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Phil. Trans. R. Soc. Lond. A 2000 **358**, 2419-2432
doi: 10.1098/rsta.2000.0657

10.1098/rsta.2000.0657

H_3^+ near dissociation: theoretical progress

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The observation of an infrared spectrum of the H_3^+ molecular ion at its dissociation limit by Carrington and co-workers has presented a tremendous challenge to theory. To compute this spectrum it is necessary to model accurately the global potential energy surface of H_3^+, vibrationally excited states at dissociation, rotational excitation, lifetimes of rotationally excited 'shape' resonances, and infrared transition dipoles near dissociation. Progress in each of these aspects is reviewed and results are presented for highly excited vibrational levels using a new *ab initio* global potential. The use of massively parallel computers in solving aspects of the problem is discussed.

Keywords: discrete variable representation; massively parallel computers; resonances

1. Introduction

In 1982, Carrington and co-workers announced the observation of a very unusual photodissociation spectrum for the H_3^+ molecular ion (Carrington *et al.* 1982). These workers made H_3^+ using electron-impact ionization of H_2, selected these ions with a mass spectrometer, and photodissociated them using a CO_2 laser:

$$H_3^+ + h\nu \rightarrow H_2 + H^+. \tag{1.1}$$

Photodissociation was monitored using an electrostatic analyser (ESA), which was set to monitor the proton current. The ESA is also sensitive to the kinetic energy of the ions monitored, and the original spectra were obtained by observing those ions with approximately zero kinetic energy in the frame of the molecule.

Simplistically, the kinetic energy released in the molecular frame corresponds to the amount of energy above dissociation contained in the fragmenting ion. However, the situation is complicated by the fact that some of the excess energy can be carried away by the molecular hydrogen fragment as vibrational or rotational excitation. Furthermore, the ESA only gives approximate kinetic energy resolution, and protons with a range of kinetic energies are, in practice, expected to contribute to the spectrum. Indeed, Carrington *et al.* (1993) showed that the spectrum varies strongly with kinetic energy release.

The experimental set-up of Carrington and co-workers is very sensitive; their spectrum results from between 0.1 and 1% of the ions in their system (Carrington &

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Phil. Trans. R. Soc. Lond. A (2000) **358**, 2419–2432

Kennedy 1984). However, Carrington *et al.* (1993) observed a very large number of well-defined transitions in the limited range of their laser, 872–1094 cm^{-1}. As the dissociation energy of H_3^+ is *ca.* 35 000 cm^{-1} (Cosby & Helm 1988; Lie & Frye 1992), this experiment monitors only those levels of the ion that lie very close to the dissociation limit. Prior to this experiment the structure of the rotation–vibration energy levels at dissociation for chemically bound molecules larger than diatomic was completely unknown. Indeed, H_3^+ and its isotopomers remains the only strongly bound polyatomic that has been studied in this fashion.

The spectrum of Carrington *et al.* (1993) was unexpected and truly remarkable. It has stimulated a whole host of theoretical studies, both (semi-)classical and quantal. Of course, H_3^+ is a highly quantal system; indeed, the very existence of the spectrum, depending as it does on tunnelling, means that classical mechanics can only have limited application. However, classical studies proved successful in interpreting the observed behaviour upon isotopic substitution (Gomez Llorente & Pollak 1987; Chambers & Child 1988).

One feature of the spectrum has provoked particular interest. Carrington & Kennedy (1984) convolved their high-resolution spectrum to show that at low resolution it showed coarse-grained structure: four peaks separated by *ca.* 50 cm^{-1}. Classical calculations show that H_3^+ is highly chaotic in the near-dissociation region. There have been several classical trajectory studies that tried to identify the regular motion embedded in the chaos that could be responsible for this coarse-grained structure. Gomez Llorente & Pollak (1989) identified the 'horseshoe' motion, where one H nucleus passes between the other two, as the key to this structure. However, subsequent calculations (Polavieja *et al.* 1994, 1996) have suggested at least one other possible candidate.

Classical work on the H_3^+ near-dissociation spectrum has been reviewed by Pollak & Schlier (1989). Carrington & McNab (1989), McNab (1994) and Kemp *et al.* (this issue) have reviewed the experimental work on this problem.

