.09
4	4^f	e	1	E''	420.515	413.24	0	−1	+1	e	A_1''	424.01	−1	o	A_2''	459.67
	3^f	o	1		420.509	413.22	2	+1		o	E_y''	412.43		e	E_x''	412.51
	2^f	e	3	A_1''	332.340	326.46	2	−1		e	E_x''	379.85		o	E_y''	379.80
	1^f	o	3	A_2''	332.333	326.45	4	+1		o	E_y''	273.65		e	E_x''	273.91

[a] Rotational levels are given relative to the $J = 0$ level of each vibrational state in cm^{-1}. Calculations used a product basis with $m \leqslant 4$, $n \leqslant 4$ and $j \leqslant 17$ and the same parameters as table 2. [b] Total parity given by $(-1)^{J+p}$, where $p = 0$ for states labelled e and $p = 1$ for states labelled f. [c] Parity of j: e = even, o = odd.

Table 4. Vibrational ($J=0$) energy levels for H_3^+ in cm^{-1} using the potential of Schinke *et al.*[42] All energies are relative to the dissociation limit of H_2+H^+. (*a*) Product basis,[10] (*b*) perturbation selection. Basis set: Morse functions of table 1, ref. (10).

	j even		*j* odd	
state no.	(*a*)	(*b*)	(*a*)	(*b*)
1	−32 580.48	−32 580.50	−30 086.2	−30 086.2
5	−27 622.3	−27 622.5	−25 129.2	−25 129.5
10	−24 840.2	−24 840.8		−22 624.5
15		−23 320.8		−21 111.3
20		−21 967.9		−19 934.6
25		−20 823		−19 002
30		−20 050	−18 056	−18 064
35		−19 265		
40	−18 483	−18 499		

calculations discussed above have been performed for $J>0$. The comparison of rotational transition frequencies (or rotational constants if some parameterised form for the Hamiltonian is assumed[61,62]) gives another test of the accuracy of the potential. Rather frustratingly, our experience[10,26] has shown that the best 'rotational' potential is that of Schinke *et al.*,[42] which was found to be relatively poor for the vibrational properties. Note that while the fundamental vibrations sample the curvature of the potential near the minimum, the rotational constants are very sensitive to the actual location of the minimum.

Of course, if theoretical rotational data are to be of help in assigning spectra, it is necessary to perform calculations not only for the ground but also vibrationally excited states of the molecule. Table 3 gives predicted rotational levels for the ground state and two fundamentals of D_3^+. The labels k and parity of j as well as the total parity are the labels used in our calculation. They do not allow for the full S_3 permutation symmetry of D_3^+.[10] Besides these, the levels of the degenerate ν_2 state are also characterised by G, U and s, which are the parameters used by Watson[62] in his fitting procedure for X_3 systems. All the levels have also been assigned according to irreducible representations of D_{3h}, which is isomorphic with $S_3 \otimes (E, E^*)$.

The splitting between components of levels which should be degenerate is a reflection of the lack of symmetry adaptation of our basis. The magnitude of this splitting gives a guide to the degree of convergence of the calculation. We note that it was necessary to use associated Legendre functions with $j \leqslant 17$ in the basis instead of $j \leqslant 15$ used for the hydrogen-containing isotopomers. This is a reflection of the smaller amplitude vibrations undergone by the heavier D_3^+ molecules.

4. Highly Excited States

While the agreement between theory and experiment for the low-lying levels of H_3^+ and its isotopomers can be considered broadly satisfactory and disagreements explained largely in terms of the fine tuning of the potential, the situation for the highly excited states is far less clear. The experiments of Carrington *et al.*[8,9] probe the potential in the vicinity of dissociation and it is clear that a quantum mechanical solution of the vibrational problem in this region would be extremely difficult.

