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MOLECULAR VIBRATIONS: FROM HARMONIC OSCILLATORS TO PENDULUMS *

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“No spectrum, no matter how simple, is dynamics-free. No dynamical process, no matter how complex, fails to reveal its essential characteristics in one or a series of well designed spectroscopic experiments.”

“...patterns are made to be broken, and the breaking of standard patterns is the key to perceiving those dynamical features that demand explanation.”

The quotes above are taken from the preface to a recent book titled *The Spectra and Dynamics of Diatomic Molecules* (Elsevier, 2004) by H. Lefebvre-Brion and R. W. Field. It elegantly sums up the current view in molecular spectroscopy. But why does one want to break the standard patterns? What are those dynamical features that demand our explanation? In short, the dynamical features refers to the intricate dance that the atoms in a molecule perform upon excitation i.e., intramolecular dynamics.

Explaining and hence understanding this molecular choreography will let us control molecular reaction dynamics. Well, at least that is what physical chemists have been fantasizing for many decades now! Parts of the fantasy have been turned into reality in the last couple of decades but attaining the “holy grail” of control requires an intimate understanding of the nature of molecular vibrations.

Chemistry is all about reactions - making and breaking of chemical bonds and the rate at which they do so. Insights into the structure of molecules and their reactivities have been, for many centuries, gained by imagining the molecule to be a tumbling network of springs. Such a “ball-and-spring” model, sketched in Fig. 1, is inherently a classical mechanical notion and one cannot help but

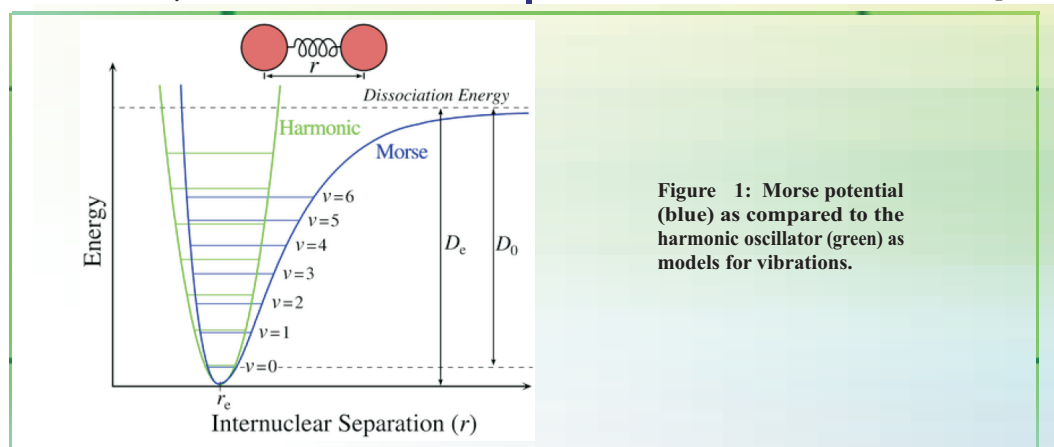


Figure 1: Morse potential (blue) as compared to the harmonic oscillator (green) as models for vibrations.

* This article is dedicated to the fond memory of Lakshmi.

wonder about its utility in the present day context of single molecule dynamics and spectroscopy. The purpose of this brief article is to argue that studying the classical dynamics is not only useful from the perspective of gaining insights into the dynamics of the molecules but perhaps such (semi)classical studies are more relevant than ever. Of course Dirac, in his landmark paper on quantum mechanics, had already anticipated this. It is interesting to note that the ever popular transition state theory of reaction rates, formulated by Wigner, Eyring, and others in the 1930s, is actually based on classical mechanics. At the same time it is a sobering thought that quantum mechanics, the correct theory for microscopic systems, is less than a century old but organic and inorganic chemists have been synthesizing complex molecules for a much longer time!

