The Dance of Molecules: New Dynamical Perspectives on Highly Excited Molecular Vibrations

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ABSTRACT

At low energies, molecular vibrational motion is described by the normal modes model. This model breaks down at higher energy, with strong coupling between normal modes and onset of chaotic dynamics. New anharmonic modes are born in bifurcations, or branchings, of the normal modes. Knowledge of these new modes is obtained through the window of frequency-domain spectroscopy, using techniques of nonlinear classical dynamics. It may soon be possible to "watch" molecular rearrangement reactions spectroscopically. Connections are being made with reaction rate theories, condensed phase systems, and motions of electrons in quantum dots.

I. Introduction

A central quest of molecular science is to understand the internal motions of molecules. The low-energy normal modes picture of regular, near-harmonic vibrations held sway for most of the twentieth century, supported by a huge amount of experimental evidence.[1] However, normal modes cannot be the whole story. Molecules undergoing reaction, including internal rearrangement, obviously fall outside the realm of near-harmonic motion. What happens on the path from regular, near-harmonic motion at low energy to the regime of irregular, often violent motions that must occur in chemical reactions?

This was pretty much a mystery until about 1980. After that, our understanding developed rapidly, and a new picture has emerged. Novel motions have been discovered that are dramatically different from the normal modes. (For some striking examples in highly excited acetylene, see the animations described in section III.E and archived at the websites listed in ref 2.)

A surprising twist is that one of the most powerful ways of seeing inside this world of internal molecular dynamics is through the window of complex frequency-domain, that is to say time-independent, spectra, rather than the complementary window of ultrafast time-domain spectra. How this comes about is one of the main themes of this Account.

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The new vista of internal molecular dynamics opens onto other domains of chemistry and physics. A major challenge is to make contact with theories and concepts of reaction rates. This is important for chemistry of systems of vital importance such as combustion and the atmosphere. Knowledge of the internal motions of molecules may help forge new tools for control of chemical reactions, using sophisticated means of ultrafast optical excitation.

Most of the work described here deals with molecules in the gas phase. The implications for molecules in condensed phase have only begun to be explored. There is even a spinoff into areas of physics and materials science: the motions of electrons in the ultrasmall electronic devices known as quantum dots.

II. Watching Molecules Dance

Most of the developments described in this Account involve use of *frequency-domain* spectra to obtain information about *time-dependent* motions in molecules. This may seem paradoxical, because frequency-domain spectra involve quantum energy eigenstates—and by definition, these have no time dependence!

The key is that the frequency and time domains are complementary.[3] Access to temporal dynamics in frequency-domain spectroscopy comes through interpretation of complex spectra, rather than through monitoring of a relatively simple time-dependent signal. Because of the exquisite detail of frequency-domain spectra, if one can learn to decode their meaning, they may actually provide a superior way of watching the dynamics of small polyatomic molecules in many situations. We will describe an array of analytical tools of growing sophistication, leading to animations of the beautiful highly excited motions of acetylene described in section III.E.

A. First Steps: Normal and Local Modes. The conventional picture of normal modes became firmly established in the first half of the twentieth century, as in the classic tome of Herzberg.[1] Figure 1, top, shows the normal stretch and bend modes of water. Striking evidence of the need for a new way of thinking came when Child and co-workers[4] showed from classical trajectory calculations that there are instances in water of local mode stretch motion: vibration predominantly in one bond. This is illustrated schematically in Figure 1, bottom. Calculations of wave functions showed that the quantum states closely reflect the classical behavior. Others soon explored the coexistence of normal and local modes using powerful tools of nonlinear classical dynamics.[5-7] We will return to this in section III.A.

B. Lighting the Way: The Spectroscopic Link. It was soon realized that the emerging nonlinear dynamics ideas could be connected to experiment through a standard tool of experimental analysis: the spectroscopic fitting Hamiltonian.

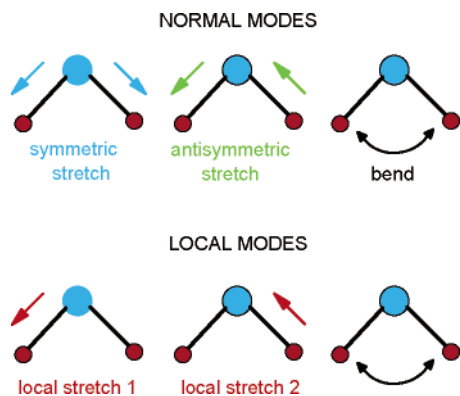* Corresponding author. E-mail: kellman@uoregon.edu.

