State- and Bond-Selected Unimolecular Reactions

F. FLEMING CRIM

Unimolecular reactions are crucial chemical events that have been the focus of increasingly sophisticated investigation in the past decade. Unraveling their details is one fundamental goal of experimental and theoretical studies of chemical dynamics. New techniques are revealing the possibilities, and challenges, of eigenstate- and bond-specific unimolecular reactions. These experiments clearly demonstrate the intimate connection between intramolecular processes and unimolecular reaction dynamics and suggest means of exploiting molecular properties to study and control reactions at the level of individual quantum states.

THE DECOMPOSITION OR ISOMERIZATION OF AN ISOLATED, energized molecule is an elementary chemical event that is central to many diverse phenomena. These unimolecular processes are ubiquitous in chemistry and play a central role in the atmosphere, combustion mixtures, plasmas, and a host of other environments. Because a chemical transformation requires a change in the equilibrium positions of the nuclei, many reactions involve vibrationally excited molecules. However, in most thermal reactions only a few molecules that have substantial vibrational energy react. Since these highly vibrationally excited molecules control the chemistry, they are fundamentally important and, in addition, are essential to schemes that might selectively influence the course of chemical reactions. The notion of exciting a particular motion in a molecule in order to control the breaking of a chemical bond is very appealing, but its implementation requires a sophisticated understanding of vibrationally energized molecules and unimolecular reactions.

Statistical theories of unimolecular reaction, which are predicated on the notion that energy flows freely among the degrees of freedom of an energized molecule, have been enormously successful in describing thermal reactions (*1*). A primary motivation for detailed experimental studies of unimolecular reaction dynamics is testing the limits of these theoretical descriptions and, potentially, the underlying assumption of rapid energy flow on the time scale of the reaction. The most detailed theoretical description of a unimolecular reaction predicts the rate of formation of products in individual quantum states from reactant molecules in a single quantum state, and the corresponding experimental goal is the observation of such fully state-resolved unimolecular reactions. The central question is the sensitivity of the reaction to the identity of the reacting state.

The possible control of the pathway of a reaction is closely related to state-resolved studies of unimolecular reactions. For molecules that are indifferent to the details of their initial excitation, one cannot hope to use some special preparation to control the identity or appearance rate of the products, but such a hope is reasonable for a molecule that "remembers" its preparation. The fundamental and practical consequences of selective chemistry have animated considerable work during the past decade, and these efforts are revealing the challenge of selective chemistry in general and delineating the requirements for its success in particular cases (*2*).

Vibrationally Excited Molecules and Intramolecular Dynamics

Performing "molecular surgery" by exciting a particular motion in a molecule requires the proper "forceps," and, because its interaction with molecules is highly specific, electromagnetic radiation is a likely implement. Lasers and nonlinear optical techniques are able to prepare highly energized molecules with the specificity of molecular spectroscopy, but initiating unimolecular reactions in stable molecules requires chemically significant energies, typically 100 to 300 kJ/mol. Such highly vibrationally excited molecules are often difficult, and in some cases perhaps impossible (*3*), to characterize by conventional spectroscopy. For example, the usual description of vibrations as normal modes (*4*), which works well for molecules at low levels of vibrational excitation, breaks down for highly excited stretching motions involving hydrogen atoms, and a different approximation, the local mode model (*5*), is more useful. The first issue in using laser excitation to prepare highly vibrationally excited molecules is the description of the excited molecule.

A bound molecular eigenstate is a stationary state that, once prepared, does not evolve in time. Transitions to these excited eigenstates from lower states are the features observed in a fully resolved spectrum of a molecule. (The linewidth of the laser, the natural widths of the transitions, and their separation determine if such a spectrum is observable in a particular case.) It is convenient to think about the behavior of a highly vibrationally excited molecule in terms of motions, such as individual bond vibrations, about which we have chemical intuition even though they do not correspond to the eigenstates of the molecule. Simple combinations of bond vibrations often correspond fairly closely to the molecular eigenstates, and they nearly always provide a useful physical picture. Figure 1 illustrates the connection between the molecular eigenstates and these zero-order states. In this picture (*6*), one zero-order state $|s\rangle$ is the "bright" state that interacts with the electromagnetic radiation, and the other zero-order states in the molecule $\{|\ell\rangle\}$ are the "dark" states that do not absorb light. The molecular eigenstates

---

The author is Helfaer Professor of Chemistry in the Department of Chemistry at the University of Wisconsin–Madison, Madison, WI 53706.

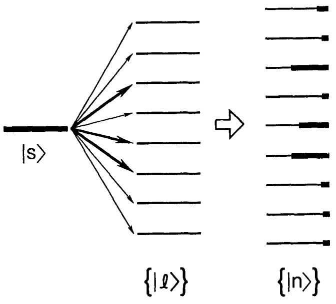

Fig. 1. Zero-order states and molecular eigenstates ordered by energy. The "bright" zero-order state |s> has a nonzero transition probability from the lower ground state, which is not shown in the figure. The "dark" zero-order states {|ℓ>} have no transition probability. The interaction of the bright state and the dark states produces the molecular eigenstates {|n>}, which share the character of the bright zero-order state to an extent determined by the interactions of the zero-order states. The amount of bright state mixed into each molecular eigenstate, as indicated by the heavy lines, determines the strength of the transition to that eigenstate from the ground state.