How does one model the molecular vibrations? The simplest model, accurate at low energies and thus sufficient to characterize the equilibrium structure, is in terms of a harmonic oscillator potential (Fig. 1 on page 47)

$$V(q) = \frac{1}{2} m \omega^2 q^2 \quad (1)$$

between two atoms of the molecule with ω being the frequency of oscillation of the diatomic bond, and q being the displacement from equilibrium. A polyatomic molecule is therefore viewed as a collection of harmonic oscillators with different frequencies and appropriate reduced masses. For a molecule with N atoms the number of such vibrational modes is $f \equiv (3N-6)$ (nonlinear geometry) or $(3N-5)$ (linear) with frequencies $(\omega_1, \omega_2, \dots, \omega_f)$. Quantum mechanics tells us that the oscillator

can only take specific, discrete (quantized) energy levels. In fact almost everyday the above picture of the molecule as a collection of harmonic oscillators is confirmed whenever someone measures and interprets the infrared spectrum of a molecule. However, bonds between atoms can and do break! The harmonic oscillators with their Hookian restoring force will never break. Clearly if one wants to describe chemical reactions then it is necessary to have a better model for the vibrations. A particularly simple but accurate and widely used model is that of the Morse potential (see Fig. 1 on page 47)

$$V(q) = D(1 - e^{-aq})^2 \quad (2)$$

with D being the dissociation energy. For small displacements (low energies) the Morse oscillations are harmonic in nature with frequency $\omega = \sqrt{2a^2 D/m}$ but for large q 's the Morse potential differs substantially from the harmonic one. In particular $V(+\infty) = D = \text{const}$ and thus the force $dV/dq = 0$ and the bond breaks. The frequency of vibrations in a Morse potential depend on the energy i.e., $\Omega = \Omega(E)$, in contrast to the harmonic vibrations. Again, for a polyatomic molecule one has a collection of frequencies $(\Omega_1, \Omega_2, \Omega_3, \dots, \Omega_f)$. Several experiments support the Morse oscillator model and thus molecular vibrations are examples of nonlinear oscillators. The classical and quantum dynamics of the Morse oscillator can also be exactly solved which makes it a very useful model.

In a polyatomic molecule the oscillators are coupled - some strongly and some not at all. Why do they couple? Since there is not much space here to go into the details of the theory

of molecular structure, and with an inevitable risk of sounding cryptic, let me just say that: The various vibrational modes couple and that is why it is a molecule. It is the coupling which makes life interesting! Coupling of the nonlinear oscillators leads to complex classical dynamics and the possibility of chaos as well. It is well known, for nearly a century, that even coupling harmonic oscillators with nonlinear coupling results in complicated motion. For example, a Hamiltonian that describes two uncoupled harmonic oscillators can be expressed as

$$H_0(x, y, p_x, p_y) = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\omega_x^2 x^2 + \omega_y^2 y^2) \quad (3)$$

and an example of nonlinear coupling between the x -oscillator and the y -oscillator is:

$$H(x, y, p_x, p_y) = H_0(x, y, p_x, p_y) + \lambda x^2 y \quad (4)$$

coupling strength λ at the same total energy. One can clearly see the drastically different nature of the classical dynamics. Are there consequences of these features of classical nonlinear dynamics in the quantum domain? What does one mean by the term “quantum chaos” if that is not a contradiction in itself? These and many more similar questions have been the focus of attention for nearly four decades now. Although the final word on these issues is yet to be said, we now know that the nonlinearity of the vibrations is crucial to understanding the molecular dynamics and its control. *In particular it is useful to think of the molecule as a set of harmonic oscillators at low energies whereas at higher energies it is more appropriate to think in terms of coupled pendulums.*

Imagine that one wants to break a specific bond in a polyatomic molecule.

