PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

Phil. Trans. R. Soc. A (2006) **364**, 2903–2916
doi:10.1098/rsta.2006.1890

The role of asymptotic vibrational states in H_3^+

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Calculations are discussed which characterize all the vibrational bound states of the H_3^+ and D_2H^+ molecular ions using a realistic *ab initio* potential energy surface. Graphical analysis and calculation of rotational constants show that both ions support a series of atom–diatom-like long-range states: asymptotic vibrational states. The role of these states in the H_3^+ system and other molecules is discussed. The vibrational calculations are extended above dissociation where the resulting (Feshbach) resonances are shown to be too short-lived to be of importance for the H_3^+ photodissociation spectrum.

Keywords: discrete variable representation; resonances; lifetimes; rotational constants

1. Introduction

How small molecules vibrate and rotate about their equilibrium structure is well understood qualitatively in terms of simple models and quantitatively by the use of computational methods based on the variational principle. Indeed, for H_3^+, such calculations can achieve near-spectroscopic accuracy (Polyansky & Tennyson 1999). The understanding of the equivalent nuclear motion states near the dissociation limit of chemically bound molecules is much more rudimentary. For diatomic systems, the situation is fairly straightforward even if such states can be very extended (e.g. Luo *et al.* 1996).

Three atom systems are qualitatively different from diatomic molecules, because, in principle, energy can be stored in non-dissociating vibrational modes leading to the presence of quasibound vibrational states lying above the dissociation limit. Such states are analogous to the Feshbach resonances found in electron collision and other similar problems. Furthermore, triatomics dissociate to an atom and a diatomic meaning that even at dissociation the system retains some zero-point energy. The significance of this will be discussed in §3*a*.

A number of calculations are now available which consider all the vibrational states of molecules up to dissociation. Chemically bound molecules for which such calculations have been performed include water (Mussa & Tennyson 1998; Gray & Goldfield 2001; Li & Guo 2001), HOCl (Skokov *et al.* 1998; Mussa & Tennyson 2002) and NO_2 (Salzgeber *et al.* 1998, 1999). A particular class of systems that have been studied in this fashion include those with three identical atoms: the argon trimer

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One contribution of 26 to a Discussion Meeting Issue 'Physics, chemistry and astronomy of H_3^+'.

(Wright & Hutson 1999), ozone (Siebert & Schinke 2003) and, of course, H_3^+ (Henderson & Tennyson 1990; Henderson *et al.* 1993; Bramley *et al.* 1994; Mandelshtam & Taylor 1997; Kostin *et al.* 2003). It transpires that the X_3 systems studied all appeared to give qualitatively similar structure of the vibrational states. Whether this is simply an accident caused by a fortuitous scaling relation between the (inverse square root of the) reduced mass and the depth of the potential well remains to be seen. Although the special case of the very weakly bound helium trimer is known to support very long-range vibrational states (Esry *et al.* 1996; Barletta & Kievsky 2001), the possibility of such states existing for the other systems cited seems to have been largely ignored.

In the specific case of H_3^+, it is hardly surprising that the possibility of long-range states has been ignored. Until recently, all calculations were performed using potential energy surfaces which did not display the correct behaviour at dissociation and therefore could not support such states. However, since potentials which show the correct long-range behaviour for the system have become available (Prosmiti *et al.* 1997; Aguado *et al.* 2000; Polyansky *et al.* 2000), it has been possible to perform calculations which probe the structure of H_3^+ vibrational states near the dissociation limit (Munro *et al.* 2005, 2006). Such studies have also been extended to one of its deuterated isotopologues (Barletta *et al.* 2006).

The particular interest in near-dissociation states of H_3^+ was sparked by the near-dissociation experiments of Carrington and co-workers (Carrington *et al.* 1982, 1993; Carrington & Kennedy 1984; Carrington & McNab 1989), which probed highly excited bound and quasibound states of H_3^+ by monitoring protons produced via the process

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

where the photon, $h\nu$, was provided by a CO_2 laser. The experiments monitored in detail a discrete spectrum, which is both dense and complicated. This work is reviewed by McNab (1995).

