All the vibrational bound states of H_3^+

James R. Henderson and Jonathan Tennyson

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

Received 8 August 1990

Vibrational calculations are presented for three H_3^+ potential energy surfaces using a discrete variable representation in all three internal coordinates. These calculations converge *all* the $J=0$ bound states of H_3^+ to within 10 cm^{-1} giving at least 881 states for each potential. The wavefunctions of these states have been analysed in an attempt to find assignable or spatially localised states of the system. The significance of this work to the unassigned near-dissociation spectra of H_3^+ is discussed.

The unassigned, near-dissociation, infrared spectra of H_3^+ recorded by Carrington and Kennedy [1,2] has given rise to much interest and speculation. The generally accepted explanation of these extremely rich spectra is that high angular momentum states are being observed with the final state undergoing rotational predissociation [3–6]. However coarse-grained versions of these spectra display regular features which have been attributed to underlying regular features in the classical motions of the system. An example of this motion is the "horseshoe" periodic orbit of Gomez Llorrente and Pollak [7].

Several limited quantum-mechanical calculations [8–11] have suggested that the "horseshoe"-like states are indeed found. All these studies have been performed or analysed in such a fashion that other families of regular states could well have been overlooked. As yet no fully coupled 3D quantum-mechanical calculations have been performed up to the dissociation limit. Indeed, until recently it would have been unthinkable to suggest such a calculation. What is required is nearly a thousand states of a classically chaotic, three-mode system. However, recent developments of theoretical techniques for treating large-amplitude vibrational motion have made such calculations possible.

The most significant new development has been the use of the discrete variable representation (DVR) by Bačić, Light and co-workers [12] for vibrational problems. This finite element technique relies on successive diagonalisations and truncations to build up a final Hamiltonian matrix with a very high information content. Thus Whitnell and Light [13] used hyperspherical coordinates and a DVR in all three internal coordinates to obtain the lowest 100 states of H_3^+. We [9] used Jacobi or scattering coordinates with a DVR in the angular coordinate to obtain the lowest 180 vibrational states which extend about half way to dissociation. The accuracy of these results has recently been confirmed by Carter and Meyer [14] who used hyperspherical coordinates and a basis set contracted using a diagonalisation and truncation procedure to calculate the same levels.

In this work we use a new implementation of the DVR method in scattering coordinates which transforms the entire internal coordinate Hamiltonian into a DVR. This method combines the efficiency of the polynomial basis sets that we have developed over a number of years to treat ro-vibrational problems [15] with the power of the DVR to give us estimates, to within 10 cm^{-1}, of the positions of *all* the vibrational bound states of the H_3^+ molecule.

In this work we used three H_3^+ potentials. The potential energy surface due to Meyer, Botschwina and Burton (MBB) [16] is of near spectroscopic accuracy at low energies [17]. However, although this surface is well behaved up to dissociation [14], it does not actually dissociate correctly. The less accurate ab initio potential due to Schinke, Dupuis and Lester (SDL) [18] was designed for scattering calculations and thus dissociating problems. However,

0009-2614/90/$ 03.50 © 1990 – Elsevier Science Publishers B.V. (North-Holland)

in the course of this work, we found that actually if one considers a coordinate where all three H atoms move apart symmetrically this potential becomes ill-behaved below the H^+–H_2 dissociation limit. This problem was circumvented by forcing an artificially high energy in the region of poor behaviour. The diatoms-in-molecules (DIM) potential [19] has been used extensively for (semi)-classical calculations. It is well behaved over the entire energy range of concern to us but, at low energy, is significantly less accurate than the ab initio potentials. Although we present results for all three potentials, we have concentrated on the MBB potential because the quantum-mechanical calculations cited above [9,13,14] all used versions of this potential.

DVR theory as applied to vibrating triatomics has been thoroughly reviewed by Bačić and Light [12] and will not be repeated here. In our implementation we have used scattering or Jacobi coordinates: r_1 is the H–H separation; r_2 is the distance from the centre of the H_2 fragment to the third H atom; θ is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. We note that unlike hyperspherical coordinates, this coordinate system does not reflect the full symmetry of H_3^+.