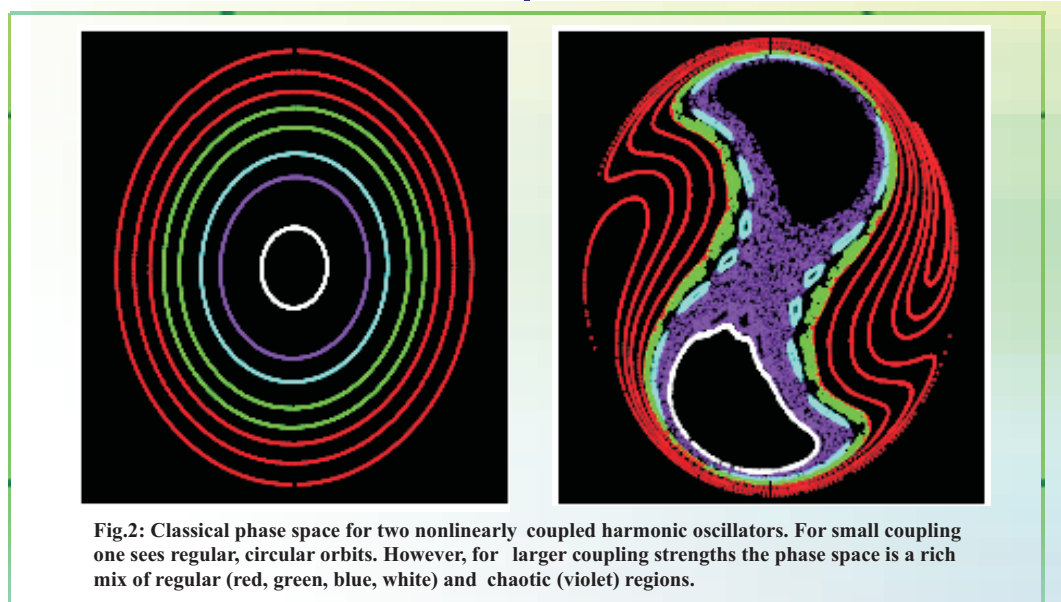


Fig.2: Classical phase space for two nonlinearly coupled harmonic oscillators. For small coupling one sees regular, circular orbits. However, for larger coupling strengths the phase space is a rich mix of regular (red, green, blue, white) and chaotic (violet) regions.

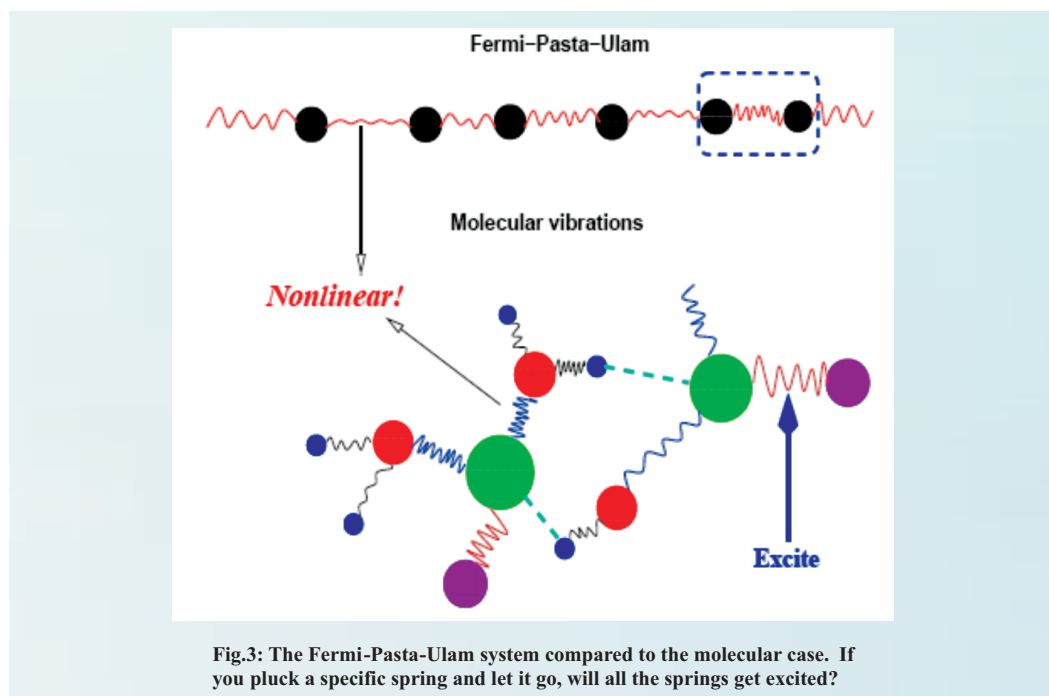
In Fig. 2 the (x, p_x) classical phase space section is shown for very small and relatively large