{|n>} are linear combinations of these zero-order states,

$$|n> = C_s^{n}|s> + \Sigma C_\ell^{n}|\ell>$$

where C_s^n and C_ℓ^n are expansion coefficients. Because each eigenstate shares some of the character of the bright zero-order state, there is a transition to each of the excited eigenstates from the ground state. The strength of the transition and, hence, the absorption intensity in the spectrum depends on the amount of the bright zero-order state contained in the eigenstate. For example, in the vibrational overtone spectra discussed below, the bright zero-order state |s> might be a pure stretching vibration, such as four quanta of O–H bond stretching, and the dark zero-order states {|ℓ>} might consist of bends and other stretching vibrations.

This picture is useful for describing intramolecular dynamics as well as spectroscopy. Because the bright zero-order state is not an eigenstate, it would change with time if initially excited. Thus, if such a nonstationary state were prepared, its excitation energy would flow among the other states with a time dependence determined by the energies of the zero-order states and the strength of their interactions (*6*). This is intramolecular energy flow from a particular vibration of a molecule to other vibrations that is part of statistical theories of unimolecular reactions. It has the classical analogue of "plucking" one bond in a molecule and observing the flow of energy into other vibrations. In statistical theories, one vibration is the reaction coordinate, and reaction occurs when sufficient energy resides in that degree of freedom. The eigenstates shown in Fig. 1 are for a small molecule, in which they are well separated compared to their widths, but in a large molecule they may be so closely spaced that they overlap within their natural widths. In this case, preparation of an eigenstate is inherently impossible, and laser excitation will always produce a nonstationary state. This situation ultimately leads to a statistical limit in the excitation of large molecules, as first described for radiationless transitions (*6*).

The assumption of rapid energy flow in a vibrationally excited molecule permits the calculation of the rate of reaction with microcanonical transition-state theory (*1, 7*). The probability of sufficient energy to overcome the barrier to reaction residing in the reaction coordinate determines the rate of reaction in this theory. Calculation of the probability involves enumeration of the quantum states in the transition state that can form products. This counting of the number of open channels requires the geometry and vibrational frequencies of the transition state, quantities that must come from ab initio theory or from inspired (and, perhaps, educated) guesses. The details of the state counting depend on the nature of the transition state for potential energy surfaces without barriers. One limiting approach is to equate the number of open channels to all of the accessible quantum states of the products. Because this scheme amounts to assessing the fraction of the phase space the products occupy, it is called phase-space theory (PST) (*8*). The tendency of PST to overestimate rate constants has motivated several modifications, most notably the statistical adiabatic channel model (SACM) (*9*) and a modified–Rica-Ramsperger-Kassel-Marcus (RRKM) theory (*10*) for dealing with systems having poorly defined transition states.

Microcanonical transition state theory predicts the rate of a reaction at a specified total energy and angular momentum but does not provide any information on the quantum states in which the products are born. Because the most detailed experiments provide the distribution of products among their quantum states, comparing these with the predictions of statistical theory is a crucial test. Prediction of the relative populations of the product states is inherent in PST, since it enumerates them in determining the number of open channels. For statistical theories in which the transition state differs from the asymptotic states of the products, one must follow the states as they evolve from the transition state to products. The SACM (*9*) and the modified-RRKM theory (*10*) as well as a modified version of PST, the separated statistical ensemble (SSE) theory (*11*), add the requisite machinery to do this. These approaches are all statistical but differ in assumptions about the evolution of the states as the interaction potential changes during the fragment separation. The test of any statistical model of unimolecular reactions is the prediction of both the rate and the product state distribution, that is, the detailed rate constant for reaction into each product state. Statistical models predict rate constants and product state distributions that depend only on the total energy and angular momentum. An ideal eigenstate-resolved experiment tests them by determining the state-to-state rate constant for different initial states of similar energy and angular momentum.

Signatures of State-Specific Reaction Dynamics

Evidence of state-specific reactions potentially appears in both rate and product state population measurements. In the first case, one can infer rates from spectra or determine them directly by

