DESCRIPTION/ABSTRACT

DYNAMICAL
ANALYSIS OF HIGHLY EXCITED MOLECULAR SPECTRA

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PROGRAM SCOPE: Spectra and internal dynamics of highly excited molecules are essential to understanding processes of fundamental importance for combustion, including intramolecular energy transfer and isomerization reactions. The goal of our program is to develop new theoretical tools to unravel information about intramolecular dynamics encoded in highly excited experimental spectra. We want to understand the formations of "new vibrational modes" when the ordinary normal modes picture breaks down in highly excited vibrations. We use bifurcation analysis of semiclassical versions of the effective Hamiltonians used by spectroscopists to fit complex experimental spectra. Specific molecular systems are of interest for their relevance to combustion and the availability of high-quality experimental data. Because of its immense importance in combustion, the isomerizing acetylene/vinylidene system has been the object of long-standing experimental and theoretical research. We have made significant progress in systematically understanding the bending dynamics of the acetylene system. We have begun to make progress on extending our methodology to the full bend-stretch vibrational degrees of freedom, including dynamics with multiple wells and above barrier motion, and time-dependent dynamics. For this, development of our previous methods using spectroscopic fitting Hamiltonians is needed, for example, for systems with multiple barriers.

FINAL REPORT BELOW:

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RECENT PROGRESS: DYNAMICS FROM SPECTRA OF HIGHLY EXCITED SYSTEMS APPROACHING ISOMERIZATION.

Intramolecular processes such as isomerization in highly excited species are of fundamental importance for combustion. The goal of our program is to develop new theoretical tools to unravel knowledge of intramolecular dynamics encoded in highly excited experimental spectra. Ordinary normal mode behavior is transcended in highly excited states, with the birth in bifurcations of new anharmonic modes, and onset of widespread chaotic classical dynamics. New spectral effects are seen on the "road to isomerization", and beyond.

Bifurcation analysis: Branchings of the normal modes into new anharmonic modes. Our approach to highly excited vibrational spectra uses bifurcation analysis of the classical version of the effective Hamiltonian used to fit spectra. We now have applied this to a bifurcation analysis of the bend degrees of freedom of acetylene. We are completing this investigation with development of a simplified independent resonance analysis. The rationale for this is connected with the necessity to simplify the bifurcation analysis for larger systems, such as addition of the stretch modes. The prospects for this continuing work are described in more detail in our Current Plans, below.

The pure bending system is a stepping-stone to the planned inclusion of the stretch degrees of freedom and an attack on the above-barrier isomerization problem for vinylidene-acetylene isomerization, both described below.

Visualization of complex molecular dynamics. One of the most important goals of our research is to convert the fairly abstract dynamical knowledge of the bifurcation analysis into a directly visualizable representation. For this, we are using computer animation techniques to make movies of the anharmonic modes born in bifurcations. Examples of our animations can be found on a web-site at http://darkwing.uoregon.edu/$\sim$meklab/, which the interested reader is urged to access.

Spectral patterns of isomerizing systems. Our earlier work has demonstrated spectral patterns associated with bifurcations and the new modes which they produce. These patterns are robust as the barrier to isomerization is approached in a system such as acetylene [3,4]. Of great interest then is to extend the bifurcation and spectral analysis to isomerizing systems. We have begun this with a thorough investigation [11] of a model of an isomerizing system of coupled stretch and bend, intended to have some of the features of a realistic model of the acetylene-vinylidene isomerization. There are indeed patterns in some was similar to those associated with below-barrier spectra. These patterns are interpreted in terms of nonlinear resonance-type couplings, similar to anharmonic Fermi resonances, between the stretch and bend. There is conventional Fermi resonance below the barrier, and a new type of ``cross-barrier" resonance.

Semiclassical quantization of systems of spectral models. Much of work seeks to assign novel quantum numbers to highly excited spectra, based on the new modes from our bifurcation analysis, when the ordinary normal modes quantum numbers no longer suffice. A fundamental question is whether these quantum numbers have any precise meaning. In a series of investigations [2,6-9] on rigorous semiclassical quantization we have answered this in the affirmative, culminating in a study with on chaotic systems [9] with favorable results.

CURRENT PLANS: TIME-DEPENDENT AND REACTIVE DYNAMICS.

Our current goal is to extend or methods to larger systems and systems undergoing intramolecular reactions, i.e. isomerization reactions involving a potential barrier. We are interested in the particular chemical problem of the acetylene-vinylidene isomerization.
 The key challenges are: (1) making current methods practical for more complex systems, with more degrees of freedom; and (2) the problem of extending the spectroscopic Hamiltonian to handle qualitatively new physical situations, in particular, motion in multiple potential wells, and very large-amplitude motion above two or more wells.