In each coordinate we used orthogonal polynomials to carry the motion. Thus the r_1 motions were carried by Morse-oscillator-like functions [20], the r_2 motions by spherical oscillator functions [21], as these behave correctly at the $r_2=0$ limit, and Legendre polynomials to represent the angular motion. Both the radial functions can be related to Laguerre polynomials. For each coordinate it is thus possible to define a Gaussian quadrature which is then used as the basis of the DVR transformation [12].

The remaining technical problem is to determine in which order the coordinates should be treated in the successive diagonalisation and truncation procedure. This question has been discussed by Light et al. [22]; the objective is to minimize the CPU time (and memory) required by obtaining the smallest possible final Hamiltonian matrix. This is done by treating the coordinate with the smallest density of states last. In the present problem, the highest density of states is in the dissociating r_2 coordinate and the lowest in the θ coordinate. The coordinates were therefore treated in the order $r_2 \rightarrow r_1 \rightarrow \theta$.

Both radial basis sets contain parameters which can be adjusted to give the variationally best functions for a given problem. The radial basis functions were optimised using a previously written [10] 2D (θ frozen) program working in a basis set rather than DVR. These tests ensured that sufficient functions were included to represent all the bound states of the problems for several values of θ. Details of the optimised radial functions are given in table 1.

As the size of the final 3D Hamiltonian was not actually dependent on the number of radial grid points used (because θ is the last coordinate included), we could be generous in our provision of radial points. Convergence is thus ensured provided the final step includes sufficient contracted radial points at each angular grid point. The final Hamiltonian was constructed by selecting the N radial contractions with the lowest eigenenergies for the 2D subproblems.

Our final results were computed using a grid of 32 Gauss–Legendre quadrature points for the θ coordinate. Because of symmetry only 16 of the points need be explicitly considered [9]. Tests showed that increasing this number actually degraded our final results as, for fixed N, less radial functions per angle could be considered. Calculations which increased the number of angular points using a fixed energy selection criterion for the radial functions showed the calculations to be stable with respect to increasing the size of the angular grid. The uncontracted DVR grids used here are equivalent to a basis set expansion comprising 23040 functions for each symmetry.

Table 2 shows the convergence of a selection of levels as a function of dimension, N, of the final

Table 1
Details of the radial basis functions used. r_e, ω_e and D_e are given in atomic units. n is the number of DVR points in each coordinate

Coordinate	Oscillator	n	r_e	ω_e	D_e
r_1	Morse-like [20]	36	3.16	0.11085	0.0060
r_2	spherical [21]	40	–	0.0095	–

Table 2
Convergence of a selection of even-symmetry H_3^+ vibrational band origins as a function of dimension, N, of the final Hamiltonian. All values are given in cm^{-1} relative to the H_3^+ ground state at 4363.5 cm^{-1} above the minimum of the surface. These results were obtained for the MBB potential function

Level	N				
	2100	2400	2700	3000	3300
1	2521.28	2521.28	2521.28	2521.28	2521.28
51	15202.9	15202.8	15202.7	15202.7	15202.6
151	22265.8	22264.3	22263.6	22263.3	22262.3
251	26170.1	26164.8	26162.1	26160.3	26158.3
351	29014.3	29008.6	29004.6	29002.8	29001.1
451	31239.8	31226.9	31218.5	31212.5	31209.7
551	33104.6	33082.7	33070.7	33063.6	33059.1
651	34733.1	34688.6	34668.0	34657.6	34652.2
701	35443.4	35368.2	35341.3	35332.0	35323.8

Hamiltonian matrix. Inspection of the table suggests that the top levels are converged to within 10 cm^{-1} (note that even level 701 is actually above the dissociation energy of the MBB potential [23]). The lower levels are considerably better converged than this. It is possible to get an independent view of the convergence by comparing the energies of the even and odd symmetry calculations. About half the $J=0$ states of H_3^+ should be of degenerate E symmetry. In this case one even and one odd eigenvalue should be degenerate. Experience [9] has shown us that the splitting between these levels (the odd level is nearly always of lower energy) gives a good measure of the convergence.

The energies of our lowest 180 states are in good agreement with previous studies [9,14]. They represent a systematic improvement on our previous work [9] where we estimated that the highest levels were only converged to 10 cm^{-1}. Carter and Meyer [14], conversely, claim convergence for all their levels to 0.2 cm^{-1}. Detailed comparison with their results suggest while their states of A_1 symmetry may well be accurate to this amount, their states of A_2 and E symmetries are often as much as 6 cm^{-1} higher than ours.

