

# Vibrational State Control of Bimolecular Reactions: Discovering and Directing the Chemistry

F. FLEMING CRIM

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received April 26, 1999

## Introduction

Molecular vibrations drive chemical reactions. Because reaction requires a rearrangement of nuclear positions as old bonds break and new ones form, a few molecules that have enough energy to overcome the barrier to reaction actually do the chemistry in most thermal reactions. Figure 1 shows the energy profile along a reaction coordinate in which an atom X attacks a molecule HAB to form the products HX + AB. Motion along the reaction coordinate can be as simple as stretching a bond to transfer an atom X, as Figure 1 illustrates, or as complex as a concerted motion of many atoms to make and break several bonds at once. This elementary view of a chemical transformation points to a conceptually simple means of controlling the rate and outcome of a bimolecular reaction: *excite motion along the coordinate that carries the reactants to the desired products*. The experimental realization is more difficult but offers both a singular understanding of how reactions occur and a view into the details of important reactions, such as those occurring in combustion, the atmosphere, and plasma chemistry. Two requirements for controlling a bimolecular reaction by vibrational excitation are preparation of a vibration that becomes motion along the reaction coordinate in a reactive encounter and retention of that excitation long enough to allow such an encounter.

There are two general approaches to exciting a vibration that maps onto the reaction coordinate in a bimolecular reaction. One is preparing a vibrational eigenstate, a time-invariant stationary state of the molecule, corresponding to motion along the reaction coordinate, and the other is preparing a nonstationary state having the proper vibrational motion. Thus far, only the first approach has selectively driven a bimolecular reaction, but

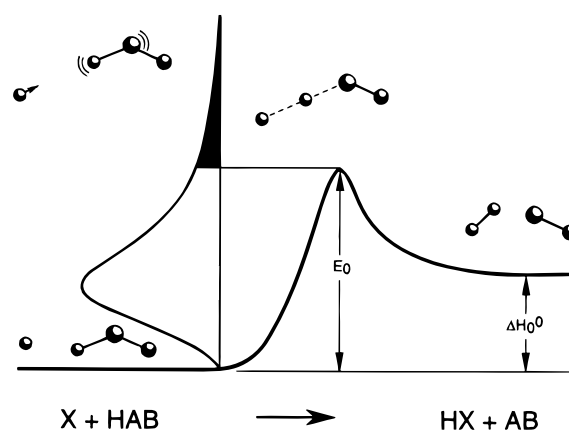


FIGURE 1. Schematic drawing of the energy profile along the reaction coordinate for a bimolecular reaction. The darkened area in the distribution on the left-hand side of the figure shows HAB molecules with enough energy to react.

in principle both schemes, which contain the common element of preparing a special vibration in a reactant molecule, can move a system along the reaction coordinate and direct the course of a chemical reaction. Because a molecular eigenstate does not evolve in time, it is relatively simple to have the vibrational excitation survive until a reactive encounter occurs. However, choosing which vibrational eigenstate to excite is more complicated since each one corresponds to a different set of vibrational motions. Fortunately, vibrational spectroscopy reveals the nature of the states and guides the selection.

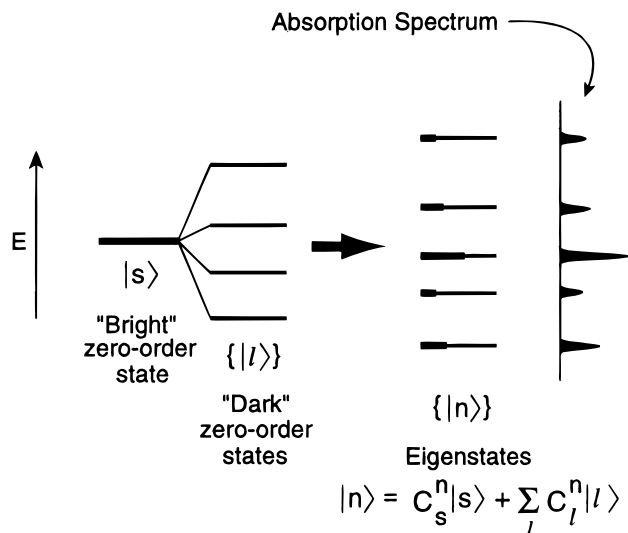
## Exciting the Reaction Coordinate

Barriers to chemical reactions are often larger than the energy provided by a single vibrational quantum. The high-energy molecules responsible for many reactions contain several quanta of excitation, and understanding the types of vibrations one can excite is crucial to controlling a bimolecular reaction. For example, in the simple hydrogen atom abstraction reaction illustrated in Figure 1, it is obvious that the H–A stretching vibration lies along the reaction coordinate since that bond lengthens in passing through the transition state.