NORMAL MODES

symmetric stretch   antisymmetric stretch   bend

LOCAL MODES

local stretch 1   local stretch 2

FIGURE 1. Normal and local modes of H_2O: top, normal modes—symmetric stretch, antisymmetric stretch, bend; bottom, local stretch modes.

In its simplest form, the spectroscopic Hamiltonian has harmonic terms proportional to the number of quanta in each normal mode and, in addition, crucial anharmonic corrections, which depend on higher powers of the quantum numbers. This Hamiltonian H_0 is diagonal, that is, depends only on the number of quanta in each mode. For example, for the two normal stretches and the bend of water (see Figure 1, top), to second order in the quantum numbers, the diagonal Hamiltonian is

$$H_0(n_s,n_b,n_a) = \omega_s\left(n_s + \frac{1}{2}\right) + \omega_a\left(n_a + \frac{1}{2}\right) + \omega_b\left(n_b + \frac{1}{2}\right) +$$

$$\gamma_{ss}\left(n_s + \frac{1}{2}\right)^2 + \gamma_{aa}\left(n_a + \frac{1}{2}\right)^2 + \gamma_{bb}\left(n_b + \frac{1}{2}\right)^2 + \gamma_{sa}\left(n_s + \frac{1}{2}\right)$$

$$\left(n_a + \frac{1}{2}\right) + \gamma_{sb}\left(n_s + \frac{1}{2}\right)\left(n_b + \frac{1}{2}\right) + \gamma_{ab}\left(n_a + \frac{1}{2}\right)\left(n_b + \frac{1}{2}\right) \quad (1)$$

This "minimal" Hamiltonian is optimized by adjusting the parameters ω_s, γ_{ss}, etc. to get the best fit to experiment.

However, this is not the most general form for the Hamiltonian. To get a satisfactory fit, it is often necessary to add couplings between the normal modes. For example, to fit the spectrum of the stretch modes of a molecule like H_2O, a large coupling between the stretches is necessary, as discovered long ago by Darling and Dennison.[1,8] Because the two stretch modes have roughly the same frequency, this is called a *resonance coupling*. The Darling—Dennison resonance takes two quanta out of the symmetric stretch and places two in the antisymmetric stretch and vice versa.

It is convenient to represent[9] the coupling in terms of raising and lowering operators a_i^+, a_i. These have the action of inserting or removing a quantum from an oscillator with n quanta:

$$a^+|n\rangle = \sqrt{n+1}|n+1\rangle; \quad a|n\rangle = \sqrt{n}|n-1\rangle \quad (2)$$

In terms of these, the Darling—Dennison coupling is

$$\mathbf{V}_{DD} = \kappa_{DD}(a_s^\dagger a_s^\dagger a_a a_a + a_s a_s a_a^\dagger a_a^\dagger) \quad (3)$$

with the coupling strength, κ_{DD}, an adjustable parameter optimized in the fit.

C. The Semiclassical Connection. The molecule is a quantum system, and the spectroscopic fitting Hamilto-

nian is a quantum Hamiltonian. Quantum mechanics is notorious for being difficult to understand in the terms in which we experience the everyday world. In the early days when scientists were groping their way toward quantum mechanics, the only way forward was to try to link classical and quantum concepts, as in the Bohr theory of the atom. The successes in this endeavor, and the ultimate failure, eventually pointed the way to the fully quantum mechanical theory. More recently, there have been efforts to go in the reverse direction, from quantum to classical pictures, via semiclassical techniques. This might strike the reader as strangely retrograde. Part of the motivation is to visualize what nature is telling us about the complex quantum systems increasingly important in science and technology—exactly the situation in highly excited molecular vibrations.

To interpret the quantum Hamiltonian semiclassically, we use the "Heisenberg correspondence",[10] reversing the procedure Heisenberg used in fabricating quantum mechanics. This connects the quantum Hamiltonian with a classical form, which can be visualized with classical images of atomic motion. This semiclassical picture is not gotten immediately in terms of the atomic positions and velocities, which constitute the molecular *phase space*.[11] Instead, it is expressed in terms of *action-angle variables,* an abstract representation of phase space whose basic meaning is familiar. The action of an oscillator mode is given by the number of quanta, plus a zero-point contribution, multiplied by Planck's constant: $(n + \frac{1}{2})\hbar$. Similarly, the angle variable ϕ is just the phase angle, familiar from the harmonic oscillator.

