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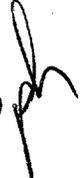
CONTINUATION PROGRESS REPORT

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***A SCALING THEORY FOR THE ASSIGNMENT
OF SPECTRA IN THE IRREGULAR REGION***

Principal Investigator: Howard S. Taylor
Department of Chemistry
University of Southern California
Los Angeles, CA 90089-0482
e-mail: taylor@chem1.usc.edu

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The ultimate object of our program is to learn how to extract information about molecular rovibrational motions from experimental spectra or calculated energy levels. This goal of spectroscopy and theoretical chemistry has historically only been possible in the regular spectral region. Our project is one of several which are aimed at spectral interpretation in the chaotic or mixed chaotic plus regular regions.^{1,2} Our particular tools involve a scaling theory developed under our previous DOE support period.³ This theory uses experimentally fitted spectral Hamiltonians or Hamiltonian's whose potentials are calculated using quantum chemistry, to obtain energy levels as a function of \hbar^{-1} . The scaling theory then uses this input to highlight the actions of the subset of all periodic orbits which control (or guide) the dynamics at any given energy up to dissociation. The periodic orbits themselves, are the skeleton of classical phase space for the molecular motions and are found by classical non-linear dynamic techniques. The finding and following of these periodic orbits by constructing a bifurcation diagram, and in 2D, Poincare surfaces of section, is labor intensive and takes much of our available man hours. We have two projects, "acetylene" and "NO₂." Below we first briefly sketch the results of the classical phase space study using the fitted spectral Hamiltonian that describes pure bending dynamics of in the acetylene $\tilde{X}^1\Sigma_g^+$ state to 15,000 cm⁻¹ of internal energy.^{4,5} The work on NO₂ will follow.

The specific purpose of this part of our work is to establish relations between experimental data and quantum mechanical results on one side and the behaviour of the dynamics given by the corresponding classical Hamiltonian function on the other side for the bend vibrations of the C₂H₂ molecule. A spectroscopic Hamiltonian is provided by the MIT group.⁵ We transform it into a classical Hamiltonian function given in action and angle variables. It describes four degrees of freedom: a two dimensional oscillator representing the cis vibrations and a two dimensional oscillator describing the trans vibrations. The Hamiltonian has two further conserved quantities beside the energy: the sum N of the actions of all four degrees of freedom, and the total angular momentum L (at the moment we are only interested in the case of L=0). Thereby the problem reduces to one with two degrees of freedom but with two parameters N and L. Therefore the number of independent conserved quantities is less by one than the number of degrees of freedom. The reduced system with two degrees of freedom is nonintegrable and shows large size chaos over wide ranges of E and N, if E is not too small. For a given value of N only a finite interval of values of E corresponds to a non empty phase space. Fixing a particular value of N corresponds to the selection of a particular polyad number in experiment. Here classically any value of N is possible, whereas after quantization N can only be an integer multiple of \hbar .

As it is usual for a system with two degrees of freedom, the best way to get information about the classical phase space is to construct Poincare sections. This shows immediately, where the most important periodic orbits are; have large KAM tori around themselves; which are sufficiently large to have influence on the corresponding quantum behaviour. Only three different periodic orbits (and

sometimes also their period doubled descendents) ever produce large size KAM islands for appropriate combinations of values of E and N . These few periodic orbits seem also to be the organizing centers of the chaotic regions in phase space for such parameter values, where large size chaos appears. Thereby we can be confident, that the behaviour of the whole systems can be understood from the properties of only a few important orbits which act as the skeleton of the whole dynamics.

This analysis indicates that in the low polyad number region the classical analysis for each polyad shows trans, beating motion and cis motions at the bottom, middle and top of the polyad respectively. Above polyad 8, due to anharmonicity, the frequencies of the cis and the trans modes each move toward an intermediate frequency. At this point the Dennison-Darling and l -doubling resonance interaction become important and cis and trans motions disappear. New modes emerge. The higher polyads generally each have local mode motion at the bottom and counter rotating modes at the top. In the middle is chaos mixed with some extraordinary regular motions that space does not allow us to here describe. In general the chaos is biggest about polyad 16 and smaller above and below. Polyad 22 is half regular while polyad 16 is only about a third regular. The classical motions and their frequencies can be correlated with the experimentally observed level spacings giving us confidence in the results. The observed experimental level patterns also correlated with our classical results.

We are continuing to push the quantum-classical correspondence and will soon assign the spectra with periodic orbit based quantum numbers. We are very proud of our achievement as for the first time high vibration state molecular motions have been extracted directly from experiment.