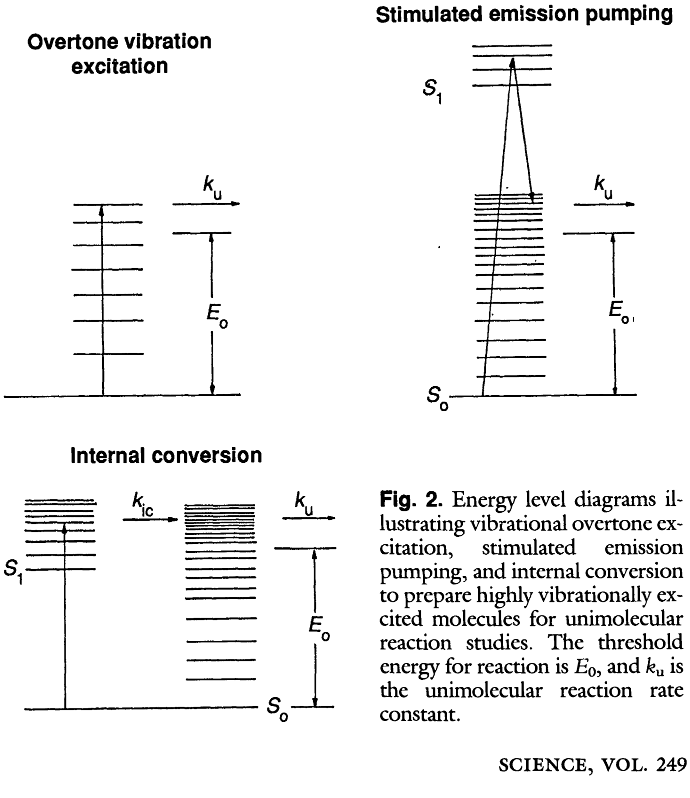

Fig. 2. Energy level diagrams illustrating vibrational overtone excitation, stimulated emission pumping, and internal conversion to prepare highly vibrationally excited molecules for unimolecular reaction studies. The threshold energy for reaction is E_0, and k_u is the unimolecular reaction rate constant.

monitoring the appearance of reaction products. Homogeneous linewidths in well-resolved excitation spectra of reactive molecules can reflect unimolecular reaction rates. If an eigenstate is coupled to the dissociative continuum, its spectral width reflects the strength of that coupling or, equivalently, the rate of the dissociation reaction. Such an inference rests on the assumption that the dissociation is the dominant source of homogeneous broadening. Measurement of the appearance rate of products requires no such assumption. In analogy with classical kinetics techniques, observation of the growth of products with time yields the first-order decomposition rate directly. The signature of an eigenstate-specific reaction in these two types of measurements is a difference in the linewidth or the product appearance rate for excitation of different quantum states that have similar energies and angular momenta. The distribution of products among their quantum states can signal state-specific reaction as well. The production of different product state population distributions in the decomposition of two initial states having similar energies and angular momenta reflects state-specific chemistry.

Clear signatures of eigenstate-specific unimolecular decomposition appear in both the spectra (*12*) and time evolution of products (*13*) for weakly bound species. The state specificity in these van der Waals molecules, in which weak forces bind two stable species by energies as large as tens of kilojoules per mole, points to the role of intramolecular couplings in ordaining statistical behavior. Because the van der Waals bond is weak, it is possible to deposit more energy than required to break it without carrying the molecule to the high energies where state mixing is extensive. In addition, the very disparate frequencies of the reaction coordinate and the initially excited vibration reduce the intramolecular coupling. The dynamics of these species are intriguing, and they are a particularly informative limiting case. What about similar phenomena in strongly bound systems? Although the target molecules are easier to obtain, performing an eigenstate-resolved experiment is a substantial challenge. The bonds are stronger, the intramolecular couplings are larger, and the number of states is greater. Nonetheless, several experimental approaches have produced state-resolved data on the unimolecular decomposition of chemically bound species.

Observations of State-Resolved Unimolecular Reactions

Preparing single quantum states of highly vibrationally excited molecules is the first experimental challenge in studying state-resolved unimolecular reactions. Three preparation schemes have provided the most highly resolved data: (i) direct excitation of overtone vibrations (*14, 15*), (ii) stimulated emission pumping (*16*), and (iii) state-specific internal conversion (*17*). Figure 2 illustrates each of these schematically. Vibrational overtone excitation creates highly vibrationally excited molecules by laser excitation of a weak transition that derives its strength from the excitation of a stretching vibration involving a light atom. In state-mixing language, the bright zero-order state corresponds to a pure stretching vibration such as an O–H, N–H, or C–H stretch. The molecular eigenstate excited in a fully resolved experiment is a mixture of this and other zero-order states. Stimulated emission pumping is a two-photon process in which one photon produces an electronically excited state and a second photon stimulates emission that leaves the molecule in a highly vibrationally excited state. The Franck-Condon overlap of the wave function of the excited rovibronic state with that of the vibrationally excited molecule in the ground electronic state determines the production efficiency of a particular excited state. Thus, the bright zero-order state that controls the initial state preparation in stimulated emission pumping is the one having a good Franck-Condon factor with the electronically excited state. State-specific internal conversion uses the coupling between a rovibrational state in an electronically excited state and a highly excited rovibrational state in the ground electronic state to create a highly vibrationally excited, electronic ground state molecule.

Vibrational overtone excitation. Unimolecular decomposition of hydrogen peroxide, HOOH, initiated by excitation of the fifth overtone of the O–H stretching vibration, $6\nu_{OH}$, provides examples of both linewidth (*18–21*) and product state distribution measurements (*22*). Laser excitation of the fifth O–H stretching overtone vibration adds 227 kJ/mol of energy to the molecule, which is enough to overcome the 207 kJ/mol dissociation threshold for the O–O bond,

$$\mathrm{HOOH}(6\nu_{\mathrm{OH}}) \rightarrow \mathrm{OH}(\nu,J) + \mathrm{OH}(\nu',J')$$

where ν and J are vibrational and rotational quantum numbers, respectively. Detecting individual quantum states of the fragments by laser-induced fluorescence (LIF) (*23*) provides the distribution of the products among their quantum states. Monitoring a single rovibrational state of the OH product while varying the wavelength of the vibrational overtone excitation laser produces the absorption spectrum of those molecules that react to form a fragment in the probed quantum state. Even for a molecule as simple as HOOH, the excitation spectrum of a room-temperature sample is quite complex because of the large number of thermally excited rotations and low-frequency vibrations from which transitions occur. Cooling the molecule in a supersonic expansion removes most of this inhomogeneous structure and reduces the spectrum to a relatively few transitions (*24*).