The reaction coordinate is formally a vibration with an imaginary frequency, the unbound motion that carries the system across the maximum in the multidimensional energy landscape of the interacting reactants.<sup>1</sup> In the reaction of X with HAB, it is a vibration in which the new X–H bond shortens as it forms and the disappearing H–A bond lengthens. Thus, the H–A stretching vibration has a large component along the reaction coordinate. Another component of motion along the reaction coordinate in this example is the translation of the X atom toward the reacting molecule. Indeed, introductory presentations often speak only of translations as providing the requisite energy, even though vibrations are at least as important in rearranging the nuclei.

**Descriptions of Vibrationally Excited Molecules.** Our approach to driving and controlling bimolecular reactions

F. Fleming Crim is the John E. Willard Professor of Chemistry at the University of Wisconsin—Madison. He was born on May 30, 1947, in Waco, Texas, and received his undergraduate training at Southwestern University, Georgetown, Texas. He earned a Ph.D. in physical chemistry from Cornell University in 1974 and joined the Engineering Research Center of Western Electric Co. He moved to Los Alamos National Laboratory as a Director's Postdoctoral Fellow in 1976 and joined the University of Wisconsin—Madison in 1977. He and his co-workers use lasers to study and control chemical reactions in gases and liquids.



**FIGURE 2.** Zero-order states and molecular eigenstates. A dipole-allowed transition connects the bright zero-order state,  $|s\rangle$ , but not the dark zero-order states,  $\{|l\rangle\}$ , to the ground vibrational state. The zero-order states interact to form the molecular eigenstates,  $\{|n\rangle\}$ .

by selective vibrational excitation uses laser light to prepare a vibrational eigenstate that has a significant component of motion along the reaction coordinate. Thus, we need a framework for describing the vibrational eigenstates. A particularly useful model, which combines intuition about vibrating bonds with the reality of the complex motions corresponding to vibrational eigenstates, describes the excited molecule in terms of zero-order vibrational states. The zero-order states correspond to simple motions, such as stretches and bends, that we can visualize easily but which do not describe the vibrational eigenstates of the molecule completely. These zero-order states are a basis for describing the actual vibrations in the same way that simple molecular orbitals are a basis for describing the complex electronic structure of a molecule.

The diagram in Figure 2 illustrates this picture of interacting zero-order states. One of the vibrational basis states,  $|s\rangle$ , is the "bright zero-order state" because it is the only basis state connected to the ground vibrational state by a dipole-allowed spectroscopic transition. For example, in the molecule HAB, it might be a state with several quanta of H–A stretching excitation. The other basis states,  $\{|l\rangle\}$ , lying nearby in energy are "dark zero-order states" that contain combinations of other vibrations. They might be states with one or more quanta of H–A stretch replaced by several quanta of other stretches or bends. Even a triatomic molecule has combinations of A–B stretching and H–A–B bending vibrations that are close in energy to the zero-order bright state, and, in general, the A and B members of HAB are polyatomic units with still more vibrational degrees of freedom.