Carrington & Kennedy (1984) found that this spectrum displayed a regular coarse-grained structure when analysed at low resolution. One explanation for this structure put forward at the time (Carrington & Kennedy 1984; Pfeiffer & Child 1987) was that this structure was due to states corresponding to a proton vibrating against an H_2 molecule. This possibility has been downplayed as other explanations for the coarse-grained structure were proposed (Gomez Llorente & Pollak 1987; Pollak & Schlier 1989). In this work, we report on recent calculations which show that the H_3^+ system does indeed display such long-range states, and on progress on using the calculations on these and other states to develop a fully quantum mechanical model of the near-dissociation spectrum of Carrington and co-workers.

2. Calculations on highly excited vibrational states

Details of the calculations have been given elsewhere (Munro *et al.* 2005, 2006; Barletta *et al.* 2006) and will only be summarized here. These calculations are based on slightly modified versions of the high-accuracy *ab initio* potential of PPKT (Polyansky *et al.* 2000). The main modification, to remove an artificial barrier in the exit channel in this potential, is detailed by Munro *et al.* (2006), who call this version the PPKT2 potential. For test purposes, calculations were also

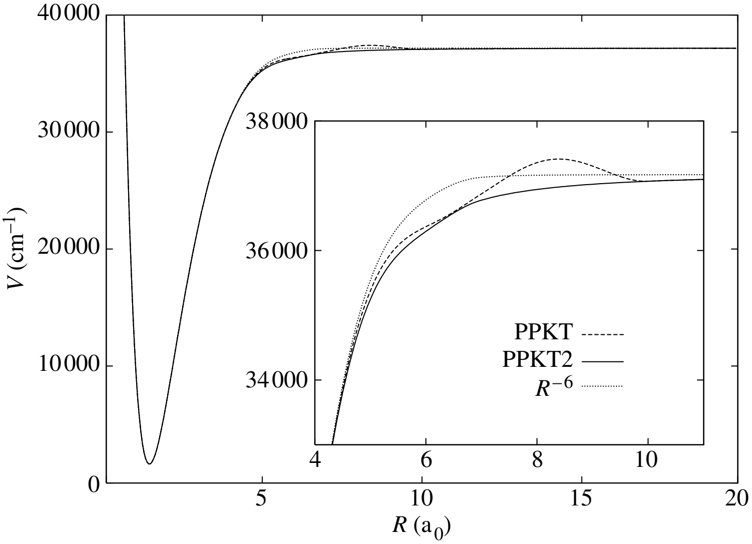

Figure 1. Cut through ground-state H_3^+ potentials for the H^+–H_2 coordinate, R, for an H_2 distance of $1.4a_0$ and an angle of 90°. PPKT, potential of Polyansky *et al.* (2000); PPKT2 as modified by Munro *et al.* (2006); and R^{-6}, PPKT2 with an R^{-6} long-range term.

performed on a further modification of the potential where the long-range portion of the potential was modified. In this version of the potential, the long-range part depends on R^{-6}, appropriate for a Van der Waals complex, rather than R^{-3} and R^{-4} appropriate for the charge-polarizability and charge-quadrupole interactions, respectively, which are appropriate for H_3^+. Figure 1 compares a cut through these different potentials showing their differing asymptotic behaviours. The potentials are all the same at short range. PPKT2 potential was also used for calculations on D_2H^+; in other words, no allowance was made for mass-dependent effects owing to failure of the Born–Oppenheimer approximation.

Nuclear motion calculations were performed with a modified (Tennyson *et al.* 2000; Kostin *et al.* 2003) version of the parallelized discrete variable representation program PDVR3D of Mussa & Tennyson (2000). All results discussed here are for the rotational ground state, i.e. $J=0$. Preliminary calculations were performed in both Jacobi (Ramanlal 2005) and Radau coordinates; however, for technical reasons (Munro *et al.* 2006), Radau coordinates (Smith 1980) give better convergence behaviour and all results presented here used these coordinates.

Obtaining converged results for the high-lying states supported by the PPKT2 potential is computationally much more demanding than for non-dissociating potentials used in earlier studies (Kostin *et al.* 2003). For this reason, it is necessary to use a large parallel computer. All calculations reported here were performed on the massively parallel HPCx supercomputer at the Daresbury Laboratory. The most demanding calculations were those on D_2H^+, as this system supports approximately twice the number of vibrational states. Largely for reasons to do with memory, studies on D_2H^+ required 1280 nodes on HPCx and took up to 4 h. Our aim was to converge calculations to within 1 cm^{-1} for all bound states of the system which was achieved by diagonalizing a final Hamiltonian matrix of dimensions 79 091 and 121 999 for H_3^+ and D_2H^+, respectively.

