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FARADAY RESEARCH ARTICLE

Why Calculate the Spectra of Small Molecules?

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Calculations on the bound nuclear motion states of molecules are now making a contribution to many areas of physical science including astrophysics, planetary atmospheres and chemical kinetics. This article discusses the various uses made of ro-vibrational calculations on small, particularly triatomic, molecules. A non-technical theoretical overview compares the three main methods for performing these calculations: the traditional perturbation theory approach, basis set methods using the variational principle and a finite-element approach, the discrete variable representation (DVR). The reasons for maintaining parallel basis set and DVR programs are given. Applications of ro-vibrational calculations to the area of traditional high-resolution spectroscopy, *i.e.* low-lying states, are discussed. These include proving and developing potential-energy surfaces, predicting and assigning spectra, calculating transition intensities and generating data for the calculation of thermodynamic and emissivity parameters. The links between highly excited ro-vibrational states, reaction dynamics and quantum chaology are discussed and the importance for improved calculations in this energy region outlined.

1. Introduction

High-resolution spectroscopy has produced a wealth of data on small and not so small molecules. Transitions are often recorded to an accuracy of eight or nine figures. This precision is impossible for the theoretician to match, particularly one working *ab initio*. Nonetheless the first-principles calculation of spectra of small molecules has been a major growth area.

The initial motivation for calculating transition frequencies was often as a test of theoretical methods against observed results. The hope was that if calculations could be made accurate enough then useful predictions could be made for as yet unobserved transitions. As theoretical methods have improved a number of other reasons for performing these calculations have come to the fore. Some of these allow theory and experiment to combine to obtain the maximum information from observed spectra. Other, more creative, uses of calculations aim to exploit the computer's ability to generate and handle very large data sets to extend studies into areas well beyond those covered by traditional molecular spectroscopy. Furthermore, while spectra may often be observed with very high precision, the nature of the transitions involved may often be far from obvious. Calculations, in which effects from various contributions may be analysed individually, have proved useful in unravelling many complicated spectra.

The development of first-principles methods of treating nuclear motion has made possible a wide variety of applications. My group at University College London (UCL) have been involved in studies ranging from the spectrum of supernova 1987A to 'quantum chaos' and from planetary aurorae to equilibrium constants for chemical reactions. These and other applications are described in this review.

The article is organised as follows. Section 2 gives a brief theoretical overview which will aim at giving a flavour rather than a rigorous exposition of how calculations are performed. Section 3 discusses results obtained for the low-lying states of small molecules. Section 4 considers the high-lying rotation–vibration states of molecules including those near dissociation.

2. Theoretical Overview

2.1 Perturbation Theory: The Traditional Approach

The low-lying states of chemically bound molecules are usually considered to undergo small-amplitude vibrational motion about some equilibrium geometry with their rotational motion approximated by the rotations of a rigid body. The interaction between vibrational and rotational motion *via* Coriolis forces is neglected. Within this simple framework vibrational wavefunctions are products of harmonic oscillators[1] and rotational wavefunctions are easily obtained as the solution of the rigid rotor model with appropriate moments of inertia.[2] Of course these models do not give an accurate picture but they provide most of the language upon which the labelling schemes ('assignments') of modern infrared and microwave spectroscopy are based.

For quantitative treatments the harmonic oscillator–rigid rotor model is improved by use of perturbation theory. Spectra are parametrized using 'force constants' for the vibrational motion (see ref. 3 for example) and 'rotational constants'.[4] The force constants are the coefficients of a Taylor expansion about equilibrium while the rotational constants are the coefficients of a power series in the rotational angular momentum and its projection. Both series contain information about the underlying potential of the system.

Thus the force constants, for example, give values for the derivatives of the potential at equilibrium. As such they give a high-order representation of the potential at a single point. A completely satisfactory scheme for extrapolating these derivatives away from equilibrium to yield values of the potential at any arbitrary molecular geometry has yet to be found. Thus, although the ro-vibrational states of a molecule are very sensitive to the potential of the system, force constant methods do not yield potentials in a form that is appropriate for other studies which rely on a knowledge of the potential far away from equilibrium.

The theory underpinning the harmonic oscillator–rigid rotor model is based on the use of the Eckart conditions[5] which maximize the separation between vibrational and rotational motion. Eckart proposed these conditions for a classical system and the simplest quantal Hamiltonian incorporating them has been given by Watson for both bent[6] and linear[7] molecules.

2.2 Variational Principle: Basis Set Methods

It has long been recognised that perturbation theory is inadequate for treating molecules with large-amplitude vibrational motion. Van der Waals complexes and chemically bound

molecules containing hydrogen are sufficiently floppy for perturbative methods to be inappropriate;[8] at higher excitation energies, all systems must undergo large-amplitude vibrational motion in one or more modes prior to dissociation.