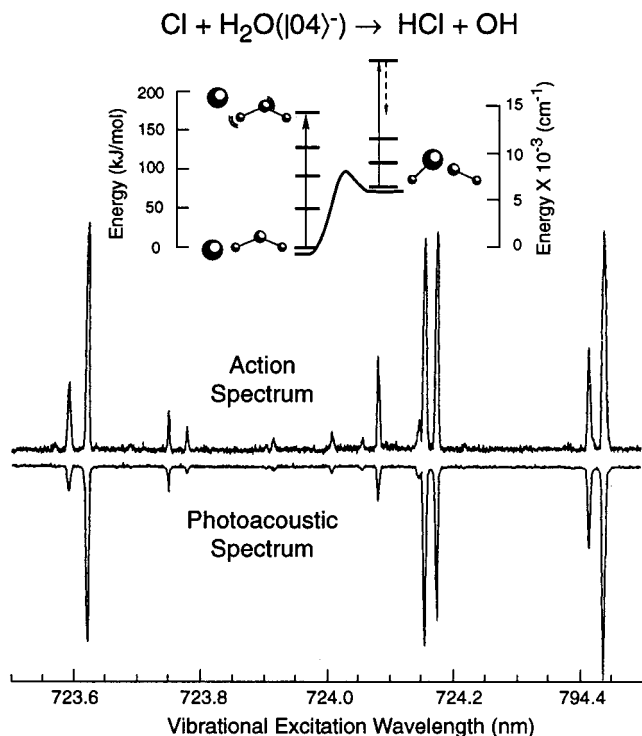
The molecular eigenstates  $\{|n\rangle\}$  are linear combinations of the basis states,  $|n\rangle = C_s^n |s\rangle + \sum_l C_l^n |l\rangle$ , with coefficients determined by the full Hamiltonian that includes terms omitted from the approximate one that describes the zero-order states. Because only the bright zero-order state has any transition probability, the amount of that state in an

eigenstate, given by  $|C_s^n|^2$ , determines the intensity of the transition to the eigenstate from the ground vibrational state, as indicated schematically by the spectrum on the right of Figure 2. Thus, excitation with a laser having enough resolution to prepare a single molecular eigenstate creates a stationary state that we describe as a linear combination of the zero-order states. It is often useful to designate the eigenstate by the identity of its predominant zero-order state, referring to a state as an O–H stretching state, for example, even though its motion is actually more complex. In using vibrational excitation to control bimolecular reactions, we prepare eigenstates that have a large component of a zero-order state that projects onto the reaction coordinate.

**Experimental Realization.** The experimental realization of a vibrationally driven bimolecular reaction requires the excitation of a well-characterized vibrational eigenstate, the interaction of the vibrationally excited molecule with a reactive partner, and the detection of the reaction products. The vibrational preparation step typically uses a pulse of laser light with a duration of about 6 ns, an energy up to tens of millijoules, a bandwidth of less than  $0.1 \text{ cm}^{-1}$ , and a wavelength in the range of 500–3000 nm. Because the energy barriers to reaction are often larger than a single vibrational quantum, experiments that excite a fundamental vibration usually require additional energy in the form of translation, while those that excite overtone vibrations do not.

The reactants can be either in a low-pressure gas or in a supersonic expansion. The densities of reactants and precursors must be low enough that a molecule has only a single collision in the time between the vibrational excitation and probe pulses. Even collisions with nonreactive molecules, such as vibrationally unexcited reactants, potentially distort the observation by transferring energy among the vibrations in the initially excited molecules.<sup>2</sup> Thus, one usually sacrifices signal to obtain single collision conditions and typically selects the time delays and pressures so that fewer than 10% of the molecules have a collision between vibrational excitation and product detection. Production of the reactive atom X uses laser photolysis or microwave discharge of precursor molecules. Both discharge and laser photolysis sources are compatible with low-pressure gas cells, but photolysis sources are best for supersonic expansions. With the reactive atoms present, a pulse of light vibrationally excites the reactant molecule, and, after a delay during which some fraction of the vibrationally excited molecules react, a spectroscopic probe detects the reaction products.

Detection of the products with a spectroscopic technique such as laser-induced fluorescence (LIF) or resonantly enhanced multiphoton ionization (REMPI) requires another laser. Because spectroscopic probes measure the relative populations of individual quantum states, they not only identify the products but also determine their energy content, information that reveals the fine details of the reaction. The approach of vibrational state preparation followed by reaction and product detection has provided