The upper trace in Fig. 3 is a portion of the vibrational overtone excitation spectrum of $\mathrm{HOOH}(6\nu_{\mathrm{OH}})$ in a supersonic expansion, and the lower curve is an asymmetric top simulation for an 8 K sample. The feature at 18,942.4 cm^{-1} arises from the two rotational transitions indicated by the vertical lines and has a total width of about 1.5 cm^{-1}. Since the laser resolution is 0.05 cm^{-1}, the width comes from homogeneous broadening of the individual transitions. In the simulation, which reproduces the spectrum rather well, a homogeneous width of $\Delta\tilde{\nu} = 1.0\ \mathrm{cm}^{-1}$ is used for each transition. The corresponding relaxation time is ~5 ps or a rate constant of $k = 2\pi c\Delta/\tilde{\nu} = 2 \times 10^{-11}\ \mathrm{s}^{-1}$. If all of the homogeneous width arises from unimolecular decomposition, this is the unimolecular reaction rate constant, and otherwise it it is an upper limit. Rizzo and co-workers (*21*) have created an even more versatile approach to producing state-selected highly vibrationally excited molecules in which they use the resolution of double resonance spectroscopy to select a single rotational state. Their vibrational overtone excitation is a two-step process in which infrared laser light first excites a rotational transition in the fundamental vibrational band, and then visible light excites the molecule from this state to a high vibrational overtone state. This approach permits the preparation of a variety of fully characterized rovibrational states for unimolecular decomposition studies. They used this scheme to prepare $\mathrm{HOOH}(6\nu_{\mathrm{OH}})$ and measure a linewidth of 0.8 cm^{-1}, in agreement with the results of the measurement in a supersonic expansion.

The rate constant inferred from these experiments is consistent with calculations that use the statistical adiabatic channel model (*25*) and with trajectory calculations (*26*), although the latter do not find completely statistical energy redistribution. Recently, Ezra and co-workers (*27*) used classical trajectory calculations to determine whether unimolecular decay or intramolecular energy redistribution controls the linewidth. They conclude that either situation is possible depending on the details of the potential energy surface used in the calculation. The important complementary experiment that should resolve this issue and, thus, shed considerable light on the intramolecular dynamics, is the direct observation of the appearance of the products. The rate of that process reflects only unimolecular decomposition while the linewidth potentially contains contributions from intramolecular energy transfer as well. Scherer and Zewail (*28*) have used picosecond laser techniques to observe the OH product appearance in vibrational overtone–initiated decomposition of HOOH($5\nu_{OH}$) directly. The excitation of this overtone vibration does not add sufficient energy to break the O–O bond, but thermal excitation contributes enough to make some states react. The direct decomposition measurement on HOOH($6\nu_{OH}$) promises to be very informative.

The distribution of the products among their quantum states in the vibrational overtone–initiated decomposition of HOOH($5\nu_{OH}$) (*29*) and HOOH($6\nu_{OH}$) (*22*) comes from detecting relative OH state populations by LIF. For excitation of the fifth overtone vibration ($6\nu_{OH}$), the product state distributions agree with PST as well as SACM treatments (*22, 25*). In my research group we have found poorer agreement with PST in the decomposition of HOOH($5\nu_{OH}$), but comparison is more difficult in this case because the reaction requires thermal energy. The SACM calculations seems to do well in the case of HOOH($5\nu_{OH}$) (*22, 25*), but improved phase space calculations appear to agree as well (*30*). We have investigated the decomposition of a similar molecule, nitric acid ($HONO_2$), initiated by excitation of the fourth or fifth overtone vibration and found that PST predicts the quantum states of the products very well (*31*). The fully state-selected experiments by Rizzo and co-workers are producing the most detailed product state distributions for HOOH, and, in preliminary experiments, they find trends that are inconsistent with both PST and the SACM (*32*). These experiments suggest that the vibrational overtone–initiated decomposition of HOOH is eigenstate specific but that uncovering it requires very highly resolved measurements.