The near-dissociation photodissociation experiments on H_3^+ probe not only high-lying bound states of the system, but also quasibound states. It is therefore important to have methods to characterize both the position and lifetime (or width) of these resonances. The complex absorbing potential (CAP) method has been used before to calculate three-body resonances in conjunction with finite basis expansions (see Muga *et al.* 2004). In this work, we have adapted the numerical procedure of Mussa & Tennyson (2002), who studied the rather less-challenging HOCl system above its dissociation limit. This procedure involves using the states obtained from diagonalizing the Hamiltonian, $\hat{H}_0$, of the system in a region about the dissociation limit as a basis to diagonalize a Hamiltonian augmented by a CAP, U,

$$\hat{H} = \hat{H}_0 + \mathrm{i}\lambda U. \tag{2.1}$$

The resulting complex eigenvalues represent the position and width of possible resonances, but it is necessary to use a search procedure based on varying the strength of the absorbing potential, λ, to identify best estimates for these parameters. An example of this is given below.

Two absorbing potentials are tested below. The first is a simple quadratic function

$$U(R) = \left(\frac{R - R_{\min}}{R_{\max} - R_{\min}}\right)^2, \tag{2.2}$$

where R is Jacobi atom–diatom distance. $R_{\min}$ and $R_{\max}$ are the parameters which define the range of the absorbing potential which assumed to be zero outside this range. The second absorbing potential tested is the more complicated but theoretically more justified form of Gonzalez-Lezana *et al.* (2004).

3. Results

(*a*) H_3^+ *asymptotic vibrational states*

The study of near-dissociation states in a triatomic brings into play an effect which is not found in diatomic molecules. Provided the triatomic dissociates to an atom and a diatom, there is an energy range where there can be quantum but not classical bound vibrational states of the system owing to zero-point energy effects of the diatomic. This region is characterized by the difference between the classical dissociation limit, D_e, and the quantal dissociation limit, D_0. As noted by Munro *et al.* (2005), in this region H_3^+ displays a number, at least 14 for the PPKT2 potential, of vibrational states which have the appearance of atom–diatom states where the atom is well separated from the diatom. Munro *et al.* labelled these states asymptotic vibrational states (AVS).

Figure 2 gives probability distributions for four even (A_1 and E symmetry) vibrational states in the near-dissociation region. These states were calculated using Radau coordinates; the plots are presented as cuts through Jacobi coordinates, as these coordinates are best for visualizing atom–diatom-type behaviour. States 668, 670 and 677 are clearly long range in nature and are the ones we would characterize as AVS; state 675 is more typical of the (chaotic?) short-range states studied extensively in earlier calculations.