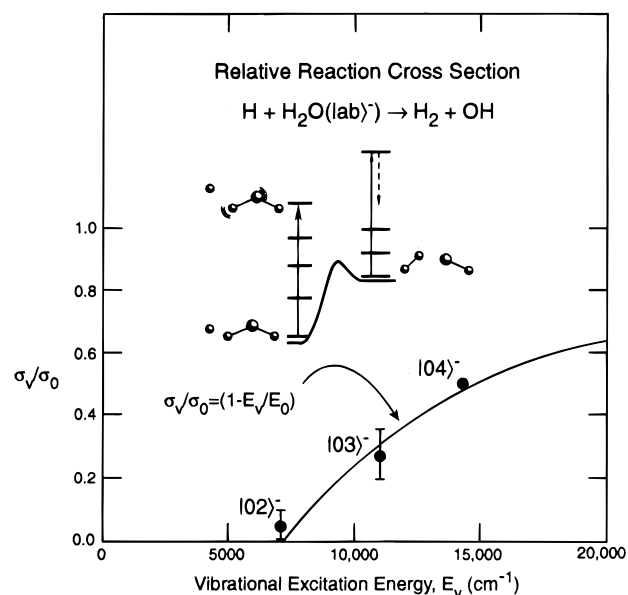


**FIGURE 3.** Photoacoustic absorption and action spectra for the reaction of Cl with vibrationally excited water. The lower trace shows the photoacoustic absorption spectrum of  $\text{H}_2\text{O}(|04\rangle^-)$ , and the upper trace shows its action spectrum, obtained by monitoring the OH product of the reaction.

the first examples of vibrationally driven bimolecular reactions in neutral<sup>3–16</sup> and ionic<sup>4,17–19</sup> systems.

## Changing Reaction Rates

The ability to prepare vibrationally excited molecules and monitor their reaction products allows us to determine the extent to which vibrational excitation accelerates a reaction. It is easiest to follow reactions that are substantially endothermic or have large barriers, both of which prevent reaction of thermal molecules. Figure 3 demonstrates the acceleration of an endothermic reaction with vibrational energy. As the diagram at the top of the figure shows, the reaction of Cl with  $\text{H}_2\text{O}$  is endothermic by about 70 kJ/mol and has a barrier of about 90 kJ/mol. The lower trace in the figure is the photoacoustic spectrum of  $\text{H}_2\text{O}$  in the region of four quanta of O–H stretching excitation and comes from detecting the acoustical signal generated by collisional relaxation of vibrationally excited water molecules prepared by laser excitation in a cell containing a microphone.<sup>20</sup> The excited state,  $|04\rangle^-$ , is the third overtone of an O–H stretching vibration in which the dominant zero-order state has four quanta of vibrational excitation in one bond.<sup>21,22</sup> The photoacoustic spectrum is the *absorption* spectrum in that region, with each feature being a transition to a rovibrational eigenstate. The upper trace in Figure 3 is the *action* spectrum obtained by scanning the vibrational overtone excitation laser through the same region while monitoring the OH product of the reaction of photolytically generated Cl atoms with vibrationally excited water molecules, Cl +



**FIGURE 4.** Relative cross sections for the reaction of water in three different vibrational states with H. The points are the relative cross sections determined by comparison to that of water in the state  $|04\rangle^-$ . The smooth curve is a fit where  $E_v$  is the vibrational energy,  $E_0$  is the threshold energy of 86 kJ/mol (7200  $\text{cm}^{-1}$ ), and  $\sigma_0$  is the maximum reaction cross section.

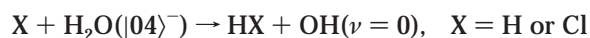
$\text{H}_2\text{O}(|04\rangle^-) \rightarrow \text{HCl} + \text{OH}$ .<sup>8,9</sup> The intensities in the photoacoustic spectrum reflect solely the vibrational excitation probability, but those in the action spectrum also reflect the probability that vibrationally excited molecules react to produce a fragment in the probed quantum state of OH. The presence of an action signal only at wavelengths where water absorbs demonstrates that vibrational excitation accelerates the reaction far beyond the thermal rate.

Preparing a series of O–H stretching states in water reveals the relative efficiency of different amounts of vibrational excitation. Figure 4 shows the relative cross sections for reaction of thermal H atoms produced in a microwave discharge with water in three different vibrational states,  $|02\rangle^-$ ,  $|03\rangle^-$ , and  $|04\rangle^-$ , that contain two, three, and four quanta of O–H stretching excitation in one bond, respectively.<sup>7</sup> As the energy level diagram in the figure shows, two quanta of excitation place the system very near the top of the barrier to reaction, and four quanta place it at twice the barrier energy. Adding energy to the O–H stretching vibration raises the reaction rate considerably, increasing it 8-fold in going from two to three quanta of excitation and doubling it again in going from three to four quanta. The relatively small amount of reaction with two quanta of excitation is consistent with the energy of the  $|02\rangle^-$  state being very close to that of the barrier. Our first experiments provided a rough estimate that the rate of reaction of  $\text{H}_2\text{O}(|04\rangle^-)$  was on the order of the gas kinetic collision rate,<sup>7</sup> and recent kinetic studies by Smith and co-workers showed that the reaction actually occurs at half the gas kinetic collision rate.<sup>2</sup> In both the reactions of H and of Cl with water,<sup>7,8</sup> vibrational excitation transforms a nonreactive molecule into one that reacts on roughly every other collision with a potentially reactive atom.

