Spectroscopy and Computational Challenges in Vibrationally Highly Excited Polyatomic Molecules

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Motivation

Solving the Schrödinger equation for the nuclear motions in small polyatomic molecules has been and will remain for this century one of the most challenging computational problems. Accurate solutions for the vibrational states of molecules which play a significant role in combustion and atmospheric chemistry as well as in biology are highly demanded since the recent advances in high resolution spectroscopy [1]. Unequivocally, the progress in experiment and theory of vibrational spectroscopy of the last twenty years is immense.

Grid methods for the solution of the Schrödinger equation are nowadays of the most powerful and exploited tools both for the time independent (here mainly known as Discrete Variable Representation - DVR [2-4]) and time dependent pictures. Concerning the last one, it was the introduction of the Fourier Pseudospectral (PS) method which provided the necessary efficiency to compete with the traditional variational techniques and to make feasible the task [5,6]. Lately, the ideas of the Chebyshev expansion of the time propagator for solving the time dependent Schrödinger equation have been extended to the energy domain, thus, producing the filtering techniques for diagonalizing the Hamiltonian matrix [7,8]. This allowed the extraction of accurate wave functions in triatomic molecules at high energies with large densities of states.

The present computational algorithms and computer technology have made vibrational calculations on triatomic molecules relatively a routine job, even on small size computers [9], and feasible the calculations with the rotational degrees of freedom included [10] and on tetratomic molecules (six degrees of freedom) [11]. However, as the size of molecule increases or the density of vibrational states increases the goal of solving the Schrödinger equation remains unsatisfied. It is interesting that in our effort to surmount the above difficulties old techniques are revisited. For example, local methods such as the Finite Difference (FD) algorithms were the first to apply in problems of Molecular Dynamics [12]. The results obtained that time were rather unsatisfactory and the appearance of global methods such as the PS ones (DVR or Fourier) dominated in solving the vibrational problem in polyatomic molecules.

However, new developments in the theory of Finite Differences [13] have led us to examine their efficiency in solving the Schrödinger equation. Thanks to new computer algorithms for computing the necessary weights in FD schemes, it was shown that the FD method may lead to a considerable saving in computer memory and time because of the local representation of the wave function [14,15].

Old ideas based on the hydrodynamic formulation of quantum mechanics going back to de Broglie and Bohm have been revived in a new scheme known as Quantum Trajectory Method (QTM) [16]. Again, the advances are due to the progress in numerical solutions of computational fluid dynamics [17]. These ideas replace the well known wave equation with trajectory - type (quantum) equations.

The molecular vibrational problem is not only that of solving the Schrödinger equation. Even if that was possible, the huge amount of data would be useless without being able to assign the vibrational states and extract their physical meaning. Assigning the vibrationally highly excited states is also a difficult task because of the non linear mechanical behaviour of the molecule. Progress in this direction has been achieved by developing methods based on effective Hamiltonians, semiclassical theories and periodic orbits [18,19]. *It turns out that up to now there has been no effort to face both problems (computation and assignment of vibrational states) simultaneously within the same theory.*
The workshop on Spectroscopy and Computational Challenges in Vibrationally Highly Excited Polyatomic Molecules aimed:

- to examine techniques for solving the Schrödinger equation in conjunction to the interpretation of vibrational spectra in highly excited polyatomic molecules. It is believed, that instead of computing the whole spectrum in a range of energies the computation of those parts of the spectrum related to experimental or other type of theoretical information will help in circumventing the difficulties in computer memory and time.
- To bring together theorists and experimentalists for better tracing the problems and stimulate new research projects.
- To review the currently used algorithms.
- During the discussion sessions ideas of designing algorithms which take in account previous experimental or theoretical information will be worked out.

Format

There were eight seminars per day of forty minutes each. The last day a round table discussion summarized the results of the meeting and planned future activities.

Program of the Meeting

- Monday, July 10th, 2000

- 9:00 - 9:15 Opening Remarks
  Chairperson : M. Child
- 9:15 - 9:55
- **Direct Fourier methods: How far can you push them?**
  Ronnie Kosloff, Hebrew University, ISRAEL

A faithful representation of a wave function is a necessary step in quantum simulations. Grid based methods have the advantage of a direct local representation in coordinate space. The Fourier method overcomes the difficulty in representing non-local operators by a fast transformation to a grid in momentum space. For a wave packet which is localized in phase space the convergence of the method is exponential. The drawback of the Fourier method is that it requires a rectangular shape in phase space. Using the restriction of an energy shell one finds that in most molecular encounters the energy shell has a convoluted shape. A general coordinate mapping based on a semiclassical idea of local momentum, optimizes the representation. Reduction of the number of grid points by more than an order of magnitude is shown for cold atom collisions where long range interactions dominate. For multi-dimensional problems the enhancement due to coordinate mapping is much larger. For free molecular encounters the elimination of the center of mass leads to the use of curvilinear coordinates. For this reason the Fourier method has been found inferior to either DVR or basis set representations which are optimized to these coordinates. A reformulation of hyperspherical coordinates allows to use a Cartesian representation. Benchmarks using a Fourier representation for NaFH and H3+ in Cartesian/hyperspherical, Jacobi and bond coordinates are shown, maintaining the simple implementation and exponential convergence.