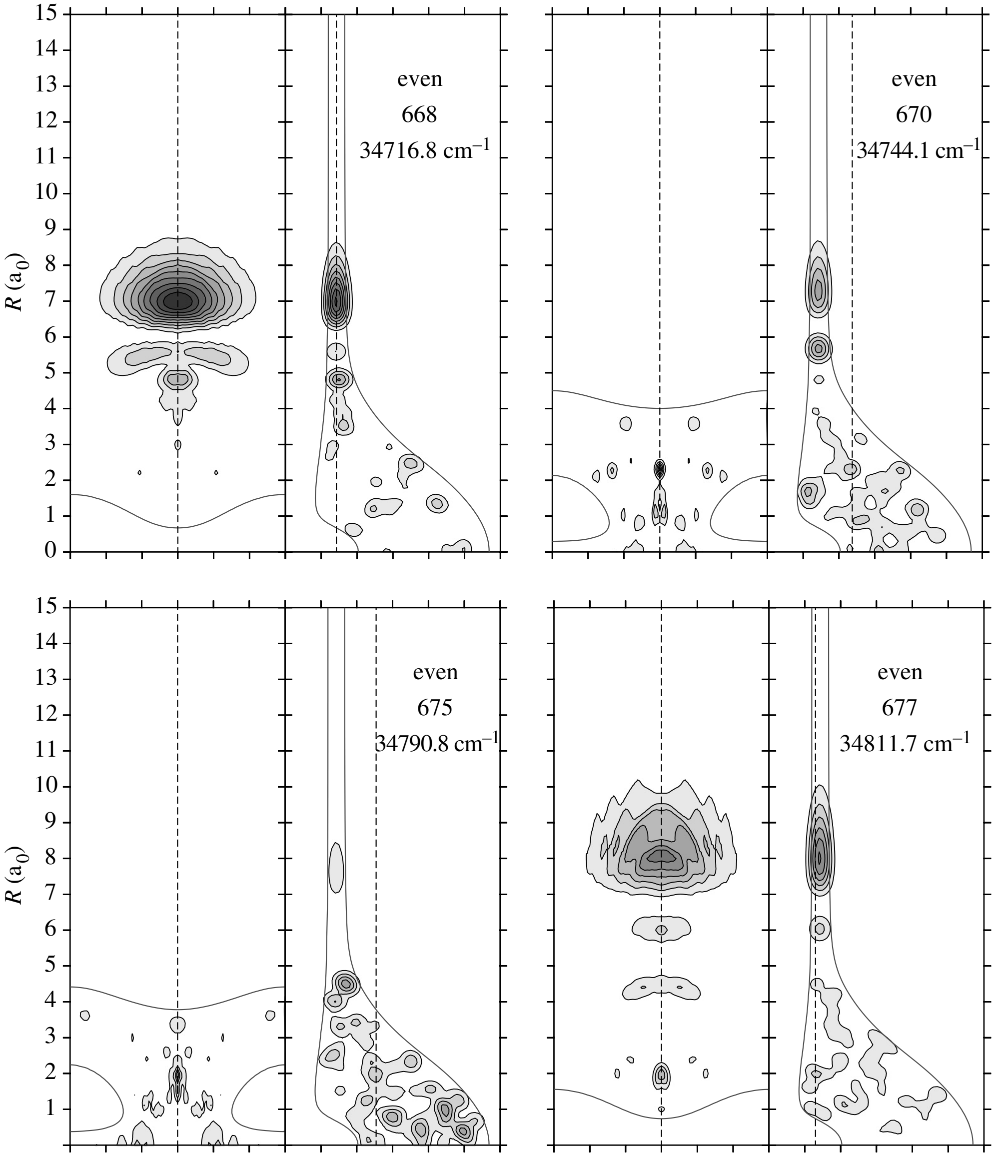

Figure 2. Probability distributions for four even near-dissociation vibrational states of H_3^+. Plots are in Jacobi coordinates with each cut taken at the maximum probability for the frozen coordinate. The value of the frozen coordinate is indicated by the dashed line on the other cut. The solid line gives the classical turning point of the potential for the particular vibrational energy, which is given in each plot as the vibrational band origin.

Although inspection of plots such as those given in figure 2 points strongly towards the existence of AVS in H_3^+, visual inspection of wave functions for systems of more than two dimensions is somewhat subjective as the images depend on both the choice of coordinates and the cuts taken. Munro *et al.* (2005)

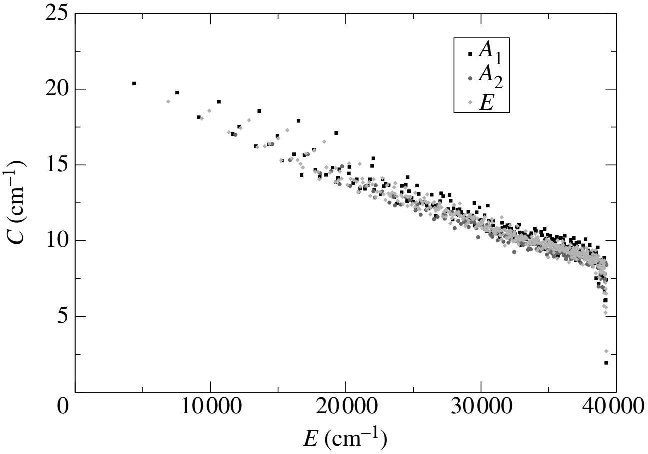

Figure 3. Rotational constants for all the bound states of H_3^+ designated by symmetry of the underlying vibrational state.

suggested a more quantitative method of identifying AVS via the C rotational constant which is associated with rotation about the axis perpendicular to the plane of the molecule. This can be calculated as an expectation value of the vibrational wave function using the procedure of Ernesti & Hutson (1994). Figure 3 presents rotational C constants calculated in this fashion for all the vibrationally bound states of H_3^+. The figure shows that in a small region near dissociation, there are indeed a series of states with smaller rotational constants than any of those found for the lower-lying vibrational states.

