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Highly excited rovibrational states of small molecules

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The use of first principles variational calculations for the calculation of high-lying energy levels, wavefunctions and transition intensities for triatomic molecules is considered. Theoretical developments are considered, including the use of generalized internal coordinates, the use of a two-step procedure for rotationally excited systems and a finite element method known as the discrete variable representation. Illustrative calculations are presented including ones for H_3^+ , LiCN and the Ar-N₂ Van der Waals molecule. A first principles 'rotational' spectrum of H_2D^+ is computed using states up to $J = 30$. The transition intensities in this spectrum are reproduced accurately in a frozen dipole approximation but are poorly represented by models that involve approximating the wavefunction.

1. Introduction

The study of nuclear motion has traditionally been divided into two fields: bound state dynamics, which has strong links with spectroscopy; and collision dynamics, of which the study of chemical reactions forms an important component. Whereas high-resolution spectroscopy has for many years provided very precise information on the bound states of molecules, until recently our quantitative knowledge of reaction dynamics has been rather crude.

The rapid advance in experimental techniques, in particular the use of molecular beams and lasers, has radically changed this situation. The measurement of state to state reaction cross sections has greatly enhanced our detailed knowledge of chemical reactions. The same experimental techniques have also greatly increased the range of bound states amenable to investigation. In particular, it is now becoming possible to probe very high-lying rovibrational states of chemically interesting systems. These states can be thought of as lying on the threshold of, or even undergoing, chemical reaction. A well known and much discussed example of this phenomenon is the near-dissociation, infrared spectra of H_3^+ recorded by Carrington & Kennedy (1984).

The observation of these high-lying states of molecular systems has opened up new and ill explored regions for theoretical analysis. These regions have a particular piquancy because in many cases they cover energy régimes where most of the classical dynamics is chaotic. The exact consequences of this classical behaviour on quantal systems are still a matter of debate.

There are relatively few systems for which a full set of bound states can be

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obtained. An important class of such systems are Van der Waals complexes where, especially for atom–diatom complexes, it has often proved possible to obtain all the rovibrational states implied by a particular potential energy surface. These systems are of great interest in their own right, but are probably atypical when compared with chemically bound species.

For a number of years we have used variational techniques to study the rovibrational states of small, particularly triatomic, molecules. While of course each individual calculation has its own aim, one of our major aims has been to obtain a better insight into molecules undergoing large-amplitude vibrational motion. This naturally leads to the study of systems in highly excited states. For chemically bound systems, these calculations can thus be thought of as approaching the chemical reaction region from below. For isomerizing systems this region may be reached for truly bound states, otherwise it is via quasi-bound or dissociating states that the link can be made.

Besides the intrinsic physical interest, this region of large-amplitude motion presents a formidable technical challenge both to understanding and to calculation. To see why this is so a brief excursion into the underlying theory of vibration–rotation calculations is appropriate.

To describe the vibrational motion of a molecule, as distinct from its other motions, it is necessary to set up a coordinate system fixed (embedded) in some way in the molecule. In doing this it is usually assumed that in first approximation the electronic motion can be decoupled from the nuclear motion and the electronic wave function integrated out of the problem for each nuclear geometry. The nuclei then can be regarded as moving in a potential that is electronic state dependent but otherwise translationally and rotationally invariant. The potential is often referred to as a potential surface of hyper-surface and the nuclei are thought of as moving on it. In many cases it is a very good approximation to consider the nuclear motion as occurring on just a single surface for such motion is generally insufficient to mix the electronic states. Most pure vibration–rotation spectra can be interpreted as associated with the ground electronic state and this will be the appropriate view for the systems discussed here.

Even within the approach of considering only the nuclear motion on a given surface the problem of body-fixing is a technically formidable one which is also very messy algebraically and it resisted solution for many years until the work of Eckart (1935). Eckart observed that if the potential had a deep minimum at a particular (equilibrium) nuclear geometry then the coordinate system could be fixed in the molecule in such a way that in the first approximation the rotation spectrum of the molecule could be understood in terms of the rotation of a rigid body whose shape was determined by the potential minimum and which corresponded to the chemical idea of the shape of the molecule. This picture is appropriate when the internal motions of the nuclei correspond to only small displacements from the equilibrium geometry and at this same level Eckart was able to show that the vibrational motion could be described in terms of products of harmonic oscillator functions. The variables of these functions were normal coordinates which were linear combinations of displacement coordinates.

