

Asymptotic vibrational states of the H_3^+ molecular ion

James J Munro, Jayesh Ramanlal and Jonathan Tennyson

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

E-mail: j.tennyson@ucl.ac.uk

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Abstract. Vibrational calculations for H_3^+ are performed using an accurate global *ab initio* potential energy surface. Fourteen bound states close to dissociation are found to have interesting long-range dynamics. These asymptotic vibrational states (AVS) are studied graphically by cuts through their wave functions and by calculating a rotational constant. These AVS, which overlap open system classical trajectories that form half-tori, should lead to an increased density of states near dissociation. Their influence on the infrared near-dissociation spectrum of H_3^+ remains to be determined.

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1. Introduction

Long-range states of molecules are important for near-threshold reaction dynamics and radiative association by which molecules were formed in the early universe; they have come to prominence with study of molecule formation and interactions in condensates. H_3^+ is the only chemically bound polyatomic for which a detailed, if poorly understood, experimental study of the states

is available. Within the Born–Oppenheimer approximation, H_3^+ is also the simplest molecular example of the quantum three-body problem. This three-body problem remains generally unsolved but can be probed very sensitively with spectroscopic experiments on molecular systems. The rotational and vibrational behaviour of chemically bound polyatomic molecules with low levels of excitation has been much studied using high-resolution spectroscopy. This behaviour is generally well understood in terms of simple models of nuclear motion based on the shape of the potential at the bottom of a deep well. Conversely, our understanding of nuclear motion states for these systems near their dissociation limit remains very limited. A fascinating glimpse into the complexities of these states was given by the very rich, infrared dissociation spectra of H_3^+ first recorded by Carrington *et al* [1] over 20 years ago. These spectra have yet to be modelled *ab initio* meaning that the theoretical framework has yet to be fully resolved.

After Carrington *et al*'s original study, Pfeiffer and Child [2] suggested that the underlying structure observed in the H_3^+ -near dissociation spectrum [3] could be explained by the vibrational motion of a proton against a hydrogen molecule. This model was dropped after further experimental studies [4] and, more importantly, the realization of the chaotic nature of the underlying vibrational states of H_3^+ [5]. Alternative models in which the underlying structure is expressed in terms of classical periodic orbits, the so-called horseshoe orbit [6, 7], were proposed. This early work has been comprehensively reviewed by Pollak and Schlier [8] and also by McNab [9].

In this paper, we report the discovery of a series of $\text{H}^+ - \text{H}_2$ asymptotic vibrational states (AVS). The existence of AVS appears to be a quantal phenomenon in that they all lie above the classical dissociation energy (D_e) of H_3^+ ; however, as we demonstrate, there is evidence for them in classical trajectory calculations. These states have no analogue for diatomic molecules, whose near-dissociation behaviour is well understood [10]. The AVS we found for H_3^+ display a complicated but generally incremental nodal structure with excitations in both the angular and radial coordinates.

2. Calculations

Nuclear motion calculations were performed using a modified *ab initio*, PPKT, global electronic ground-state potential energy surface [11]. This potential, unlike those used for previous studies [12]–[14] of the near-dissociation vibrational states, treats correctly the long-range interaction between H^+ and H_2 which determines the potential in the dissociation region. This interaction [15] consists of both charge–quadrupole, which depends on R^{-3} , and charge–polarizability, which depends on R^{-4} . This leads to a long, shallow well in the dissociation coordinate (R). A previous study of rotational–vibrational states using this potential [16] had insufficient computational power to converge the near-dissociation states.

The present calculations used 384 IBM Power4+ processors, which are part of the HPCx supercomputer at the Daresbury Laboratory, UK. Calculations were performed using an adapted version of the PDVR3D program [17]. They were performed in both Jacobi and Radau coordinates, each of which gave a clear signature for AVS. The results reported here come substantially from the Radau coordinate calculations which, for technical reasons discussed elsewhere [18], are better converged.

Rotation-less Radau coordinate calculations were performed using a discrete variable representation (DVR) method, which represents the amplitude of the wave function as an

optimized grid of points. The Radau coordinate system used is that defined by Sutcliffe and Tennyson [19]. The present calculations used an effective grid of 696960 points. PDVR3D uses a two-step diagonalization and truncation procedure. The first step solves the complete symmetrized two-dimensional (2D) radial problem for each fixed angle, using a grid of 120 DVR points in each of the radial coordinates. The points were determined from spherical oscillator functions [20]. The solutions are then truncated by energy and used as a 2D radial basis along with 96 angular grid points determined from Legendre polynomials. A 2D energy cut-off gave a final Hamiltonian matrix of dimension 79091, which is constructed and then diagonalized in the second step.