Once the quantum—classical link has been made, approximate techniques are used[12] to convert the action-angle representation into visualizable dynamics in the real space of the atoms in the molecule.

III. Basic Structures: Polyads and Bifurcations

The semiclassical Hamiltonian gives us a way to visualize the molecular dynamics, but this does not yet mean that we can make sense of what we see! In general, the dynamics are highly complex and often chaotic. If there is order in the dynamics, a systematic framework is needed to bring this out. This section tells how we obtain the motions in the animations of the Dance of Acetylene in section III.E. Two indispensable ideas are *bifurcations* of normal modes into new modes and approximate conserved *polyad numbers*.

A. Birth of New Modes in Bifurcations. Our point of view emphasizes the *natural motions* or *anharmonic modes* as the framework for thinking about the molecular dynamics. What are these natural motions? At low energy, they are the familiar normal modes.

What happens to the normal modes with increasing excitation? Tremendous insight comes from *bifurcation analysis*. New anharmonic modes are born in bifurcations, or branchings, of the original low-energy normal modes. The new modes, together with the original normal modes,
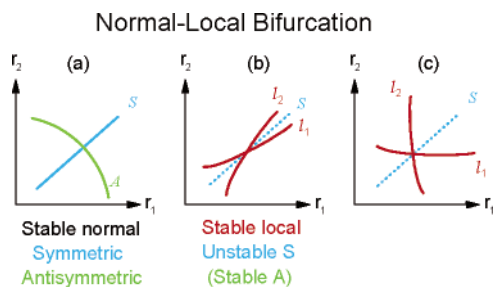
Normal-Local Bifurcation

FIGURE 2. Birth of local modes in a bifurcation. See section III.A for a detailed description.

which persist in altered form, are the framework around which the phase space is organized.

An analogy can be made to a village, nestled in a valley and surrounded by mountains. In the valley, streets are laid out in a regular grid, analogous to the normal modes of a molecule. (The streets may be curved but still laid out in an orderly pattern.) Climbing out of the valley, the grid cannot continue indefinitely, and the streets branch into twisting trails and paths. The savvy mountaineer learns enough about the paths to avoid becoming lost in the enveloping chaos.

To see what a bifurcation means, we return to the stretch modes of water. Figure 2 shows what comes out of the bifurcation analysis of the classical version of the Darling–Dennison Hamiltonian. In panel a, before bifurcation there are stable symmetric and antisymmetric stretch modes, like the schematic normal modes in Figure 1. One of the normal modes—in water, the symmetric stretch—suddenly becomes unstable. The antisymmetric stretch remains as a stable mode; for clarity, it is not shown in panels b and c. Immediately, from the symmetric stretch there emerge two new stable modes. As the energy increases, the new modes migrate away from the symmetric stretch, which survives as an unstable mode. Eventually, the new modes point along the zero-order bond displacements but as curvilinear trajectories. Anharmonic *local modes* have been born in the bifurcation. Detailed techniques of the bifurcation analysis are found in refs 13–18.

B. Polyad Numbers. The *polyad number* is a concept that is remarkably simple yet essential to the techniques described in this Account. The idea can be understood by reference to the Darling–Dennison coupling, $\hat{V}_{DD}$, of eq 3. Because $\hat{V}_{DD}$ exchanges quanta between the symmetric and antisymmetric stretch, the individual n_s and n_a are no longer good quantum numbers. However, the *total* number of stretch quanta

$$n_{str} = (n_s + n_a) \tag{4}$$

is left unchanged. Thus, $\hat{V}_{DD}$ preserves n_{str} as a good quantum number, often referred to as a *polyad* number.

As an analogy, consider the United States interstate highway system of east–west and north–south routes. The east–west routes are like polyads. There is free east–west traffic, like the free energy flow within a polyad. Imagine blockades that prevent access to north–south routes, so traffic can never switch from one east–west

route to another. Similarly, the polyad number acts as a bottleneck to energy flow between polyads.