- 9:55 - 10:35

- **A new iterative method for calculating energy levels and wave functions**

  Tucker Carrington Jr., Universite de Montreal, CANADA

  We present an efficient iterative method for calculating energy levels and wave functions. The method requires storing only a small number of vectors but allows one to calculate energy levels and wave functions with fewer matrix-vector products than the filter diagonalizations method of Mandelshtam and Taylor. A zeroth-order Hamiltonian is used to precondition a spectral transform Lanczos method.

- 10:35 - 11:05 Coffee Break

- 11:05 - 11:45

- **The Jacobi-Wilson method : A new approach to the calculation of excited rovibrational bound states of semi-rigid molecules**

  Claude Leforestier, LSDSMS - Montpellier, FRANCE

  We present a new method adapted to the calculation of excited rovibrational states of semi-rigid molecules. It first relies on a description of the molecule in terms of polyspherical coordinates, in order to obtain a compact expression for the kinetic energy operator. This general description is then adapted to the molecule considered by defining curvilinear normal modes from a zero order harmonic Hamiltonian H0, the solutions of which being used as the working basis set. As a result, only the difference H-H0 has to be worked out numerically, H0 being handled fully analytically. An application to the excited rovibrational states of the HFCO molecule is presented.

- 11:45 - 12:25

- **Quantum fluid dynamics (QFD) in the Lagrangian and Eulerian representation**

  Attila Askar, Koc University, TURKEY

  The quantum fluid dynamics (QFD) formalism, the associated numerical formulation and the application of the formulation to multidimensional wave packet dynamics are presented. The applications include wave packets in four dimensional quadratic potentials and two coordinate photo-dissociation problems for NOCl and NO2. The QFD formulation is based on the separation of the amplitude and phase of the complex wave function in Schrödingers equation. The approach leads to two conservation laws, one for mass and one for momentum, similar to those in hydrodynamics. In the QFD analogy, the solution of the time dependent equation is transformed to observing the dynamics of an equivalent gas continuum. The classical fluid dynamics equations are treated numerically in two equivalent but conceptually different formats called as the Lagrangian [1]and Eulerian [2] approaches. These correspond respectively to following the particles of the fluid continuum and observing the dynamics at the points of a fixed coordinate frame. The numerical implementation of the QFD equations leads to a dramatically short times as compared with other integration methods of the time dependent Schrödinger equation. This special computational efficiency comes from the combination of QFD representation in dealing with the near monotonic amplitude and phase of the complex wave function and the use of an explicit time integrator where the computational effort grows only linearly with the number of discrete points. Moreover, the Lagrangian description concentrates the computation effort to regions of highest probability as an optimal adaptive grid and the Eulerian scheme allows the formulation of multidimensional problems as a set of one-dimensional problems within an alternating direction methodology.

1. Quantum fluid dynamics (QFD) in the Lagrangian representation with applications to photo-dissociation problems, F. Sales, A. Askar and H. A. Rabitz, J. Chem Phys. 110, 2423 (1999)

2. Multidimensional wave packet dynamics within the fluid dynamical formulation of the Schrödinger equation, B. Dey, A. Askar and H. A. Rabitz, J. Chem. Phys. 109, 8770 (1998)

- 12:25 - 14:15 Lunch Break
- Chairperson : R. Schinke
- 14:15 - 14:55
- **Recent developments in spectral analysis of time correlation functions**

  Vladimir Mandelshtam, University of California at Irvine, USA

  The Fourier Transform (FT) is commonly accepted as the central (and often the only) method of spectral analysis. It is also a common belief that the "uncertainty principle", which is only a property of the Fourier Transform, is the very general one that defines the spectral resolution in terms of the length of the time signal. Under certain assumptions about the time signal which are often justified in quantum dynamics problems the spectral information can be extracted much more efficiently using the Filter Diagonalization Method (FDM), which is a linear algebraic technique using local spectral analysis. I will present several recent developments of FDM, in particular, the multi-scale FDM based on using a non-uniform Fourier basis that can perform a local spectral analysis in high resolution while describing the rest of the spectrum in low resolution. The problem of high resolution (non-linear) spectral analysis is often very ill-defined in that the result is highly sensitive to the input data, usually making the application of the corresponding technique (e.g., the FDM) a state-of-the-art. This instability problem will be addressed. In particular, I will discuss the noise averaging idea to stabilize FDM. Another way to circumvent the said instability problem corresponds to the recently proposed Regularized Resolvent Transform (RRT) which is a direct linear algebraic transformation of the signal from the time to frequency domain, that has the high resolution property, is stable, fast, robust, etc., and can be used to replace FT. I will discuss some applications of these general techniques to several diverse problems, such as calculating the quantum bound and resonance spectra of small molecules, spectral analysis of semiclassically obtained time correlation functions, extracting the spectral information from experimentally measured signals, etc.
- 14:55 - 15:35
- **Six-dimensional quantum treatment of the vibrations of diatomic adsorbates on solid surfaces with application to CO on Cu(100)**