Then, as shown in Fig. 3 on page 51, all that has to be done is to excite that bond and dump

energy in excess of the bond strength. With some luck the deposited energy will stay put in that bond for a few vibrational time periods (about a few hundred femtoseconds) or chemically significant timescales and then snap the specific bond. Turns out that this viewpoint is far too naive mainly due to the fact that molecules excited to such high energies have complicated intramolecular dynamics. The excited mode is coupled to many other modes and thus the initially localized energy flows rapidly into many other, perhaps undesirable, modes. In other words the molecular choreography is very complicated. Sometimes it is so complicated that it is simple! Underlying this complicated song and dance sequence of excited molecules is a dynamics of indescribable beauty which, amazingly enough, is the same as one observes while studying celestial mechanics. Indeed one could say that what was termed nearly a century ago by Poincaré as the fundamental problem of dynamics is relevant to the intramolecular motions as well. This might sound very strange given the disparity between mass, length, and time scales for molecular and celestial phenomena and yet very recently astronomers, mathematicians, chemists, and physicists have come together to work on space missions! It is appropriate to quote from the recent account by Porter and Cvitanović: *In a turn of events that would have astonished anyone but N. Bohr, we now know that chaotic trajectories identical to those that govern the motion of comets, asteroids, and spacecraft are traversed on the atomic scale by highly excited Rydberg electrons. This almost perfect parallel between the governing equations of atomic physics and celestial mechanics implies that the transport mechanism for these two situations is virtually identical... The orbits used to design space missions thus also determine the*

ionization rates of atoms and chemical-reaction rates of molecules!

This flow of energy within a molecule is called as the phenomenon of Intramolecular Vibrational energy Redistribution or IVR for short. The questions that we are, as many other chemical physicists in the world are, interested in: Where does the energy flow? How? Why? How fast? How is this *classical* notion of ball-and-spring vibrational motion encoded in the quantum eigenstates? The significance to reaction dynamics has to do with the fact that IVR is at the heart of one of the best known and widely applied approach to estimating reaction rates- the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. In essence RRKM, proposed in the 1950s, make the assumption that for most molecules the time scale for IVR is much smaller than typical reaction timescales; this neglects dynamics and renders the theory statistical. Does this basic, seemingly reasonable, assumption ring the death bell for mode-specific chemistry? Before answering this question let me point out that around the very time that RRKM was proposed a famous computational study was performed by Fermi, Pasta, and Ulam (FPU). They took a large number of nonlinearly coupled oscillators, excited one of them and numerically studied the subsequent flow of energy through the system (Fig. 3 on page 51). Surprisingly the initial energy did not distribute statistically - energy was sloshing back and forth between a few select modes with other modes being mere spectators. The FPU system was a one dimensional network of nonlinear oscillators and a polyatomic molecule is much the same but now in three dimensions. So, if FPU system exhibits mode-specific dynamics then is it