In this paper we address the problem of constructing a full quantum mechanical model of the H_3^+ near-dissociation spectrum. This is a formidable problem that requires consideration of many aspects of the problem: the electronic potential energy surface, highly excited vibrational motion, rotational excitation, lifetimes of the quasi-bound states, transition moments between the states, and other more-detailed considerations such as the validity of the Born–Oppenheimer approximation and modelling the initial conditions of the experiment. In the following sections we consider each of these aspects in turn and report on the latest progress in each case.

2. Potential energy surfaces

H_3^+ is a two-electron system and is, therefore, amenable to very-high-accuracy treatment of its electronic structure. Indeed, for spectroscopic studies, *ab initio* electronic structure calculations have been performed which are accurate in the absolute energy to better than 0.05 cm^{-1} (Cencek *et al.* 1998). This has led to *ab initio* spectroscopic studies that reproduce experiment to a similar level of accuracy (Polyansky & Tennyson 1999).

The situation is very different at energies near the H_3^+ dissociation limit. All the (semi-)classical studies and, until very recently, all the quantal studies were conducted using H_3^+ potential energy surfaces, which cannot be considered reliable, let alone accurate. The two most popular potentials, the diatomics-in-molecule (DIM) surface of Preston & Tully (1971) and the adjusted *ab initio* Meyer–Botschwina–Burton (MBB) surface (Meyer *et al*. 1986), both suffered from the same defect, which would appear to be crucial to modelling near-dissociation behaviour. Neither surface accurately models the potential energy of the system as it dissociates. Indeed, the MBB potential, used for nearly all quantal studies, was only designed for spectroscopic studies and can only be considered reliable below halfway to dissociation.

The long-range, near-dissociation behaviour of H_3^+ is actually relatively easy to model as the leading terms can be obtained accurately using perturbation theory (Giese & Gentry 1974). Indeed, Schinke *et al*. (1980) produced a surface that is globally correct using this long-range behaviour. However, this surface suffered from problems with symmetry and joins between different regions of the surface.

Recently, we (Prosmiti *et al*. 1997; Polyansky *et al*. 2000) have attempted to rectify this problem using two different approaches. In both cases two coupled surfaces were actually constructed to allow for the crossing of the $H^+ + H_2$ and $H + H_2^+$ dissociation channels at large diatomic bond lengths.

Our earlier work (Prosmiti *et al*. 1997), although it used some *ab initio* data from Schinke *et al*. (1980), was largely constructed from experimental data. It used the known long-range behaviour and spectroscopically determined portions of the surface (Dinelli *et al*. 1995) to create a reliable, global surface for the H_3^+ system. This surface proved relatively easy to construct and calculations using it have already been reported (Prosmiti *et al*. 1998). However, the lack of assigned spectroscopic data on H_3^+ for anything except the low-energy region means that the potential is not strongly constrained.

More recently, we (Polyansky *et al*. 2000) determined the global H_3^+ surface entirely from *ab initio* data. For this we used the ultra-high-accuracy, but limited, data of Cencek *et al*. (1998), augmented by further calculations of our own, giving about 200 high-accuracy *ab initio* electronic energies. At high energies, the surface was constrained using the data of Schinke *et al*. (1980). It proved surprisingly difficult to obtain a satisfactory fit to all the *ab initio* data to 5 cm^{-1} accuracy, leading us to present two alternative fits. Results presented below used fit 2, which removed unphysical features from the potential at the price of giving a slightly poorer fit to the *ab initio* data. The difficulty of fitting the *ab initio* data to its intrinsic accuracy suggests that the true surface displays really quite subtle behaviour, which will require further development of potential functions and a denser grid of *ab initio* points to model accurately.

It should be noted that Aguado *et al*. (2000) have also recently presented a global *ab initio* surface for H_3^+. These workers performed *ab initio* calculations at a very large number of geometries, 8469, which they fitted to the DIM form of Preston & Tully (1971) with an accuracy of *ca*. 20 cm^{-1}. Calculating many points defines the whole surface but at the cost of using lower-accuracy *ab initio* calculations. Perhaps more disappointingly, Aguado *et al*. (2000) did not ensure that their surface has the correct long-range behaviour at the near-dissociation limit.