Zlatko Bacic,New York University, USA

We will present our computational methodology for exact quantum 6D diatomic molecule adsorbed on a rigid corrugated surface. It is aimed at adsorbates executing coupled, strongly anharmonic large-amplitude vibrations. Surface nonrigidity is introduced in an approximate way, by means of a simplified surface-mass model. With this methodology, we have calculated excited vibrational levels of CO molecule adsorbed on Cu(100) surface, for all four isotopomers of CO, using the empirical potential by Tully and co-workers. Our calculated fundamental frequencies of CO/Cu(100) vibrations are in good overall agreement with the experimental frequencies and isotope frequency shifts; an important exception is the CO stretch fundamental. Comparison between the 6D results and those of 5D (rigid CO) and 4D (fixed-site) quantum calculations provide quantitative information about the couplings among the vibrational modes of CO on Cu(100). Excited states of the lowest-frequency (doubly degenerate) frustrated translation mode are analyzed and assigned. Extension of this methodology to nonlinear polyatomic molecules will be discussed.

- 15:35 - 16:00 Coffee Break
- 16:00 - 16:40
- **Variable order finite difference algorithms for quantum molecular dynamics**

  Stavros C. Farantos, IESL, FORTH, GREECE

  The problem of interpreting vibrational spectra of polyatomic molecules is twofold; first, we must find the solutions of the Schrödinger equation, and second, we must assign the energy levels with quantum numbers. In spite of the impressive advances in solving the Schrödinger equation for triatomic and tetratomic molecules limitations remain especially for excited molecules. Significant is also the progress in the physical interpretation of vibrational spectra thanks to the links with non-linear mechanics and semiclassical theories [1]. Recently we have addressed the problem of solving the time dependent and time independent Schrödinger equation via Finite Differences (FD). The view of considering global Pseudospectral methods (Sinc and Fourier) as the infinite order limit of local Finite Difference methods [2], and vice versa, Finite Difference as a certain sum acceleration of the Pseudospectral methods has been exploited to investigate high order Finite Difference algorithms for solving the Schrödinger equation in Molecular Dynamics. Radial and angular variables are treated on the same ground with centered equi-spaced grids as well as non uniform Legendre and Chebyshev grids [3-5]. Results from 1D to 5D systems will be presented which demonstrate the stability and accuracy of High Order Finite Difference approximations of wave functions compared to global Pseudospectral techniques.

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3. R. Guantes and S. C. Farantos, J. Chem. Phys. 111, 10827 (1999).
4. R. Guantes, A. Nezis and S. C. Farantos, J. Chem. Phys. 111, 10836 (1999).
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- 16:40 - 17:20
- **Vector parametrization of a N-atom problem: Application to vibrational calculations**

Christophe Iung, LSDSMS - Montpellier II, FRANCE

This communication aims to present a general method that enables one to build kinetic energy operators in getting rid of the heaviness of differential calculus. In the present formulation [1,2], the system is described by any set of n vectors (Jacobi, Valence, Radau,... vectors). We will show how the kinetic energy can be written in terms of the (n-1) angular momenta associated to the (n-1) vectors and the total angular momentum J [3]. Application of such an approach [4] has been done for studying the ammonia spectroscopy [5]. We will show also show how this formalism can be adapted in order to study semi-rigid molecules. In this latter case, our formalism provides a very compact, simple expression of the kinetic energy in terms of the BF projection of vector J and the conjugate momenta associated to the spherical coordinates of the vectors chosen in order to parametrize the molecule.

1. "Vector Parametrization of the N-atom problem in quantum mechanics : I - Jacobi coordinates", F. Gatti, C. Iung, M. Menou, Y. Justum, A. Nauts et X. Chapuisat, J. Chem. Phys., 108, 8804 (1998).
2. "Vector Parametrization of the N-atom problem in quantum mechanics : II - Coupled-angular-momentum spectral representation four four-atom systems" F. Gatti, C. Iung, M. Menou, et X. Chapuisat, J. Chem. Phys. 108, 8821 (1998).
3. "Vector Parametrization of the N-atom problem in quantum mechanics with non orthogonal Coordinates" C. Iung, F. Gatti, A. Viel et X. Chapuisat, Phys. Chem. Chem. Phys., 1, 3377 (1999).