Adding complexity. The acetylene/vinylidene isomerization involves the stretches as well as the bends. As the dimensionality of the problem becomes larger, one of the challenges is whether our analysis can be performed in a way that is understandable and useful.

One key to making larger systems tractable is use of the polyad quantum number. Even for many degrees of freedom with multiple resonances couplings and chaos, the bifurcation problem thereby is reduced from numerical searching to the much simpler task of finding the solutions of analytical (polynomial) equations. Still, the results are formidably complex to interpret. To address this, in completing our investigation of the pure bends system, we are developing an approximate independent resonance analysis that is much easier to understand, is scalable to larger systems, and which furthermore can be *exactly* extended to the full, exact spectroscopic Hamiltonian.

Time dependent dynamics. Our prior work has focused on extracting information from spectra, i.e. time-independent phenomena. A major goal is to understand dynamics. Part of this is understanding the new modes that take over from the normal modes after bifurcations. However, dynamics must also certainly include time-dependent phenomena, for example to understand isomerization. We are currently applying our spectroscopic Hamiltonians to time-dependent dynamics. One goal is to understand Coulomb explosion and other studies of the vinylidene/acetylene system. The system is believed to "cycle" between the vinylidene and acetylene forms in a very highly excited condition. This goes on for an extremely long time, up to a microsecond, and the reason for this is a mystery. The question is why the system doesn't relax out of the reaction coordinate into the "bath" modes when it is on the acetylene side of the reaction barrier. We are currently modeling this with the spectroscopic Hamiltonian, and attempting to understand it in terms of the knowledge of the molecular phase space which we have gained from the bifurcation analysis.

Spectroscopic Hamiltonians for multiple wells and above barrier spectroscopy. The remaining and least-explored challenge in dealing with isomerization problems in our approach is to include above barrier spectroscopy, and multiple wells, in the spectroscopic Hamiltonian; and to develop techniques such as bifurcation analysis to obtain dynamical information. We have begun this, using model systems until such time as experimental data become available. We are using some of the ideas developed in our paper [11] on spectral patterns of isomerizing systems.

Recent publications (in print or in press since 2000) related to DOE supported research:

1. M. Joyeux, D. Sugny, V. Tyng, M.E. Kellman, H. Ishikawa, R.W. Field, C. Beck, and R. Schinke, "Semiclassical Study of the Isomerization States of HCP", J. Chem. Phys. 112, 4162 (2000.)

2. S. Yang and M.E. Kellman, "Direct Trajectory Method for Semiclassical Wavefunctions", Phys Rev A 62, 022105 (2000).

3. J.P. Rose and M.E. Kellman, "Spectral Patterns of Chaotic Acetylene", J. Phys. Chem. A. 104, 10471 (2000).

4. M.E. Kellman, J.P. Rose, and Vivian Tyng, "Spectral Patterns and Dynamics of Planar Acetylene", European Physical Journal D 14, 225 (2001).

5. M.E. Kellman, "Internal Molecular Motion", Encyclopedia of Chemical Physics and Physical Chemistry, J.H. Moore, Ed. (Institute of Physics, London, 2001).

6. S. Yang and M.E. Kellman, "Addendum: Direct Trajectory Method for Semiclassical Wavefunctions", Phys. Rev. A. 65, 034103 (2002).

7. S. Yang and M.E. Kellman, "Semiclassical Wave Function Near a Strong Resonance", Phys. Rev. A 65, 064101 (2002).

8. S. Yang and M.E. Kellman, "Perspective on Semiclassical Quantization: How Periodic Orbits Converge to Quantizing Tori", Phys. Rev. A. 66, 052113 (2002).

9.. S. Yang and M.E. Kellman, "Semiclassical wave function from a quantizing cantorus", submitted to Phys. Rev. A.

10. C.Zhou, D. Xie, R.Chen, G.Yan, H.Guo, V. Tyng, and M.E. Kellman, "Highly Excited Vibrational Energy Levels of $CS_2(\tilde{X})$ on a New Empirical Potential Energy Surface and Semiclassical Analysis of the 1:2 Fermi Resonance", Spetrcochimica Acta A 58, 727-746 (2002).

11. S. Yang, V. Tyng, and M.E. Kellman, "Spectral Patterns of Isomerizing Systems", in press, J. Phys. Chem. A.

12. M.E. Kellman, M.W. Dow, and Vivian Tyng, "Dressed Basis for Highly Excited Vibrational Spectra", in press, J. Chem. Phys.