3. Highly excited vibrational states

Following early, but limited, attempts to perform full quantum mechanical, nuclear motion calculations on the H_3^+ near-dissociation problem (Tennyson & Sutcliffe 1984;

Pfeiffer & Child 1987; Gomez Llorente *et al.* 1988; Tennyson & Henderson 1989; Tennyson *et al.* 1990), H_3^+ has become something of a benchmark system for studies of highly excited vibrational states. The first calculations that successfully obtained all the bound vibrational states of a chemically bound polyatomic molecule were performed on H_3^+ (Henderson & Tennyson 1990; Henderson *et al.* 1993). Since then a number of other workers have addressed this problem using methods of increasing accuracy. The work of Bramley *et al.* (1994) and Mandelshtam & Taylor (1997) is particularly notable. However, all these studies were performed on the non-dissociating MBB surface.

A common feature of our recent potentials, when compared with the MBB surface, is the much more attractive nature of the surface in the $H_2 + H^+$ dissociation channel. It is more difficult to compute all the bound vibrational states of these new more-realistic surfaces. This is because these surfaces support significantly more bound states and many of the new states cover a much greater range in the dissociative coordinate, generally denoted R.

To help address these problems we have been performing calculations on the highly excited vibrational states of H_3^+ using the PDVR3D program (Mussa *et al.* 1998; Mussa & Tennyson 2000). This program is an implementation of the DVR3D program (Tennyson *et al.* 1995) for performing calculations on highly excited states of triatomic species. The present calculations were performed on the 576-node Cray-T3E system located at the University of Manchester Computer Centre as part of the ChemReact computing consortium.

Besides the sheer size of a calculation designed to compute 10^3 or more states of a system, there are a number of severe technical problems specific to calculating high-lying states of H_3^+. The first of these involves the correct inclusion of symmetry. Coordinates that can easily be fully symmetrized, such as hyperspherical coordinates (Wolniewicz & Hinze 1994) and interparticle coordinates (Watson 1994), have been used successfully for high-accuracy studies of low-lying states. However, there are difficulties with employing any of these at high energy. Instead, all the near-dissociation calculations so far have used scattering (or Jacobi) coordinates, which are expressed in terms of H–H distance, r, the H^+–H_2 centre of mass distance, R, and the angle between $\underline{r}$ and $\underline{R}$, θ. In these coordinates the only symmetry for the rotationless, $J = 0$, problem is given by whether the basis has even or odd parity about $\theta = \pi/2$ (Tennyson & Sutcliffe 1984).

The second problem, which is more severe, involves the barrier to linearity. H_3^+ can probe linear geometries at energies of approximately one-third the dissociation energy. In Jacobi coordinates these geometries are handled correctly at $\theta = 0$ or π but with difficulty for $R = 0$ (Henderson *et al.* 1993). One result of this is that a number of calculations in Jacobi coordinates (Bačić & Zhang 1992; Tennyson 1993; Henderson *et al.* 1993) show differential convergence between odd and even symmetries. This can be at least partly cured by using symmetry-dependent basis functions in the R coordinate (Henderson *et al.* 1993; Mandelshtam & Taylor 1997; Prosmiti *et al.* 1998).

However, as discussed below, calculations on rotationally excited states involve mixing between calculations with different 'k' blocks, where k is the projection of the rotational angular momentum onto the body-fixed z-axis. For the best z-axis embedding, different k blocks employ 'even' and 'odd' R basis sets. Under these circumstances, both differential-convergence and k-block-dependent radial basis sets are undesirable.

For these reasons we are exploring the use of an alternative coordinate system for modelling the H_3^+ system. Radau coordinates (Smith 1980) are, like Jacobi coordinates, orthogonal and therefore simple to use in discrete variable representation (DVR) calculations. They have been used very successfully for a number of challenging calculations on rotationally excited water (Polyansky *et al*. 1997; Mussa & Tennyson 1998). Radau coordinates do not give a particularly good physical model of the H_3^+ system, but numerical studies have demonstrated (Bramley & Carrington 1994) that Jacobi coordinates do not either. Radau coordinates have the important advantages that linear geometries can be modelled without any of the radial coordinates going to zero and the same functions can be used for even and odd symmetries.