4. "Vector Parametrization of the N-atom problem in quantum mechanics : III- Separation into two subsystem : Application to NH3", F. Gatti, J. Chem. Phys,111, 7225 (1999).

5. "Fully Coupled 6D Calculations of the Ammonia Vibration-Inversion-Tunneling State with a Split Hamiltonian Pseudo-Spectral Approach" F. Gatti, C. Iung, C. Leforestier et X. Chapuisat.

- Tuesday, July 11th, 2000, Chairperson : C. Leforestier

- 9:00 - 9:40

- **Bifurcations and level structures in the spectra of simple molecules**

  Mark Child, Oxford University, UK

  1. A variety of cases of Fermi resonance will be used to demonstrate how the energies of quantized periodic orbits of the system provide natural divisions between different regions of the quantum mechanical spectrum. The discussion will be set in the context of Kellman's catastrophe map, which will be extended to include physically important situations that have not hitherto been considered notably by including higher terms in the coupling function and considering non-zero angular momentum. 2. The concept of quantum monodromy will be used to demonstrate certain generic vibrational-rotational energy level patterns around the energy thresholds at which a bent molecule becomes linear, or parts of a linear molecule begin to rotate around each other. 3. Applications to possible observables in the spectrum of HCP will be discussed.

- 9:40 - 10:20

- **From complex molecular vibrational spectra to detailed molecular motions without a PES: C_2H_2 (bending) and Bromochlorofluoromethan**

  Howard Taylor, University of Southern California, USA

  The complex FTIR spectra involving the excitation of the CH bond in CHBrClF is analyzed to yield the detailed motions of the hydrogen atom that when quantized yield the observed energy levels. The starting point for the analysis is the encoding by the Quack group of their spectra into an effective spectroscopic, four resonance, algebraic Hamiltonian. This is followed by a classical nonlinear dynamic analysis in the reduced phase space of the system. For polyad 5, the highest for which the parametrization of the Hamiltonian has been shown to hold, five different types of motion are shown to underlay the dynamics. The relation between the classical phase space structures found in the analyses and the observed and fitted quantum levels is established most often by the use of semiclassical KAM quantization to obtain agreement with the quantum spectra. The molecular motions associated with an eigenstate are then obtained by transforming the corresponding reduced phase space structure back to displacement coordinates. Besides the expected Fermi resonances, a secondary resonance zone associated with a resonance between the two bend normal modes is found. The motions associated with the quantum states in this zone are shown to cause such states to appear to have symmetries as Cs and C3v; as such this chiral molecule, excited properly will not act in a manner typical of a chiral molecules. It will also be shown how the use of the polyad constant of the motion greatly simplifies the dynamic analysis by causing the reduced phase space of each high polyad to be reduced to a point at its maximum and minimum energy. This intern causes a great simplicity in the search for and the bifurcation structure of the periodic orbits relative to an analysis using a potential surface. The phase space of the latter is unbounded from above and leads to an evermore complicated and uninterpretable periodic orbit pattern as energy increases.

- 10:20 - 10:50 Coffee Break
- 10:50 - 11:30
- **Bifurcations, spectral patterns, and ultrafast dynamics in highly excited molecules**

  Mike Kellman, University of Oregon, USA

  Spectral patterns associated with bifurcations in the vibrational dynamics of highly excited molecules will be considered in a series of cases of increasing complexity. Early work on a spectroscopic Hamiltonian with a single resonance will be briefly reviewed, with an emphasis on spectral patterns associated with a separatrix. Multiresonance systems will then be considered. It will be shown how the bifurcation analysis can be performed for systems with a conserved polyad number. Specific cases include water, acetylene bends, and a planar model of acetylene bends and stretches. A spectral assignment technique based on correlation diagrams, effective quantum numbers, and a "dressed basis" technique will be presented. Spectral patterns associated with these assignments, even in the presence of chaos, will be presented and evaluated for their dynamical information.
- 11:30 - 12:10
- **Quantum vibrational chaos: how subtle a concept is it ?**

  Marc Joyeux, Universtie Joseph Fourier-Grenoble I, FRANCE

  Recent global surfaces fitted against ab initio points (and eventually slightly adjusted against experimental data) are able of describing the highly excited vibrational dynamics of small (triatomic) molecules up to the dissociation threshold or the isomerization barrier with reasonable accuracy. Classical studies at these high energies generally indicate wide spread chaos.The goal of this presentation is to lay emphasis on the fact that the quantum dynamics might be much more regular than the classical one. Two examples will be discussed.

