

Vibrational Energy Flow and Chemical Reactions

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ABSTRACT

How vibrational energy flows in molecules has recently become much better understood through the joint efforts of theory, experiment, and computation. The phenomenology of energy flow is much richer than earlier thought. We now know energy flow depends on the local structure of molecular vibrational state space. The details of the theoretically predicted transition from localized vibrations to free flow, where the molecule can act as its own heat bath, are now well-established experimentally. Energy flow is a quantum diffusive process leading to nonexponential decays, also seen in experiment. The slowness of energy flow in activated molecules causes substantial deviation from statistical Rice–Ramsperger–Kassel–Marcus (RRKM) theories for low barrier rate processes, such as isomerization. Quantitative calculations of rates in those cases are now possible.

Introduction

Ever since Arrhenius explained the dramatic temperature dependence of reaction rates using the idea of energetically activated molecules, chemists have been curious about how activation occurs. This curiosity was sharpened by Lindemann's explanation of the unimolecular reaction mechanism that invoked the metastable nature of highly activated molecules.¹ What is the origin of this metastability? One possibility was that quantum energy flow was intrinsically slow. Another explanation that finally caught on was provided by Rice, Ramsperger, and Kassel, who realized that an entropy barrier arises from the improbability of concentrating the vibrational energy in a few degrees of freedom prior to reaction.^{2,3} This effect, now enshrined in the Rice–Ramsperger–Kassel–Marcus (RRKM) theory,⁴ is undoubtedly the major contributor to metastability. RRKM theory merely needs to assume that facile energy flow occurs—the details are unimportant. Nevertheless, the stubborn curiosity of physical chemists made the attempt to understand intramolecular energy flow a recurrent theme of experimental and theoretical research into the 21st century.^{5–9} Despite the consensus on the wide applicability of RRKM theory, the possible role of restricted vibrational energy flow in modifying the rate of unimolecular reactions has resurfaced many times.^{10–14} It has also been proposed that controlling vibrational energy flow using phase coherent laser pulses may represent the best hope of guiding chemical reactions

into normally disfavored outcomes.¹⁵ Several difficulties confront those interested in intramolecular vibrational redistribution (IVR), as energy flow in isolated molecules is now called. On the experimental side, clever techniques are needed to access the necessary time and energy scales with sufficient resolution and dynamic range.^{16–18} Composite processes may take very long, while the elementary events of vibrational energy flow occur on the subpicosecond time scale.

Theorists have faced equal challenges. While time and energy scales present no special problems to them, the high dimensionality of state space discourages direct computational assaults on IVR, except by individuals with especially heroic dispositions.^{19–22} Thus theorists are tempted to resort to classical mechanical approximations.^{8,23} The classical approximation is justified for very small molecules, the vibrational modes of which are likely to have a high degree of excitation if the molecule has sufficient energy to react. This is not the case for larger molecules, the state spaces of which are so huge that they can harbor enough overall energy to react while the average energy per mode remains small. Translating the classical results to the quantum regime also requires the theorist to confront “quantum chaos”—a problem rife with conceptual puzzles.²⁴ A useful and popular approach unties the Gordian knot by not lamenting but rather exploiting the large phase space. Freed, Rice, Jortner, and others have argued that the density of levels in the state space allows it to be treated as a continuum, allowing the use of the Golden Rule to estimate how fast energy flows in a molecule.^{5,6} This approach provides the language most used to describe IVR, although it has its limitations.⁹ The key difficulty pointed out many times is that measured rates of IVR do not scale with the total density of states,^{25–30} as the direct application of the Golden Rule approach would imply.⁵ Of course the Golden Rule can be rescued by noticing that the “bath states” into which energy flows are themselves highly mixed objects the coupling strength of which decreases as the global density grows. Such an interpretation, although strictly correct, verges on tautology.^{15,31} Despite these difficulties, in the past decade renewed progress has been made toward understanding IVR. The purpose of this Account is to summarize the main ideas and results of one approach, the local random matrix theory (LRMT) of energy flow in molecules,^{25,32–34} comparing it with experiments^{35–39} and large quantum dynamical computations.^{20–22,34,40–42} LRMT provides a simple way of visualizing quantum energy flow in molecules. It has suggested several unsuspected aspects of energy flow now confirmed in the laboratory. When supplemented with appropriate scaling rules for intramolecular vibrational couplings,^{43,44} the theory produces at least semiquantitative predictions of absolute IVR rates.