Table 1 lists vibrational band origins and C constants for the top even (A_1 and E) vibrational levels supported by the PPKT2 potential. This potential, as is appropriate for H_3^+, decays only as R^{-3}. It is interesting to ask if such a long-range decay is necessary to support AVS. As a numerical test, we also performed calculations on the R^{-6}-modified PPKT2 potential. At low energy, this potential gives the same results as the PPKT2 and PPKT potentials, since these states are not sensitive to the asymptotic form of the potential. Table 1 shows that unsurprisingly this is not true for states close to dissociation. However, even for the R^{-6}, there are states with significantly reduced rotational constants which we take to be the signature of an AVS. Our calculations find that the potentials support the same number of short-range vibrational states, but the R^{-6} potential supports six fewer even AVS and hence six fewer vibrational states in total. When considering these numbers, it should be remembered that our calculations are essentially variational in nature and only give a lower bound to the number of bound states of the system. In particular, we consider it probable that further even longer-range states would be revealed by using more extended radial grids in the calculation.

(*b*) D_2H^+ *asymptotic vibrational states*

Besides the H_3^+ vibrational calculations discussed previously we have also made a study of the vibrational states of D_2H^+. This system was extensively studied by Carrington *et al.* (1993), who monitored isotope effects in their photodissociation

Table 1. Near-dissociation H_3^+ vibrational levels and rotational constants. Near-dissociation even vibrational band origins, in cm^{-1}, for H_3^+ calculated in Radau coordinates for the PPKT2 and R^{-6} potentials. N_e gives the state number and $\langle C \rangle$ is the effective C-axis rotational constant. Levels given in bold are the ones identified as AVS.

PPKT2 potential			R^{-6} potential		
N_e	level (cm^{-1})	$\langle C \rangle$ (cm^{-1})	N_e	level (cm^{-1})	$\langle C \rangle$ (cm^{-1})
660	34606.788	8.727			
661	34619.147	8.365	657	34622.251	8.971
662	34633.690	8.163	658	34633.287	8.199
			659	34639.221	7.788
663	34646.539	7.650	660	34649.220	8.311
664	34667.981	8.498	661	34666.773	8.346
665	34668.158	8.515	662	34672.213	8.866
666	34677.211	8.594	663	34686.188	8.602
667	34685.077	7.562	664	34686.673	8.232
668	**34716.850**	**5.704**	665	34712.221	7.700
669	34726.958	8.482	**666**	**34726.256**	**6.853**
670	**34744.139**	**6.572**	667	34740.021	8.510
671	34745.815	8.858	668	34752.664	8.925
672	34750.744	8.128	669	34754.039	8.681
673	34763.433	8.679			
674	**34769.659**	**6.759**	670	34768.022	8.753
675	34790.860	7.751	671	34800.405	8.404
676	34795.457	7.840	672	34804.481	8.661
677	**34811.712**	**6.048**	673	34806.041	7.831
678	34823.961	7.227			
679	34825.222	7.343			
680	**34836.529**	**5.200**	674	34834.842	8.374
681	**34852.006**	**6.085**	675	34848.322	8.609
682	**34858.105**	**6.825**	676	34861.900	7.947
683	**34865.425**	**5.606**	**677**	**34864.658**	**6.447**
684	**34882.977**	**6.483**			
685	**34891.348**	**1.941**	**678**	**34887.905**	**6.252**
686	34897.999	7.423	679	34896.232	7.068
687	**34901.023**	**2.371**	**680**	**34906.264**	**5.840**
			681	**34913.519**	**4.460**

spectra. It should be noted that for technical reasons, their results for D_2H^+ are more extensive than those for H_2D^+, which would have been easier for us to study since it is lighter and therefore supports fewer bound states. Isotopic effects appear to be the aspect of the near-dissociation photodissociation spectra that can be clearly interpreted in terms of semi-classical models (Chambers & Child 1988). Such mixed isotopologues are also of interest as their wave functions in the near-dissociation region have a link to isotope exchange reactions such as

$$HD + D^+ \rightarrow D_2 + H^+, \tag{3.1}$$

which is exothermic by 334 cm^{-1}.