The polyads constitute an important type of pattern in complex, highly excited spectra.[19,20] It was predicted for very highly excited states of acetylene[20,21] that a polyad number

$$N_{total} = 5n_1 + 3n_2 + 5n_3 + n_4 + n_5 \tag{5}$$

involving all the normal modes, $\nu_1-\nu_5$, would be a good approximate quantum number. This has been confirmed by experiment,[22–24] with identification of remarkable spectral patterns.

The reason for the approximate polyad number is that couplings that break it are relatively ineffective. This is due to the frequency ratios of the normal modes (approximately 5:3:5:1:1 in acetylene). This almost guarantees that couplings that break the polyad constant are far off-resonance and enfeebled or else are high-order and inherently weak. Either way, the polyad-breaking couplings are nearly ineffective. (In our traffic analogy, polyad-breaking terms are like the presence of very inefficient secondary roads.)

For our purposes, the key use of the polyad number is in bifurcation analysis. But first, it is necessary to generalize the Darling–Dennison Hamiltonian that has served thus far for illustration.

C. Fermi Resonances. In the example of H_2O, the Darling–Dennison coupling between the stretches led to a profound change in the dynamics, the birth of local modes in a bifurcation from one of the normal modes. A natural question is whether other types of coupling are possible, between other modes than the stretches. In H_2O, there is an approximate 2:1 resonance condition satisfied between the symmetric stretch and bend frequencies: $\omega_s \approx 2\omega_b$. In fitting the H_2O spectrum, when bending quanta are present, it turns out to be necessary to include a 2:1 coupling term of form

$$\kappa_{sbb}(a_s^\dagger a_b a_b + a_s a_b^\dagger a_b^\dagger) \tag{6}$$

which exchanges two quanta of bend for one of symmetric stretch. (The analogous coupling between antisymmetric stretch and bend is forbidden by symmetry.) The 2:1 resonance, also known as Fermi resonance,[1] is very often prominent in spectra. It is easy to verify that the 2:1 coupling preserves as polyad number the sum

$$n_{sb} = (n_s + n_b/2) \tag{7}$$

Other resonances, of order $n{:}m$, are possible in other systems.[25]

Still another type of coupling is a multimode resonance. For example, in C_2H_2 an important coupling[26,27] is

$$\kappa_{2345}(a_3^\dagger a_2 a_4 a_5 + a_3 a_2^\dagger a_4^\dagger a_5^\dagger) \tag{8}$$

which transfers one quantum from antisymmetric C–H stretch ν_3 to C–C stretch ν_2 and bends ν_4 and ν_5. To avoid confusion, the general term *anharmonic resonance* is often used to include all the special cases.
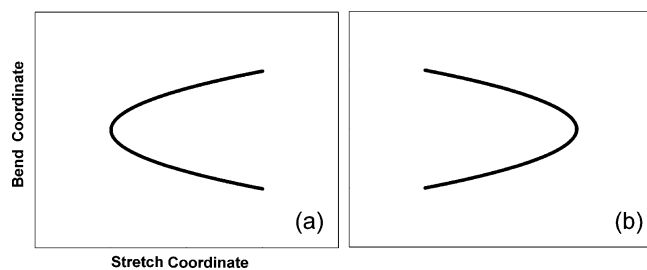
FIGURE 3. Resonant collective modes of the Fermi resonance system of coupled stretch and bend with approximate 2:1 frequency ratio.

We saw in Figure 2 how the language of normal and local modes comes out of the bifurcation analysis of the Darling−Dennison Hamiltonian. It turns out that this language is not the way to describe the general anharmonic resonance case. For example, in 2:1 Fermi systems, a bifurcation gives rise to "resonant collective modes",[28−30] illustrated in Figure 3. Their difference from the local modes of the Darling−Dennison system is evident.

D. Putting Chaos Where It Belongs: Many Modes, Multiple Resonances. With multiple resonances present, as in H_2O, we cannot always think about each resonance and its bifurcation behavior apart from other resonances in the system. In H_2O, the Darling−Dennison resonance couples the symmetric and antisymmetric stretches; the Fermi resonance couples the symmetric stretch and bend. Indirectly, the resonances are linked, and all three modes are coupled. Classically, this means that the molecular motion may be chaotic, and this is clearly observed in numerical studies.[16,31−33]

With chaotic dynamics, do we lose the conserved polyad number? The stretch polyad number ($n_s + n_a$) is no longer conserved, because it is broken by the 2:1 Fermi coupling (eq 6); nor is the Fermi polyad number ($n_s + n_b/2$) conserved, because it is broken by the Darling−Dennison coupling (eq 3). However, there is still a total polyad number

$$n_{total} = (n_s + n_a + n_b/2) \qquad (9)$$

that is preserved by both couplings, as is readily verified.