Because computation was difficult the body-fixed Eckart hamiltonian was not used in an *ab initio* way to explain spectra but rather was used as a tool to assign and to rationalize experimental spectra. However, the work of Watson (1968) led to the development of a form of the Eckart hamiltonian that was amenable to calculation

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and developments in computers made *ab initio* calculations possible. Such calculations were attempted in the pioneering work of Carney & Porter (1974), and of Whitehead & Handy (1975).

In these works a variational approach was used with basis functions of the kind described above, namely a product of a vibrational part and a rotational part:

$$\Psi_n^J = \Phi_n(\mathbf{Q}) \sum_{k=-J}^{+J} C_k^J |JMk\rangle, \quad (1)$$

where $|JMk\rangle$ is a standard symmetric-top function with M the (arbitrary) quantum number along the space-fixed axis and k the quantum number along the body-fixed z -axis. \mathbf{Q} denote the normal coordinates and $\Phi(\mathbf{Q})$ consists of a product of harmonic oscillator functions, one for each normal coordinate. In the pioneering work referred to above only the cases $J = 0$ were considered but nevertheless it was confirmed, at least for triatomics, that the Eckart approach gave an accurate account of the lower vibrational states of water and of H_3^+ .

Following this pioneering work, Bartholomae *et al.* (1981) attempted to use similar techniques to understand the vibration-rotation spectrum of CH_2^+ , a molecule of some interest in astrophysics. It was in this attempt that the difficulties, which were known in principle to arise in any body-fixed formulation, were first encountered in an *ab initio* calculation.

To fix a coordinate system in a molecule it is necessary to do a nonlinear coordinate transformation from the lab-fixed frame to the body-fixed one. The jacobian for this transformation is thus coordinate dependent and can vanish for particular coordinate values. Indeed simple topological arguments show that in any coordinate transformation that separates rotations from other motions the jacobian must have a vanishing region. In the case of the Eckart embedding it emerges that the singular region is determined by vibrations of sufficiently large amplitude to cause one or more of the generalized moments of inertia to vanish. To be specific, for a triatomic molecule these regions occur when the molecule becomes linear.

Of course the coordinate transformation is not valid for a region in which the jacobian vanishes even though the body-fixed hamiltonian has a structure which takes no explicit account of this possibility. The failure manifests itself in divergent expectation values of the body-fixed hamiltonian between trial wavefunctions that put the molecular motion into the singular region. This sort of failure was encountered by Bartholomae *et al.* in respect of the bending motion of CH_2^+ , which is particularly 'soft'. It emerged from this work that the traditional Eckart approach, relying on the idea of an equilibrium geometry was not a good way to treat this molecule. It was necessary therefore to use a different coordinate system and although it is not possible to choose a system without singular regions altogether it is possible to alter where these regions occur. From this it is clear that the singular regions are entirely artificial and have no real physical cause but are still not avoidable.

In work begun in 1982 two of the present authors began to develop the theory of the construction of coordinate systems for triatomic systems which were definable in a general way to include all possible placings of the singular regions. The work has developed successfully and its present status is summarized in Sutcliffe & Tennyson (1986, 1990).

In parallel with the theoretical developments computational methods have been developed; in particular, the introduction of two step variational procedures (Chen

et al. 1986; Tennyson & Sutcliffe 1986) has effectively solved the problem of dealing with rotationally excited states. The use of a coordinate based, rather than function based, finite element method called the discrete variable representation (DVR) by Light and co-workers (see the recent review by Bačić & Light 1989) has led to a near order of magnitude increase in the number of bound states that can be obtained for a given system. Finally, the use of *ab initio* wavefunctions and dipole (hyper)-surfaces has led to the development of methods of generating complete spectra from first principles (Miller *et al.* 1989; Carter *et al.* 1989).

In this paper we discuss how we have used these techniques to try to obtain understanding of the behaviour of large amplitude rovibrational states. We will only present a brief outline of the theories involved, instead referring the reader to the original papers and a recent review (Tennyson *et al.* 1990). We will concentrate on results obtained for the high lying levels of contrasting triatomic systems: H_3^+ , LiCN, Na_3 and the Ar- N_2 Van der Waals complex. Of particular note are predicted hot (2000 K) rotational spectra for the H_2D^+ molecule. The asymmetry and strong Coriolis couplings in this system mean that accurate transition frequencies and wavefunctions can only be obtained using sophisticated variational techniques. In contrast to this we find that the predicted line intensities are almost entirely given by the small, permanent H_2D^+ dipole.