To estimate the total number of bound states we obtain it is necessary to assign all the E levels, some thing that becomes increasingly difficult near the dissociation limit where the splitting of the E states becomes greater than the mean spacing between states. Alternatively, at high energy, it is possible to make a statistical assumption about the symmetry of the states calculated. We assumed that two-thirds of the odd states were E, the remaining being A_2. With this assumption the total number of states below a particular energy is given by the number of even states plus one-third the number of odd states. Table 3 compares this approximation with the actual numbers for the lowest 400 MBB states which have been assigned. The lowest 180 were assigned by comparison with Carter and Meyer [14], the remainder by looking for degeneracies in the even and odd calculations. This latter method is likely to overestimate the total number of E states slightly, and hence

Table 3
The number of bound states supported by each of the three surfaces for a range of energies. The energies (column 1) are given relative to the H_3^+ ground state for each surface. D_0 is the dissociation energy [23]: 35035.2 cm^{-1} for MBB, 37810.6 cm^{-1} for DIM, and 34424.5 cm^{-1} for the SDL surface

Energy (cm^{-1})	MBB (assigned)	MBB	DIM	SDL
10000	19	21	22	20
14000	44	47	52	47
18000	95	100	106	100
22000	174	183	192	184
26000	303	314	317	315
28000	397	401	398	404
30000	–	502	495	510
32000	–	624	607	637
34000	–	781	739	792
D_0	–	881	1071	828

underestimate the total number of states, because pairs of A_1 and A_2 states which happen to be close in energy will be assigned as E.

Table 3 shows that the statistical approximation is a reasonably good one. Using it we predict that the MBB potential supports 881 states. As these calculations are essentially variational in nature (see ref. [12] for a fuller discussion on whether the DVR method is variational), this number gives a lower bound on the actual number of bound states. However our tests strongly suggest that it is unlikely that we are missing more than 10 states. The statistical approximation may add a further error of 10 states, giving a total maximum error of 20 states.

Table 3 also presents results for the SDL and DIM potentials. The SDL results are very similar to those obtained using the MBB potential; this potential supports a slightly higher density of states at higher energies but a smaller total number of states because of its lower dissociation energy. At low energies the DIM potential supports more states than the other two, but the density drops near dissociation. The DIM potential overestimates the dissociation energy of H_3^+ and this results in the potential supporting over 1000 bound vibrational states. Although we have not done a detailed convergence analysis on the DIM potential we suspect that the DIM calculations are not quite so well converged as the others. Previous studies [10,11] have shown the DIM potential to be classically more chaotic (strongly coupled) than the MBB potential and hence harder to obtain converged results for.

In previous studies [9–11,24], contour plots of the wavefunction have proved very useful as a method