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In several cases, LRMT calculations suggest that restrictions of energy flow indeed modify unimolecular reaction rates.⁴⁵

Visualizing Energy Flow in Vibrational Quantum Number Space

The successes of RRKM theory suggest that energy flows readily within a molecule, yet our spectroscopic experience suggests there are privileged quantum basis states that simplify looking at the quantum dynamics of a molecule. Low-resolution infrared spectroscopy identifies vibrational energy as belonging to functional groups. Molecules not too high in symmetry—the vast majority—have many localized normal modes.⁴³ The harmonic normal modes of a weakly excited organic molecule have “almost good” quantum numbers in the language of the Bohr–Sommerfeld theory.⁴⁶ Ultimately, the harmonic picture of the forces is a good approximation because nuclei are much heavier than electrons, so the low-energy wave functions for nuclear motion can be more precisely localized than the electron clouds.^{43,47,48} This harmonic picture breaks down for weak bonding. Yet for ordinary covalently bonded molecules, normal or local modes, supplemented by torsional modes for conformational isomerizations, represent slowly varying degrees of freedom and can be used to label privileged quantum mechanical states.⁴⁴ For rate theory, a pure harmonic system represents a molecule the kinetics of which would be described by Slater’s theory,⁴⁹ in which one waits for the classical motions of the modes to be in phase with each other for a bond to break, much like a grand conjunction of the planets in Ptolemaic astrology. The anharmonicity of bonds, however, clearly reveals limits to the harmonic character of molecules. Even weak anharmonicity allows energy to flow slowly between modes—even the privileged states are not eigenstates.

Classical mechanics teaches us that weak nonlinear couplings are most effective in resonance, as when a child pumps his or her legs in synchrony with the period of a swing. Likewise, certain paths of motion through the quantum state space represented in a normal mode basis are more facile than others. Such paths follow local resonances, in which a few quanta in one mode are transformed into quanta of other modes such that the approximate total mode energy is nearly conserved.

A schematic view of the state space of a molecule in the privileged basis is shown in Figure 1. States are labeled by the number of quanta in each vibrational mode. IVR is most rapid to states that differ only by a few quanta in a few modes because the direct anharmonic couplings get weaker when more quanta are transferred through higher order nonlinearities. The zeroth-order energy of each privileged state is the sum of the energies in each mode. If the modes were exactly harmonic this would be $\sum_i \hbar \omega_i (n_i + 1/2)$, but the modes have a self-nonlinearity that changes their frequencies slightly with excitation.⁵⁰ The approximate energies are thus $\sum_i \hbar \omega_i (n_i + 1/2) - \sum_{i,j \neq i} \hbar \omega_{ij} (n_i + 1/2)(n_j + 1/2)$. Because modes go in and out of

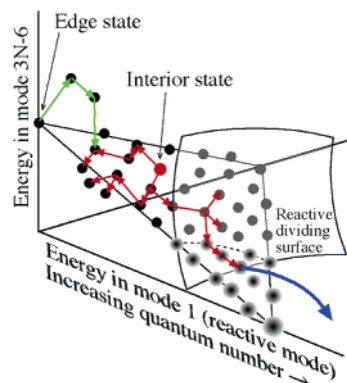


FIGURE 1. Three of the $3N - 6$ dimensions of the molecular quantum state space, including “fuzzy” states with a finite lifetime due to chemical reaction. A typical state on the energy shell (red circle), because it lies in the interior, has many choices of where to move next, while nearly conserving energy. These paths are shown in red. Overtones correspond to states near the edge of the energy shell. Such edge states can only reach isoenergetic states by first tunneling off the energy shell; a tunneling path is shown in green. When energy is localized in a reactive mode, the molecule can directly react with a rate indicated by the blue arrow. When the IVR processes (red and green arrows) are slower than the reactive process (blue arrow), RRKM theory must be modified.

resonance as a function of energy, the resulting paths of easy quantum motion can meander quite wildly (unlike the child on a swing who constantly adjusts the period of pumping, always staying in resonance).