Table 1 presents both even and odd $J = 0$ results for the MBB potential. Comparison is made with the highly converged calculations of Bramley *et al*. (1994). Calculations are presented for both Radau and Jacobi coordinates using the program PDVR3DRJ (Mussa & Tennyson 2000). For even symmetry, a similar level of convergence is found in both coordinates for a final Hamiltonian size of $N = 8500$. However, for odd symmetry, there are significant differences between the Radau and Jacobi calculations, with the Radau calculations again giving reasonable agreement with those of Bramley *et al*. (1994).

The odd-symmetry Jacobi calculations give energies that are too low and are, therefore, non-variational. This problem was extensively analysed by Henderson *et al*. (1993) and attributed to the use of the quadrature approximation, standard in DVR approaches (Bačić & Light 1989). As $R \rightarrow 0$, integrals over the moment of inertia, which behaves as R^{-2}, are not correctly evaluated with this approximation. Henderson *et al*. (1993) were able to solve this problem by transforming between basis set and grid representations, but only at considerable computation expense. Their method would be very hard to implement efficiently on a parallel computer.

It should be noted that $N = 8500$ is not sufficient to fully converge our calculations and that larger calculations give close agreement with the results of Bramley *et al*. (1994) for the MBB potential. However, it is of more interest to converge the results on our more recent, global potentials. Table 2 presents preliminary results for the *ab initio* fit 2 of Polyansky *et al*. (2000). These results show uniform convergence for both even and odd symmetry with the $N = 11\,000$ results converged to *ca.* $1\ \mathrm{cm}^{-1}$. As was anticipated from their shape and because of their slightly higher dissociation energy, the new potentials support nearly 50% more vibrational states than the MBB potential. Full results of these calculations will be reported elsewhere.

4. Rotational excitation

While nearly all quantal studies of H_3^+ near dissociation have been performed for $J = 0$, rotational excitation is actually an essential ingredient of the observed spectrum. It has been established both from the experimental data and from early calculations that the states observed are trapped behind rotational barriers, or, in the standard terminology of scattering theory, are shape resonances. It is therefore essential to consider rotational excitation as part of a proper analysis of the observed near-dissociation experiments. Indeed, it is impossible to correctly model the lifetime effects, discussed in the next section, without considering rotational excitation.

There have only been two fully quantal attempts to compute rotationally excited states of H_3^+ in the near-dissociation region. Miller & Tennyson (1988) looked for the

Table 1. H_3^+ *band origins for the MBB potential*

(Vibrational band origins, in cm^{-1}, for H_3^+ calculated in Radau coordinates (E_R) using the MBB potential (Meyer *et al*. 1986) and a final Hamiltonian of dimension $N = 8500$. Differences with a Jacobi (E_J) coordinate calculation and the results of Bramley *et al*. (1994) (E_B) are given for comparison.)