Diatomic molecules have only one vibrational mode and hence only one internal coordinate. This means that for a given potential, $V(R)$, the Schrödinger equation can be solved accurately by direct numerical integration.[9] Early attempts to treat large-amplitude motion in polyatomic molecules identified a single large-amplitude mode which could be treated in a similar fashion to a diatomic molecule, with the other modes kept (near) rigid.[10]

For triatomic (and to a lesser extent tetratomic) molecules, ro-vibrational energy levels and wavefunctions are now usually obtained using basis set expansions and the variational principle. For example, energy levels and wavefunctions for Watson's Hamiltonians have been obtained by Whitehead and Handy[11,12] and others.[13–15] These calculations use products of harmonic oscillators (Hermite polynomials) as a basis to represent the vibrational motions and Gauss–Hermite quadrature to evaluate the matrix elements of the Hamiltonian, particularly over the potential.

Watson's Hamiltonian has generally fallen out of favour for variational calculations. This is because of the difficulty of going smoothly from bent to linear systems as illustrated by a series of calculations on the quasi-linear CH_2^+ molecule.[13,16–19] The preferred solution to these problems is to use internal coordinates which are defined in terms of interatomic distances and related geometric parameters. One general scheme for defining internal coordinates for triatomic molecules is given in Fig. 1.

For any set of internal coordinates, $\boldsymbol{Q}$, it is necessary to derive the appropriate Hamiltonian. How this is done is discussed in a recent review by Sutcliffe.[20] However, we should note that the process of transforming from $3N$ particle coordinates to three translational, three rotational and $3N-6$ vibrational (internal) coordinates inevitably introduces singularities into the Hamiltonian. This means that not all physically desirable coordinate choices are actually usable. The Hamiltonian implied by the coordinates of Fig. 1 is given by Sutcliffe and Tennyson,[21] who also discuss these problems in some detail.

Given a coordinate system, $\boldsymbol{Q}$, and a Hamiltonian the next step in the variational approach is to choose basis functions to represent the motions of the nuclei. Usually vibrational motion is represented as products of suitable one-dimension functions, $P(Q)$, so that the wavefunction of vibrational state i can be written

$$\Psi_i(Q_1, Q_2, Q_3, \ldots) = \sum_{j,k,l,\ldots} c^i_{j,k,l,\ldots} P_j(Q_1)P_k(Q_2)P_l(Q_3)\ldots \quad (1)$$

where the expansion coefficients $\boldsymbol{c}^i$ are obtained by diagonalising the secular matrix constructed in terms of the basis functions. This method has been labelled the finite basis representation (FBR).[23]

Suitable basis functions include harmonic oscillators (Hermite polynomials), Morse oscillators (Laguerre polynomials) and related functions, and free rotor functions (Legendre polynomials). In the case of the Morse and harmonic oscillators these functions contain parameters that can be optimised using the variational principle to obtain compact one-dimensional basis sets.

For a given basis set it is necessary to integrate over all coordinates to form the secular matrix. While some integrals may be evaluated analytically, integration over arbitrary potential functions requires numerical quadrature. A very satisfactory way of doing this is to note that all the basis functions mentioned above can be expressed in terms of orthogonal polynomials. The integrals can be evaluated numerically using the appropriate Gaussian quadrature scheme[24] for each function.

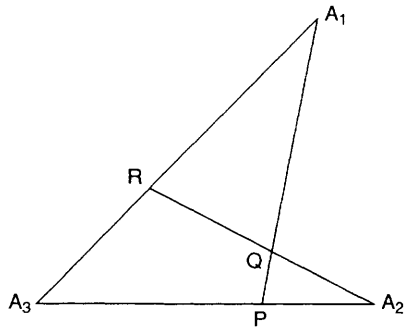

Fig. 1 General triatomic internal coordinate system.[21] A_i represents atom i. The coordinates in the text are given by $r_1 = A_2$–R, $r_2 = A_1$–P and $\theta = A_1\hat{Q}A_2$. The Hamiltonian is defined by geometrical parameters, see ref. 21

$$g_1 = \frac{A_3 - P}{A_3 - A_2}; \qquad g_2 = \frac{A_3 - R}{A_3 - A_1}$$

For triatomic molecules the computational bottleneck in variational calculations is diagonalisation of the secular (Hamiltonian) matrix. It is for this reason that care must be chosen to use appropriate, compact, basis sets. However, operations on matrices, including diagonalisation, are very efficiently handled by computers with vector processing capability and calculations with several thousand basis functions are now routinely performed. In this context it should be noted that the matrices being diagonalised are small in comparison with those used routinely *ab initio* electronic structure calculations using configuration interaction (CI). However, in contrast to CI calculations one is usually interested in tens or hundreds of the solutions. Furthermore, although the matrices being diagonalised may be sparse,[25,26] they are usually much less sparse and less diagonally dominant than the CI ones.

Rotational motion is carried in these calculations by Wigner rotation matrices, $D^J_{k,M}(\alpha, \beta, \gamma)$. Unlike the vibrational basis functions discussed above, these form a finite set: for a given value of the rotational angular momentum quantum number, J, it is necessary to include only the $2J+1$ functions with $-J \leqslant k \leqslant +J$, where k is the projection of J on the molecular z axis.