So one of our key notions, the polyad number, has survived the introduction of multiple resonances and chaos. What about the other key idea, of new modes born in bifurcations? This too survives intact. The polyad number again yields great service. It turns out that the bifurcation problem is essentially analytically solvable when there is a conserved polyad number.[13,16,18] This is an enormous simplification over numerical solution of Newton's laws. The analytical bifurcation analysis of the chaotic polyad Hamiltonian has now been performed for triatomics[16,31,32] and for C_2H_2.[18] A related numerical analysis for C_2H_2 has been performed by Jacobson and co-workers.[33]

E. The Dance of Acetylene. Everything is now in place for our goal of visualizing molecular dynamics by decoding the information inherent in their spectra. The websites in ref 2 show animations of the bending dynamics of
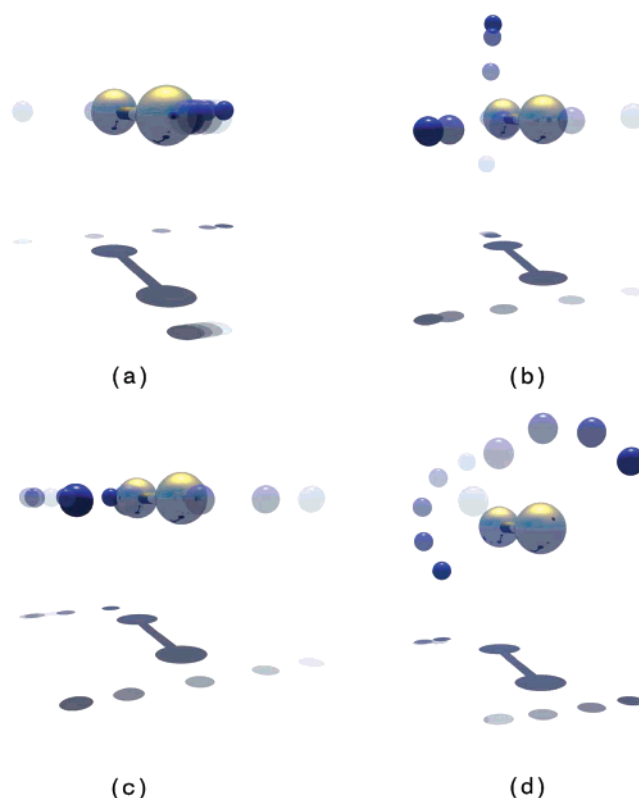

FIGURE 4. Time-lapse still frames from animations described in text of the new modes born in bifurcations. Panels a−d are the local (L), orthogonal (O), precessional (P), and counter-rotator (CR) modes, respectively. Reprinted from ref 18 with permission. Copyright 2006 American Chemical Society (http://pubs.acs.org).

acetylene, obtained[18] using the methods just described. We use the experimental fitting Hamiltonian[34] of Field and co-workers, who have explored spectra that place many quanta in the bending modes. The animations show that the bend normal modes of acetylene undergo an elaborate series of bifurcations, giving birth to four new kinds of anharmonic modes. The modes in the animations are depicted in time-lapse still frames in Figure 4. These modes are for vibrational angular momentum $l = 0$. Figure 5 shows the "orthogonal" mode when $l > 0$. Now there is precession of the vibrational angular momentum. The viewer may find these new motions surprising, even startling. They are far different from the low-energy normal modes. One would not guess just by looking at the raw spectrum that it is telling us that these are the natural motions of the molecule at high energy.

F. What Does a Bifurcation Look Like? We have seen that the spectrum encodes a wealth of information about the complex dynamics of the molecule, including new anharmonic modes born in bifurcations from the original normal modes. Are there direct spectral markers of these bifurcations? The answer is yes. Associated with the 2:1 Fermi system, a pattern is predicted[14] of a minimum in the spacing of adjacent energy levels within a polyad. This pattern has been observed[17] in isomerization spectra of the molecule HCP.