The local nature of the energy flow in this basis imposes an interesting structure on the way energy moves around. Most of the states have excitations in many modes—these are called interior states.^{34,39} Interior states have the possibility of a rich set of possible direct nonlinear connections, allowing the energy to flow in many ways. If the molecule is sufficiently excited, many of these possible energy flow paths can be realized. Motion in the interior can be thought of as sequential hopping to nearby states, limited to states differing by changes of only a few quantum numbers in a few modes.³² The local ways of hopping can be quantified through a local density of states (or set of local state densities, if hops of various lengths are involved), which is a function of the (unperturbed) energy change, ΔE . This local density $\rho_{loc}(\Delta E)$ is crucial in determining the rate and manner of energy flow in the interior states. It measures the likelihood that a resonant local transfer can occur.

At the periphery of state space, a qualitatively different form of energy flow occurs. The so-called “edge states” have all (or nearly all) their energy concentrated in a single mode.³⁴ The direct paths for energy flow from edge states are limited. Instead these states decay by a “dynamical tunneling” process in which intermediate states are never populated but facilitate hopping to energy states that are nearly resonant and that are found in the interior with very different quantum numbers.^{30,51} This dynamical tunneling resembles superexchange electron transfer in large biomolecules.^{52,53} In small molecules, it is relevant to notice that if one local energy transfer in a particular direction can occur resonantly, a further hop in the same

direction is likely to be also resonant, until anharmonicity or the finite size of the quantum state space finally terminates the chain. This leads to “polyad” structure⁵⁴ in the state space.

A model that captures much of the organization of state space is the local random matrix model introduced by Logan and Wolynes.²⁵ The model Hamiltonian has the standard form of normal mode harmonic oscillators coupled by anharmonic couplings. The locality of quantum motion encoded by this Hamiltonian leads to a variety of interesting phenomena that we will discuss in the next section. These include a transition from facile energy flow throughout the phase space at high energies to strictly localized energy flow at low excitation. Generically the energy flow among interior states is diffusive.

The anharmonically coupled Hamiltonian can be made into a quantitatively predictive model to treat energy flow in large classes of molecules.^{21,40,44} The unperturbed frequencies are accessible from low-resolution spectroscopy or can be found via normal-mode analysis from simple energy functions or quantum chemical calculations. Knowledge of the frequencies is sufficient to characterize the local density of states. Finding the nonlinear couplings would seem to require high-quality quantum chemical calculations, but the main features of energy flow only depend on their statistical properties—typical size, variation, etc. The couplings can be modeled as random quantities (hence the “random” of local random matrix theory) subject to certain scaling laws and correlations dependent on the bonding properties of the molecule.^{34,42–44,55} Unperturbed modes often mix stretching and bending of many parts of the molecule, so the magnitude of the nonlinearities depends on the bonding pattern of the molecule. A simple implementation of the scaling, suitable for semiquantitative IVR calculations, is given in refs 26 and 34.

The Transition to Energy Flow and Diffusion in State Space

A dramatic prediction of LRMT is the transition from localized quantum states to highly mixed quantum states when the local density of states gets large enough. A computational simulation is shown in Figure 2A.²¹ The transition was inferred by Logan and Wolynes, using techniques borrowed from the theory of Anderson localization of electron motion in disordered conductors.²⁵ It was predicted to occur when $T(E) = 2\pi(\sum_{\Delta n} V_{\Delta n} \rho_{\Delta n})^2$ exceeds 1. $V_{\Delta n}$ is the average coupling strength involving states Δn quanta away from the state under consideration; $\rho_{\Delta n}$ is the corresponding local density of states. A similar transition criterion was obtained by Kuzmin and Stuchebukhov⁵⁶ using anharmonic perturbation theory and by Bigwood and Gruebele using a pairwise interaction approximation.³⁴ All these criteria increase with energy and molecular complexity.