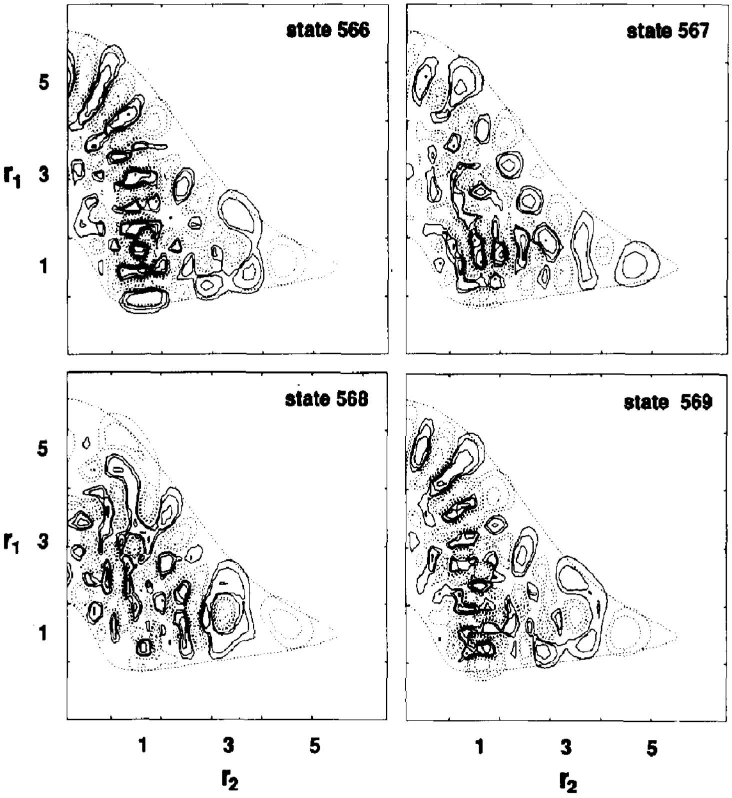

Fig. 1. Cuts through the wavefunction of four even H_3^+ vibrational states calculated using the MBB potential with $\theta = 90°$. Contours are for 64%, 32%, 16% and 8% of the maximum amplitude with solid (dashed) curves enclosing regions of positive (negative) amplitude. The outer contour gives the classical turning point. The band origins of the states are 33311, 33317, 33326 and 33335 cm^{-1}. The radial coordinates are given in atomic units (a_0).

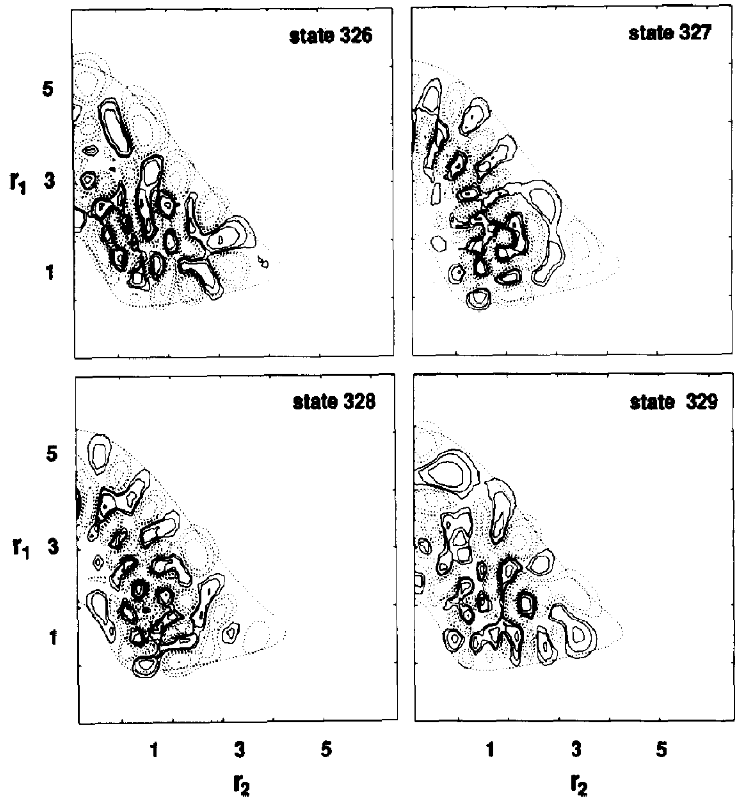

Fig. 2. Cuts through the wavefunctions of four even H_3^+ vibrational states calculated using the MBB potential with $\theta=90°$. Contours as in fig. 1. The band origins of the states are 28014, 28055, 28091 and 28138 cm^{-1}.

of obtaining insight into the nature of individual states. However analysing many hundreds of 3D states with 2D plots is a formidable undertaking. So far we have only looked at the even states and at the DVR point nearest $\theta=90°$; this corresponds to the previous analysis of H_3^+ wavefunctions. This particular cut through the wavefunction is appropriate for finding "horseshoe" states. These "horseshoe" states are perhaps better thought of as highly excited bending states of a quasilinear molecule. We find such states extending in a single progression all the way from the bending fundamental (ν_2) to dissociation – and indeed above it; we found a $19\nu_2$ state just above the dissociation limit of the MBB potential.

Figs. 1 and 2 illustrate typical contour plots of the wavefunctions of the high-lying states. Note that because we are confined to the coordinate range $r_2 \geqslant 0$, only half horseshoes appear in the plots. Fig. 1 shows two even states with $18\nu_2$ (numbers 566 and 569) and their immediate neighbours. Fig. 2 shows even states (numbers 327 and 328) with $14\nu_2$ as well as a quantum of excitation in the transverse stretching mode (ν_1). Again neighbouring states are included for comparison. The high-lying states that we assign to horseshoe modes have a large gathering of amplitude in the vicinity of the horseshoe periodic orbit, or in other words are scarred by it. However, none of the assignments we make in the high-energy region are particularly clear cut. This is in contrast to the intermediate energy horseshoe states analysed previously which showed very clear nodal structures [9].