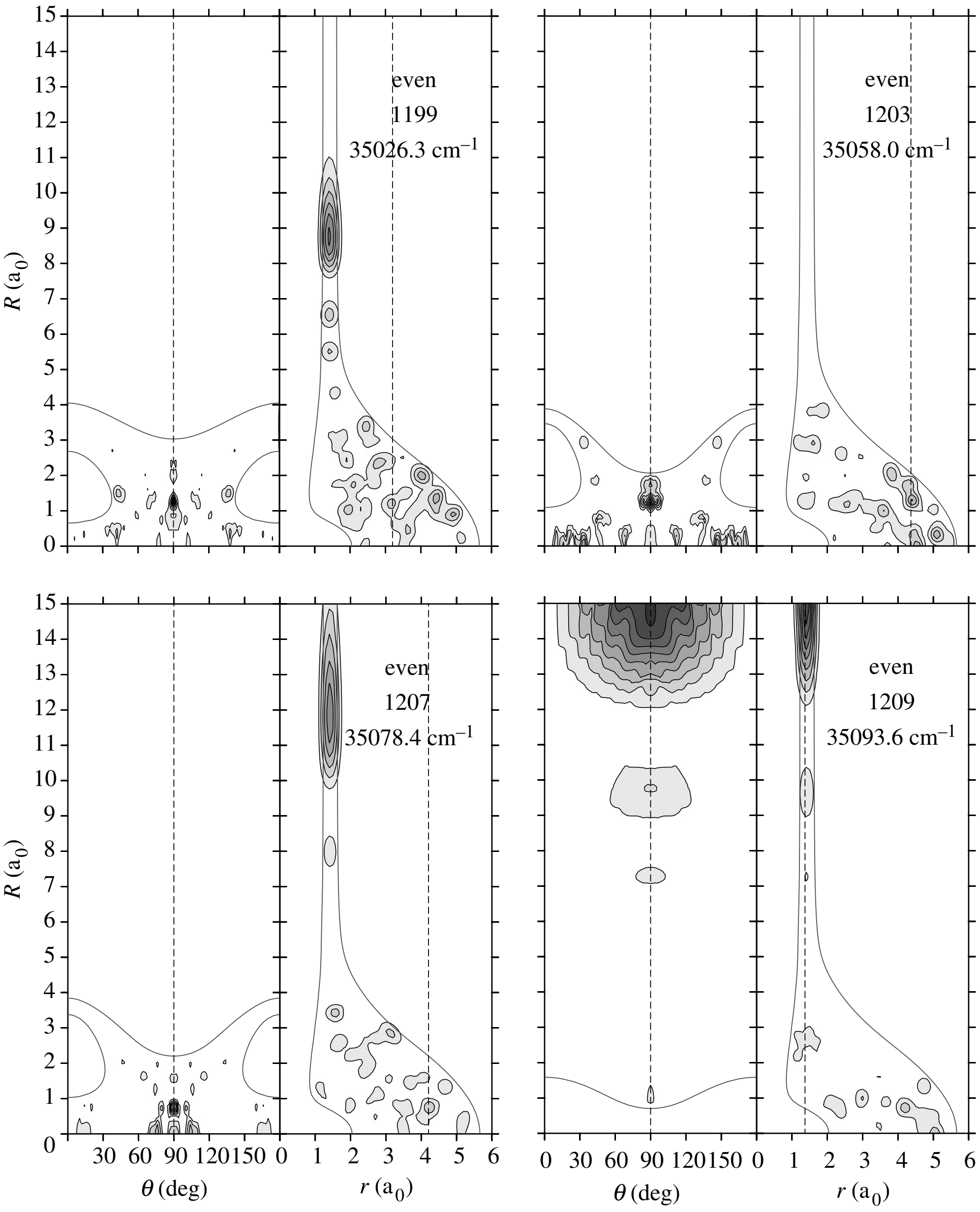

Figure 4. Probability distributions for four even near-dissociation vibrational states of D_2H^+. Plots are in Jacobi coordinates corresponding to H–D_2 scattering. The value of the frozen coordinate is indicated by the dashed line on the other cut. The solid line gives the classical turning point of the potential for the particular vibrational energy, which is given in each plot as the vibrational band origin.

Figure 4 gives four sample probability distributions for even (A_1) symmetry near-dissociation states of D_2H^+. The plots are chosen to emphasize dissociation into the lowest dissociation limit, $H^+ + D_2$. D_2H^+ also appears to support AVS. This view is confirmed by an analysis of the C rotational constant for D_2H^+ (figure 5). A thorough analysis of the D_2H^+ calculations is given by Barletta *et al.* (2006).