The first example is 2-dimensional HOCl. The quantum spectrum will be shown to be governed by the classical stable POs up to the dissociation threshold. The connection between Husimi distributions, Poincare surfaces of section and Intramolecular Vibrational energy Redistribution (IVR) will also be discussed in some detail. The second example is HCN/CNH. We have recently derived a modified version of canonical perturbation theory, which applies to floppy systems. Upon application of this procedure to two well-known ab initio surfaces for the HCN/CNH isomers, it will be shown that the three degrees of freedom can be considered to remain totally decoupled up to and above the isomerization barrier.

- 12:10 - 14:15 Lunch Break
- Chairpeson : J. Tennyson
- 14:15 - 14:55
- **Nonlinear dynamics effects in vibrational spectra: HCP, DCP, and HOCl**

  Reinhard Schinke, Max-Planck-Institut fur Stroemungsforschung, Goettingen, GERMANY

  The vibrational spectra of triatomic molecules will be discussed from the perspective of exact quantum mechanical calculations using accurate and global potential energy surfaces. The examples include HCP, DCP, and HOCl. In all these examples anharmonic resonances between two modes play an essential role. At high energies these resonances lead to bifurcations in the classical phase space, which leave profound hallmarks in the quantum mechanical spectra. For HCP, the theoretical predictions can be directly compared with detailed experimental results and very good overall agreement is obtained.
- 14:55 - 15:35
- **Spectroscopic investigation of the isomerization of HCP: Recent developments of experimental observation of highly excited vibrational levels**

  Haruki Ishikawa, Tohoku University Aoba-ku, JAPAN

Our observation of highly excited vibrational levels of HCP has attracted many theoretical interests. In the case of HCP, it was revealed that an anharmonic resonance between the bend and the CP stretch modes plays an important role in the vibrational dynamics from both the experimental and theoretical studies. The agreement between experimental and theoretical analyses of the highly excited vibrational levels was excellent. In our previous experimental observation and analysis, vibrational levels in rather low energy region are treated. In much higher energy region, the interaction between the bend and the CH stretch modes becomes strong. To extend our experimental study on the highly excited levels of HCP, it is necessary to get the information about levels which involves the excitation of CH stretch. Thus, we have developed an IR-UV-DF and IR-UV-SEP spectroscopies. In both techniques, we use the IR-UV double resonance excitation as a pump scheme of the DF and/or SEP spectroscopies. As a result, highly excited vibrational levels involving the CH stretch excitation could be observed for the first time.

- 15:35 - 16:00 Coffee Break
- 16:00 - 16:40
- **Bond-breaking internal rotation: Experimental and theoretical challenges**

  Matthew Jacobson, Oxford University, UK

  The acetylene-vinylidene isomerization is a prototypical example of a 1,2-hydrogen shift. Over the past several years, I have carried out experimental and theoretical studies of acetylene when it has *nearly* enough vibrational excitation for it to be capable of isomerizing to the quasi-stable vinylidene species. These studies have uncovered indirect but unambiguous evidence for a class of vibrational states, the "local benders", that sample the isomerization pathway and, in a classical sense, spend much more time near the transition state than they do near the linear equilibrium configuration. However, this talk will primarily look forward rather than backward, and examine the experimental and theoretical challenges that face the study of isomerization in acetylene (and similar systems) when the vibrational energy exceeds the transition state energy, and the hydrogen(s) can undergo bond-breaking internal rotation (i.e., the hydrogens can rotate around the CC core). Recent experimental data will be presented which show tantalizing signs of probing the nascent "isomerization states" in acetylene. In addition, possible spectroscopic signatures of bond-breaking internal rotation in acetylene and other molecules will be discussed, including changes in rotational fine structure constants and the breakdown of the polyad approximation.

- 16:40 - 17:20

- **Experimental studies of vibrationally highly excited molecules: Comparison with effective polyad model Hamiltonian calculations for the reaction DCO (X 2A') → D + CO**

  Friedrich Temps, Christian-Albrechts-Universitaet zu Kiel, GERMANY

  Stimulated Emission Pumping (SEP) spectra have provided detailed information on the vibrational structure and the state-specific unimolecular decay constants of DCO (X) up to energies of Ev = 18200 cm-1, far above the asymptotic D-CO dissociation limit at 5400 cm-1 [1]. The available experimental data were used to develop a simple effective polyad model Hamiltonian for the system which was applied to rationalize the observed unimolecular dynamics. The parameters occurring in the model were determined by fitting to the measured vibrational bound and resonance state energies up to Ev = 15000 cm-1. The vibrational states predicted by the model were found to be in excellent agreement with the experimental data and with data from published quantum dynamics work [2]. Based on the fitting results, the rates and pathways were investigated for intramolecular vibrational energy redistribution (IVR) in the highly excited DCO (X). Decay constants could be predicted for the progressions of excited local mode CO stretching overtone states and excited DCO bending overtone states. The results of these calculations show a mode specificity which reflects the different strengths of the couplings between the internal coordinates and explains the observed large discrepancies between the decay constants from the SEP measurements and the statistical rate theory calculations. Using a complex version of the model Hamiltonian, state specific decay constants could be calculated for the individual eigenstates near the threshold of the reaction which reflect the coarse experimental trends.