2. Theory

The general triatomic coordinate system of Sutcliffe & Tennyson (1990) is defined in figure 1. This coordinate system reduces to a number of special cases which are summarized in table 1. With the body-fixed z -axis embedded parallel to either the r_1 or r_2 coordinate, the hamiltonian for these coordinates can be written

$$\hat{H} = \hat{K}_V^{(1)} + \hat{K}_V^{(2)} + \hat{K}_{VR}^{(1)} + \hat{K}_{VR}^{(2)} + V(r_1, r_2, \theta). \quad (2)$$

The kinetic energy operators depend on the particular coordinate choice only via the moments of inertia of the problem which in turn can be related to g_1 and g_2 . This hamiltonian has thus been used as the basis for a computer program in general coordinates (Tennyson & Miller 1989).

In equation (2), V is the potential energy function. The vibrational kinetic energy operators, \hat{K}_V , determine the rotation free hamiltonian and are independent of the axis embedding used. The operators $\hat{K}_V^{(2)}$ and $\hat{K}_{VR}^{(2)}$ are null for orthogonal coordinate systems such as scattering and Radau coordinates (see table 1). The exact form of these kinetic energy operators is given in Sutcliffe & Tennyson (1990).

If k is assumed to be the projection of the total angular momentum, J , on the body-fixed z -axis, then only the \hat{K}_{VR} couple terms off-diagonal in k . For the z -axis embedded along either r_1 or r_2 , this off-diagonal Coriolis coupling is only between k and $k \pm 1$ terms. The two step rotational procedure of Tennyson & Sutcliffe (1986) involves first solving a series of problems that neglect these Coriolis coupling terms and then using these solutions as a basis to solve the full problem given by hamiltonian (2). This method is very efficient (Sutcliffe *et al.* 1988) and has been used to obtain rotational levels up to dissociation even for chemically bound systems such as H_3^+ (Miller & Tennyson 1988*a*).

The traditional method of solving hamiltonian (2), as used by the program TRIATOM (Tennyson & Miller 1989), is to use a product of truncated basis set expansions in each coordinate. This approach has been labelled the finite basis

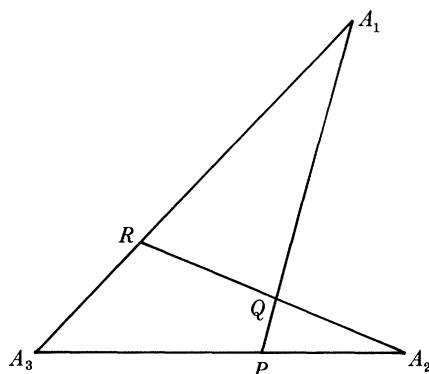


Figure 1. Coordinate system of Sutcliffe & Tennyson (1990). A_i represents atom i . The coordinates are given by $r_1 = A_2 - R$, $r_2 = A_1 - P$ and $\theta = A_1 \hat{Q} A_2$. The geometric parameters are defined by

$$g_1 = (A_3 - P)/(A_3 - A_2) \quad \text{and} \quad g_2 = (A_3 - R)/(A_3 - A_1).$$

Table 1. *Special cases of the general Sutcliffe & Tennyson (1990) coordinate system*
(Parameters g_1 and g_2 are defined in figure 1. Atom i has mass m_i .)

| coordinate type ^a | g_1 | g_2 |
|------------------------------|---|--|
| scattering or Jacobi | $m_2/(m_2 + m_3)$ | 0 |
| bondlength–bondangle | 0 | 0 |
| geometric midpoint | $\frac{1}{2}$ | 0 |
| Radau ^b | $1 - [\alpha/(\alpha + \beta - \alpha\beta)]$ | $1 - [\alpha/(1 - \beta + \alpha\beta)]$ |

^a In this definition neither the Jacobi nor Radau coordinates are mass weighted.