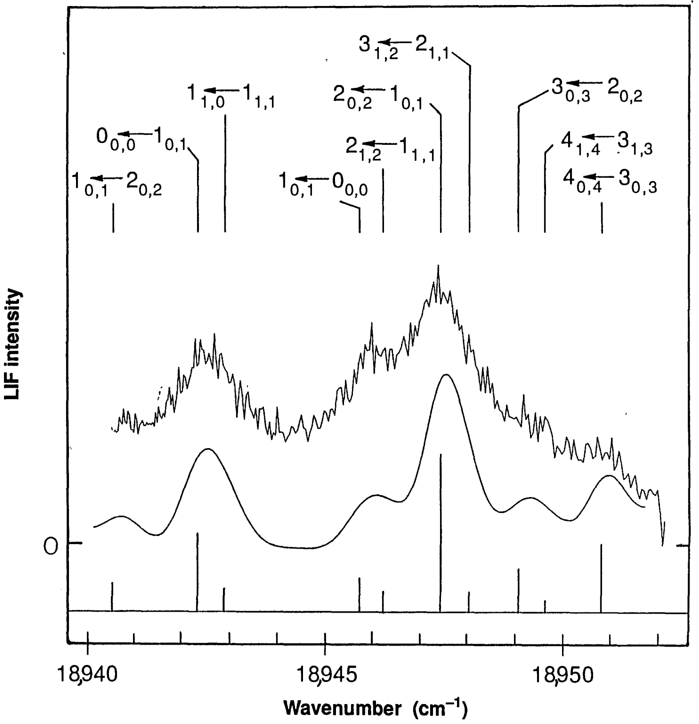

Fig. 3. The vibrational overtone excitation spectrum for the fifth O–H stretching overtone vibration ($6\nu_{OH}$) of hydrogen peroxide molecules cooled in a supersonic expansion. All transitions are of the S_0^0-type *A* band. The signal is the laser-induced fluorescence intensity from the OH product of the unimolecular decomposition. The lower curve is an asymmetric rotor simulation of the spectrum in which a temperature of 8 K and a linewidth of 1.0 cm^{-1} are used. The vertical lines show the calculated intensities of the rotational transitions that are labeled above.

Hydrazoic acid, N_3H, is a molecule with a potential energy surface that differs qualitatively from those for hydrogen peroxide and nitric acid. Time-resolved vibrational overtone–initiated decomposition studies by Foy *et al.* (*33, 34*) on molecules cooled in a supersonic expansion show eigenstate-specific reaction rates and clear evidence of state-specific level mixing. The decomposition of hydrazoic acid,

$$N_3H \rightarrow N_2 + NH$$

occurs over a barrier of ~150 kJ/mol that arises from the avoided crossing of two surfaces that correlate with different electronic states of the NH product. Because there is a substantial barrier of ~90 kJ/mol to the reverse reaction, the transition state in a statistical calculation is well defined. However, the crossing of the two potential energy surfaces can produce very state-specific decomposition since some vibrations might promote the coupling between the two much more efficiently than others. The excitation spectrum in the region of the fourth ($5\nu_{NH}$) overtone vibration, obtained by varying the vibrational excitation wavelength while detecting the NH fragment by LIF, shows sharp structure with no evidence of lifetime broadening, but dissociation does broaden the individual features in the region of the $6\nu_{NH}$ transition. The average appearance times of the NH products are 210 and 0.95 ns for the fourth and fifth overtone excitations, respectively. This measured lifetime for $6\nu_{NH}$ excitation is consistent with the broadening of the features. The variation in the rate with small changes in the excitation energy provides clear evidence of eigenstate specificity in the decomposition of $N_3H(5\nu_{NH})$. Two states, with $J = 2$ but differing in energy by 0.1 cm^{-1}, have NH-fragment appearance times that differ by a factor of 2. The structure in the vibrational overtone excitation spectrum reflects specific-state mixing in the vibrationally excited molecule, and it is the different character of those mixed states that produces the various decay rates, probably through vibrational state–specific coupling between the two electronic states that cross at the barrier. At higher energies, the eigenstate specificity disappears as intramolecular couplings to the more numerous background states produce highly admixed eigenstates that contain a number of different modes (*34*).

Internal conversion and stimulated emission pumping (SEP). State-specific internal conversion in formaldehyde (H_2CO) (*35, 36*), ketene (CH_2CO) (*37*), nitrosylcyanide (NCNO) (*38*), and formaldehyde (*39*) as well as SEP in fluoroformaldehyde (HFCO) (*40*) have permitted the observation of eigenstate-resolved unimolecular reactions through linewidth, lifetime, and product state population measurements. For example, in internal conversion experiments, Dai *et al.* (*39*) found rates that differed by a factor of 2.5 for states lying within 10 cm^{-1} of each other, probably reflecting state-specific tunneling through a barrier. Moore and co-workers have observed substantial variation in the lifetimes of different initial highly vibrationally excited states of H_2CO produced by internal conversion in Stark level crossing experiments (*35*). From detailed analysis and theoretical modeling, they argue that this variation is consistent with a quantum statistical model that includes the fluctuation in the lifetimes expected for the distribution of states and couplings in H_2CO (*41*). This analysis makes the important point that reaction rates that depend strongly on the particular state prepared can be consistent with quantum ergodic dynamics in the excited molecule and arise from statistical variations. The average rate measured in their experiments agrees with RRKM theory with a tunneling correction included, but there are large variations among the initial states. Some of the first SEP measurements on HFCO show different linewidths and, hence, lifetimes for nearby states as well

(*40, 42*). These spectra may reflect reactions that are slower than predictions of RRKM theory and seem to indicate the presence of rather stable highly excited states.