Previous calculations by us[10] failed to converge states even half-way to dissociation. The use of perturbative basis set selection, as discussed for D_3^+ above, does improve this convergence, see table 4. However, the improvement is insufficient to suggest that

Table 5. Convergence of H_3^+ $J = 1^e$ rotational levels (potential as for table 4) with increasing vibrational basis (N_{vib}). All frequencies, in cm^{-1}, are relative to the $J = 0$ level of the corresponding vibrational state. (*a*) *z* axis is embedded along *r*, eqn (2.10); (*b*) *z* axis embedded along *R*, eqn (2.9).

	(0, 0)		(0, 1)			
	$K = 1$	$K = 1$	(2, 1, 0)[a]	(2, 1, 0)	(0, −1, 1)	(0, −1, 1)
$k =$	0	1	0	1	0	1
parity of *j*	e	o	e	o	o	e
(*a*) no Coriolis	83.858	86.870	79.492	88.129	81.449	85.822
$N_{vib} = 10$	64.071	64.197	27.926	27.685	106.687	95.579
20	64.051	64.049	25.877	25.766	104.788	93.652
50	64.048	64.046	25.847	25.738	104.759	93.622
exact[b] (200)	64.048	64.046	25.847	25.738	104.759	93.622
(*b*) no Coriolis	83.964	86.870	90.035	72.138	88.129	85.822
$N_{vib} = 10$	64.411	64.455	29.899	29.720	96.206	107.532
20	64.076	64.081	26.168	26.242	93.841	104.979
50	64.047	64.048	25.758	25.845	93.613	104.761
exact[b] (200)	64.047	64.048	25.753	25.845	93.612	104.760

[a] (G, U, s),[62] see table 3. [b] Results for the fully coupled calculation given by table 6 of ref. (10).

significant progress can be made in this fashion without a great improvement in computer technology. Already at energies about a third of the dissociation energy the convergence is sufficiently poor for degenerate pairs to be not readily identified.

At first sight the situation concerning the calculation of fully coupled highly excited rotational states is equally hopeless. This is because the size of the full rovibrational problem is too large to be tractable. Indeed absent from table 3 are the levels with $J = 4$ and even total parity because with $j \leqslant 17$ we could no longer handle the secular matrix. However, the reformulation of the nuclear motion problem into two separate variational steps has allowed us to tackle accurately rotational states up to $J = 20$.[37]

The basis of this separation is the initial neglect of all off-diagonal Coriolis couplings, *i.e.* terms off-diagonal in *k* in the Hamiltonian of eqn (2.5). The solutions of these calculations are then used as a basis to express the solutions of the full Hamiltonian. This method has two distinct advantages. First, only a fraction of the solutions from the first step are required to converge the rotational levels belonging to low-lying vibrational states. Secondly, the structure of the secular matrices obtained in the second variational step is such that only a small portion of it need be calculated, leading to a large consequent saving in computer requirements. Table 5 presents illustrative results of this procedure. Good convergence is obtained even though for both embeddings the neglect of Coriolis interactions is a poor approximation.

There are, as yet no assigned experimental transitions for these highly excited rotational states, so it is too early to comment on the accuracy of these calculations. However, the relatively large rotational constant of a molecule such as H_2D^+ means that the manifold of states, for say $J = 20$, spans several vibrational states. There is evidence from our calculations that as a consequence of this it is no longer possible to assign the parent vibrational state for many of the rotational levels.[37]

5. Conclusions

We have shown that H_3^+ and its isotopomers have proved themselves of fundamental importance in the interplay between theory and experiment. These electronically simple species nevertheless give rise to complex rovibrational properties partially as a consequence of their lightness. In the low-energy regime, the first half of this decade has seen their spectroscopy go from being non-existent to being well recorded and reasonably well understood. Although there are some disagreements between *ab initio* calculation and experiment, these are small, of order 0.1%, and directly attributable to errors either in the calculation of the electronic potential or its fitting to a suitable analytical function for use in nuclear motion calculations. Indeed the development of accurate fitting techniques is a priority if the results of high-accuracy electronic structure calculations are not to be degraded.