The trend toward ergodic delocalized behavior with increasing molecular complexity has long been expected. The clearest evidence for a transition came from the

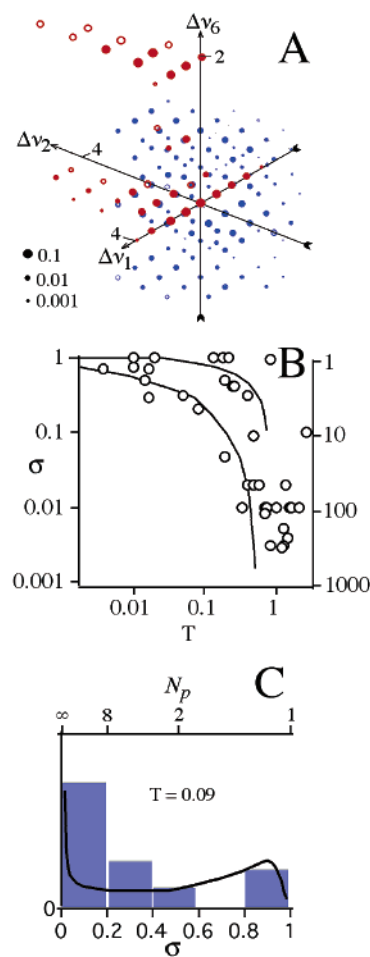


FIGURE 2. (A) Two thiophosgene (SCCl_2) eigenstates near 8000 cm^{-1} with nominal normal mode assignments $|700\ 000\rangle$ (red, edge state with fractal dimension 1.2) and $|233\ 222\rangle$ (blue, interior state with fractal dimension 3.0). A projection onto the three most active normal modes is shown. The axes label basis states by how they differ from the assigned state in the ν_1 , ν_2 , and ν_6 modes. For example, a point at $(-2,1,3)$ for the red state corresponds to the $(5,1,0,0,3)$ harmonic oscillator basis state. The size of circles is proportional to the magnitude of the amplitudes on a log scale, and the hollow circles correspond to negative amplitudes.⁸⁷ (B) Number of participating states N_p and dilution factors $\sigma = 1/N_p$ obtained by McDonald and co-workers by IR fluorescence⁵⁷ are plotted against the criterion $T(E)$ of LRMT. Numerical simulations using the local random matrix model from ref 42, indicated by the region between the two black curves, agree with the experimental variation of σ as a function of $T(E)$. (C) The bimodal probability distribution of the dilution factors from McDonald's data is consistent with the local random matrix theory (black curve) from ref 33.

beautiful survey of infrared fluorescence in organic molecules undertaken by McDonald in the 1980s.^{57,58} An excited CH bond in a set of 20 organic molecules ranging in size from methane to oxirane was created using infrared light. The promptly reemitted IR photons were gathered, and the vibrational fluorescence yield was measured. This yield is determined by the number of states the excitation can flow to before emission occurs. The yield is then a measure of the degree of localization. Models based on the total density of states predict the trend toward delocalization with increasing size, but when the number

of states participating in IVR is plotted as a function of total density of states, at best a ragged transition is seen. When the same data are plotted versus T (local density of states), the transition now is seen to occur sharply over a very small range of T near 1 (Figure 2B) as a continuous network of states is established for energy flow.