## Discovering and Controlling Reaction Mechanisms

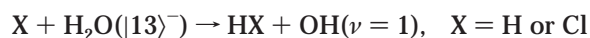
Preparing molecules having very different nuclear motions but similar amounts of vibrational energy while detecting individual quantum states of reaction products provides a detailed view of the mechanism of a reaction. One can discover the fate of the energy initially deposited in the reacting molecules and can determine the ability of different vibrations to accelerate the reaction. Such an approach shows which vibrations move the system along the reaction coordinate and points the way to controlling the course of the reaction.

**Spectator Reactions—Energy Disposal and Product States.** Vibrational excitation clearly promotes the abstraction of a hydrogen atom from water by either H or Cl atoms, an observation that raises the question of the distribution of energy among reaction products. The  $|04\rangle^-$  state of  $\text{H}_2\text{O}$  makes 110 kJ/mol ( $9500\text{ cm}^{-1}$ ) of energy available for disposal in the products. Detection of the OH product of the reaction of water with Cl shows that it contains less than 6 kJ/mol ( $500\text{ cm}^{-1}$ ) of rotational energy and no vibrational excitation,<sup>7–10</sup>



Measuring the Doppler width of LIF transitions used to detect the recoiling OH fragment shows that only about 20% of the available energy appears in translation and that roughly 75% of the available energy resides in the HCl product, most likely as vibrational excitation of the new HCl bond.<sup>9</sup> The reaction with H follows a similar pattern.<sup>10</sup> The appearance of most of the available energy for the reactions of Cl and H with  $\text{H}_2\text{O}(|04\rangle^-)$  in the new bond suggests that the O–H stretch, the “old bond”, is a spectator that does not participate in the disposal of the energy into the products.

Preparation of other vibrational states with similar energy but different nuclear motions further supports the spectator picture for reactions of water. The  $|13\rangle^-$  eigenstate is predominantly the zero-order state containing one quantum of O–H stretching excitation in one bond and three quanta in the other.<sup>21</sup> Reaction of water in that state with either H or Cl produces nearly all of the OH product in  $\nu = 1$ ,<sup>7–10</sup>

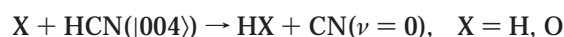


The nonreacting bond is a spectator that retains its initial excitation, in this case one quantum of O–H stretch, during the reaction. This spectator behavior strongly suggests that we can cleave a selected bond preferentially, since reactions with H or Cl break only the bond containing energy in excess of the barrier.

The reactions of H atoms with water provide particularly good opportunities for comparison to theory. Well before the observation of the reaction of highly vibrationally excited water with H atoms, Schatz et al.<sup>23</sup> used quasiclassical trajectory calculations to predict the sub-

stantial acceleration of the reaction by stretching vibrations. Quasiclassical calculations recover many of the details of the experimental observations,<sup>24</sup> and the agreement is even better for recent trajectories on improved potential energy surfaces.<sup>25</sup> In addition, both Clary and co-workers<sup>26</sup> and Bowman and co-workers<sup>27</sup> have performed quantal calculations for the same reaction.

The hydrogen atom abstraction reactions of water are particularly simple, and one must be cautious in extrapolating to seemingly similar systems. The reactions of vibrationally excited hydrogen cyanide (HCN) with H, Cl, and O atoms are a case in point, and experiments for several levels of vibrational excitation reveal subtle behavior.<sup>13,14</sup> The reactions of H and O with HCN containing four quanta of C–H stretch,  $\text{HCN}(|004\rangle)$ ,<sup>28</sup> produce mostly (78% and 85%, respectively) vibrational ground-state CN radicals,



This energy disposal pattern suggests that the C–N bond is a spectator much like the surviving bond in the reactions of water. The situation changes dramatically for reaction with Cl atoms, where there is much more vibrational excitation in the old bond, and only 58% of the CN fragments appear in the ground vibrational state. The interaction potential of Cl with HCN changes the dynamics from those with H or O, making the surviving bond a participant rather than a spectator to the reaction. Calculations of the ab initio potential energy surfaces for the H and Cl systems<sup>29</sup> suggest that the Cl reaction occurs for larger approach angles and involves the CN moiety more completely than do the reactions with H and O.<sup>14</sup> The differences between the reaction with Cl and those with H and O emphasize the important role of both the initially selected vibrational state and the attacking atom.