Detailed state distribution measurements for the internal conversion–initiated decomposition of NCNO (*38*) and of CH_2CO (*37*) have motivated direct, time-resolved measurements of the decomposition rate (*43, 44*). The result is particularly informative for ketene, where the photofragment excitation measurements show that the product state populations for different excitation energies agree quite well with the predictions of PST. The observed populations are also consistent with the modified RRKM theory. A direct measurement of the appearance rate of the CH_2 fragment shows that the actual rate is less than that predicted by PST, as expected, but that its magnitude and energy dependence agree with the predictions of the modified RRKM theory (*44, 45*). This measurement is an example of the power of combining experiments that use state-specific reactant preparation and product detection with direct reaction-rate measurements.

Experiments that use different excitation schemes have clearly demonstrated quantum state–resolved unimolecular reactions in several molecules. They also show that eigenstate-specific unimolecular reactions may arise from tunneling, surface crossings, statistical variations in reaction rates, and selective couplings into the dissociative continuum. A question that remains is whether this state specificity in unimolecular reaction can be translated into bond-selected chemical reactions.

Bond-Selected Reactions

The key to initiating a bond-selected chemical reaction is the deposition of energy in the reaction coordinate, either by its direct excitation or by preferential coupling of energy into it from another vibration. Excitation of overtone vibrations, which derive their transition strength from stretching vibrations involving light atoms, is a likely means of such selective energy deposition. For example, Jasinksi *et al.* (*46*) have attempted to enhance hydrogen atom transfer reactions by exciting C–H bond stretching vibrations. They find no difference between the excitations that primarily involve the atom to be transferred and excitations of those that do not. This reflects the highly admixed nature of the initial state or, in the language of intramolecular energy transfer, the rapid redistribution of energy on the time scale of the reaction.

An intriguing example that points to the subtlety of vibrational overtone excitation is an experiment by Reddy and Berry (*47*) on the isomerization of allylisocyanide

$$H_2C{=}CHCH_2NC \rightarrow H_2C{=}CHCH_2CN$$

Excitation of different regions of the C–H vibrational overtone spectrum produces reaction rates that change nonmonotonically with energy content of the molecule, apparently at variance with the predictions of statistical theories. However, recent experiments by Segal and Zare (*48*) that have partially unraveled the vibrational overtone excitation spectrum indicate that the inhomogeneous structure of the spectrum is different in the regions of the various transitions. Thus the energy deposited in the excitation depends not only on the identity of the transition but also the hot-band contribution to that particular portion of the spectrum. The observed differences are unlikely to reflect mode-selected reaction (*48*).

Preferential coupling from one vibration into the reaction coordinate does occur to some extent in the vibrational overtone–initiated unimolecular decomposition of *tert*-butylhydroperoxide,

$$tert\text{-}BuOOH \rightarrow tert\text{-}BuO + OH$$

My research group has studied the vibrational overtone–initiated reaction using time-resolved techniques that directly determine the decomposition rate and has obtained results that are consistent with the predictions of statistical theories (*49*). Zare and co-workers (*50*) have found that in high-pressure samples or liquids, where collisions inhibit the slow reaction of molecules that behave statistically, there is a small amount of rapid reaction that apparently comes from molecules in which energy has first migrated into the O–O bond, which is the reaction coordinate. This experiment suppresses the dominant slow component of the reaction to uncover the small portion that proceeds along a preferential pathway.

It seems difficult to excite the reaction coordinate in stable molecules, and recently my research group has taken a slightly different approach to bond-selected reactions (*51*). We excite a well-isolated vibration in a molecule and then convert that vibration into the reaction coordinate with a photon or a reactive atom. The process using a photon is vibrationally mediated photodissociation (*52*), in which a second photon dissociates a highly vibrationally excited molecule prepared by vibrational overtone excitation. We have excited four quanta of the O–H stretching vibration in HOD and preferentially cleaved the O–H bond by subsequently exciting the vibrationally excited molecule to a dissociative electronic surface (*52, 53*). The vibrational excitation in the ground electronic state controls the bond cleavage in the electronically excited state since, for the proper photolysis energies, transitions from the vibrationally excited molecule occur into only the dissociation channel on the excited potential in which the O–H bond breaks. The consequence is that severing the O–H bond is at least 15 times more likely than breaking the O–D bond. Our other approach, in which a reactive atom is used to convert the O–H stretching vibration into the reaction coordinate, is the first example of a bond-selected bimolecular reaction (*54*). In that case we preferentially cleave the O–H bond in vibrationally excited HOD by reaction with a hydrogen atom. Reaction of the vibrationally excited end of the molecule is 100 times more likely than reaction of the unexcited end. In both of these experiments, the interaction with a photon or a reactive atom effectively converts the isolated O–H stretching vibration into the reaction coordinate. This demonstrates the substantial acceleration of the reaction rate and the large bond selectivity that chemical intuition suggests should occur but which has previously eluded experimental observation.