^b $\alpha = [m_3/(m_1 + m_2 + m_3)]^{\frac{1}{2}}$, $\beta = m_2/(m_1 + m_2)$.

representation (FBR). Typically we have used (associated) Legendre polynomials for the θ coordinate and Morse oscillator-like functions (Tennyson & Sutcliffe 1982) for the radial coordinates, although spherical oscillators have proved useful for some applications (Tennyson & Henderson 1989). Numerical integration, for example over the potential function, is then done using gaussian quadrature in the appropriate polynomials. For further details see Tennyson (1986) and Tennyson *et al.* (1990).

The DVR involves formally obtaining the hamiltonian in the FBR and then transforming one or more of the coordinates to a finite element representation. The special feature of the DVR is that this transformation is based on the use of gaussian quadrature points and weights. This yields formal similarities with the FBR problem (Dickinson & Certain 1968). The advantage of DVR methods over standard FBR implementations is that they define a hierarchy of problems that can be diagonalized and their solutions used as a basis for expanding the next problem. This successive diagonalization and truncation leads to compact final hamiltonian matrices with high information content. This approach thus has similarities with that of Carter & Handy (1986*a, b*) who develop FBR expansions by diagonalizing one or more model problems.

A good review of the DVR approach has recently been given by Bačić & Light (1989). Tennyson & Henderson (1989) extended this work to the problem of rotational excitation using an adaptation of the two-step method discussed above. Recently Henderson *et al.* (1990) have shown how the DVR approach can be formulated in the general coordinates of figure 1.

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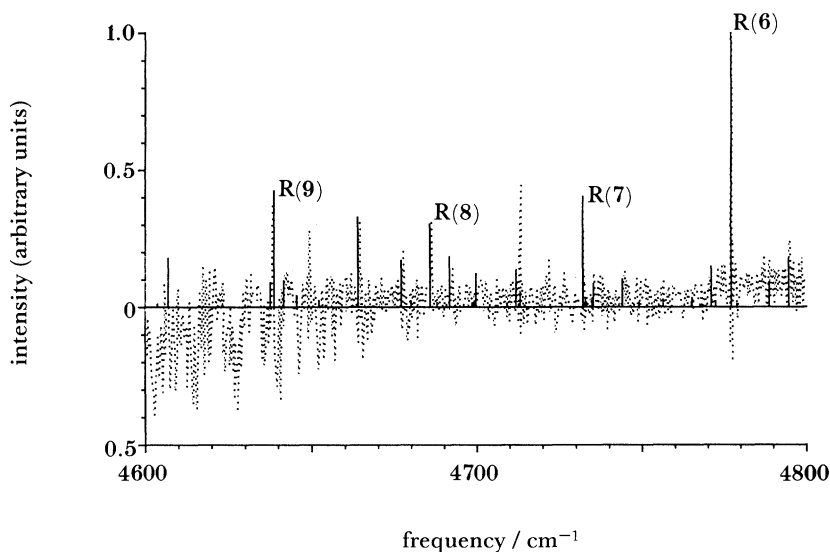


Figure 2. Simulated first principles $\text{H}_3^+ 2v_2(2) \rightarrow v_0$ emission spectrum compared with that measured by Drossart *et al.* (1989) in the southern auroral 'hot spot' on Jupiter. The simulation is for a temperature of 1000 K. The emission line at 4712 cm^{-1} in the observed spectrum is due to an H_2 quadrupole transition. \cdots , Jupiter auroral spectrum.

3. Results

3.1. H_3^+ and H_2D^+

Since the work of Carney & Porter (1974), H_3^+ and its isotopomers have been the subject of considerable theoretical interest. The advent of an *ab initio* potential energy surface of near spectroscopic accuracy and an associated dipole surface (Meyer *et al.* 1986) has meant that predictions of high accuracy can be made for these systems (Miller & Tennyson 1987).

An outstanding example of this work is the assignment of an H_3^+ overtone emission spectrum in the southern auroral 'hot spot' in Jupiter (Drossart *et al.* 1989). The aim of these observations was to record H_2 quadrupole transitions, which were indeed observed, but many other unexpected transitions were also seen. These lines were assigned by comparison with *ab initio* calculation of the individual transitions and comparison with an unassigned laboratory spectrum. Figure 2 compares our simulated spectrum with that observed on Jupiter. The more extensive laboratory spectrum has now been assigned by comparison with *ab initio* calculations (Majewski *et al.* 1989).