The CH stretching overtones of two organic molecules, pyrrole and triazine, provide another clear example of the localization threshold.²² Tuning the anharmonic coupling in computer simulations shows that both molecules lie just at the threshold for IVR, which occurs by dynamical tunneling as expected for edge states. Lehmann showed that several nearly isoenergetic states of the molecule propyne have different IVR properties, depending on how close they are to the edge of state space, and such behavior has been analyzed in detail for edge and interior states of SCCl_2 .^{21,35,39} The total density of states in these cases is nearly identical, but the local densities of states differ. Another prediction of the LRMT concerns the probability distribution of the number of “participating states”—the number of states coupled strongly enough to a privileged state to “light up” in the spectrum. The simple Golden Rule predicts that the number of participating states smoothly increases from 1 as the IVR threshold is passed. LRMT theory predicts that the distribution is bimodal near the threshold: either a state is very prone to IVR, or it is not; intermediate cases are comparatively rare.⁵⁹ This is confirmed by the McDonald data (Figure 2C)³¹ and within a single molecule by recent stimulated emission pumping experiments on SCCl_2 .⁶⁰

A third striking characteristic of quantum energy flow predicted by LRMT is its gradual nature—the energy does not disappear into a morass of states immediately. For interior states, the flow to nearby states proceeds first, and the wave function spreads until a significant part of the state space is filled. Figure 3A shows how probability spreads when an interior state of SCCl_2 is initially excited. Using the analogy to Anderson localization in disordered solids, Schofield and Wolynes suggested this spreading would follow a diffusion law.³² A power-law decay of the probability of being found in the initial state as a function of time is predicted. The experimental IVR decay for an initial state of SCCl_2 is shown in Figure 3B. While the initial decay is exponential, a much slower power-law decay quickly ensues. Quantum dynamics simulations with a six-dimensional anharmonic vibrational Hamiltonian also agree with this result.²¹

Power-law decays are found in other systems. Time-resolved fluorescence monitoring IVR in fluorene and cyclohexylaniline revealed power laws.⁶¹ Multiscale dynamics are observed in methanol (Figure 4) and in the CH overtones of benzene.^{29,62,63} Two time scales have been observed by Pate for IVR in small organic molecules (personal communication) and by Crim in CH_2I_2 .⁶⁴ Over short time windows, multiscale decays may appear as double-exponentials: as shown in Figure 2, there are “quantum beats” superimposed on the decay. The beats occur because state space, albeit large, is finite and the couplings among states are not entirely uniform.

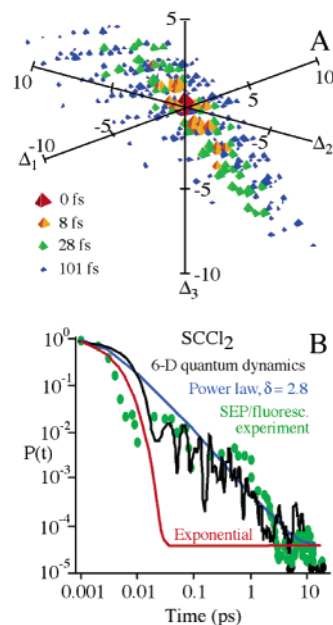


FIGURE 3. (A) Time evolution of an interior quantum state of thiophosgene well above the IVR threshold, at 8000 cm^{-1} ;²¹ only three of the six dimensions of state space are shown (cf caption to Figure 2). (B) Experimental IVR decay (in green) corresponding to interior states of thiophosgene is compared with a six-dimensional quantum dynamics simulation using a full Watson vibrational Hamiltonian (in blue) and the predictions from global (in red) and local random matrix theory (in blue) (both averaged over quantum beats evident in the experiment and full 6-D quantum calculation).

Energy Flow and Non-RRKM Dynamics

The deeper understanding of IVR provided by LRMT gives us insight into when RRKM theory will be valid and how to correct it. For RRKM to be valid, the molecule must be excited above its energy flow threshold. Below the threshold, one sees resonances of many different widths in experiments due to the coexistence at the same energy of molecules with wave functions initially near the transition state region and others far from it.⁶⁵ The dramatic breakdown of RRKM from complete nonergodicity has been the target of many studies. A particularly interesting result is the observation by Pate of medium-sized organic molecules with quantum states spanning a superposition of different isomers—organic molecule Schrödinger cats.⁶⁶ The situation of the energy flow threshold being higher than the reaction barrier however seems rare.