  1. Stoeck et al., J. Chem. Phys.106, 5333 (1997).
  2. Stoeck et al., J. Chem. Phys.106, 5359 (1997).

- Wednesday, July 12th, 2000, Chairperson : M. Joyeux

- 9:00 - 9:40

- **Techniques for the calculation of highly excited rovibrational bound, quasibound, and reactive L2 eigenstates**

  Joel Bowman, Emory University, USA

  I will review calculations we have performed on rovibrational states of HOCl using exact and adiabatic rotation methods, and using a highly accurate ab initio potential energy surface due to Kirk Peterson. The striking dependence of experimentally observed resonances on the angular momentum will be also be rationalized, based on calculations of the resonances using the adiabatic rotation approximation. Finally, reactive scattering using real L2 eigenfunctions, with damping, will also be reviewed for 3D D+H2 and other reactive systems.

- 9:40 - 10:20

- **Calculating Quantum States of Molecules at Dissociation**

  Jonathan Tennyson, University College London, UK

  A typical chemically bound triatomic molecule may have up to million bound states. Although the majority of these state are not accessible in current spectroscopy experiments, characterizing them is important for modeling radiative properties of hot molecules, in cool stellar atmospheres or rocket exhausts for example, and for predicting thermodynamic properties such as specific heats at high temperature. We have adapted discrete variable representation (DVR) based codes used for spectroscopic studies to run on a variety of MPP machines. Using these codes we have obtained all the bound levels of rotationally excited water up to dissociation [1]. A particular challenge is to represent quasibound states of these molecules which lie just above the dissociation limit. This region forms a bridge between high resolution spectroscopy and reaction dynamics. In particular there is spectroscopic data available on the H3+ molecule here which has defied interpretation for nearly two decades [2]. Recently we have extended our codes to address this problem [3], latest results will be reported at the meeting.

  1. H. Y. Mussa and J. Tennyson, J Chem Phys, 109, 10885 (1999).
  2. A. Carrington, J. Buttenshaw and R.A. Kennedy, Mol. Phys, 45, 753 (1982).
  3. H. Y. Mussa and J. Tennyson, Computer Phys Comms (Special issue on Parallel Computing), in press

- 10:20 - 10:50 Coffee Break

- 10:50 - 11:30

- **Spectroscopy and quantum dynamics of highly excited chiral molecules: Experiment and theory including parity violation**

  Martin Quack, ETH Zurich (Zentrum), SWITZERLAND

  In the early 80ies my research group embarked on a project to derive the primary processes of intramolecular kinetics in highly excited polyatomic molecules from their high resolution rovibrational spectra. The key steps in the new methods developed in this context by us are : 1.

Development of the new experimental techniques allowing for obtaining complete analysis and assignments of complex spectra. 2. Description of the spectra in terms of adequate effective Hamiltonians containing a limited number of parameters. 3. Deriving new descriptions of the full molecular Hamiltonian including also new developments for accurate analytical representations of multidimensional potential hypersurfaces as well as new, often very small terms in the Hamiltonian. 4. Solving multidimensional rovibrational Schrödinger equations with finite basis or discrete variable representations as well as Quantum Monte Carlo methods. 5. Deriving the time dependent quantum wave packet motion for highly excited states for individual molecules in isolation as well as under intense coherent infrared radiation. 6. Obtaining quantum statistical approximations. The combination of experimental and theoretical methods is essential in this project. As is well but perhaps not widely known, this approach has led to the first multidimensional femtosecond wave packets from experiments on polyatomic molecules and has also been the basis for a proposal of the most sensitive experimental test of CPT symmetry. The earlier work has been reviewed [1-6]. In the lecture, we will briefly discuss our current experimental and theoretical methods and then present our most recent results on the spectroscopy and quantum dynamics of chiral molecules [7] in the low and the high barrier limit [8,9,10], including the new theory of parity violation in polyatomic molecules [7-13]. Depending on the time available, we will discuss also the symmetry and rovibrational quantum dynamics of the absolute molecular clock [14].