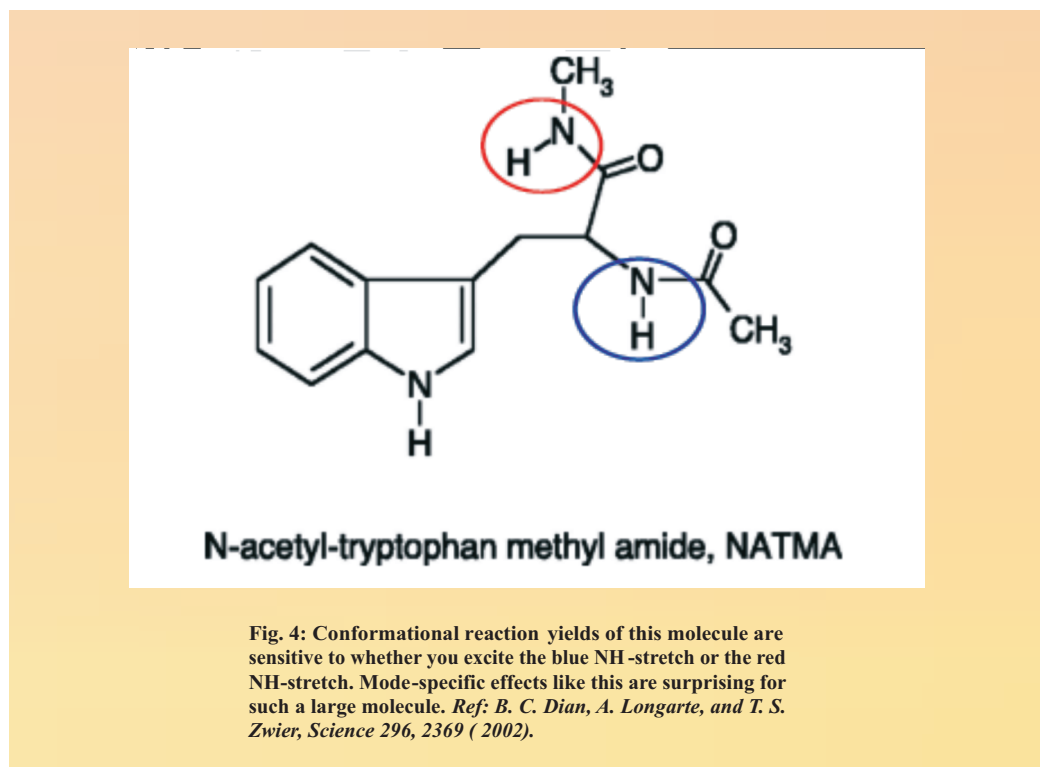


reasonable to expect the molecular system to do the same? Or is it that RRKM wins? Recent detailed and beautiful experiments in both time and frequency domains indicate that consolations regarding the death of mode-specific chemistry are indeed premature. Even fairly large molecules at high levels of excitations can exhibit non-statistical dynamics. That is good and bad news. The good news is that one can hope to control the molecular dance. The bad news is that dynamical details cannot be ignored and thus simple and elegant expressions for rates *a la* RRKM cannot be written down.

The issues involved are quite subtle and the following two of the recent examples are worth highlighting. For example a recent experiment showed that mode-specific effects can exist

even in a large molecule like N-acetyltryptophan methyl amide (NATMA). This molecule is shown in Fig. 4 on page 52 and has two NH-stretches (highlighted in red and blue). The stretching frequencies of these are very close, about 3440 cm^{-1} and 3466 cm^{-1} . Dian *et al.* were interested in studying the conformational reaction of NATMA (which has 164 minima connected by 714 transition states!) upon exciting one or the other NH-stretch using a laser. They found that the reaction yields were sensitive to the specific NH-stretch being excited. As another example consider the molecule *trans*-formanilide (TFA, shown in Fig. 5 on page 53).

A water molecule can bind to two sites of TFA via hydrogen bonding. One site involves the C=O group and the other site is the NH-group.



Clarkson *et al.* performed an interesting experiment to understand the shuttling dynamics of this water molecule between the two sites. One can think of this water shuttling as an isomerization reaction - what is the rate for this reaction? How would IVR in the TFA-water complex influence the shuttling dynamics? Amazingly, RRKM rates are quite reasonable despite the fact that the barrier to the reaction is small! I say amazing because researchers expect that deviations from statisticality are strongest for such small barrier isomerization reactions. It seems like the single water molecule really scrambles the energy throughout the complex. Hydrogen bonds seem to have this uncanny ability to act as conduits for the flow of energy. But the H-

bonds are among the weakest of the lot. So, how do they do this? People are trying to get to the bottom of this because insights into the mechanism here is of importance to biomolecular systems.

There are many such examples now which indicate that IVR could be specific to the functional group in a molecule. Methyl groups (acting like rotors), H-bonds (acting as pipelines) seem to be particularly good at accelerating the rate of energy flow. So within the same molecule, exciting a CO-stretch, a NH-stretch, or a OH-bending could lead to very different rates of IVR. And that is exciting because if we understand the mechanism and the pathways then we can actually try and

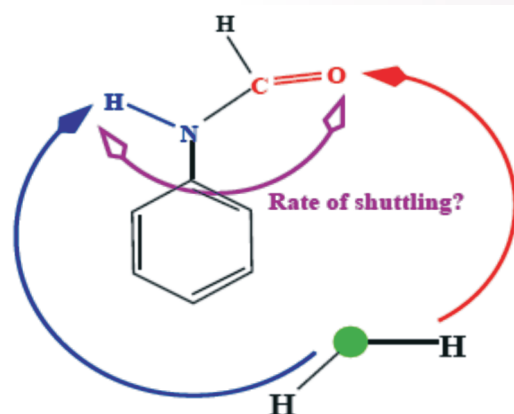


Fig. 5: The rate of shuttling of water between NH-site (blue) and CO-site (red) agrees with RRKM estimate. A single water molecule is capable of inducing extensive IVR throughout the molecule? Ref: J. R. Clarkson, E. Boquero, V. A. Shubert, E. M. Myshakin, K. D. Jordan, and T. S. Zwier, *Science* 307, 1443 (2005).

control the molecular dance. How can classical mechanics help in understanding the IVR process? Which of the classical mechanisms survive quantization and which of them do not? In order to address these issues, our group is working on unraveling the pathways for energy flow in molecules from classical, semiclassical and quantum viewpoints. The same question, from a time-independent standpoint, has to do with the nature of the highly excited eigenstates - can we assign them? Quantum eigenstates encode the details of the energy flow dynamics and thus assignment of eigenstates implies an intimate knowledge about the IVR processes.