Experience has shown that the best way of solving the coupled rotation–vibration problem is in two steps.[14,27] In our method, the first step involves solving $J+1$ vibrational problems, one for each value of $|k|$. The lowest solutions of these problems are selected as a basis for the fully coupled problem.[28] This method is so effective that rotational levels can even be found at the dissociation limit for chemically bound molecules;[29] the two-step procedure has effectively solved the rotational problem for small molecules.

2.3 Finite Elements: The Discrete Variable Representation

Variational calculations using basis sets have been very successful in predicting spectra for a wide variety of triatomics and some larger molecules. However usually in these calculations only a small proportion (*ca.* 5%) of the solutions obtained by diagonalising the secular matrix are of any significance. This means that basis set calculations normally perform poorly when a large number of energy levels are required.

In the last few years a number of finite-element methods have been proposed for solving the nuclear motion Schrödinger equation. The most widely used of these is the discrete variable representation (DVR) which was originally suggested in the sixties[22] but has since been extensively developed by Light and co-workers for ro-vibrational problems. A comprehensive review of the DVR has been given by Bačić and Light.[23]

Although the DVR method is not strictly variational, it has strong formal[30] and practical links with the basis set methods discussed above. This is because the formulation of the problem in a DVR first requires, at least in principle, the construction of the secular matrix in terms of appropriate (polynomial) basis functions. This matrix is then transformed to a grid of points determined by the appropriate Gaussian quadrature scheme for each function.

Superficially this transformation achieves nothing as the DVR and FBR matrices are isomorphic.[30] However, in the DVR it is easy to define a hierarchy of problems which can be diagonalised and the lowest solutions selected and used to expand the next problem. In this fashion final Hamiltonian matrices are constructed with a very high information content—up to half the solutions of the final matrix may be physically significant.[31] An illustrated discussion of this diagonalisation and truncation procedure, which is similar to the two-step method for rotationally excited states discussed above, is given by Light *et al.*[25]

2.4 DVR *vs.* FBR

Given that the DVR typically yields many more physically significant solutions for a final matrix of given size (and hence for a given amount of computer time) one might expect it to be universally the method of choice. However, the FBR and DVR methods have rather different numerical characteristics which means that it is the policy of the UCL group to maintain parallel and complementary FBR and DVR codes for given problems.

In the DVR method the quadrature points also serve as the expansion points for the wavefunction. This means that numerical integration and basis set size are inextricably linked so that the only way of improving the accuracy of integrals which have to be determined numerically is by increasing the number of points used to represent the wavefunction and hence the size of the problem. The pitfalls in this approach have recently been extensively analysed for a problem where DVR calculations appeared to give converged results which violated the variational principle.[32–34]

In the FBR method, quadrature schemes may be selected simply to give integrals to the required precision with no other consequences for the calculation. This means that a converged FBR calculation is inherently more accurate than the corresponding DVR one. FBR calculations will therefore continue to be used when very accurate results are required for low-lying states. This is the most common situation when calculations are performed for comparison with conventional high-resolution spectroscopy.

Furthermore, the coupling of quadrature and matrix size means that it is generally impossible to perform a small DVR calculation as the numerical quadratures become too unreliable and the results lose all significance. It is, in principle, possible to circumvent this problem by transforming matrix elements determined numerically using the appropriate FBR (as has been done in other circumstances[34,35]), but there is little advantage in doing this rather than a small FBR calculation. Small calculations are important for developing appropriate basis functions,[36] the derivation of spectroscopically determined potentials (see below) and other tests.

DVR calculations on rotationally excited systems have now been performed by a number of groups.[35,37–40] However, because of the large bases used for the vibrational degrees of freedom in these calculations, they tend to be computationally expensive. This again suggests that FBR calculations will continue to be used for studies involving many rotational levels especially at low levels of vibrational excitation.

3. Low-lying States

3.1 Proving Potential-energy Surfaces

Much of chemical physics is concerned with properties which are determined by inter- and intra-molecular potentials. High-resolution spectroscopy in particular is very sensitive to the details of potential-energy surfaces. As spectra contain much information about these surfaces, it would seem natural to use these data to construct accurate surfaces which can be used for further spectroscopic studies or in other contexts. However, only for the simple one-dimensional curves governing the nuclear motion of diatomic systems is it possible to go directly from observed energy levels to the potential.

For polyatomic molecules potential-energy surfaces must be constructed by some other means. This surface can then be used to predict known ro-vibrational transition frequencies for comparison with experiment. From this comparison the accuracy of the surface can be determined, at least in the region to which the observed data are sensitive.

The traditional way of fitting the experimental data to force constants and rotational constants using perturbation theory has been discussed above. These approaches do not really yield true global potentials of the system and are gradually being superseded by other methods.

The improvement in electronic structure calculations means that at least for small, triatomic and tetratomic, molecules containing light atoms it is possible to calculate potential-energy surfaces *ab initio*. Although in few cases can these surfaces hope to meet the demanding standards of accuracy produced by high-resolution spectroscopy, they can be used for predictive purposes and as the starting point for further refinements.