Convergence tests were performed on all the variational parameters, of which there are five. Three of them show monotonic convergence with increasing size or value, the size of the radial basis (N_R), the size of the angular basis (N_θ) and the 2D cut-off energy (E_{2D}). While the other two control the character of the radial basis set and are optimizable parameters. The degree of convergence depends upon the state and generally the low-energy states converge better than the high-energy states. Below D_e , energy levels for the Radau calculations are converged to within 0.7 cm^{-1} . Above D_e , the majority of levels are still converged to better than 0.7 cm^{-1} but some states converge slower; the last state may only be converged to $\approx 3.0 \text{ cm}^{-1}$. It is possible to converge lower energy states to much better than this by using less spatially extended radial grids of the same dimension, but here we have intentionally tried to resolve the very long-range states, this required sacrificing some convergence in the lower-energy states.

In Radau coordinates, there is a symmetry in the radial terms of the Hamiltonian, we therefore get an even and odd radial basis parity. Both of these parity calculations were performed. The odd parity calculations perform better because fewer states need to be converged and a similar basis has a reduced size. The full symmetry of each state within the D_{3h} point group was determined by calculating the scalar product of the wave functions with themselves under coordinate permutations. Vibrational states were then numbered by energy, starting with 1 for the ground state. With this procedure, we were easily able to assign A_1 , A_2 and E symmetries to all but two states. In our calculations, state numbers 830 and 831 differ by only 0.18 cm^{-1} and they appear to be of mixed (A_1 , E) symmetry. This is an accuracy problem as our calculations are performed in the reduced symmetry of Radau coordinates. While the potential is invariant to D_{3h} operations. The complete Hamiltonian is only invariant to operations in C_{2v} and therefore the perfect D_{3h} result is only achieved in the complete basis set limit. Thus, we can assume that those two states are converged to worse than 0.18 cm^{-1} .

Convergence was also estimated in a semi-independent manner by examining the difference in energy between the degenerate E symmetry states of the even and odd parity calculations. The majority of differences are better than 0.1 cm^{-1} . But as can be expected some states do not converge as well. The worst case is for the last state (859) with a difference of 3.6 cm^{-1} at an energy of $34\,902.8 \text{ cm}^{-1}$ above the ground vibrational state.

3. Results

Our calculations show that the PPKT potential supports at least 260 bound vibrational states of A_1 symmetry, 172 of A_2 symmetry and 427 of the degenerate E symmetry. Of these, 52 A_1 , 38 A_2 and 88 E states lie above the classical dissociation limit of H_3^+ at $D_e = 37\,170.4 \text{ cm}^{-1}$ (or more than $32\,808.8 \text{ cm}^{-1}$ above the H_3^+ vibrational ground state). Graphical analysis of the wave functions of