Over the years several studies have shown that crucial information on the intramolecular dynamics can be gained with a careful study of the classical dynamics. For example, consider the bending motions of the linear molecule acetylene CH. At low energies of excitation there are the *cis*-bending and the *trans*-bending modes - something that every spectroscopy textbook would show. The nature of these motions is shown in Fig. 6 on page 54.

What happens if we start pumping more and more energy i.e., exciting the bends? At first guess one would predict that the bending motions would simply speed up. This is true upto some energy but beyond this energy completely new types of motion set in. Only one of the hydrogens bends or one hydrogen rotates clockwise about the bond axis with the other hydrogen doing the same but anticlockwise! (Fig. 6 on page 54). Turns out that this appearance of new types of motion is due to certain changes in the classical phase space - technically known as *bifurcations*. Amazingly enough, acetylene's dynamical behaviour mirrors the large scale changes happening in the classical phase space. It seems certain that Poincaré and Bohr would have a lot to talk about in this millenium.

A very important insight, originating from classical dynamics, is that IVR is facilitated in a molecule by chains of nonlinear resonances *i.e.*, energy flows between two modes if their frequencies are in near-integer ratios. So, for instance if two of the vibrational modes, call them *a* and *b*, at some energy *E* satisfy

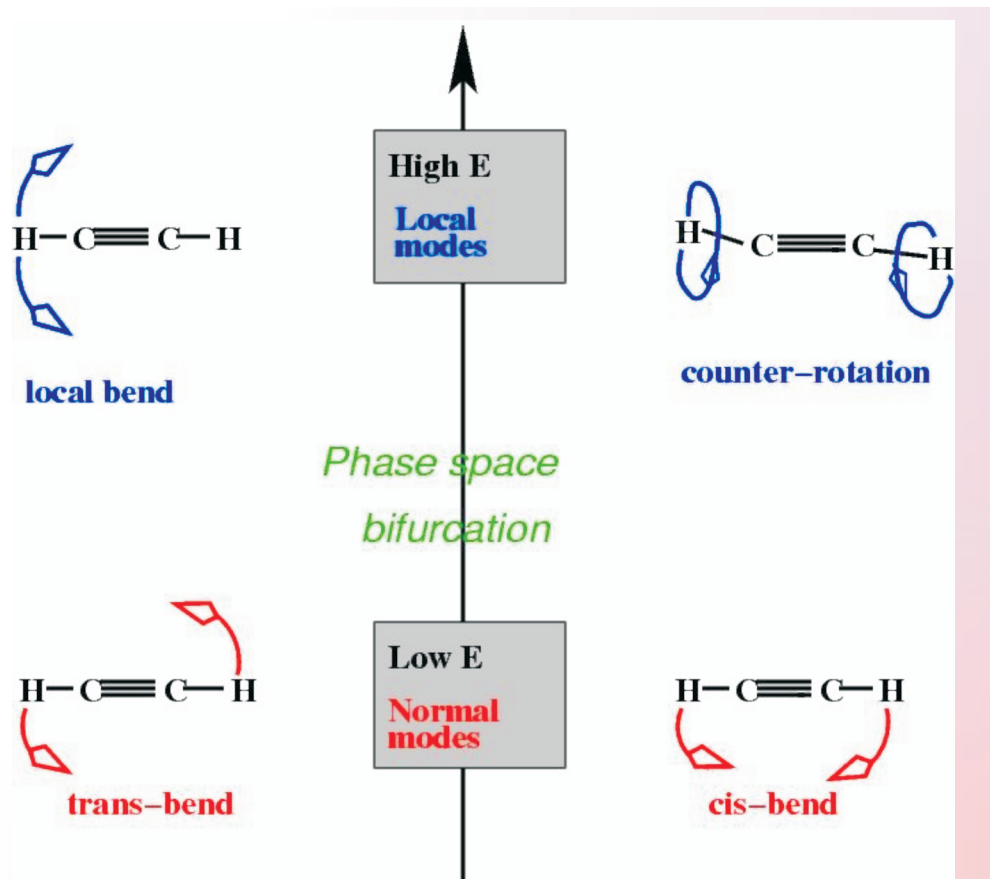


Fig. 6: The low energy bending normal modes of acetylene give way to completely different modes at higher energies. Birth of these new modes is predicted by classical mechanics and the fingerprints can be seen in the quantum domain.