Actually electronic structure calculations yield values for the potential only at a grid of points. To obtain the full potential it is necessary to interpolate analytically between these points. This is usually done by means of least-squares fitting a surface of suitable functional form and with adjustable parameters. This step in the calculation remains something of a black art (see for example ref. 15). An appropriate functional form should be capable of (*a*) displaying (near) harmonic behaviour about the equilibrium geometry, (*b*) reflecting the (permutation) symmetry of the molecule, (*c*) going smoothly to dissociation products and (*d*) showing saddle points at appropriate places, for example linear geometries for a non-linear molecule. Functions used to fit potentials in the region of equilibrium rarely satisfy (*d*) and none that I know of satisfy (*c*). Alternatively, potentials such as the Sorbie–Murrell one,[41] which dissociate correctly usually have difficulty giving the required accuracy about equilibrium. This problem is becoming a barrier to the development of high-quality global potentials with at least one very accurate *ab initio* calculation remaining unfitted because of difficulties finding a suitable functional form.[42]

Alternatively it is possible to construct spectroscopically determined surfaces by guessing a suitable potential, calculating its ro-vibrational levels, comparing them with experiment, adjusting the parameters in the potential and repeating the procedure until the calculations reproduce experiment.

This method has been used extensively for Van der Waals molecules[43] and is now becoming a significant source of potentials for chemically bound triatomics.

Fig. 2 summarizes these two procedures. In both cases the calculation of ro-vibrational levels is a key step in the comparison with experiment.

One system for which many potential-energy surfaces have been constructed is water. The better *ab initio* surfaces reproduce the fundamental frequencies to within a few wavenumbers (see ref. 44 for a survey). Conversely there are four spectroscopically determined surfaces available all of which reproduced the 63 observed band origins of water lying up to 22 000 cm^{-1} with a standard deviation of *ca.* 10 cm^{-1}. Table 1 summarizes the results of a systematic test of these surfaces by Fernley *et al.*[45] and shows that the surface due to Jensen[46] gives reliable results for a large range of levels.

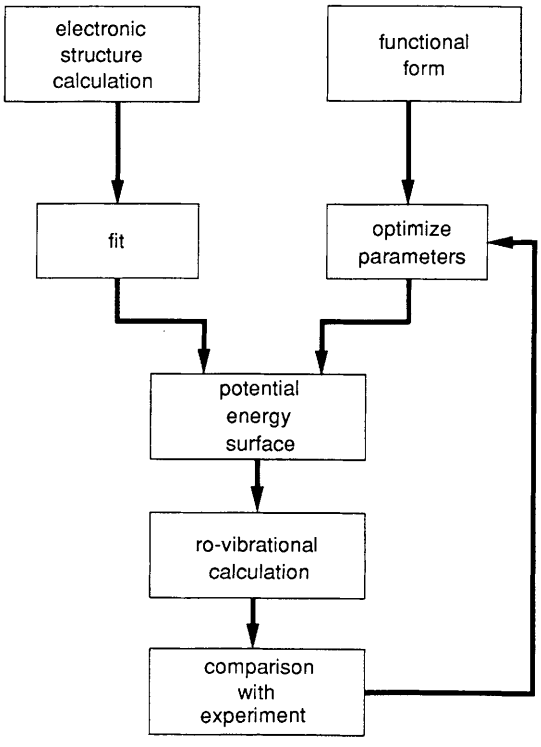

Fig. 2 Scheme showing how potential-energy surfaces are constructed and tested against observation. The left-hand side depicts the first-principles route and the right-hand side spectroscopically determined potentials. Hybrids between the two methods are also possible

Table 1 Statistical comparison of four spectroscopically determined water potential-energy surfaces for the 63 observed vibrational band origins and rotational term values for the lowest 10 vibrational states[45] [given are the mean (observed − calculated) error and standard deviation (σ), both in cm^{-1}]

	band origin		term values	
potential[a]	mean	σ	mean	σ
CH	4.1	11.5	0.10	0.35
HC	−1.2	7.2	−0.59	1.20
J	−1.1	6.4	0.01	0.14
KH	0.2	10.3	−0.05	0.37

[a] The potentials are: CH, S. Carter and N. C. Handy, *J. Chem. Phys.*, 1987, **87**, 4294; HC, L. Halonen and T. Carrington Jr., *J. Chem. Phys.*, 1988, **88**, 4171; J, P. Jensen, *J. Mol. Spectrosc.*, 1989, **133**, 438; KH, E. Kauppi and L. Halonon, *J. Phys. Chem.*, 1990, **94**, 5779.

3.2 Predicting and Assigning Spectra

In spectroscopy it is possible to observe large numbers of transitions to high accuracy without knowing what it is that is being measured. Theory is rarely able to compete with this accuracy but can often help with the understanding.

The usual procedure by which spectra are understood is called assignment. Both levels in a transition are assigned vibrational and rotational quantum numbers. In fact most of these quantum numbers are only approximate, a theme I will return to in section 4. It is often true that once a few transitions have been assigned patterns emerge which allow the assignment of many others.