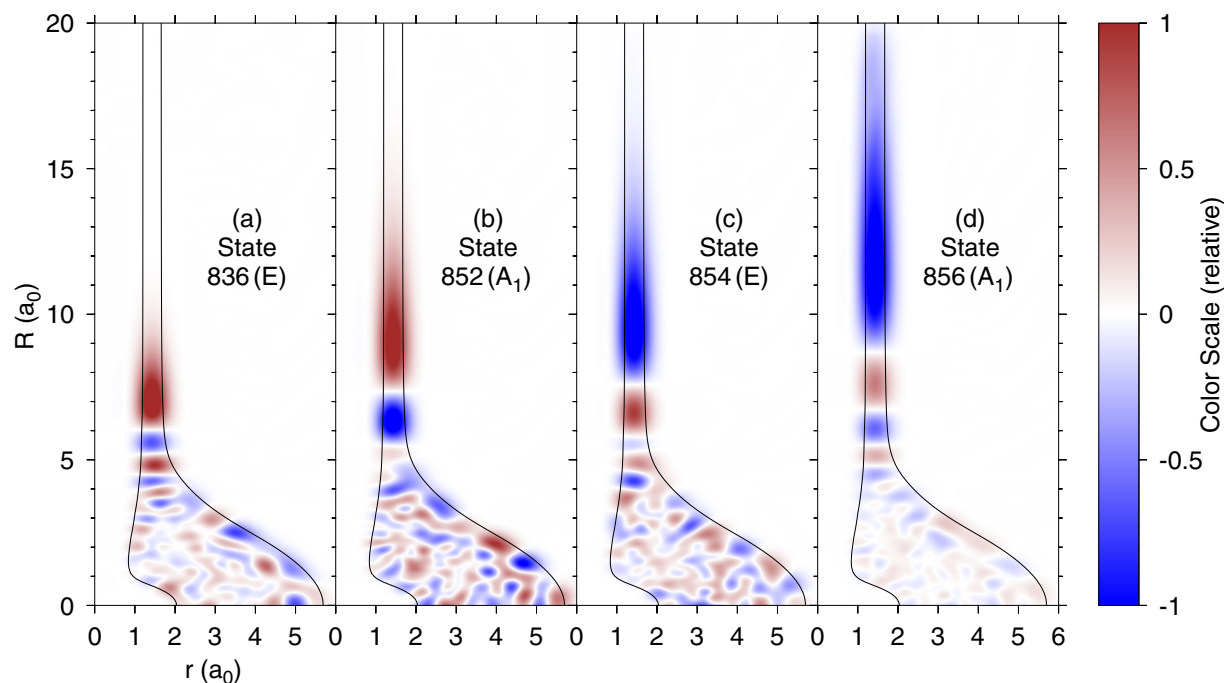


Figure 1. 2D cuts through the DVR wave functions at a Jacobi angle of 90° . The classical turning points for each wave function are displayed as a black contour. Wave function amplitude is plotted using a colour scale (shown), each plot is scaled according to the maximum amplitude within each cut of the wave function.

all our bound states was performed by taking a variety of 2D cuts through the wave functions for several coordinate positions (for both Radau- and Jacobi-based calculations), paying particular attention to states lying above D_e . These cuts revealed a number of states whose amplitude can be regarded as lying substantially in the asymptotic region of the potential.

Figure 1 gives four examples of such states. Figure 1 depicts wave functions calculated in Radau coordinates but then transformed into Jacobi coordinates since these are more natural for displaying the dissociative R and intra H_2 r motions. Each DVR grid point was transformed and any points with a Jacobi angle of between 89.5° and 90.5° were plotted.

Figure 1 is strongly suggestive of the presence of AVS. However, analysis of wave function plots is somewhat subjective. In order to quantify the presence of AVS, we computed rotational constants for the states as expectation values of the wave functions. We did this for each vibrational state of H_3^+ using the method of Ernesti and Hutson [21]. We anticipated that the large average H^+-H_2 separation found in AVS would lead to significantly reduced values for the C rotational constant, which governs the rotational motion of the system about the axis perpendicular to the plane of the molecule.

Figure 2 plots the rotational constant C for all the bound vibrational states of H_3^+ . The initial drop from $C \approx 20 \text{ cm}^{-1}$ to $10 \leq C \leq 14 \text{ cm}^{-1}$ is associated with states possessing sufficient energy to sample linear geometries. Above D_e there are 14 states for which C is less than 7 cm^{-1} . These are precisely the AVS, we identified graphically. Furthermore, there is a close and unsurprising correlation between the extent of the AVS and a low value of C . Thus, for example, state 856 (see figure 1(d)), a very extended state, has the lowest value of C , 1.94 cm^{-1} .