For high-lying states, the main theoretical focus is still on the nuclear motion calculations themselves. A technique has recently been developed for the calculation of highly excited rotational states which shows much promise for advancing our understanding here, where traditional concepts based on the harmonic oscillator and rigid-rotor hamiltonians are no longer useful. However, the goal of quantum-mechanical calculations explaining the fascinating experiments of Carrington and coworkers still appears to be distant.

Note added in proof: Recent observations of D_3^+ by Watson *et al.*[63] agree with the results of table 3 to within 0.3%.

References

1 J. J. Thomson, *Philos. Mag.*, 1912, **24**, 20.
2 T. Oka, *Phys. Rev. Lett.*, 1980, **45**, 531.
3 J. O. Hirschfelder, *J. Chem. Phys.*, 1938, **6**, 795.
4 G. D. Carney and R. N. Porter, *J. Chem. Phys.*, 1974, **60**, 4251.
5 G. D. Carney and R. N. Porter, *J. Chem. Phys.*, 1976, **65**, 3547.
6 T. Oka, in *Molecular Ions: Spectroscopy, Structure and Chemistry*, T.A. Miller and V. E. Bondybey (North-Holland, Amsterdam, 1983), p. 73.
7 R. N. Porter, *Ber. Bunsenges. Phys. Chem.*, 1982, **86**, 407.
8 A. Carrington, J. Buttenshaw and R. A. Kennedy, *Mol. Phys.*, 1982, **45**, 753.
9 A. Carrington and R. A. Kennedy, *J. Chem. Phys.*, 1984, **81**, 91.
10 J. Tennyson and B. T. Sutcliffe, *Mol. Phys.*, 1984, **51**, 887.
11 W. D. Watson, *Rev. Mod. Phys.*, 1976, **48**, 413.
12 D. Smith, *Philos. Trans. R. Soc. London, Ser. A*, 1981, **303**, 535.
13 M. Bogey, C. Demynck, M. Denis, J-L. Destombes and B. Lemoine, *Astron. Astrophys.*, 1984, **137**, L15.
14 H. E. Warner, W. T. Conner, R. H. Petrmichl and R. C. Woods, *J. Chem. Phys.*, 1984, **81**, 2514.
15 S. Saito, K. Kawaguchi and E. Hirota, *J. Chem. Phys.*, 1985, **82**, 45.
16 T. G. Phillips, G. A. Blake, J. Keene, R. C. Woods and E. Churchwell, *Astrophys. J.*, 1985, **294**, L45.
17 J. K. G. Watson, S. C. Foster, A. R. W. McKellar, P. Bernath, T. Amano, F. S. Pan, M. W. Crofton, R. S. Altman and T. Oka, *Can. J. Phys.*, 1984, **62**, 1875.
18 J-T. Shy, J. W. Farley, W. E. Lamb Jr and W. H. Wing, *Phys. Rev. Lett.*, 1980, **45**, 535.
19 J. K. G. Watson, personal communication.
20 G. D. Carney, *Can. J. Phys.*, 1984, **62**, 1871.
21 J. Tennyson and B. T. Sutcliffe, *Mol. Phys.*, 1985, **54**, 141.
22 S. C. Foster, A. R. W. McKellar, I. R. Peterkin, J. K. G. Watson, F. S. Pan, M. W. Crofton, R. S. Altman and T. Oka, *J. Chem. Phys.*, 1986, **84**, 91.
23 J-T. Shy, J. W. Farley and W. H. Wing, *Phys. Rev. A*, 1981, **24**, 1146.
24 J-L. Destombes, personal communication.
25 V. Spirko, P. Jensen, P. R. Bunker and A. Cejchan, *J. Mol. Spectrosc.*, 1985, **112**, 183.
26 J. Tennyson and B. T. Sutcliffe, *Mol. Phys.*, 1985, **56**, 1175.
27 H. F. Schaeffer III, *The Electronic Structure of Atoms and Molecules* (Addison-Wesley, New York, 1972).
28 K. S. Sorbie and J. N. Murrell, *Mol. Phys.*, 1975, **24**, 1387.
29 P. E. S. Wormer and J. Tennyson, *J. Chem. Phys.*, 1981, **75**, 1245.
30 C. Eckart, *Phys. Rev.*, 1935, **45**, 552.
31 J. K. G. Watson, *Mol. Phys.*, 1968, **15**, 476.
32 G. D. Carney and R. N. Porter, *Chem. Phys. Lett.*, 1977, **50**, 327; *Phys. Rev. Lett.*, 1980, **45**, 537.
33 G. D. Carney, *Chem. Phys.*, 1980, **54**, 103.
34 G. D. Carney, *Mol. Phys.*, 1980, **39**, 923.
35 P. G. Burton, E. von Nagy-Felsobuki, G. Doherty and M. Hamilton, *Chem. Phys.*, 1984, **83**, 43; P. G. Burton, E. von Nagy-Felsobuki and G. Doherty, *Chem. Phys. Lett.*, 1984, **104**, 323.