A molecule in which theory has played and is continuing to play a particularly strong role is H_3^+. This unusual triangular ion is believed to be the cornerstone of most gas-phase reaction cycles in the interstellar medium.[47,48] Yet it was only in 1980 that the first H_3^+ spectrum was observed: Oka[49] observed infrared absorptions of the degenerate bending fundamental v_2 following pioneering theoretical calculations by Carney and Porter.[50]

Since then a series of calculations by Miller and Tennyson[51] have lead to the assignment of the bands $2v_2 \leftarrow 0$,[52] $2v_2 \leftarrow v_2$,[53] $v_1 + v_2 \leftarrow v_2$[53] and $3v_2(l = 1) \leftarrow 0$.[54] Most recently, following the predictions of Miller *et al.*,[55] the 'forbidden' $v_1 + v_2 \leftarrow v_2$ band has been observed.[56] This work also reported the first observations of transitions in the 'infrared-forbidden' breathing fundamental, v_1. Table 2 compares the observed transition frequencies with those predicted from theory for this band.

The importance of the H_3^+ work was shown by the serendipitous observation of its $2v_2 \rightarrow 0$ emission spectrum from the southern polar regions of Jupiter.[59] This observation has led to a flurry of observational activity and the assignment of H_3^+ emission spectra in both supernova 1987a[60] and Uranus.[61]

3.3 Calculating Transition Intensities

It is often said that a spectrum acts like a fingerprint, giving a unique characterization of a particular species. While this is true, most applications of spectroscopy actually aim at more than a simple diagnosis of the presence of a particular molecule. Quantitative information is also required.

A ro-vibrational spectrum contains considerable physical information about the system under study. For systems in

Table 2 Observed and predicted transition frequencies of the 'infrared-inactive' stretching fundamental, v_1, of H_3^+; the transitions are observable due to intensity stealing from nearby transitions of the infrared-active bending fundamental, v_2

transition[a]	wavenumber/cm^{-1}	
$J',K' \leftarrow J,K$	obs.[56]	calc.
7,5 ← 6,2	3282.308	3282.27
6,5 ← 5,2	3202.169	3202.15
7,6 ← 6,3	3144.454	3144.33
5,5 ← 4,2	3120.199	3120.24
6.6 ← 5,3	3066.561	3066.55
7,7 ← 6.4	3026.154	3025.96
6,5 ← 6,2	2709.479	2709.61
6,6 ← 6,3	2569.726	2569.85
7,7 ← 7,4	2454.417	2454.39

[a] Quantum numbers J,K denote the total angular momentum and its projection along the H_3^+ symmetry axis.[57]

thermodynamic equilibrium, spectra can give the absolute quantity of the species being observed and the temperature, as well as information on isotopic and spin isomer abundance if appropriate. In non-equilibrium conditions, a spectrum can give the amount of the species in each level absorbing/emitting radiation. However, to extract any of this information it is necessary to know the strength of the individual transitions observed.

While many ro-vibrational transition intensities have been measured,[62] certain set-ups make the measurement of absolute transition intensities nearly impossible. This is true, for example, of non-equilibrium observations such as those made of cold plasmas, flames or transient species. In this case the calculation of transition intensities may be vital for any useful applied spectroscopy even though the actual transitions involved have been well characterised in the laboratory.

H_3^+ provides a prototype of this approach. The extensive laboratory measurements have all been made in plasmas for which it is very difficult to determine the occupancy of individual levels of the ion. Thus the experiments yield little information on the transition intensities. However, these can be calculated from first principles[63] and extensive lists have been compiled.[58]

Fig. 3 shows a recent infrared emission spectrum of Uranus taken with a resolution of 0.0031 μm.[61] It is easy to assign the 11 most prominent features of this spectrum to lines or blends of known transitions in the fundamental bending mode of H_3^+, ν_2. However, use of the transition intensities also yields a column density, ρ, a temperature, T and an *ortho* fraction, f_o. T and n are important for modelling auroral processes in Uranus—in particular they are sensitive monitors of both the energy deposition and emission in the ionosphere. f_o is important as values near $\frac{1}{2}$, as observed, suggest that the H_3^+ has thermalised before emitting. This is because H_3^+ formed from cold H_2 might be expected to have an f_o value nearer $\frac{1}{3}$.[61] The ro-vibrational spectrum of H_3^+ is now routinely being used as a monitor of auroral activity in the Jovian planets.[64,65]

3.4 Generating Thermodynamic Data

The development of reliable and fairly automatic programs for calculating ro-vibrational energy levels and spectra[66] means that it is possible to compute comprehensive sets of energy levels or transitions. These in turn can be used to generate thermodynamic or emissivity data of interest.

For example, sums over energy levels, E_i, give partition functions, z, as a function of temperature, T:

$$z = \sum_i (2J_i + 1)g_i \exp(-E_i/k_B T) \quad (2)$$

where g_i is the nuclear spin degeneracy factor. Note that this formulation makes no separation between rotational and vibrational motion and hence z is the combined partition function for these motions. Besides their use for calculating temperature-dependent spectra, partition functions can be used to derive equilibrium constants as a function of temperature.