$\alpha\Omega_a(E)=\beta\Omega_b(E)$ then the modes are locked in a $\alpha:\beta$ nonlinear resonance and they will exchange energy between themselves. In the quantum world such a classical resonance condition translates to the statement that the mode a will lose (gain) α units (quanta) of excitation with mode b gaining (losing) β units of excitation. Since one mode is getting de-excited with simultaneous excitation of the

other mode it is nothing but transfer of energy between the two modes. Thinking of a three mode system, a general locking condition can be

$$\alpha\Omega_a(E)+\beta\Omega_b(E)+\lambda\Omega_c(E)=0 \quad (5)$$

In fact the nonlinear resonances, for various (α,β,λ) , form an intricate network - sort of a transport network complete with highways,

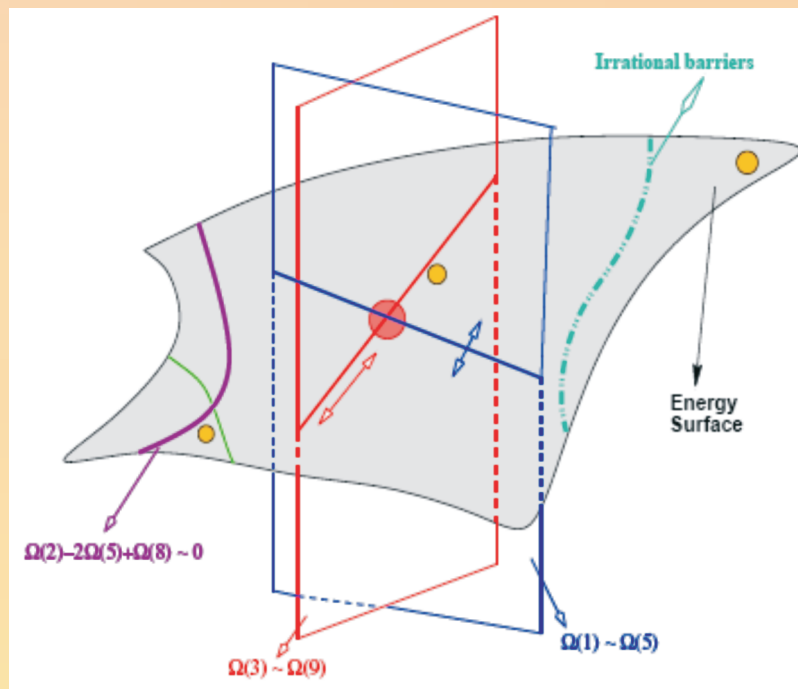


Fig. 7: Geometry of the resonance network. The energy surface is interested by various planes corresponding to nonlinear resonances. This network leads to energy flow. Part of the network are akin to road-blocks and have to do with irrational commensurability between the mode-mode frequencies.

bylanes and dead-ends. A sketch of this network is shown in Fig. 7. Locally, around each resonance the dynamics is that of a *pendulum*. Loosely speaking one can think of the width of a highway as being inversely related to the order of the resonance ($\alpha + \beta + \lambda$). The dead-ends are like traffic road blocks on the energy transport map. One possible location of the road blocks have to do with regions where the frequency ratio between modes is irrational - and the most irrational, in a number theoretic sense, is the golden mean $(\sqrt{5}-1)/2$. Do these irrational regions have any effect? The jury is still out on this issue but there are hints that

such dead-ends might check the rate of energy flow in molecular systems.