even parity				odd parity			
state	E_R	$E_\mathrm{R} - E_\mathrm{J}$	$E_\mathrm{R} - E_\mathrm{B}$	state	E_R	$E_\mathrm{R} - E_\mathrm{J}$	$E_\mathrm{J} - E_\mathrm{B}$
530	32 698.39	0.13	1.80	442	32 389.75	1.49	−1.83
531	32 714.31	−0.37	0.78	443	32 392.43	1.14	0.70
532	32 714.98	−0.13	0.86	444	32 412.84	5.89	0.64
533	32 748.22	−0.40	0.82	445	32 425.08	5.54	0.36
534	32 777.92	1.76	2.40	446	32 436.30	8.98	−0.35
535	32 803.84	0.49	1.34	447	32 438.57	0.93	−0.27
536	32 823.48	0.97	1.44	448	32 510.02	5.47	1.16
537	32 833.91	0.95	1.80	449	32 525.10	7.87	0.17
538	32 840.00	0.24	1.11	450	32 542.36	10.90	0.87
539	32 849.06	−0.23	0.49	451	32 548.40	1.73	−0.15
540	32 866.05	−1.11	−0.10	452	32 587.23	1.67	0.18
541	32 899.86	−0.69	0.21	453	32 618.68	4.28	0.14
542	32 901.44	0.07	0.93	454	32 623.04	4.51	0.12
543	32 906.08	−0.36	0.16	455	32 643.22	1.62	−1.11
544	32 919.33	−0.24	1.38	456	32 649.35	3.74	−0.13
545	32 943.88	0.40	1.21	457	32 674.80	7.76	0.51
546	32 968.82	0.44	1.39	458	32 715.07	3.89	0.95
547	32 984.50	−0.04	0.97	459	32 748.69	3.96	1.29
548	32 987.12	0.28	1.05	460	32 769.47	7.53	−0.21
549	32 994.81	−1.76	−0.96	461	32 775.96	1.05	0.44
550	33 017.58	−0.28	−0.35	462	32 803.03	2.62	0.53
551	33 043.58	−0.69	0.65	463	32 820.09	0.97	−1.95
552	33 054.01	0.80	0.27	464	32 831.02	0.89	−1.09
553	33 064.76	0.17	1.73	465	32 847.32	7.23	−1.25
554	33 085.69	−1.09	1.31	466	32 866.43	4.51	0.28
555	33 118.70	−0.04	1.23	467	32 875.00	6.18	0.26
556	33 132.63	−0.17	0.68	468	32 892.62	12.45	0.32
557	33 154.78	0.44	1.93	469	32 902.19	7.30	1.68
558	33 157.48	−0.44	0.80	470	32 915.31	3.84	0.38
559	33 189.87	−1.03	0.23	471	32 919.23	4.00	1.28
560	33 199.61	−0.18	0.57	472	32 943.22	5.89	0.54
561	33 205.74	0.33	1.79	473	32 967.70	3.48	0.27
562	33 220.69	0.87	1.92	474	32 986.30	3.89	0.23
563	33 231.42	−0.96	0.70	475	32 996.71	4.66	0.94
564	33 282.87	0.46	1.34	476	33 043.25	3.03	0.32
565	33 292.92	−0.51	1.70	477	33 054.08	2.38	1.13
566	33 301.23	2.60	5.44	478	33 054.55	2.15	0.81
567	33 304.94	−2.11	−2.39	479	33 085.87	7.75	1.49
568	33 314.23	−0.12	1.92	480	33 117.72	2.95	0.25

Table 1. (*Cont.*)

even parity				odd parity			
state	E_R	$E_R - E_J$	$E_R - E_B$	state	E_R	$E_R - E_J$	$E_J - E_B$
569	33 325.70	−1.26	0.33	481	33 132.29	4.24	0.34
570	33 332.45	3.37	4.64	482	33 139.85	10.31	0.52
571	33 348.47	−1.00	0.34	483	33 156.59	3.52	−0.09
572	33 354.75	−1.90	−0.22	484	33 178.98	1.42	0.77
573	33 396.54	−0.75	0.28	485	33 189.97	2.66	0.33
574	33 401.44	−0.55	0.18	486	33 204.42	2.74	0.47
575	33 403.27	0.76	1.88	487	33 219.36	2.89	0.60
576	33 422.95	0.17	0.90	488	33 228.24	3.97	−0.23
577	33 434.61	−0.19	0.65	489	33 231.98	5.80	1.26

highest rotational state that was still bound. Their results are in good agreement with a recent semi-classical study by Kozin *et al*. (1999), which used the concept of relative equilibria to map out the behaviour of H_3^+ as the molecule is rotationally excited. This work has recently been extended to H_2D^+ and D_2H^+ (Kozin *et al*. 2000).

The other quantal near-dissociation study was performed by Henderson & Tennyson (1996), who computed states with $J = 0$, 1 and 2 up to dissociation. These calculations were limited by the available computer resources; some of their calculations took more than two weeks' computer time, and even then were not highly converged.

Recent studies of rotationally excited states of water in Radau coordinates by Mussa & Tennyson (1998) were able to converge all $J = 2$ up to dissociation in *ca.* 1 h using 64 processors on a Cray-T3E. As water is both heavier and has a higher dissociation energy than H_3^+, there is no reason why Mussa & Tennyson's method should not work well for H_3^+. Indeed Mussa & Tennyson (1998) performed calculations for water with $J = 10$; $J \leqslant 10$ should be sufficient to cover the critical portions of the low kinetic energy release spectrum (Gomez Llorente & Pollak 1989).