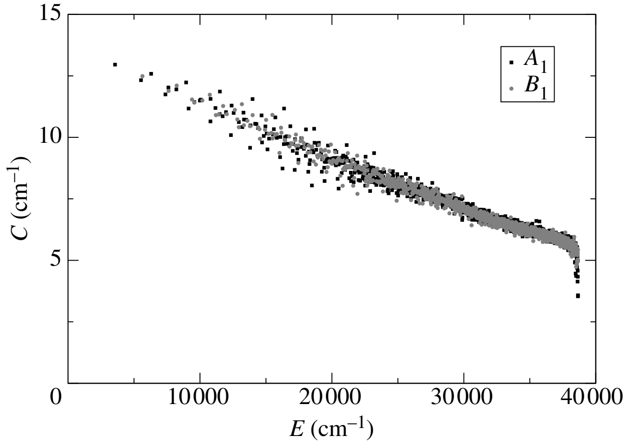

Figure 5. Rotational constants for all the bound states of D_2H^+ designated by symmetry of the underlying vibrational state.

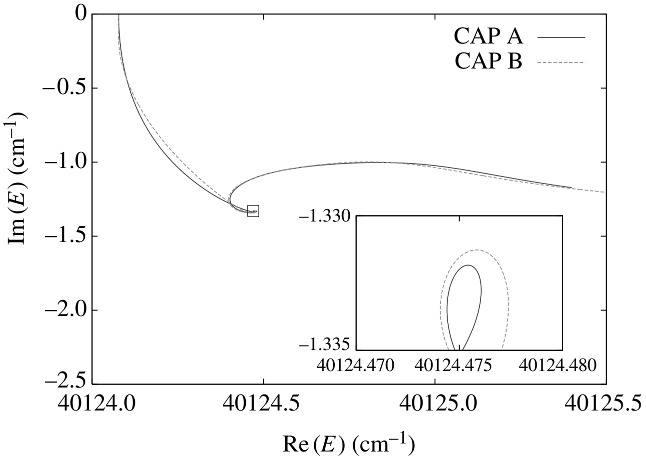

Figure 6. Resonance position and width as a function of the strength of the CAP for two resonance states of H_3^+. CAP A is given by equation (2.2) and CAP B is the function proposed by Gonzalez-Lezana *et al.* (2004).

(*c*) *Lifetime effects*

The near-dissociation photodissociation experiments of Carrington and co-workers, by construction, probe states that lie just above the dissociation limit of the H_3^+ system and therefore have a finite lifetime. Indeed, the details of the experimental set-up used have an important role in determining the lifetime window to which the experiments are sensitive and hence which states are observed. Therefore, any complete understanding of these experiments has to address the lifetime effects in the quasibound states as well.

As discussed previously, we have started to study the lifetimes of low-lying resonances for both H_3^+ and D_2H^+. Figure 6 compares the results of calculations on H_3^+ performed using the quadratic CAP and that proposed by Gonzalez-Lezana *et al.* (2004). As the parameter λ is tuned, the eigenvalues of equation (2.1) follow trajectories in the complex energy plane. In the infinite basis set case, the resonance widths and energies could be obtained by the limit $\lambda \rightarrow 0$. With a finite basis set, a resonance can be identified by searching for cusps of the above trajectories. This corresponds to local maxima in the curvature. However, the use of two different CAPs leads to two different sets of resonances, and we accept results only when the two match. Finally, the computed resonance lifetime is sensitive to both the CAP parameters and the convergence of the basis set. Our work is still preliminary; further work is required on these aspects of the H_3^+ resonance problem.

So far, our analysis of resonance parameters has concentrated on pure vibrational states. For these states, we find that the resonances are rather broad, with widths typically greater than 1 cm^{-1}. Such states are too short-lived to be of importance for the observed near-dissociation photodissociation. This finding is in agreement with previous semi-classical studies (Schlier & Vix 1985).