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2. M. Quack, Annual Rev. Phys. Chem. 41, 839-874 (1990).
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4. M. Quack, chapter 27 in : 'Femtosecond Chemistry', J. Manz and L. Woeste eds., Proc. Berlin Conf. Femtosecond Chemistry, Berlin (March 1993), Verlag Chemie, Weinheim (1994), p. 781-818.
5. M. Quack and M.A. Suhm, in 'Advances in Molecular Vibrations and Collision Dynamics, Vol. III, Molecular Clusters', p. 205-248, Z. Bacic and J. Bowman eds., JAI Press, Stamford, Conn. (1998).
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13. M. Quack and J. Stohner, Phys. Rev. Lett. 84, 3807-3810 (2000); M. Quack and J. Stohner, Z. Phys. Chem. 214, 5, 675-703 (2000).
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- 11:30 - 12:10

- **New experimental and theoretical aspects of overtone spectroscopy**

Lauri Halonen, University of Helsinki, FINLAND

The laser-induced dispersed fluorescence method has been developed to investigate vibration-rotation states of gaseous polyatomic molecules in the ground electronic state [1 - 3]. A specific molecular rovibrational state in the wave number region 10 500 - 14 000 cm-1 is pumped by a high-resolution Titanium:Sapphire ring laser. The sample cell with a parabolic mirror is placed inside the ring-laser cavity. The resulting fluorescence from the sample is collected and then dispersed by an interferometer. We have applied this technique to acetylene and water, in which collision-induced spectra are observed. The strongest fluorescence transitions correspond to the Delta(v) = 1 change in the hydrogen stretching vibrational quantum number. In C2H2, we have observed a number of symmetrical states ([40+]0, [30+]0, and [20+]1, where the first two numbers refer to the CH oscillators and the last one refers to the CC oscillator). These would not be accessible by one-photon transitions from the ground vibrational state. Neither in acetylene nor in water changes in nuclear spin states due to molecular collisions have been detected. In water, we have verified the experimental fluorescence intensity patterns using the discrete variable method with an exact kinetic energy operator and an Eckart frame dipole surface.

Overtone Hamiltonians have been developed and applied to molecular systems involving large amplitude motions [4 - 6]. Our general strategy is to assume that both the kinetic and potential energy parameters are functions of the large amplitude coordinates. In practice, these functional dependencies can be determined by electronic structure calculations. We have applied our methods particularly to methanol and ammonia, which include a large amplitude torsional and inversion mode, respectively.

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- 12:10 - 14:15 Lunch
- Chairpeson : S. C. Farantos
- 14:15 - 14:55
- **Highly excited vibrational states in the methyl halides**

  Mark Law, University of Aberdeen Meston Walk, UK

  The methyl halide molecules and their isotopomers have been the subjects of extensive spectroscopic investigations over many years. Here we review the most recent experimental and theoretical work and discuss the major challenges for future development of our understanding of the vibrational quantum states in these prototype systems. The mid- and near-infrared overtone absorption spectra of the methyl halides are dominated by features arising from C-H stretching excitation. However in all cases (including the deuterated derivatives) the C-H(D) stretching manifolds are strongly perturbed by Fermi resonances involving some or all of the CH3 bending overtones and combinations. These and other important resonances ensure that nearly all vibrational degrees of freedom are strongly coupled. Comparisons between the methyl halides are particularly interesting in view of the changes, with substitution of successively heavier halide atoms, in the densities of states and the patterns of vibrational couplings. Approximate computations of highly excited vibrational states in these molecules have included studies using the perturbation-resonance approach in which most terms in the complete Hamiltonian are treated by low order perturbation theory whilst resonant terms are taken into account exactly but using a substantially reduced basis. More accurate variational calculations have been attempted on the methyl halides for low internal energies. The prospects for extending such methods to high excitations are discussed.

- 14:55 - 16:00 Concluding Remarks
- POSTERS
- **Variational calculation on methane: a progress report**

  Junkai Xie and Jonathan Tennyson, University College London, UK

  Methane is the third most important greenhouse gas and is present in many planetary atmospheres. The way methane absorbs and emits light remains poorly understood, particularly when it is hot. A better theoretical understanding of the methane rovibrational spectrum would undoubtedly lead not only to more information being obtained from the astronomical spectra, but also to better modeling of methane in many other situations. Some variational vibration-rotation calculation have already been performed for methane. However these studies are tractable because they make approximations based on the molecule being semi-rigid. It is unlikely that these approaches will be reliable for the highly excited states necessary to treat the hot methane problem. Here we report on progress in developing a full variational treatment of the methane rotation-vibration problem. The procedure we have adopted is general to AX4 type molecule and makes no assumption about any decoupling in their potential energy surface. This lack of decoupling leads to perform full nine-dimensional quadrature over the potential. However this cost is moderated by taking advantage of the symmetry inherent in these AX4 systems, itself a subject of considerable study. So far we have developed a procedure for treating the stretching and bending motion of methane. For the non-rotating methane, the vibrational motions can be divided into stretches (four coordinates) and bends (five independent coordinates). Here, our strategy is to solve separate, reduced Hamiltonian for the stretches and the bends, and to use the results of these to solve the full coupled problem. For the stretch problem, we evaluate the kinetic energy matrix elements for each of five possible total symmetry types and eight different basis types. A similar approach is used to deal with the bending methane vibration (five dimensional problem) in symmetry coordinate variables. These coordinates lead a very complicated symmetrized wave functions. To overcome this problem, we transform the coordinates. In the new coordinate system, we use Jacobi polynomial for the four degrees of the angular motion, and the sine and cosine function for the other angle. For the bends, we also evaluate the bends kinetic energy matrix each of five possible total symmetry types and 12 different basis types. Results of the separate stretching and bending calculation will form a basis of the fully coupling nine dimensional methane vibration problems.