The ability to compute complete spectra unbiased by any physical approximation beyond the Born–Oppenheimer approximation allows one to make critical comparisons of various standard approximations. The accuracy of the calculations on H_3^+ and isotopomers make these systems particularly attractive for this theoretical analysis. The non-rigidity of these systems also means that they provide a particularly stringent test of approximations based on the perturbation of (near) rigid structures.

Over a number of years we have analysed the vibration–rotation spectrum of H_2D^+ under conditions of extreme rotational excitation (Tennyson & Sutcliffe 1986; Tennyson *et al.* 1988). This molecule is a particularly good test case because it is a

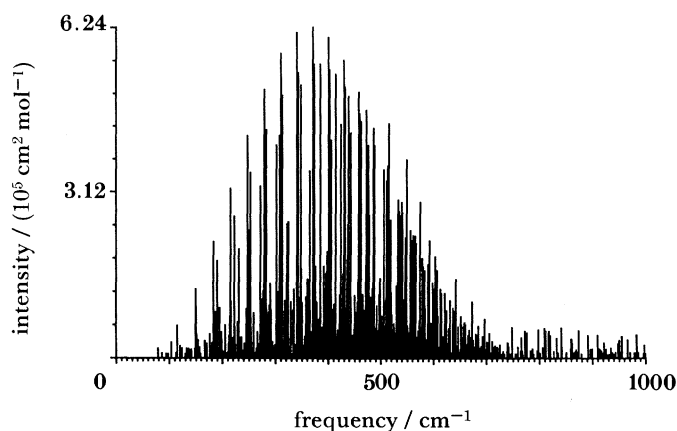


Figure 3. First principles H_2D^+ absorption spectrum in the range 0–1000 cm^{-1} . The spectrum was calculated assuming a Boltzmann distribution at 2000 K and using the Meyer–Botschwina–Burton (MBB) dipole surface.

very asymmetric top ($\kappa \approx -0.07$) and is known to be subject to very strong Coriolis effects (Foster *et al.* 1986). Analysis of its energy levels has shown that while levels with total angular momentum, J , of 10 or less can be at least approximately represented by perturbational expansions, it has so far proved impossible to analyse the higher J levels using these ideas (Tennyson *et al.* 1988).

It is interesting to ask if the rotational linestrengths are affected by this behaviour. We have therefore undertaken a systematic study of the hot rotational spectrum of H_2D^+ . Calculations were done for all rotational levels with J less than or equal to 30 using the MBB (Meyer *et al.* 1986) potential energy surface.

These calculations were done in scattering coordinates and used the two step variational procedure of Tennyson & Sutcliffe (1986). The first, ‘vibrational’ step was converged using the lowest 800 functions selected on energy grounds and basis functions (Morse oscillator-like functions for the radial coordinates and associated Legendre functions for θ) previously optimized (Miller & Tennyson 1987). The rotational calculations were done with a basis of $300 \times (J + 1)$ functions selected from the $J + 1$ first step calculations using an energy ordering criterion (Sutcliffe *et al.* 1988). This basis converged levels with $J = 30$ to better than 1 cm^{-1} and lower J levels to considerably better than this. The full wavefunctions from these calculations were then used to generate transition dipoles subject only to the strict angular momentum selection rules

$$\Delta j = 0, \quad \Delta p = \pm 1; \quad \Delta J = \pm 1, \quad \Delta p = 0, \quad (3)$$

where p is a parity label defined such that the total parity of the system is given by $(-1)^{J+p}$. The transition moments file was then processed, using suitable physical conditions and nuclear spin factors, to give synthetic stick spectra. All calculations were done with the TRIATOM program suite (Tennyson & Miller 1989).

Figure 3 shows a typical stick spectrum computed at 2000 K. Although we refer to this spectrum as rotational, we should stress that we have made no assumption about rovibrational separation in its construction.