The search for other regular features in the vibrational wavefunctions of this system is underway. This will be done both by plotting different cuts through the wavefunctions and also by transforming the wavefunctions to coordinates which better display other classical periodic orbits.

In summary, we have developed a 3D DVR method in scattering coordinates with which we obtain converged vibrational wavefunctions for H_3^+ up to dissociation. This is a major advance in our ability to treat this challenging and dynamically rich system. We believe that a proper quantal treatment of the predissociating states of H_3^+ observed by Carrington and co-workers [1,2] is near.

Finally we note that, compared for example to the cost of constructing 3D ab initio potential energy surfaces, these calculations are computationally fairly modest. For example a calculation with $N=2400$ took 2 min to perform all the steps up to and including constructing the final Hamiltonian matrix and 22 min to diagonalise this matrix, all timings are for a single processor of a Cray-XMP. Our decision to stop the calculation at $N=3300$ was solely determined by memory constraints.

We would like to thank the staff of the University of London Computer Centre for their help in performing these calculations. This work was supported by SERC grant GR/F/14550.

References

[1] A. Carrington, J. Buttenshaw and R.A. Kennedy, Mol. Phys. 45 (1982) 753.

[2] A. Carrington and R.A. Kennedy, J. Chem. Phys. 81 (1984) 91.

[3] E. Pollak, J. Chem. Phys. 86 (1987) 1645.

[4] M.S. Child, J. Phys. Chem. 90 (1986) 3595; R. Pfeiffer and M.S. Child, Mol. Phys. 60 (1987) 1367.

[5] M. Berblinger, E. Pollak and Ch. Schlier, J. Chem. Phys. 88 (1988) 5643.

[6] A. Carrington, J. Chem. Soc. Faraday Trans II 82 (1986) 1089.

[7] J.M. Gomez Llorente and E. Pollak, J. Chem. Phys. 88 (1988) 1195; 90 (1989) 5406.

[8] J.M. Gomez Llorente, J. Zakrewski, H.S. Taylor and K.C. Kulander, J. Chem. Phys. 89 (1988) 5959; 90 (1989) 1505.

[9] J. Tennyson and J.R. Henderson, J. Chem. Phys. 91 (1989) 3815.

[10] J. Tennyson, O. Brass and E. Pollak, J. Chem. Phys. 92 (1990) 3005.

[11] O. Brass, J. Tennyson and E. Pollak, J. Chem. Phys. 92 (1990) 3377.

[12] Z. Bačić and J.C. Light, Ann. Rev. Phys. Chem. 40 (1989) 469.

[13] R.M. Whitnell and J.C. Light, J. Chem. Phys. 90 (1989) 1774.

[14] S. Carter and W. Meyer, J. Chem. Phys. (1990), in press.

[15] J. Tennyson, S. Miller and J.R. Henderson, in: Methods in computational chemistry, Vol. 5, ed. S. Wilson (Plenum Press, New York, 1990).

[16] W. Meyer, P. Botschwina and P.G. Burton, J. Chem. Phys. 84 (1986) 891.

[17] S. Miller and J. Tennyson, J. Mol. Spectry. 128 (1987) 183.

[18] R. Schinke, M. Dupuis and W.A. Lester Jr., J. Chem. Phys. 72 (1980) 3909.

[19] Ch. Schlier and U. Vix, Chem. Phys. 95 (1985) 401.

[20] J. Tennyson and B.T. Sutcliffe, J. Chem. Phys. 77 (1982) 4061; 79 (1983) 43.

[21] J. Tennyson and B.T. Sutcliffe, J. Mol. Spectry. 101 (1983) 71.

[22] J.C. Light, R.M. Whitnell, T.J. Pack and S.E. Choi, in: Supercomputer algorithms for reactivity, dynamics and kinetics of small molecules, ed. A. Laganà, NATO ASI series C 277 (Kluwer, Dordrecht, 1989) p. 187.

[23] S. Miller and J. Tennyson, Chem. Phys. Letters 145 (1988) 117.

[24] J.R. Henderson and J. Tennyson, Mol. Phys. 69 (1990) 639.