For a long time, it was widely believed that identifiable spectral patterns could not persist in systems with mul-
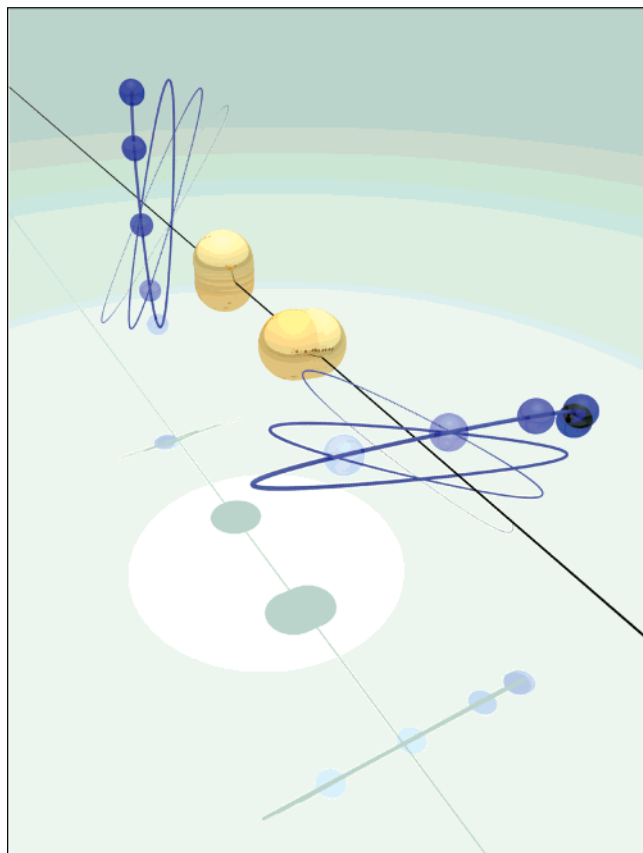
FIGURE 5. Trajectory of an orthogonal mode born in a bifurcation of the trans normal mode. The carbon–hydrogen local bends vibrate in orthogonal planes. The trajectory precesses because it has vibrational angular momentum $l > 0$.

tiple resonances and chaotic dynamics. However, tools using correlation diagrams enable identification[31,35–37] of regular patterns very much like those found in single-resonance, nonchaotic systems. Applications to spectral patterns of C_2H_2 are found in refs 35 and 36.

IV. Energy Flow and Chemical Reactivity

So far we have considered internal motions of molecules in their own right. But chemistry is largely about chemical reactions. The internal motions of molecules must surely have much to do with reactions. This is evident especially for internal molecular rearrangement or isomerization reactions, where the internal motion is all there is! But it must also be true for unimolecular decompositions and bimolecular reactions. It is desirable to connect the notions of polyad number and bifurcations to ideas used in thinking about reactions. Consider isomerization of acetylene, HCCH, to form the radical vinylidene, CCH_2. This reaction is important in several contexts, for example, combustion,[38] but detailed understanding has been elusive. The reaction coordinate for this process is illustrated in Figure 6.

A. Leaping the Barrier: A Challenge to Theory. Consider first the role of the modes born in bifurcations of the normal modes. In the isomerization of acetylene in Figure 6, the reaction coordinate must involve something very much like the local bend mode, one of the
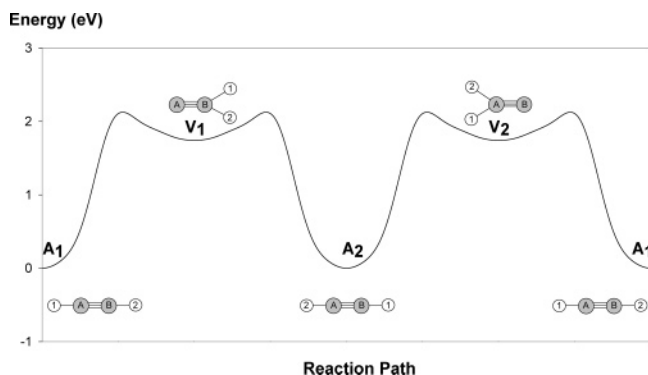

FIGURE 6. Potential for acetylene–vinylidene isomerization. To isomerize, acetylene (A) must rise above the energy of the barrier, cross over to the vinylidene side, and settle into the shallow vinylidene well (V).

modes born in bifurcations of the normal modes. It seems that there should be a general connection of the new molecular modes discovered through spectra and theories of reaction dynamics.