Consider the reaction

$$A + B \rightarrow C + D \quad (3)$$

Then the temperature-dependent equilibrium constant, $K(T)$, is given by the formula

$$K = \frac{z'_C z'_D}{z'_A z'_B} \exp(-U/k_B T) \quad (4)$$

where U, the heat of the reaction at absolute zero, is given by the difference between the zero-point energies of the products and reactants measured on a common (absolute) energy scale. Note that z' differs from z defined above in that it also includes the translational partition functions which can be incorporated as a simple mass factor for reactions which conserve the number of particles.[67]

Isotope-exchange reactions are important for isotope separation schemes, for the formation of exotic molecules (*e.g.* ref. 68) and astrophysically. The thermodynamics of these reactions can be characterised by using the ro-vibrational levels of the species involved.

Thus, for example, the deuterium fractionation reactions

$$H_3^+ + D \rightarrow H_2D^+ + H; \qquad U = -509K \quad (5)$$

and

$$H_3^+ + HD \rightarrow H_2D^+ + H_2; \qquad U = -139.5K \quad (6)$$

are both exothermic by amounts significant for temperatures of 100 K or less. They are thus very important in the cool interstellar medium where they can lead to an H_2D^+/H_3^+ ratio several orders of magnitude greater than the natural abundance of D.[69] Fig. 4 shows the temperature dependence of the equilibrium constants of the two reactions.[70] These data are important input for models such as that of Millar *et al.*[69]

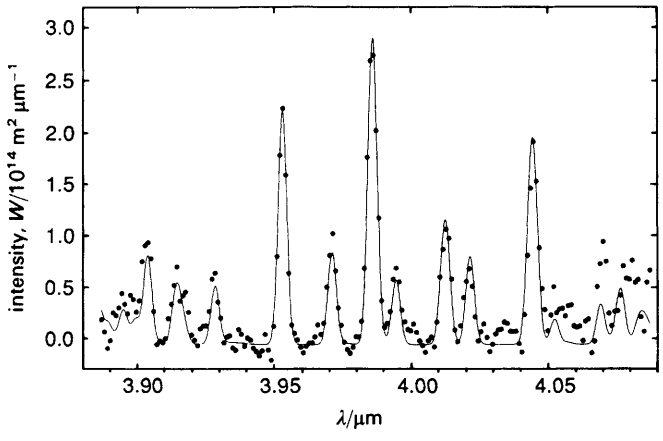

Fig. 3 Emission spectrum from Uranus (April 1st, 1992) recorded by Trafton *et al.*,[61] points, and fit to the spectrum using the H_3^+ data of Kao *et al.*,[58] curve. A telescope resolution of 0.0031 μm was assumed in the fit. H_3^+ parameters: $T = 740$ K, $f_o = 0.51$, $\rho = 6.5 \times 10^{10}$ cm^2

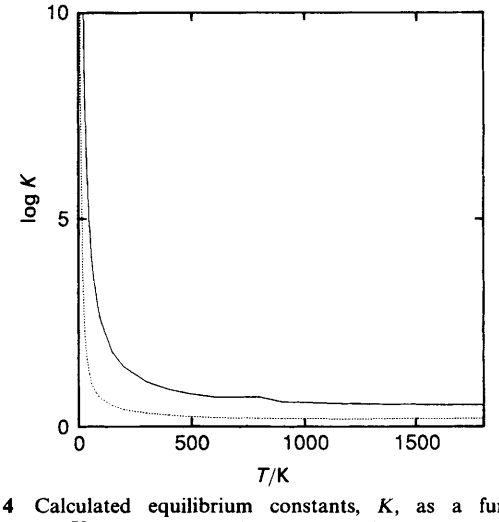

Fig. 4 Calculated equilibrium constants, K, as a function of temperature[70] for reactions $H_3^+ + D \rightarrow H_2D^+ + H$ (solid curve) and $H_3^+ + HD \rightarrow H_2D^+ + H_2$ (dashed curve)

Knowledge of the total absorption of a medium, often called the opacity, as a function of molecular composition, wavelength and temperature is important for modelling planetary and cool stellar atmospheres. On Earth it is vital for understanding the 'greenhouse effect'. Traditionally such absorption profiles have been constructed from databases of transitions individually measured in the laboratory, of which HITRAN[62] is a much used example.

Even for a triatomic molecule, such as water, depending on the temperature of interest, it may be necessary to know between 10^4 and 10^7 transitions in order to synthesize an accurate opacity function. Generating this large amount of data experimentally is tedious and expensive. Conversely computers are well suited to the repetitive nature of such tasks. So far, datasets of all the possible ro-vibrational transitions of a molecule have only been generated for simple systems.[71] However, a number of groups, including the one at UCL, are working on extending these methods to molecules of general atmospheric and astrophysical interest.