At high kinetic release it seems likely (Carrington *et al*. 1993) that the sparser and stronger photodissociation spectrum is actually sampling states of much higher rotational excitation. Experience with water (Viti 1997) and the early H_3^+ calculations of Miller & Tennyson (1988) have shown that because there are fewer bound states for high J values, such calculations are actually easier. However, present methods (Mussa & Tennyson 2000), which scale linearly with J for low J, would probably need to be adapted for this situation.

5. Lifetime effects

One problem with any theoretical attempt to model the H_3^+ spectrum of Carrington and co-workers is that the experiment is only sensitive to states that fall inside certain lifetime windows. Particularly the lower states, some or all of which are quasi-bound (Carrington & Kennedy 1984), must live long enough to enter the portion of the apparatus with the photodissociating laser. Conversely, the upper states must be

Table 2. *Convergence of* H_3^+ *band origins*

(H_3^+ vibrational band origins, in cm^{-1}, as a function of the size of the final Hamiltonian matrix, N. Calculation in Radau coordinates for fit 2 of the *ab initio* potential of Polyansky *et al.* (2000). For $N < 11\,000$, differences to the $N = 11\,000$ results are given.)

even parity				odd parity			
state	$N = 11\,000$	10 000	8500	state	$N = 11\,000$	10 000	8500
753	35 849.93	−0.84	−2.05	660	35 842.43	−0.44	−1.49
754	35 855.98	−0.78	−2.14	661	35 858.33	−0.42	−1.17
755	35 864.92	−0.70	−1.70	662	35 863.43	−0.45	−1.29
756	35 884.62	−1.46	−2.92	663	35 868.16	−0.58	−1.81
757	35 906.57	−0.74	−2.08	664	35 880.33	−0.46	−1.47
758	35 917.26	−0.53	−1.70	665	35 902.20	−0.48	−1.51
759	35 926.10	−0.97	−2.46	666	35 918.11	−0.43	−1.30
760	35 938.88	−0.80	−1.82	667	35 955.49	−0.74	−1.98
761	35 958.35	−0.67	−1.76	668	35 962.39	−0.50	−1.37
762	35 969.75	−1.11	−2.92	669	35 981.56	−0.74	−2.17
763	35 988.71	−0.69	−1.81	670	35 988.90	−0.31	−1.07
764	35 992.06	−0.61	−1.54	671	35 994.67	−0.79	−2.23
765	36 002.35	−0.83	−2.29	672	36 014.00	−0.51	−1.83
766	36 019.37	−0.81	−1.89	673	36 026.28	−0.32	−0.95
767	36 029.49	−0.98	−1.95	674	36 043.44	−0.47	−1.35
768	36 037.82	−0.47	−1.31	675	36 050.89	−0.55	−2.30
769	36 060.54	−0.64	−1.74	676	36 075.07	−0.67	−1.74
770	36 082.28	−0.74	−1.52	677	36 087.24	−0.53	−1.59
771	36 100.55	−0.66	−1.75	678	36 092.60	−0.49	−1.68
772	36 119.35	−0.72	−1.98	679	36 121.79	−0.66	−1.94
773	36 134.49	−1.01	−2.63	680	36 125.85	−0.68	−1.81
774	36 136.98	−0.75	−1.82	681	36 139.53	−0.59	−2.10
775	36 153.87	−0.79	−2.25	682	36 148.68	−0.64	−1.96
776	36 165.03	−0.89	−2.19	683	36 159.17	−0.67	−1.89
777	36 182.41	−0.73	−2.01	684	36 163.88	−0.59	−1.63
778	36 190.20	−0.59	−1.59	685	36 174.04	−0.74	−2.44
779	36 198.62	−0.85	−1.87	686	36 186.48	−0.49	−1.32
780	36 203.71	−0.66	−1.93	687	36 197.86	−0.94	−2.40
781	36 230.84	−0.74	−1.81	688	36 216.33	−0.55	−1.61
782	36 253.46	−0.97	−2.33	689	36 231.19	−0.48	−1.54
783	36 265.99	−0.96	−2.12	690	36 242.43	−0.49	−1.39
784	36 276.01	−1.01	−3.00	691	36 262.76	−0.69	−2.09
785	36 291.96	−0.52	−1.47	692	36 287.47	−0.75	−2.69
786	36 300.25	−0.75	−2.05	693	36 296.06	−0.59	−1.88
787	36 312.29	−0.71	−1.86	694	36 313.23	−0.39	−1.21
788	36 326.74	−0.71	−1.79	695	36 343.42	−0.92	−2.60
789	36 341.36	−0.75	−2.04	696	36 357.03	−0.63	−1.98
790	36 359.90	−0.60	−1.60	697	36 374.51	−0.58	−1.88
791	36 376.42	−0.47	−1.38	698	36 388.81	−0.58	−1.74