As mentioned above, experience has shown perturbation theory to be poor at representing the energy levels of the high J states considered. The standard method of representing the rotational contribution to the linestrength of a particular

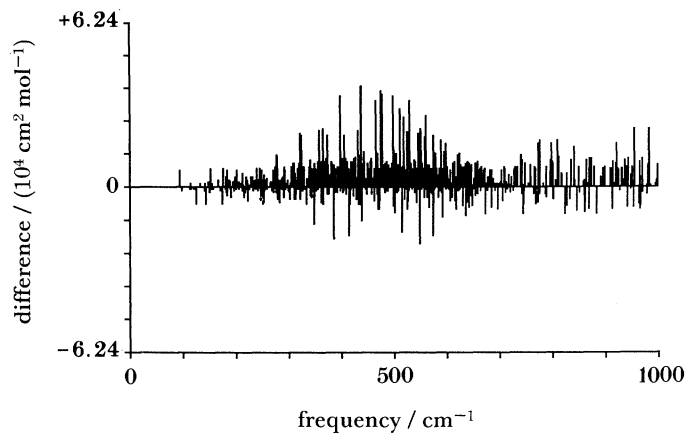


Figure 4. Difference between the full first principles H_2D^+ absorption spectrum (figure 3) and that calculated using a frozen dipole approximation. Note the larger scale than figure 3.

transition is to consider an appropriate transition moment multiplied by some angular factor, such as a Hönl–London factor, which is a function of rotational quantum numbers alone. This approximation is based on the assumption that the wavefunction is a product of vibrational and rotational functions, as (1), and that the vibrational component of this function is independent of the rotational state of the system. Our experience with the rovibrational transitions of H_3^+ (Miller & Tennyson 1988*b*; Miller *et al.* 1990) suggests that this approximation is poor for this system.

Qualitatively, the intensity of the pure rotational spectrum of H_2D^+ is due to its permanent dipole moment. This dipole arises from the separation of the centre of mass from the centre of charge caused by the isotopic substitution. In producing the simulated spectrum of figure 3 we used the full *ab initio* dipole surface of MBB adapted for H_2D^+ . It is possible, however, to produce a spectrum using simply a constant dipole moment. We have therefore undertaken such a calculation, freezing the H_2D^+ dipole at its rovibrational ground state average value of 0.6055 Debye. In our embedding this dipole lies purely along D– H_2 coordinate, which is our body-fixed *z*-axis.

Figure 4 shows the difference between the ‘exact’ synthesized spectrum and that computed in frozen dipole approximation. It should be noted that figure 4 is plotted on a scale an order of magnitude larger than figure 3. It would thus appear that for the important transitions lying below about 700 cm^{-1} the frozen dipole approximation is better than 90% accurate. This approximation differs from the standard one in that full allowance is made for the variation of the ‘vibrational’ wavefunction with rotational state via the overlap contribution to the transition moment of the upper and lower levels.

Above 700 cm^{-1} the frozen dipole approximation appears to be less valid. Transitions in this region appear to be substantially vibrational in nature and thus should have a different zeroth-order dipole transition strength. Our plan is to test this supposition by doing a similar analysis on our ‘vibrational’ spectra.

Of course much interest in the high-lying levels of H_3^+ and its isotopomer has been provoked by the challenging experiments of Carrington & Kennedy (1984). Their spectra are very dense, they resolved over 100 lines per cm^{-1} , and also show some coarse grained regularity. As yet there is no widely accepted explanation for these