36 W. Meyer, P. Botschwina and P. G. Burton, *J. Chem. Phys.*, 1986, **84**, 891.
37 J. Tennyson and B. T. Sutcliffe, *Mol. Phys.*, in press.
38 J. Tennyson and B. T. Sutcliffe, *J. Chem. Phys.*, 1982, **77**, 4061; 1983, **79**, 43.
39 J. Tennyson and B. T. Sutcliffe, *J. Mol. Spectrosc.*, 1983, **101**, 71.
40 J. Tennyson, *Comput. Phys. Rep.*, in press.
41 B. T. Sutcliffe and J. Tennyson, *Mol. Phys.*, in press.
42 R. Schinke, M. Dupuis and W. A. Lester Jr, *J. Chem. Phys.*, 1980, **72**, 3909.
43 P. G. Burton, E. von Nagy-Felsobuki, G. Doherty and M. Hamilton, *Mol. Phys.*, 1985, **55**, 527.
44 B. Martire and P. G. Burton, *Chem. Phys. Lett.*, 1985, **121**, 479.
45 P. Jensen, V. Spirko and P. R. Bunker, *J. Mol. Spectrosc.*, 1986, **115**, 269.
46 C. E. Dykstra and W. C. Swope, *J. Chem. Phys.*, 1980, **72**, 3909.
47 G. D. Carney and S. Adler-Goldem, paper presented at 40th Symposium on Molecular Spectroscopy, Ohio State University, June 1985; G. D. Carney, S. Adler-Golden and D. C. Lesseski, *J. Chem. Phys.*, 1986, **84**, 3921.
48 T. Amano and J. K. G. Watson, *J. Chem. Phys.*, 1984, **81**, 2869.
49 K. G. Lubic and T. Amano, *Can. J. Phys.*, 1984, **62**, 1886.
50 S. C. Foster, A. R. W. McKellar and J. K. G. Watson, *J. Chem. Phys.*, in press.
51 F. Mentch and J. B. Anderson, *J. Chem. Phys.*, 1981, **74**, 6307.
52 P. Bartlett, *D. Phil. Thesis* (Oxford University, 1985).
53 P. Botschwina, personal communication.
54 L. Halonen, M. S. Child and S. Carter, *Mol. Phys.*, 1982, **47**, 1097.
55 S. Carter and N. C. Handy, *Mol. Phys.*, 1984, **53**, 1033.
56 J. L. Dunham, *Phys. Rev.*, 1931, **41**, 713; 1932, **41**, 721.
57 G. Simons, R. Parr and J. M. Finlan, *J. Chem. Phys.*, 1973, **59**, 3229.
58 J. F. Ogilvie, *Proc. R. Soc. London, Ser. A*, 1981, **378**, 287.
59 J. Tennyson, *Comput. Phys. Commun.*, 1983, **29**, 307.
60 J. Tennyson, *Comput. Phys. Commun.*, 1984, **32**, 109.
61 M. R. Aliev and J. K. G. Watson, *J. Mol. Spectrosc.*, 1976, **61**, 29.
62 J. K. G. Watson, *J. Mol. Spectrosc.*, 1984, **103**, 350.
63 J. K. G. Watson, S. C. Foster and A. R. W. McKellar, to be published.

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