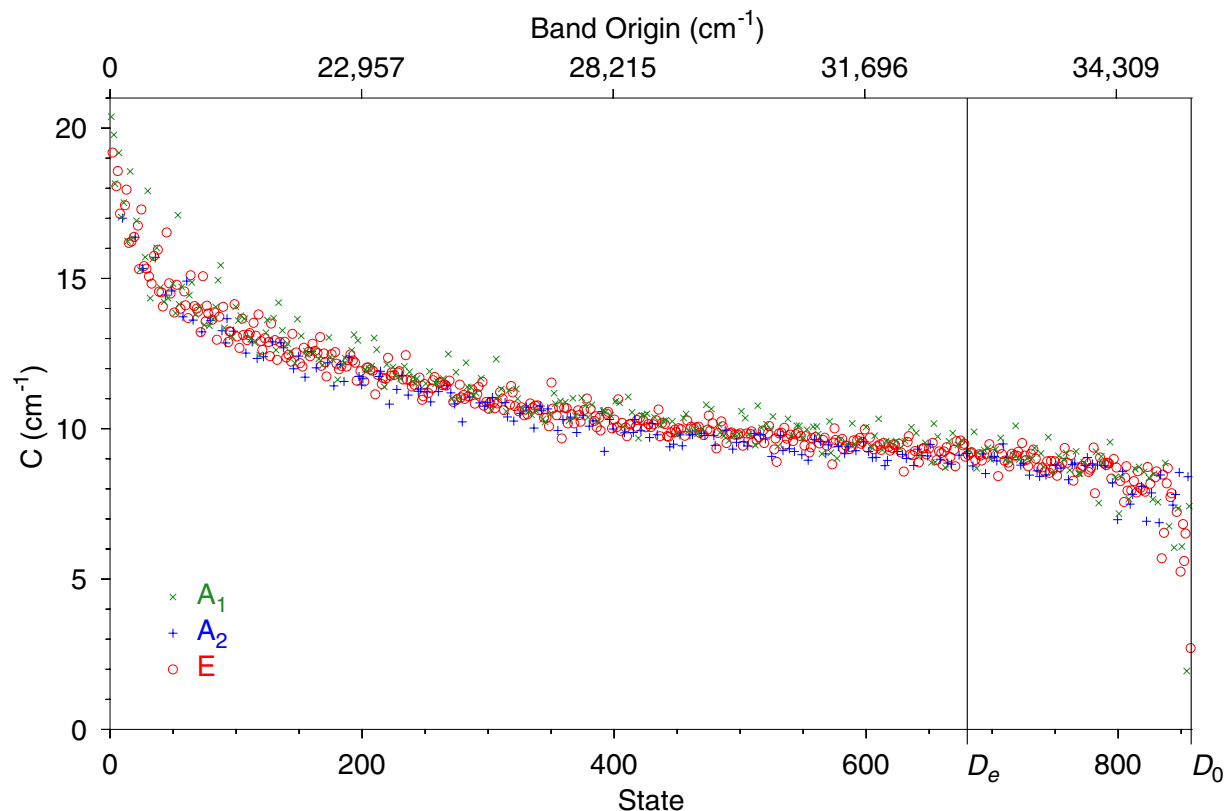


Figure 2. Plot of rotational constant C against state numbers. The classical dissociation energy (D_e) is after state 681 and the first dissociation energy (D_0) allowed in our calculation is after state 859. The state number is not linear in energy; however, representative values for band origins are given on the top axis.

We also examined the wave functions by cutting along R and θ for fixed r (the H_2 equilibrium bond length). We found that there are a series of long-range states with excitations in both the radial R coordinate and the angular θ coordinate. These states retain the complicated short-range behaviour which ensures orthogonality to the other high-energy states and do not have any excitation in the H–H distance, r . This is to be expected because of the almost 1D nature of the potential at long range.

In practice, the potential almost certainly supports more AVS than we identify here. The grid in Radau coordinates only covers radial values less than $14.6a_0$ when transformed to the Jacobi R coordinate and the grid is no longer uniform, but along the dissociation channel displayed in figure 1 our grid extends to $20.0a_0$. More extended states than this, which seem likely, will not be adequately represented by our grid and are therefore absent from our calculations.

We have performed 2D classical trajectory calculations at energies between D_e and D_0 for Jacobi coordinates with θ frozen at 90° . These calculations, which will be discussed in detail elsewhere, show no periodic orbits in the asymptotic (large R) region. However, Poincaré surfaces of the section, figure 3, show what appear to be half-tori trapped in the dissociating portion of the potential, which merge with chaotic orbits at small R . These half-tori emerge because of the simple nature of trajectories in long-range part of the potential due to its almost 1D nature.