The NO_2 project aims at producing a scaling diagram for this system. This will highlight the important periodic orbits which (non-trivially) must be found as a function of energy. Experiments up to dissociation have been done on this system but no spectral Hamiltonian has been developed that is valid over a large energy range. Hence our first job, which has been completed, has been to develop good potential surfaces for the ground and the intersecting first excited states.

Though there has been some great improvement in constructing semiempirical effective surfaces for the \tilde{X}^2A_1 ground state of NO_2 ,¹⁰ it was decided to use the ab initio potential energy surface by Leonardi, Petrongolo, Hirsch and Buenker.⁸ Although this surface gives less accurate results an rms deviation of 17.13 cm^{-1} for the states below $10,000 \text{ cm}^{-1}$ compared to the deviation of about 3 cm^{-1} in the above mentioned surface, it is the only surface for NO_2 which provides the user with both the ground and the first excited \tilde{A}^2B_2 state in the diabatic representation. Additionally it also gives the coupling potential between both surfaces. Only the existence of these three surfaces makes it possible to compute the nonadiabatic bound states of the molecule. Any adiabatic computation of only the ground state will not give the experimentally measured states above $11,000 \text{ cm}^{-1}$ since here the breakdown of the Born-Oppenheimer approximation will occur. The

chosen surface had two major drawbacks. One was unphysical kinks, which we smoothed out, and the other was a too high density of states. We chose a smoothing of the kinks such that phase space was reduced yielding a lower density of states than observed, but with only half the deviation than obtained prior to our modifications.

Now, according to Delon, measurements show that the NO_2 molecule possesses more than 3,000 eigenstates in the 3.226 eV deep well.⁷ This gives rise to a measured density of states no larger than 5 per cm^{-1} . Such densities are a formidable challenge for theory. The only method, available today, which is capable of handling that many dense eigenstates, is the filter diagonalization method in combination with signal processing, both of which were products of prior DOE support.¹¹ For example, a direct matrix diagonalization in a adapted basis by Leonardi et al., gives only half of the states up to about 2 eV. To realize, why signal processing made the calculation of ALL states possible, one has to understand, that filter diagonalization alone, is only able to compute the states in a narrow energy window. This is done by generating an effective basis for this energy range. To ensure that one gets all states lying in this range, one has to generate more basis functions than there are eigenstates in this range, i.e., so that the density of the basis functions matches the real ones. Since the real density is a function with fluctuations of about one order of magnitude and more, it is practically not possible to do the trial and error calculations needed to find a sufficiently dense number of basis functions for each energy window. This is so as every test for each trial window size and bases would require a separate Chebyshev iteration (the time consuming step). Since signal processing is basically the extraction of states out of a huge time signal (generated by only one iteration procedure), the convergence of the energy window parameters is easy, because the signal processing is a fast running code. Actually we needed on average ten tries with different grid adjustments until we converged a window to extract the states with six figures accuracy (finally we had about fifty windows per symmetry).

For a system as large as NO_2 , one has to setup an efficient strategy which minimizes the computational effort. We have done this by using Radau coordinates which makes it easy to account for the symmetry of the system and which gives a simple expression for the kinetic energy. To get only the states of one symmetry species at a time, we applied a symmetry operator to a potential adapted grid, which was constructed by using a combination of a Legendre DVR with a one dimensional NO diatom adapted basis (which was generated out of a sinc DVR). We identified the three dimensional potential energy cutoff as the principal parameter with which we checked the convergence of our iteration. We ran four grids, consistent with cutoffs of 4, 6, 8, and 8.1 eV for the even symmetry of the adiabatic ground state to check that the accuracy of our states is better than 10^{-4} which is one magnitude better than the average distance between the states of the surface. Since the adiabatic first excited state has only about one fifth of the number of states of the ground states, and the nonadiabatic state has approximately the same density, we used the two largest grids for the other electronic states and the odd

parity without any further check of the convergence. A number of recalculations with different grids and variation of other computational parameters gave us confidence that we had extracted all the bound states for each symmetry for both the adiabatic and the nonadiabatic coupled surfaces.

The comparison of the state density with experiment is quite good and gives a density of 0.3 cm^{-1} per symmetry just below dissociation (adiabatic and nonadiabatic states). This is less than the one found in experiments (0.5 cm^{-1}) but is in accordance with semiempirical expectations.^{7,10} The states below $10,000 \text{ cm}^{-1}$ differ, only slightly from those of Leonardi.

We are now undertaking calculation at other \hbar^{-1} ; will try to get the relevant periodic orbits and in general will attempt to get enough data for a full scaling analyses (which is easy compared to the full classical and quantum calculations). We will also apply our energy independent statistical analysis methods⁽³⁾ to further reveal information about the evolving dynamics.

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