This works in reverse as well, with challenges from reaction dynamics for spectroscopy. Consider the steps needed for the isomerization reaction along the reaction coordinate in Figure 6. To get to the small region of stability of the vinylidene isomer, one way is for the molecule to leap across the barrier into the vinylidene isomer form, in a process promoted by chaos. Another way is to tunnel quantum mechanically through the barrier. A leading challenge is to extend the spectroscopic Hamiltonian and bifurcation analysis to systems with multiple wells and above barrier motion, to detect these intricate motions of isomerizing species. The solution of this challenge is just in the beginning stages.[39,40] If this can be accomplished, a dream will become reality: watching unimolecular rearrangement reactions with the precision tool of high-resolution, frequency-domain spectroscopy.

The challenge of connecting internal molecular motions and chemical reactions is particularly acute because there have recently been very significant theoretical advances[41,43] in understanding the real meaning of the transition state, one of the cardinal ideas of reaction dynamics. These ideas have application not only to chemical reactions but also to seemingly unrelated systems such as an atom in a magnetic field and planetary dynamics.[44]

B. Blocking and Channeling Energy Flow. If energy flow in a molecule is inhibited or enhanced, this can lead to reaction rates orders of magnitude different from those predicted by unimolecular reaction theory,[45] which supposes randomization of energy in a molecule (via intramolecular vibrational relaxation, or IVR). A polyad constant restricts energy flow from one polyad to another, as discussed in section III.B. Does the polyad constant act as a blockade to IVR? Two empirical observations make this a pressing issue.

1. Caught in a Cycle. First, consider once again the acetylene–vinylidene isomerization. In Coulomb explosion experiments,[46] the molecule is prepared in the

vinylidene form. Astonishingly, the system appears to cycle back and forth between the vinylidene and acetylene forms of Figure 6 for several microseconds. Further evidence comes from classical[47] and quantum[48] simulations of the isomerization. Above the barrier, the molecule interconverts many times between the two forms.

The puzzle is that when the system is in the acetylene part of the cycle, it does not relax out of the reaction coordinate by fast IVR into the "bath" of acetylene bend and stretch states at nearby energy. One explanation could be severe inhibition by the approximate polyad number. One way to test this idea is to extend the spectroscopic Hamiltonian with polyad-breaking terms and then perform time-dependent dynamics.

2. Trapped by a Bottleneck. A second curious instance of inhibition of IVR has been observed in molecules for which acetylene is a prototype[49] with a dramatic decrease in isomerization rate. There is reason to suspect that this too is connected with the ability of the polyad constant to act as a severe constraint on energy flow. It is straightforward via light absorption to place several quanta into C−H stretching motion. It is likely that six quanta of C−H stretch have more than enough energy to isomerize. However, this energy must first find its way into the presumptive local bend reaction coordinate. In C_2H_2, it has been demonstrated[20,21] that there are *two* polyad numbers: the usual total quantum number (eq 5) and a second, less familiar type. These are equivalent to an approximate energy transfer rule[27] that one C−H stretch quantum is redistributed as one C−C stretch and two C−H bend quanta. So, putting six quanta into C−H stretch results in just 12 quanta in the bend, only half the number needed for isomerization.

Polyad numbers therefore look like a key bottleneck to IVR. Gruebele and Bigwood have found[50] in computer simulations that it is possible to "freeze" IVR with coherent laser pulses, slowing it by 2 orders of magnitude. They ascribe the possibility of this IVR blockade to there being a severely limited set of states to which the excited "bright" state can couple in the absence of the laser control. This is exactly what one would expect with fast energy flow confined within a polyad. The polyad bottleneck therefore appears a likely key to control of IVR with intense ultrafast laser pulses.

It may be significant that extreme selectivity with respect to the two resonant modes shown in Figure 3 has been observed[51] in electron impact excitation of the Fermi resonance system CO_2.