Conclusions

Several experiments have selected single quantum states of reactants and measured populations of individual quantum states of products to investigate state-resolved unimolecular reactions. They illustrate the feasibility of such detailed measurements and the wealth of information available for comparison to theory. State-specific unimolecular reactions, in which the rate of the reaction or the energy disposal in the products depends on the identity of the initially excited state, certainly do occur. One challenge is to place these observations in a theoretical framework that includes the possibility of statistical behavior in a fully quantum system. There are examples where the excited molecule "remembers" its preparation, and we need to understand whether that memory is vague, for example, reflecting only a restricted access to some of the energetically allowed phase space, or highly specific. Another challenge is to use the state specificity of reaction to control the course of chemical change and, in particular, to break a bond preferentially. Qualitatively the key is to excite the reaction coordinate, but a number of experiments have shown that molecules are not particularly inclined to aid in that endeavor. Recent experiments in which we selectively break a bond by using a photon or a reactive atom to turn an isolated vibration into the reaction coordinate illustrate the possibility of controlling chemistry by exciting the reaction coordinate. These measurements on the prototypical water molecule suggest approaches to bond-selected chemistry in other systems (*51*).

The detailed studies of intramolecular dynamics and unimolecular reaction briefly described here have reduced our naiveté about the complexity of intramolecular interactions. Understanding the means by which energy flows in highly vibrationally excited molecules and the intramolecular couplings that control unimolecular reaction requires fundamental information from both theory and experiment. Sophisticated experimental and theoretical approaches are providing new insights into chemical reactions and the possibility of their control with light.