Even when energy flow occurs, the quantitative validity of RRKM theory is still not guaranteed. If energy flow is slower than the reaction coordinate vibration itself, the simple RRKM rate will be in error because states depleted by reaction must be refilled via IVR. Diffusion through state space to the activated configurations becomes rate-limiting and shows up in the pressure dependence of the rate constants because state space diffusion is facilitated by collisions. Because collisions must compete with an internal flow rate, rather than the much longer metastable decay of activated molecules, slow energy flow leads to changes of the rate at pressures considerably higher than would be expected from strict RRKM theory. A beautiful

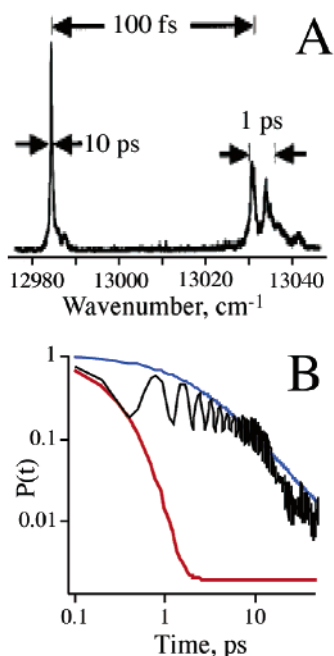


FIGURE 4. (A) Spectrum of a mixed CH/OH stretching vibrational state of methanol from ref 88. Three IVR time scales are shown, and time scales slower than 100 ps exist but are not resolved in these spectra. (B) Survival probability computed from the spectrum sampled at 188 points (black) is shown. A single exponential fit can only capture one time scale (earliest shown in red), while the simple power-law fit shown in blue captures the envelope of the full dynamics (but not the quantum beats).

example of this way of diagnosing slow IVR was provided by the pressure-dependent NMR studies of the boat/chair isomerization of cyclohexane carried out by Jonas.⁶⁷ The important role of restricted energy flow in this case was pointed out first using classical calculations.⁶⁸ A much-studied example of non-RRKM behavior is the photoisomerization of stilbene.¹² This process has been extensively investigated because it is similar to the photoisomerization of retinal that initiates the events of vision⁶⁹ and that mediates photosynthesis in some bacteria.⁷⁰ The biological isomerization process is extraordinarily fast (subpicosecond), but stilbene isomerizes more slowly, reflecting an entropy barrier as predicted by RRKM theory. In the first analyses, detailed RRKM modeling of the rates in the isolated stilbene molecule in beams did not reproduce the experimental data.^{71,72} The possibility of corrections arising from nonadiabatic effects from a curve crossing diminishing the rate was raised. Nordholm suggested that restricted energy flow modifies the rate.^{73,74} The validity of this explanation is buttressed by experiments from the Hochstrasser and Fleming groups, showing a pressure enhancement of the rate up to 100 atm.^{12,75} Although stilbene is fairly large, LRMT can be applied to estimate the IVR threshold, energy flow rates, and rate changes for photoexcited stilbene. Using the same potential surface as the original RRKM calculations, Leitner and Wolynes showed that the energy flow threshold is near 1200 cm^{-1} ,⁴⁵ very close to the barrier used in the early RRKM calculations. Zewail has directly measured energy flow via overtone excitation at these energies. His results show the energy

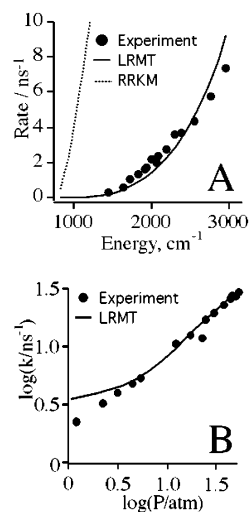


FIGURE 5. (A) Experimental isomerization rate for trans-stilbene,^{71,76} along with RRKM predictions and RRKM corrected for slow IVR from ref 79. (B) Plot of log of the isomerization rate vs log of the pressure is shown: the circles are experimental results; the solid line is the LRMT. At the lower pressures, the populations decay nonexponentially, reflecting lack of equilibration in the isolated molecule below the IVR threshold or laser cooling effects.^{65,89}

flow to be slow and agree quite well with LRMT.⁷⁶ Finally, the dynamical corrections from slow energy flow agree well with both isolated molecule values and pressure dependences.