- **Dynamical chirality and the quantum dynamics of bending vibrations of the CH chromophore in methane isotopomers**

Roberto Marquardt, Universite de Marne-la-Vallee, FRANCE, and Martin Quack and Ioannis Thanopulos, ETH-Zurich (Zentrum), SWITZERLAND

We investigate the time dependent quantum dynamics of the CH chromophore by calculation of the wave packet evolution during and after coherent excitation of the bending modes of the methane isotopomers CHD3, CHD2T and CHDT2 [1]. For this purpose realistic potential energy surface [2] and electric dipole moment functions [3] are used, which have been derived previously from ab initio calculations and high resolution spectroscopic information. The results are obtained in two steps: firstly, the vibrational spectrum and eigenfunctions for the field-free molecular Hamiltonian are calculated with a discrete variable representation (DVR) technique; then the time dependent Schroedinger equation for the molecule in interaction with the external electromagnetic field is solved in the basis of the molecular eigenstates within the quasiresonant approximation (QRA) [4]. Different excitation pathways depending on the bending direction in an internal coordinate frame, the role of semiclassical and delocalized intramolecular vibrational redistribution [5] on these processes and the possibility of controlling the dynamics by localization of the wave packet motion in subspaces of the relevant configuration space are discussed. The excitation of a bending mode is further used to generate dynamical chirality [6], which can be quantified by the enantiomeric excess. The free evolution of the wave packet after generation of a chiral molecular structure corresponds to a stereomutation reaction on the femtosecond time scale superimposed by a racemization reaction, which is understood to arise from quantum delocalization effects due to intramolecular vibrational redistribution.

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6. M. Quack, Angew. Chem. Int. Ed. Engl., 28, 571-586 (1989).

- Chris Cooper, Oxford University, ENGLAND
- Raul Guantes, Instituto de Matematicas y Fisica Fundamental, Consejo Superior de Investigaciones Cientificas, SPAIN
- **The Vague Torus Revisited: Semiclassical Quantization of Chaotic Vibrations Using Fourier Transforms of Intermediate Length Classical Trajectories**

  Randall B. Shirts, Brigham Young University Provo, USA

  We are interested in the spectra of molecules which are vibrationally excited to high levels. Because of the enormous number of states, the quantum mechanics of such systems is intractable, so we have been applying semiclassical methods. However, most coupled oscillator systems exhibit classically chaotic motion at high energies, and standard Einstein-Brillouin-Keller quantization is formally inapplicable. In 1982 however, W. P. Reinhardt and I [1] noted a surprising degree of intermediate-term order in classically chaotic coupled oscillator motion and dubbed the resulting phase space structure the "vague torus." At that time, we justified the success of several methods of semiclassical quantization on the existence of vague tori. In this poster, I will exhibit the explicit construction of vague tori and their use for semiclassical quantization [2]. In addition, I will demonstrate how the same Fourier transform formalism can be used to get approximate transition dipole matrix elements using the Heisenberg correspondence principle. The combination of semiclassical eigenvalues and matrix elements thus allow construction of approximate spectra using only Fourier transforms of classical trajectory data.

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Conclusions and perspectives

The current numerical algorithms and techniques to solve the time independent and time dependent Schrödinger equation for small polyatomic molecules were examined in association to high resolution vibrational-rotational spectroscopy of excited states. The dynamical interpretation of the theoretical and experimental spectra via semiclassical theories, bifurcation diagrams and generally non-linear mechanics were the focus of extensive discussions in this three days CECAM meeting.

It was concluded that the discrete variable representation (DVR) pseudospectral methods remain the most accurate and efficient in calculating the quantum

vibrational levels in molecules. Old methods such as the Finite Differences and Quantum Trajectory Method revisited and discussed in the light of more recent developments.
Accurate calculations for highly vibrational excited states at present are feasible for four atom molecules (six degrees of freedom). However, the need for introducing schemes which couple these methods with approximate ones was underlined in order to treat large molecules where quantum effects such as tunneling in isomerization processes are important.

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