REFERENCES AND NOTES

1. P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley, New York, 1972).
2. Special issue on Mode Selectivity in Unimolecular Reactions, J. Manz and C. S. Parmenter, Eds., *Chem. Phys.* **139** (1989).
3. J.-P. Pique *et al.*, *Adv. Laser Sci.* **4**, 673 (1989); J.-P. Pique, Y. Chen, R. W. Field, J. L. Kinsey, *Phys. Rev. Lett.* **58**, 475 (1987).
4. E. B. Wilson, J. C. Decius, P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).
5. B. Timm and R. Mecke, *Z. Phys.* **98**, 363 (1936); R. Mecke, *Z. Elektrochem.* **54**, 38 (1950); B. R. Henry, *Acc. Chem. Res.* **10**, 207 (1977); M. S. Child and L. Halonen, *Adv. Chem. Phys.* **47**, 293 (1981).
6. P. R. Stannard and W. M. Gelbart, *J. Phys. Chem.* **85**, 3592 (1981).
7. I. W. M. Smith, *Kinetics and Dynamics of Elementary Gas Reactions* (Butterworths, London, 1980).
8. P. Pechukas, J. C. Light, C. Rankin, *J. Chem. Phys.* **44**, 794 (1966); P. Pechukas and J. C. Light, *ibid.* **42**, 3281; J. C. Light, *Faraday Discuss. Chem. Soc.* **44**, 14 (1967).
9. M. Quack and J. Troe, *Ber. Bunsenges, Phys. Chem.* **78**, 240 (1974); J. Troe, *J. Chem. Phys.* **75**, 226 (1981).
10. R. A. Marcus, *J. Chem. Phys.* **85**, 5035 (1986); *Chem. Phys. Lett.* **144**, 208 (1988); D. M. Wardlaw and R. A. Marcus, *Adv. Chem. Phys.* **70**, 231 (1988); S. J. Klippenstein, L. R. Khundkar, A. H. Zewail, R. A. Marcus, *J. Chem. Phys.* **89**, 4761 (1988).
11. C. Wittig, I. Nadler, H. Reisler, J. Catanzarite, G. Radhakrishnan, *J. Chem. Phys.* **83**, 5581 (1985).
12. See, for example, Z. S. Huang, K. W. Jucks, R. E. Miller, *ibid.* **85**, 3388 (1986); C. M. Lovejoy and D. J. Nesbitt, *ibid.* **86**, 1098 (1986); Z. S. Huang and R. E. Miller, *ibid.* **90**, 1478 (1989).
13. See, for example, J. C. Alfano, S. J. Martinez, D. H. Levy *ibid.* **91**, 7302 (1989); K. W. Butz, D. L. Catlett, G. E. Ewing, D. Krajnovich, C. S. Parmenter, *J. Phys. Chem.* **90**, 3533 (1986); M. P. Casassa, A. M. Woodward, J. C. Stephenson, D. S. King, *J. Chem. Phys.* **85**, 6235 (1986); D. H. Semmes, J. S. Baskin, A. H. Zewail, *ibid.* **92**, 3359 (1990).
14. F. F. Crim, *Annu. Rev. Phys. Chem.* **35**, 657 (1984).
15. ———, in *Molecular Photodissociation Dynamics*, J. Baggott and M. Ashfold, Eds. (Royal Society of Chemistry, London, 1987), pp. 177–210.
16. C. E. Hamilton, J. L. Kinsey, R. W. Field, *Annu. Rev. Phys. Chem.* **37**, 493 (1986).
17. H. Reisler and C. Wittig, *ibid.*, p. 307.
18. L. J. Butler, T. M. Ticich, M. D. Likar, F. F. Crim, *J. Chem. Phys.* **85**, 233 (1986); *ibid.*, p. 6251.
19. T. M. Ticich, thesis, University of Wisconsin, Madison (1988).
20. ———, M. D. Likar, F. F. Crim, unpublished results.
21. X. Luo, P. T. Rieger, D. S. Perry, T. R. Rizzo, *J. Chem. Phys.* **89**, 4448 (1988).
22. T. R. Rizzo, C. C. Hayden, F. F. Crim, *ibid.*, **81**, 4501 (1984).
23. J. L. Kinsey, *Annu. Rev. Phys. Chem.* **28**, 349 (1977).
24. C. Douketis and J. P. Reilly, *J. Chem. Phys.* **91**, 5239 (1989).
25. L. Brouwer, C. J. Cobos, J. Troe, H-R. Dübal, F. F. Crim, *ibid.* **86**, 6171 (1987).
26. T. Uzer, J. T. Hynes, W. P. Reinhard, *ibid.* **85**, 5791 (1986).
27. C. Getino, B. G. Sumpter, J. Santamaria, G. S. Ezra, *J. Phys. Chem.* **93**, 3877 (1989).
28. N. F. Scherer and A. H. Zewail, *J. Chem. Phys.* **87**, 97 (1987).
29. T. M. Ticich, T. R. Rizzo, H. R. Dübal, F. F. Crim, *ibid.* **84**, 1508 (1986).
30. A. Sinha and F. F. Crim, unpublished results.
31. A. Sinha, R. L. Vander Wal, F. F. Crim, *J. Chem. Phys.* **92**, 401 (1990).
32. T. R. Rizzo, personal communication.
33. B. R. Foy, M. P. Casassa, J. C. Stephenson, D. S. King, *J. Chem. Phys.* **90**, 7037 (1989).
34. ———, *ibid.* **92**, 2782 (1990).
35. D. R. Guyer, W. F. Polik, C. B. Moore, *ibid.* **84**, 6519 (1986); W. F. Polik, D. R. Guyer, C. B. Moore, *ibid.* **92**, 3453 (1990).
36. T. J. Butenhoff, K. L. Carleton, C. B. Moore, *ibid.*, p. 377; T. J. Butenhoff, K. L. Carleton, M. C. Chuang, C. B. Moore, *J. Chem. Soc. Faraday Trans. 2* **85**, 1155 (1989).
37. I-Chia Chen, W. H. Green, Jr., C. B. Moore, *J. Chem. Phys.* **89**, 314 (1988).
38. I. Nadler, M. Noble, H. Reisler, C. Wittig, *ibid.* **82**, 2608 (1985); C. X. W. Qian, M. Noble, I. Nadler, H. Reisler, C. Wittig, *ibid.* **83**, 5573 (1985).
39. H. L. Dai, R. W. Field, J. L. Kinsey, *ibid.* **82**, 1606 (1985).
40. Y. S. Choi and C. B. Moore, *ibid.* **90**, 3875 (1989).
41. W. F. Polik, D. R. Guyer, W. H. Miller, C. B. Moore, *ibid.* **92**, 3471 (1990).
42. C. B. Moore, *Philos. Trans. R. Soc. London*, in press.
43. L. R. Khundkar, J. L. Knee, A. H. Zewail, *J. Chem. Phys.* **87**, 77 (1987).
44. E. D. Potter, M. Gruebelle, L. R. Kundkar, A. H. Zewail, *Chem. Phys. Lett.* **164**, 463 (1989).
45. S. J. Klippenstein and R. A. Marcus, *J. Chem. Phys.* **91**, 2280 (1989); *ibid.* **93**, 2418 (1990).
46. J. M. Jasinski, J. K. Frisoli, C. B. Moore, *J. Phys. Chem.* **87**, 2209 (1983); *ibid.*, p. 3826; *Faraday Discuss. Chem. Soc.* **75**, 289 (1983).
47. K. V. Reddy and M. J. Berry, *Chem. Phys. Lett.* **56**, 223 (1979).
48. J. Segall and R. N. Zare, *J. Chem. Phys.* **89**, 5704 (1988).
49. T. R. Rizzo and F. F. Crim, *ibid.* **76**, 2754 (1982).
50. J. H. Gutow, D. Llenerman, R. N. Zare, *J. Phys. Chem.* **92**, 172 (1988); M. C. Chuang, J. E. Baggott, D. W. Chandler, W. E. Farneth, R. N. Zare, *Faraday Discuss. Chem. Soc.* **75**, 301 (1983); D. W. Chandler, W. E. Farneth, R. N. Zare, *J. Chem. Phys.* **77**, 4447 (1982); T. R. Rizzo, C. C. Hayden, F. F. Crim, *Faraday Discuss. Chem. Soc.* **75**, 350 (1983).
51. F. F. Crim *et al.*, *Philos. Trans. R. Soc. London*, in press.
52. M. D. Likar, J. E. Baggott, A. Sinha, R. L. Vander Wal, F. F. Crim, *J. Chem. Soc. Faraday Trans. 2* **84**, 1483 (1988).
53. R. L. Vander Wal, J. L. Scott, F. F. Crim, *J. Chem. Phys.* **92**, 803 (1990).
54. A. Sinha, M. C. Hsiao, F. F. Crim, *ibid.*, p. 6333.

55. The work from the University of Wisconsin–Madison described in this article is supported by the Office of Basic Energy Sciences, Division of Chemical Sciences of the Department of Energy.