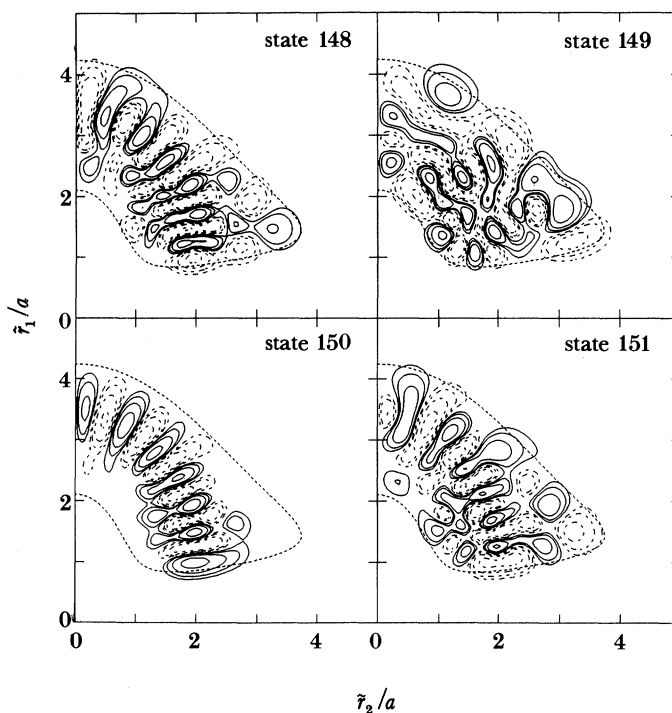


Figure 5. Cuts through 3D $J = 0$ H_3^+ wavefunctions (Tennyson & Henderson 1989). The coordinates are scattering (Jacobi) coordinates. For the plots the angle θ has been fixed at 90° and the states shown are all symmetric about this point. Contours are for 8%, 16%, 32%, and 64% of the maximum amplitude with solid (dashed) curves enclosing regions of positive (negative) amplitude. The outer dashed contours represent the classical turning point of the potential for the associated eigenvalue. The radial coordinates are mass weighted so that $\tilde{r} = \alpha r_1$ and $\tilde{r}_2 = r_2/\alpha$ where $\alpha = (3/4)^{1/2}$.

features. One proposal is that the regularity may be explained by the presence of a classically stable periodic orbit undergoing a 'horseshoe' motion (Gomez Llorrente & Pollak 1989). Classically, this orbit has a very small region of stability, but the interesting question is how does it affect the quantum mechanical properties of the system.

We have done a number of calculations to try to probe the quantal behaviour of these high-lying regions. Our best calculations, which used a DVR for the angular coordinate θ , gave wavefunctions for the lowest 180 $J = 0$ states of H_3^+ using the MBB potential (Tennyson & Henderson 1989). The highest of these states is only about two thirds of the way to dissociation, but nonetheless it is apparent from analysis of these wavefunctions (Brass *et al.* 1990) that the 'horseshoe' motion has a strong influence on the quantum dynamics.

In the high-energy region (i.e. anywhere above the barrier to linearity which is reached by state number 12), there are many irregular states for which no assignment can be made by analysing the nodal structure of the wavefunction. However, throughout the entire energy region it is possible to find highly excited bending modes which follow the classical 'horseshoe' (see state 150 of figure 5 for example). The observation of these states in the intermediate energy region, where they are classically unstable, does not prove that these states are the cause of the regularity

in the Carrington–Kennedy spectrum, but their existence is at least a confirmation of the growing impression that classically stable orbits have a disproportionately strong influence on the quantum mechanical behaviour of a system.

3.2. Other systems

In the previous subsection we considered several aspects of the high energy behaviour of the H_3^+ system. Although we have done many studies on this system our methods are designed to be flexible enough to treat any triatomic. Indeed our methods are not particularly well suited to H_3^+ because they are unable to incorporate the full symmetry of the system. However, consideration of the higher energy regions of other chemically bound systems tends to be more qualitative in nature because of the absence of reliable potential energy surfaces.

One system that has attracted considerable interest is LiCN. Several calculations have been performed on the two-dimensional (r_{CN} frozen) SCF potential energy surface of Essers *et al.* (1982). These calculations have been stimulated by the isomerizing nature of this system (it has an absolute minimum for linear LiNC and a local minimum for linear LiCN). These minima are separated by a relatively small barrier (3455 cm^{-1} from LiNC). Comparison with classical calculations on a number of systems suggest that the behaviour of LiCN is typical of small systems with an internal barrier (Tennyson & Farantos 1985).

Several calculations have concentrated on the behaviour of the lowest 100 states of LiCN, which cover the region up to and including the isomerization barrier (see, for example, Benito *et al.* 1989). Recently we (Henderson & Tennyson 1990) have been able to utilize the full power of the DVR method to obtain wavefunctions for the lowest 900 vibrational ($J = 0$) states of the system with CN frozen. These calculations extend our knowledge of this system to well above the barrier region.

Analysis of contour plots of the LiCN wavefunctions shows that while the majority of the vibrational states are irregular in appearance and cannot be assigned (e.g. state 811, figure 6), even at high energies states associated with three different zeroth-order hamiltonians could be observed. These states correspond to normal mode states of LiNC (e.g. state 725, figure 6), normal mode states of LiCN (e.g. state 360, figure 6) and free-rotor states (e.g. state 459, figure 6).

The large number of levels obtained in these calculations means that it is possible to use statistical methods to analyse the distribution of nearest neighbour spacings between levels. At high energy we found that the level spacing distribution tends towards a Wigner distribution, which has often been associated with ‘quantum chaos’. Furthermore we found a good correlation between the degree of ‘chaos’ as measured by these distributions and the number of states for which no reasonable assignment could be made.