Table 2. (*Cont.*)

even parity				odd parity			
state	$N = 11\,000$	10 000	8500	state	$N = 11\,000$	10 000	8500
792	36 385.85	−0.61	−1.64	699	36 395.72	−0.81	−2.27
793	36 390.15	−0.88	−2.26	700	36 406.95	−0.28	−0.86
794	36 399.05	−0.88	−2.22	701	36 413.77	−0.66	−2.03
795	36 410.36	−0.76	−2.02	702	36 428.56	−0.49	−1.69
796	36 422.48	−1.08	−2.00	703	36 435.45	−0.71	−2.21
797	36 423.73	−0.88	−2.49	704	36 449.86	−0.51	−1.50
798	36 443.04	−0.88	−2.21	705	36 463.81	−0.47	−1.52
799	36 455.26	−0.82	−1.89	706	36 474.91	−0.61	−1.60
800	36 468.25	−0.75	−2.03	707	36 483.68	−0.61	−2.00

short enough lived to decay before the excited H_3^+ ions leave the apparatus altogether. In addition, for a few transitions, Carrington *et al.* (1993) were able to determine lifetimes from measurements of linewidths, although in most cases the states were too long lived for this to be possible.

Mandelshtam & Taylor (1997) have computed positions and widths for resonances in the H_3^+ system. However, these calculations were only performed for vibrationally excited states with $J = 0$. It is well established (Pollak & Schlier 1989; Drolshagen *et al.* 1989) that such Feshbach resonances are much too broad, i.e. decay much too quickly, to be important for the observed near-dissociation spectrum.

There are essentially no calculations on quasi-bound rotationally excited states for chemically bound systems. An exception are the studies by Skokov & Bowman (1999*a*, *b*) on the simpler HOCl system. However, even these calculations employed an approximation which neglects all coupling between k-blocks, i.e. all the off-diagonal Coriolis interactions. This decoupling approximation is valid for HOCl but not useful for H_3^+.

We have adapted the PDVR3D program suite to study resonances using procedures similar to those adopted by both Mandelshtam & Taylor (1997) and Skokov & Bowman (1999*a*, *b*). Initial results, as reported by Mussa & Tennyson (2000), are only for $J = 0$, but we have recently generalized this method to deal with fully Coriolis coupled rotationally excited states. The new procedure will be applied to H_3^+ in the near future.

6. Dipole transitions

To model any spectrum successfully it is necessary to consider transition moments as well as energy levels. Indeed, the near-dissociation spectrum of H_3^+ shows pronounced variation in line intensities both through the structure in the coarse-grained spectrum at low kinetic energy release (Carrington & Kennedy 1984) and the stronger lines with high kinetic energy release (Carrington *et al.* 1993).

The quantum manifestation of the classical chaos found for highly excited H_3^+ might be expected to display itself in spectra that show little or no structure. However, the vibrational band strength calculations of Le Sueur *et al.* (1993) suggest that transitions in the near-dissociation region may well show strong propensity rules due to transition-moment effects. The only attempt to compute actual dipole transition strengths at the frequencies covered by Carrington *et al.*'s CO_2 laser was by Henderson & Tennyson (1996). This, necessarily simplified, calculation could not reproduce the observed coarse-grained structure observed in the H_3^+ photodissociation spectra. Henderson & Tennyson (1996) concluded that it is necessary to combine lifetime and transition-moment effects in any attempt to model the near-dissociation spectrum of H_3^+.