4. Conclusion

We have studied bound (and quasibound) vibrational states of the H_3^+ system using a realistic global potential, which, in particular, displays the correct asymptotic behaviour at the dissociation limit. For this potential, we have converged a large number of vibrational states for both H_3^+ and D_2H^+; among these, we have identified near-dissociation vibrational states in both molecules which behave like atom–diatom complexes. These AVS are a direct consequence of the long-range interaction potential, but test calculations reported here appear to suggest that this behaviour is robust enough to survive even in an R^{-6} potential. R^{-6} behaviour, which characterizes dispersion forces, is the weakest possible long-range interaction between molecular fragments. It would therefore seem possible that AVS will be a general feature of the near-dissociation behaviour of chemically bound species. Indeed, similar states appear to have been identified in recent calculations on ozone near its dissociation limit (Grebenshcikov *et al.* 2003). Given their greatly reduced rotational constants, one would anticipate that the presence of AVS will significantly increase the density of states in the near-dissociation region, a feature that has already been observed experimentally, if not fully understood, in nitrogen dioxide (Jost *et al.* 1996).

To determine whether AVS play an important role in the near-dissociation spectrum of H_3^+ requires further work on modelling the spectrum. In particular, it is necessary to combine the lifetime effects discussed previously with treatment of rotational excitation and dipole transitions. Rotational excitation calculations have been performed at the H_3^+ dissociation limit (Miller & Tennyson 1988; Kostin *et al.* 2003), but such calculations remain computationally expensive. A number of dipole studies (Le Sueur *et al.* 1993; Henderson & Tennyson 1996; Ramanlal 2005) involving near-dissociation, but not resonance, states of H_3^+ have been reported. Calculations tackling these aspects of the problem are presently being performed.

We thank Hamse Mussa and Jayesh Ramanlal for their contribution to preliminary parts of this project. This work has been supported by the UK Engineering and Physical Sciences Research Council via the ChemReact Computing Consortium and other grants.

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Discussion

J. M. Bowman (*Emory University, Atlanta, USA*). The asymptotic vibrational states are another name for 'Van der Waals' states which are of course well known. For reactive and recombination dynamics, they may also play an important role and this has been seen by us for the $O(^3P)+HCl$ reaction and also possibly for O_3 recombination via a third body.

J. Tennyson. It has indeed been known for some time that Van der Waals molecules, such as the $O(^3P)+HCl$ reaction complex, support long-range bound states, see Tennyson (1985) for example. However, it was not widely anticipated that chemically bound molecules would support such Van der Waals molecule-like states near their dissociation limit. Indeed for the specific case of H_3^+, this possibility had been widely discounted.

L. Wiesenfeld (*Université Joseph-Fourier, Grenoble, France*). What is the stability of the motion in the θ direction in Jacobi coordinates as the energy increases towards dissociation?

J. Tennyson. At large R, the potential becomes increasingly flat in the θ direction and the motions thus become isotropic. Classically, most of our calculations, in common with previous studies, have concentrated on the special case of $\theta=90°$ about which the motions are stable due to symmetry.

M. Larsson (*AlbaNova, Stockholm University, Sweden*). If the behaviour of H_3^+ near dissociation is chaotic, would that not imply that the spectrum is not reproducible?

J. Tennyson. Experimentally, the near-dissociation spectrum of H_3^+ was found to be highly reproducible by Carrington and co-workers. Theoretically, the possible sensitivity of the spectrum to the finer details of the calculation does indeed raise the question whether it will ever be possible to perform a detailed line-by-line calculation which reproduces all aspects of the observed spectrum. However, there are two features of the spectrum which should be reproducible by theory. The first is the well-publicized low-resolution structure first observed by Carrington & Kennedy (1984) and the second is the much sparser, strong-line spectrum obtained for experiments which probed the higher kinetic energy release of the proton (Carrington *et al.* 1993).

B. J. McCall (*University of Illinois at Urbana-Champaign, Urbana, USA*). In the context of future work on even higher vibrationally excited states, is there any idea how the intensity of the $n\nu_2\leftarrow 0$ overtone bands scales, with n for $n>5$?

J. Tennyson. This problem was studied by Le Sueur *et al.* (1993), who calculated the vibrational band intensity for transitions to every vibrational state of H_3^+ starting from the ground vibrational state. They found that while, of course, the intensity dropped for the higher bending states, transitions of the type $n\nu_2\leftarrow 0$ remain much stronger than all other transitions all the way to dissociation. Specific numbers can be found in their paper. Le Sueur *et al.*'s findings were supported by Ramanlal (2005), who repeated these calculations using the more reliable PPKT2 potential. It should be noted in this context that Le Sueur *et al.* also found that low-energy ν_2 bending modes and the high-energy so-called horseshoe states formed a single set of states in the quantum mechanical calculations, in contrast to classical studies which associate these motions with different families of periodic orbits (Depolavieja *et al.* 1994).

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