What part of this network is utilized by the classical dynamics? Does the quantum dynamics use similar regions of the resonance network or is it significantly different? Recent progress in our understanding of IVR and its control suggests that the crucial issue has to do with the nature of diffusion on the energy surface - which is classically decorated by the resonance network. If one had two states, one which is at the edge of the energy surface and another in the interior, as shown in Fig. 8

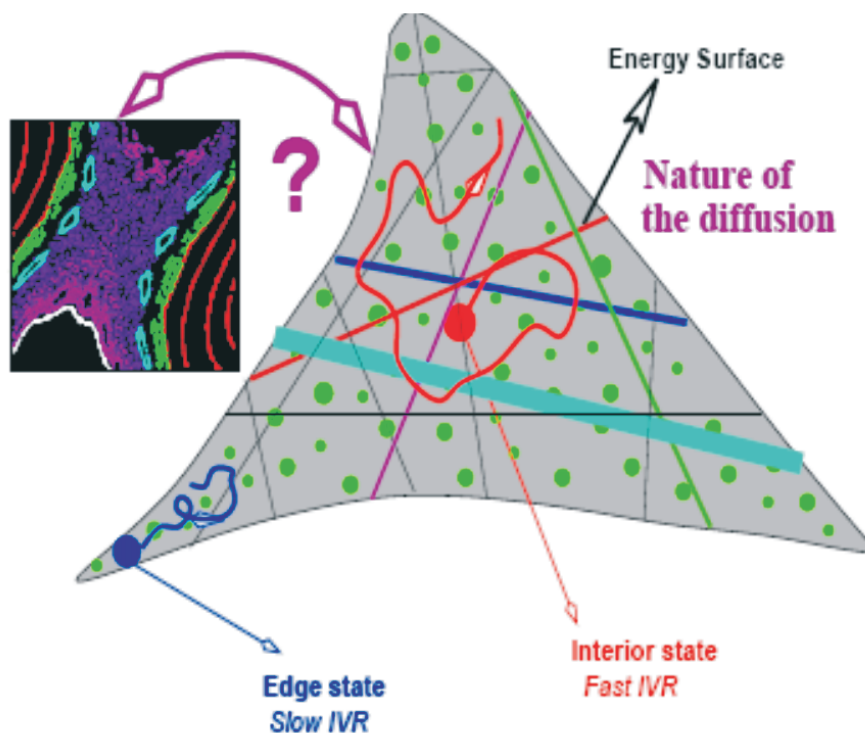


Fig. 8: IVR as diffusion on the energy surface showing some of the important nonlinear resonances. Two optically bright states which are isoenergetic are shown. State shown in blue is an edge state and the one in red is a combination state. The optically dark states are shown in green. How different is their IVR dynamics? The diffusion process here has intimate links to the nature of regular-chaos border in the underlying phase space.

above, then how would their IVR dynamics differ? Experimentally, the edge state corresponds to an overtone mode and the interior state is a combination mode which have approximately the same energy. There are other states (shown as green dots in Fig. 8) with

similar energies but optically 'dark' i.e., they cannot be prepared. In contrast the edge and interior states are optically 'bright'. A first guess, based on the number of dark states nearby, is that IVR will be fast from the interior state and comparatively slow out of the edge state. This

would be more or less correct if the diffusion in the energy space is normal. However this need not be the case - in fact one can have dynamical traps which render the diffusion anomalous! The interesting thing here is that such traps have to do with the complex nature of the phase space regions corresponding to the border between regular and chaotic dynamics. Such a border region is shown in Fig. 8 (on page 10) and corresponds to a blow-up of the phase space shown earlier for the nonlinearly coupled harmonic oscillators. Amazingly, in systems with more than two degrees of freedom (regime of interest for most molecular systems) one still does not understand the regular-chaotic border in sufficient detail. Strictly speaking, even the definition of what constitutes a border, if any, in high dimensional systems is unclear - let alone the quantum manifestations.

Finally, it is natural to ask as to whether purely quantum routes to IVR exist in a molecule. In other words, is it possible that the quantum dynamics could "short-circuit" the network? The answer is yes - quantum mechanics can transport energy even though classical mechanics cannot. This is known as *dynamical tunneling* which may be the reason for observing non-trivial intensity and splitting patterns in a high resolution frequency domain spectrum. However ironically, as shown by recent work from our group and others, even this dynamical tunneling is intimately linked to the classical resonance network!

The competition between classical routes to IVR via nonlinear resonance network and quantum routes via dynamical tunneling

depends nontrivially on value of the "effective" Planck constant \hbar of the system. What is the impact of this competition on the energy flow dynamics and mechanism? Several questions arise at this juncture, and we hope that a detailed knowledge of transport on the resonance network will allow us to shut down some of the highways thereby controlling IVR and thus give mode-specific chemistry a fair chance to happen.

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