In fact, at UCL we have a very extensive, but far from exhaustive, dataset of H_3^+ transition frequencies and line intensities. Part of an earlier version of this dataset has been published,[58] but one of the problems of this work is presenting the large quantities of data involved in a form accessible to other workers. So far our attempts at guessing which portions of this dataset are the most important to publish have not proved very accurate!

4. High-lying States

4.1 Spectroscopy and Reaction Dynamics

Much of high-resolution spectroscopy is concerned with transitions between low-lying levels of molecules, but this is not always the case. Laser-based techniques, such as stimulated emission pumping, allow high-lying levels of molecules to be probed. Besides the intrinsic interest in these levels, it is in this region that spectrosocopy links up with other areas of chemical physics and in particular the study of reaction dynamics.

Unimolecular reactions in the form of isomerisation should be amenable to study using ro-vibrational techniques, provided the reaction occurs on a single electronic potential-energy surface. A prototype system of this form which has been much studied is LiCN.[72–79] This molecule has a linear isocyanide structure[80,81] and is predicted to also have a metastable linear cyanide isomer.[81]

A study by Henderson and Tennyson using the DVR technique and a model which froze the CN bond obtained 900 vibrational wavefunctions for LiCN.[82] These results covered an energy region up to four times the barrier to isomerisation in the LiCN system. The calculations found vibrational states localised in both LiNC and LiCN minima, some of which persisted throughout the entire energy region. Above the barrier to isomerisation an increasing proportion of the states are completely delocalised. Of these states, a few are free-rotor like (or 'polytopic'[83]) in appearance, but most are highly irregular in nature, meaning that no sensible assignment of vibrational quantum numbers could be attempted.

The study on LiCN parallels similar but less complete 3D studies on isomerisation in HCN.[84,85] Vibrational wavefunctions for highly excited states of HCN have been used to estimate the relative formation rates of HCN and HNC[86] in an attempt to explain the anomalously high population of HNC observed in the interstellar medium.

A decade ago Carrington *et al.*[87] reported an infrared photodissociation spectrum of H_3^+ showing a very large number of narrow transitions between what proved to be quasibound (or predissociating) ro-vibrational states of the ion.[88] This spectrum, which remains largely unexplained and completely unassigned,[89] has provided a major challenge to theory.

Initially theoreticians focussed on the classical behaviour of the H_3^+ nuclear motion problem. This showed that while much of the H_3^+ phase space in the near dissociation region was chaotic, quasiperiodic trajectories were found by a number of workers (*e.g.* ref. 90). H_3^+ is, however, a highly quantal system.

Henderson and co-workers performed a series of calculations using a DVR in one[37] and three[33,34,91] dimensions obtaining approximate energies and wavefunctions for all the vibrational bound states of H_3^+. This work has taken theory into the realms of the dissociation for chemically bound polyatomic systems although there is still some way to go before it yields a full explanation of the predissociation spectrum of Carrington *et al.*

An interesting comparison between (semi-)classical and quantal calculations on H_3^+ can be obtained by comparing the density of states predicted by the two methods. The function is important for partition functions and for statistical models of chemical reaction. Fig. 5 shows a comparison of semi-classical and quantal estimates of the $J = 0$ density of H_3^+ states based on the work of Berblinger *et al.*[92] As can be seen, the agreement is excellent, suggesting that direct integration of phase space gives a reliable method of obtaining densities of states for highly excited molecules.

4.2 Quantum Chaology

The subject of chaos in classical systems has aroused much recent research and popular interest. A particular branch of this work involves the behaviour of conservative (*i.e.* constant energy), non-linear Hamiltonian systems.[93] Anharmonically coupled oscillators are a particular example of such a system and as such their general properties have received much attention.

More controversial is the behaviour of systems which are known to be classically chaotic under quantum mechanics (*e.g.* ref. 94). The phrase 'quantum chaology'[95] has been coined to describe this area of research.

Molecular vibrations give some of the simplest and most easily observed examples of anharmonically coupled quantal oscillators. Indeed a number of observed molecular spectra

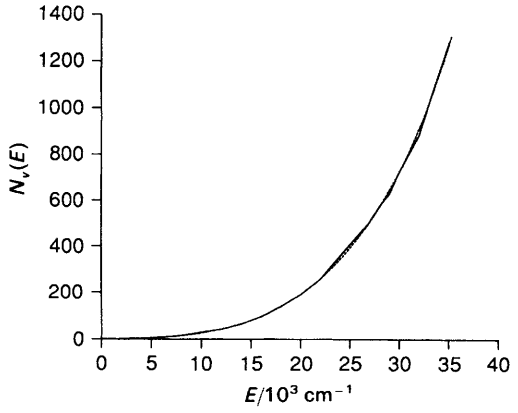

Fig. 5 Number, $N_v(E)$, of vibrational ($J = 0$) states of the H_3^+ molecular ion lying below a particular energy, E. The solid line gives quantal predictions[91] and the dashed line gives semi-classical results obtained by Monte Carlo integration of the volume of phase space.[92] For ease of comparison doubly degenerate vibrational states have been counted twice. The dissociation energy of H_3^+ is *ca.* 35 000 cm^{-1}

have been pronounced 'chaotic' on the basis of the behaviour with respect to some indicator of 'quantum chaos'. Small molecules so studied include HCN,[96] CH_2OH,[97] C_2H_2,[98] NO_2,[99] SiH_2[100] and Na_3.[101]