V. Beyond Molecules in the Gas Phase

So far we have mostly considered novel motions of isolated molecules in the gas phase. We now turn to systems where investigation of bifurcation phenomena is just beginning. We first consider the natural extension to molecules in the condensed phase. Then, we explore surprising connections between the discoveries being made in molecular systems and the seemingly unrelated field of nanoscale electronic materials.

A. Molecules in the Condensed Phase. With all that has been learned about novel motions of molecules, an obvious question is whether these phenomena are important in the condensed phase. At present, little is known. The reason is that solvent interactions wash out most of the detail in frequency-domain spectra that in the gas phase allows us to "watch" the molecular dynamics. It is necessary to take the more direct, but in some ways more limited, approach of pulsed time-domain spectroscopy.

One question is the effect of the solvent bath on energy flow within a solvated molecule. Recent work points to the possible importance of bifurcations. Reid and co-workers[52] found in ultrafast laser probes of solvated ClO_2 that there is a bottleneck to vibrational energy flow within the ClO_2 molecule when it is excited to high vibrational states. Blocked by the bottleneck within the molecule, energy slowly leaks into the solvent bath. When enough energy has leaked out, the solute reaches a critical vibrational state, the bottleneck is broken, and there is a sudden onset of rapid energy flow within the molecule. Whether coincidental or not, the breaking of the bottleneck is associated with a bifurcation predicted[16] on the basis of gas-phase spectroscopy of ClO_2.

There are questions as well about the role of polyad numbers in energy transfer in condensed phase. For example, does polyad number conservation within the molecule act as a bottleneck to energy flow to the bath? At present, we can only speculate, looking ahead to future research.

B. Quantum Dots: Electronic Molecules in Artificial Atoms. An almost fantastic connection with motions of atoms in molecules appears with new developments in *quantum dots*. These systems have attracted great interest, largely because their electronic and optical properties have revolutionary potential for computational technology.

One of their most interesting features is that it is possible to add excess electrons one at a time. Hence, quantum dots are sometimes called artificial atoms. Amazingly, the motion of the electrons in artificial atoms may have many properties in common with molecules. The existence of *real* "molecular atoms" has been known for two decades.[53,54] These are highly excited helium atoms in which the motion of the electrons is much like the rotations and vibrations of a highly nonrigid linear XYX triatomic molecule. Similar molecular atoms are now being found[55] in quantum dots, with an interesting twist.

Electrons in an artificial atom see a central potential due to the semiconductor nanostructure. This is like an attractive oscillator potential, rather than the Coulomb potential exerted by the nucleus of a real atom. So, these systems may turn out to be more like real molecules than the helium molecular atoms discovered earlier.[53,54] All the basic effects of anharmonicity may be present, such as bifurcations, local and normal modes, Fermi resonances, and approximate polyad numbers. If these molecule-like effects turn out to have uses in electronic devices, this will be yet another example of a fundamental research area that quickly proves to be of practical importance in unforeseen ways.

VI. Summary and Outlook

For most of the last century, the study of internal molecular motion was concerned primarily with molecules at low energy near their equilibrium configuration. Now the focus has changed dramatically to the study of highly excited systems. Pulsed lasers have played a major role, but there is growing awareness as well of the immense potential of frequency-domain spectroscopy for probing dynamical processes. This involves measurement of very complex spectra of excited states and sophisticated theoretical analysis to unlock the dynamical information encoded in spectra. A primary tool is bifurcation analysis of the Hamiltonians used to fit experimental spectra. This gives information about the birth of new anharmonic motions born in bifurcations of the low-energy normal modes.

This is yielding remarkable information about motions of high-energy molecules, including molecules undergoing isomerization. A major challenge is to connect these new insights with reaction dynamics and theories of chemical reaction. Another challenge is to relate novel molecular motions to methods to control molecular reactions; some approaches to control[56,57] clearly rely in part on knowledge of molecular motions, including bifurcation phenomena.

Ramifications are beginning to be explored for molecules in the condensed phase. Here, the experimental tool is ultrafast time-domain laser spectroscopy, but the requisite knowledge of internal molecular dynamics is obtained from frequency-domain, gas-phase experiments.

This fruitful interplay between gas- and condensed-phase systems, probed with sophisticated frequency- and time-domain techniques, is likely to yield fascinating insights and discoveries about molecules for a long time to come. Moreover, exciting connections are forming with frontier areas of physics and materials, such as electron motion in quantum dots.

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