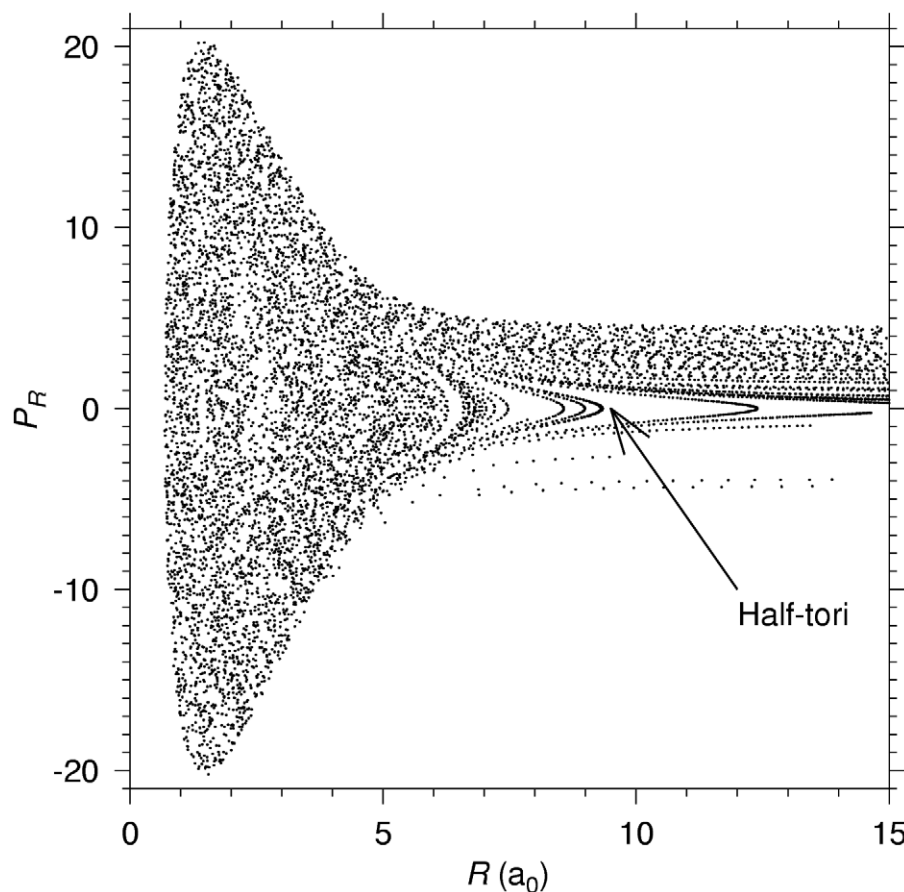


Figure 3. Poincaré surface of the section for classical trajectories intersecting the R and P_R plane, where P_R is the momentum along R . The plane lies along $r = 1.4a_0$ (the equilibrium H_2 bond length). Trajectories have an energy of $39\,000\text{ cm}^{-1}$ above the potential minimum.

This situation is similar to the ‘quasi-Landau’ orbits observed in another classically unbound system, the H atom in a magnetic field [22].

4. Concluding remarks

There is no direct evidence for previous observations of AVS, although similar states were recently identified in a study of ozone near its dissociation limit [23]. These states are accompanied by an increase in the density of states in the region between D_e and D_0 . Furthermore, Jost *et al* [24] observed an unexplained increase in the density of states for NO_2 near its dissociation limit. The few AVS found for H_3^+ could make a significant contribution to the density of states since their small rotational constants will mean that they support many more rotationally excited states than the more usual near-dissociation states. A similar situation should occur if, as is likely, NO_2 also supports AVS.

$\text{H}^+ + \text{H}_2$ is, of course, a prototypical collisional system. The many-bound states supported by the short-range deep well of the electronic ground state of this system are known to play an important role in inelastic collisions [25]. The long-range nature of the AVS is likely to be particularly significant for this; indeed recent collisional studies have shown a strong sensitivity to the potential used [26].

There is another class of three-body asymptotic states which lie between D_e and D_0 , Efimov states [27]. These occur for some weakly bound triatomics such as $^4\text{He}_3$ [28]. Theoretically, given a special enough system there can be infinitely many of these states. Though in practice only a few have been found (e.g. 1 or 2 for $^4\text{He}_3$), the number of such states depends critically on the potential strength in the dissociative region. Exactly how many AVS H_3^+ supports remains to be seen. It is clear that these too could have a critical dependence on the potential in the dissociative region. Long-range attractive potentials are universal between molecular fragments, hence AVS, rather than Efimov states which require rather special circumstances, will determine the behaviour of chemical-bound species at large separations.

The role, if any, of AVS in the near-dissociation spectra of Carrington *et al* [1, 3, 4] remains uncertain. It is clear, however, that the large-charge separation that these states possess will lead to a large dipole effect and that, because of their spatial separation, they may not couple strongly to many states. Our graphical analysis and classical trajectory calculations suggest that the so-called horseshoe states [6, 7] are less pronounced in the dissociation region for the more realistic PPKT potential than for other potentials studied previously. Whether these states are just masked by other features and are still effective in the way proposed by previous investigations [7] remains unclear. An understanding of the role of AVS in the enigmatic near-dissociation spectrum of H_3^+ requires further work, including the explicit treatment of rotational excitation which is currently underway.

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