This is an area where quantum-mechanical calculations are probably more reliable and easier to interpret than experiment. Direct comparison between experiment and classical calculations relies on a series of assumptions about such things as the accuracy of the potential-energy surface, the Born–Oppenheimer approximation, neglect of nuclear and electronic angular momentum couplings and assumptions about unobserved transitions. In conventional spectroscopic studies, these effects can often be ignored or allowance made for them using perturbation theory. However, chaotic trajectories are unstable with respect to perturbations and it is thus difficult to decide *a priori* how a seemingly small perturbation may affect a spectrum.

Conversely it is possible to set up and solve, at least in principle, a well defined model using quantum mechanics. For molecular vibrations this same model can usually be studied classically (*e.g.* ref. 75, 76). Direct unambiguous quantum–classical comparison is then possible. If these results also agree with observation, then the model is a valid one. If not, it may be possible to improve the model used for both the quantal and classical calculations.

As the wavefunction of a system contains all the information knowable about that system, it is possible to interrogate calculated wavefunctions using several different methods. Table 3 gives the results of such an analysis for the LiCN calculations of Henderson and Tennyson[91] discussed in the previous section. The two parameters compared are the distribution of the spacings between neighbouring vibrational energy levels of the system, as parametrized by the Brody parameter q, and the proportion of states in the same energy region which could not be assigned approximate quantum numbers by visual inspection of plots of the vibrational wavefunction, u. The Brody distribution is a generalization which gives a Poisson distribution, the usual distribution displayed by the spacing between neighbouring levels of a regular system, for $q = 0$, and a Wigner distribution, the distribution of eigenvalues obtained by diagonalising matrices of random numbers, for $q = 1$. In practice the parameter q is least-squares fitted to the nearest-neighbour distribution (see ref. 102). It can be seen here that there is a high degree of correlation between the two measures: one based on energy levels and the other directly on the wavefunctions.

The one major conclusion of the various comparisons of classical and quantal calculations concerns 'scarring' of the wavefunction. This is the observation that the wavefunction tends to collect amplitude disproportionately about quasi-periodic classical orbits. This is the basis for the explanation of coarse-grained regularity in a number of otherwise irregular spectra.[90,101] Indeed scarring of the quantal wavefunction has actually lead to the identification of otherwise unnoticed stable orbits.[103,104]

Table 3 Level spacing distribution Brody parameter,[102] q, for the levels of LiCN calculated by Henderson and Tennyson[91]

levels	energy range/cm^{-1}	$\bar{S}$	q	σ	u
1–30	0–2240	77.5	0.154	0.034	7%
31–100	2286–4090	26.0	0.588	0.030	44
101–300	4090–7150	15.3	0.785	0.012	81
201–400	5768–8358	13.0	0.798	0.015	85
301–500	7150–9427	11.4	0.764	0.017	88
401–600	8350–10445	10.5	0.794	0.013	91
501–700	9427–11388	9.8	0.859	0.011	93
601–800	10445–12247	9.0	0.830	0.012	94
701–900	11388–13086	8.6	1.049	0.011	95

The energy range of each bin is given relative to the LiNC ground vibrational state. The average level spacing, $\bar{S}$, in cm^{-1} and the standard deviation, σ, of the fit in units of probability as well as the percentage of unassigned states, u, in each fit are also given.

5. Conclusion

In 1978 Carney, Sprandel and Kern[105] published a much quoted review on the state of rotation–vibration calculations for chemically bound small (triatomic) molecules. This work gave a comprehensive summary of variational techniques in use at the time. Its major concerns were (*a*) whether the (Eckart) Hamiltonians used by different groups were actually the same and (*b*) whether the different solution strategies employed actually gave the same answers. All except one work quoted used normal coordinates, and all studies concentrated on the vibrational fundamentals and, perhaps, a low level of rotational excitation.

During the 1980s geometrically defined internal coordinates have largely superseded normal coordinates and a number of benchmarked internal coordinates codes have become generally available (*e.g.* ref. 106). Methods have been developed for dealing with very high degrees of vibrational[23] and rotational[27] excitation.

The first principles calculation of molecular spectra using the variational principle has thus become a mature technique capable of making useful contributions to a number of areas of physical science. In this review I have tried to illustrate the range of problems that can be tackled using these techniques.

Perhaps the most compelling illustration of this progress can be seen from the role of first-principles ro-vibrational calculations in the development of accurate potential-energy surfaces. A major driving force for the development of these techniques was the progress in electronic structure calculations and hence the availability of good *ab initio* potential-energy surfaces. Ro-vibrational calculations were required to make comparisons between these surfaces and high-resolution spectroscopy. Now it is becoming a standard procedure to use variational ro-vibrational calculations to derive potential-energy surfaces directly from the observed spectra.

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