7. Other considerations

The sections above discuss a series of issues that have to be addressed in any attempt to model the H_3^+ spectra of Carrington and co-workers. However, even if all the above steps are accomplished one would still not expect perfect agreement between theory and experiment. Before this can be achieved at least two other aspects of the problem have to be considered.

All the discussion above has been presented in terms of the Born–Oppenheimer separation between nuclear and electronic motion. H_3^+ is a light molecule for which the Born–Oppenheimer approximation is only known to be valid to an accuracy of *ca.* 1 cm^{-1} for the well-studied, low-energy, high-resolution spectra of H_3^+ and its isotopomers. Any attempt to give a line-by-line interpretation of the H_3^+ near-dissociation spectrum will, therefore, inevitably have to address the Born–Oppenheimer problem. Although the possibility of doing this is still some way off, it is encouraging to note that Polyansky & Tennyson (1999) were able to perform *ab initio* non-Born–Oppenheimer calculations that reproduced the high-resolution spectrum of H_3^+ to within a few hundredths of a wavenumber, nearly two orders of magnitude better than the best possible Born–Oppenheimer calculation. Furthermore, it would not be difficult to implement Polyansky & Tennyson's (1999) procedure in a near-dissociation calculation.

A second consideration is experimental. As in all laboratory spectroscopic experiments on H_3^+, the ions are produced in a hydrogen discharge. This is an efficient method of creating H_3^+, and one which, by cooling the discharge, can tune the level of H_3^+ excitation produced. However, the resulting population of H_3^+ vibration and rotation states is not well characterized. Indeed, any thermal or quasi-thermal population would be unlikely to yield the near-dissociation states accessed in the experiments discussed here. Clearly, any thorough theoretical model of these experiments will need to make some assumptions about the initial population.

8. Conclusion

It is now a considerable time since Carrington *et al.* (1982) reported the detection of a very detailed near-dissociation spectrum of H_3^+. This work and its subsequent refinements (Carrington & Kennedy 1984; Carrington *et al.* 1993) have presented a considerable challenge that theory has yet to fully meet. However, advances in computer technology matched with algorithmic developments suggest that the first fully quantal models of the spectrum, if not the first quantum number assignments, should not be very far off.

There is one aspect of the H_3^+ problem that merits comment. There has been considerable work, both experimental and theoretical, on the high-resolution spectrum of H_3^+ and its isotopomers using standard spectroscopic techniques (see contributions by McCall and by Watson in this issue). The H_3^+ system is well characterized at energies extending maybe as far as 10 000 cm^{-1} above its ground state. There is then a gap of some 25 000 cm^{-1} to the region about dissociation probed by Carrington and co-workers. As yet there is no experimental information on this region. This is despite theoretical predictions of relatively high-intensity spectra with a pronounced structure (Le Sueur *et al*. 1993) and the availability of high-accuracy calculations (Cencek *et al*. 1998; Polyansky & Tennyson 1999) that could be extended to give good frequency predictions for a possible experiment. There is no doubt that experimental information on this intermediate-energy regime would be of great help to those trying to perform reliable calculations for energies near dissociation.

This work has been supported by the UK Engineering and Physical Sciences Research Council via the ChemReact Computing Consortium and other grants. The work of O.L.P. was partly supported by the Russian Fund for Fundamental Studies. R.P. acknowledges a TMR Fellowship, under contract ERBFMBICT 960901.

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Discussion

B. SUTCLIFFE (*Université de Bruxelles Libre, Belgium*). It is well known that it is extremely difficult to get potential energy surfaces without ‘holes’ in them, particularly in the asymptotic regions. Are you confident that your surface for H_3^+ is without holes?

J. TENNYSON. It is indeed difficult to construct potential energy surfaces free from spurious features, of which deep unphysical minima, ‘holes’, is the worst example. In the particular case of our H_3^+ potentials (Prosmiti *et al.* 1997; Polyansky *et al.* 2000), we have taken particular measures to stop this happening in the asymptotic region by using the known behaviour of the potential when one atom or ion is well separated from the rest of the molecule. We believe this method is good for dealing with the asymptotes, but is not a cure for all problems with unphysical behaviour. In constructing our most recent and most accurate H_3^+ potential (Polyansky *et al.* 2000), we had considerable difficulty with what appears to be an unphysical shoulder in the potential at certain near-linear geometries.