Similar calculations have also been done for Na_3 (Henderson *et al.* 1990) using Radau coordinates. However, the complexity of the potential-energy surface makes it difficult to obtain reliable wavefunctions for this system and to analyse these wavefunctions.

Finally, we end with a mention of the Ar– N_2 Van der Waals complex. We (García Allyón *et al.* 1990) have just completed a series of calculations aimed at interpreting the infrared spectrum obtained for this system by McKellar (1988). As the spectrum was obtained ‘hot’ at liquid nitrogen temperatures, it was necessary for us to consider all bound rovibrational states of the system. Calculations were therefore done for J values up to 33. The levels obtained yielded 30 000 transitions between

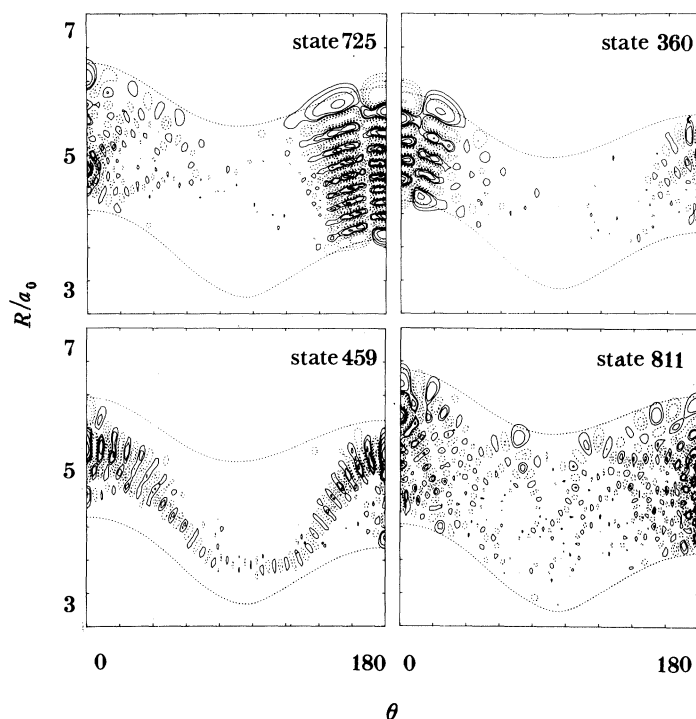


Figure 6. Contour plots of typical LiNC/LiCN vibrational states (Henderson & Tennyson 1990). The coordinates are scattering coordinates with r_{CN} frozen. $\theta = 0^\circ$ for linear LiCN and 180° for linear LiNC. Solid (dashed) contours enclose regions where the wavefunction has positive (negative) amplitude. Contours are drawn at 4%, 8%, 16%, 32% and 64% of the maximum amplitude of the wavefunction. The outer dashed contours represent the classical turning point of the potential for the associated eigenvalue.

truly bound states of the complex. 15000 of these transitions were intense enough to be retained in our convolution to give a spectrum that could be compared with experiment.

Although the Ar-N₂ potential energy surface is reasonably well known (Candori *et al.* 1983), there is no information readily available on the dipole surface. We therefore chose to construct a suitable surface from the appropriate long-range contributions with short-range functions adjusted to give approximate agreement with the intensities observed by McKellar (1988). This tuning procedure is still in progress.

4. Conclusions

We have outlined the theoretical techniques available for studying the high-lying rovibrational states of triatomic molecules. The application of these techniques has been illustrated using a number of our recent calculations.

Calculations of the 'rotational' spectrum of H₂D⁺ at high temperature has shown that the intensity distributions predicted from a full calculation can be well modelled by an approximation which freezes the dipole at its ground state value. Conversely attempts to approximate the wavefunctions by perturbation theory or by separating rotational and vibrational motion lead to poor values not only for the transition frequencies but also for the transition intensities themselves.

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As a final observation it is worth recording that our calculations often exceed the limitations of available potentials. Not only is the potential energy surface probably the major source of error for all systems discussed above, but also the region of validity of a given potential can also constrain the calculations that can be done. For example the recent DVR calculations on H_3^+ (Tennyson & Henderson 1989) obtained estimates for all the vibrational states in the energy region for which the accurate MBB (Meyer *et al.* 1986) potential is valid. The absence of a potential of similar accuracy to that of MBB for the dissociating regions of H_3^+ is a deterrent to doing detailed quantum mechanical calculations in this important energy region.

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