The analysis of stilbene isomerization as an IVR-modulated reaction has met with some controversy. Adjustments of the early potential surface were made, allowing RRKM to fit the isolated molecule rates.⁷⁷ For the adjusted surface, new mechanisms have to be invoked to explain the pressure dependence. Gershinsky and Pollak suggested that stilbene is cooled by the laser owing to mode softening upon photoexcitation.⁷⁸ Schroeder and Troe invoked specific van der Waals clustering at high pressure to modify the reaction barrier and give a pressure dependence in the right range.⁷⁷ Martinez's recent high-level quantum chemical calculations resolve the issue.⁷⁹ These calculations show little mode softening in the excited state, so laser cooling contributes mainly for very slow IVR. When LRMT is applied to the new surface, the energy flow thresholds and rates agree with the earlier calculations. In addition, without adjustable constants, the isolated molecule results are predicted quite well (Figure 5A,B). The pressure effects predicted using RRKM theory corrected by LRMT energy flow rates agree quantitatively with Fleming's experiments in Figure 5B. If the zero-point corrected barrier for reaction and the IVR threshold are close, this may explain the nonexponential isomerization kinetics seen at low buffer gas densities in bulb experiments, although laser cooling effects can also contribute.⁷⁸ The model also quantitatively explains the "flipped" rates for d_2 - and d_{10} -deuterated stilbenes, which are caused by zero-point energy effects.

Stilbene is not an isolated exception to the RRKM theory.^{12–14} Low-barrier processes such as isomerization occur when the local density of states is still rather low. Leitner has shown that isomerizations in fluoroethanol

and allyl fluoride, studied recently by multiresonance ultrahigh resolution spectroscopy by Pate, are also influenced greatly by slow isomerization rates.^{38,80} Ironically, both early explanations of metastable activated molecules can apply.

Outlook for Quantum Energy Flow and Chemical Reactivity

Molecular energy flow has become a topic with rich experimental and theoretical underpinnings. The organized exploration of quantum energy flow now enters a new phase. More tunable systems that explore the transition to energy flow need to be developed to test all details of the theory. We need experiments that allow any part of molecular state space to be probed, not just those parts easily accessible with one or two laser pulses, to distinguish the dynamics in the interior of state space from the dynamical tunneling expected for edge states.

The role of energy flow in reaction kinetics, the problem that motivated the field, remains somewhat controversial. Arguments about the accuracy of input parameters still cloud our understanding of gas-phase observations.⁷⁷ The quantum energy flow problem for reactions in condensed phases has been broached,⁸¹ but little has yet been tested in the laboratory.⁷² Direct experimental probes of energy flow in reacting molecules would be most welcome.

The emerging local picture of energy flow gives cause for much optimism about another Holy Grail of physical chemistry—laser control of reactivity.^{82,83} Because quantum diffusion leads to a very slow spreading through state space, relatively simple laser pulses can control this spread.⁸⁴ Thus, the dynamics of a large organic molecule with a huge state space can be made to look like that of a small polyatomic, where quantum control has already been achieved. Global densities of states (i.e., thermodynamics) would no longer be the main factor determining the fate of an excited molecule.

The molecular energy flow problem is an example of a deep issue of concern in many parts of physical science—the transition from orderly to disorderly motion in a many body system. We can expect the ideas from this field to have an impact in other areas including quantum dots⁸⁵ and quantum computation.⁸⁶

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