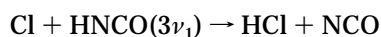
**Inferring Mechanisms and Directing Reactions.** The energy disposal in the reactions of vibrationally excited water shows that the surviving bond is a spectator, and these spectator dynamics make the reaction rate depend strongly on the details of the vibrational excitation. As shown above, the  $|03\rangle^-$  state reacts about half as fast as the  $|04\rangle^-$  state, while the  $|02\rangle^-$  state reacts at a barely detectable rate. The slightly more energetic state, having one quantum in one bond and two in the other,  $|12\rangle^-$ , reacts much more slowly than the  $|03\rangle^-$  state, which has all the energy in one bond. In fact, it seems to react no better than the  $|02\rangle^-$  state, suggesting that *only* the energy in the bond that becomes part of the reaction coordinate counts.<sup>7–9</sup> This mode-selective chemistry occurs in part because removing one quantum from the reaction coordinate leaves barely enough energy in that degree-of-freedom to surmount the barrier. At higher energies, the differences are less dramatic although clearly present.<sup>9</sup>

All of the energy to drive a reaction does not have to come from vibration, and it is possible to trade some vibrational energy for translational energy in many hydrogen atom abstraction reactions. For example, a detailed study of vibrationally excited methane,  $\text{CH}_4$ , reacting with



translationally energetic Cl atoms reveals much about the dynamics of the reaction.<sup>12</sup> Simpson et al. excited a quantum of stretching vibration in CH<sub>4</sub> molecules and observed their reaction with photolytically produced Cl atoms using REMPI detection of the HCl product. Their detection scheme provided information not only about the quantum state populations of the HCl product but also about its recoil direction, and they found that the 30% of the HCl born in  $\nu = 1$  preferentially scatters in the forward direction (with respect to the incoming Cl atom) for low rotational states. Because the photolysis laser imposes a preferential direction on the Cl atoms in the laboratory frame, they were able to investigate a steric effect directly by changing the approach of the Cl atom to the vibrationally excited C–H bond and show that the Cl approaches the vibrationally excited CH<sub>4</sub> through a relatively large cone of acceptance. They inferred that the methyl fragment carries away little internal energy, providing another example of spectator behavior but with subtle features of the product formation.

The vibrational eigenstate selected chemistry of a four-atom molecule, isocyanic acid (HNCO), shows yet another competition between possible reaction pathways. Vibrational overtone spectroscopy of HNCO molecules cooled in a supersonic expansion reveals couplings between the N–H stretching zero-order state and other states containing bending quanta.<sup>30</sup> Although the spectroscopic analysis provides many details of the interactions among vibrational states, the most important point in the present context is that the highly vibrationally excited eigenstates in the region of three quanta of N–H stretching excitation are different mixtures of N–H stretching and bending excitation. The result of reacting HNCO in these states with Cl atoms,



is striking. States containing only stretching excitation react almost twice as fast as isoenergetic states containing a mixture of stretching and bending excitation.<sup>16</sup>

Action spectra, in which one observes the relative reactivity of pairs of states that are different mixtures of the same zero-order states, show that the bending vibration actually *inhibits* the hydrogen abstraction reaction. Ab initio calculations of the interaction potential of HNCO with Cl shown in Figure 5 reveal the means by which bending excitation stymies the H atom abstraction reaction.<sup>16</sup> The interaction potential for a Cl atom approaching an HNCO molecule becomes increasingly attractive in the vicinity of the carbon atom as the N–C–O bending angle decreases. The attraction arising from bending excitation effectively “steals” some of the incoming Cl atoms that would otherwise react with the H atom and directs them toward the C atom, where they form a complex or recoil without reacting, a diversion that inhibits the production of HCl. This change in the interaction potential to reduce the reactivity bears a close connection to a recent inference that bending excitation enhances the reaction of Cl

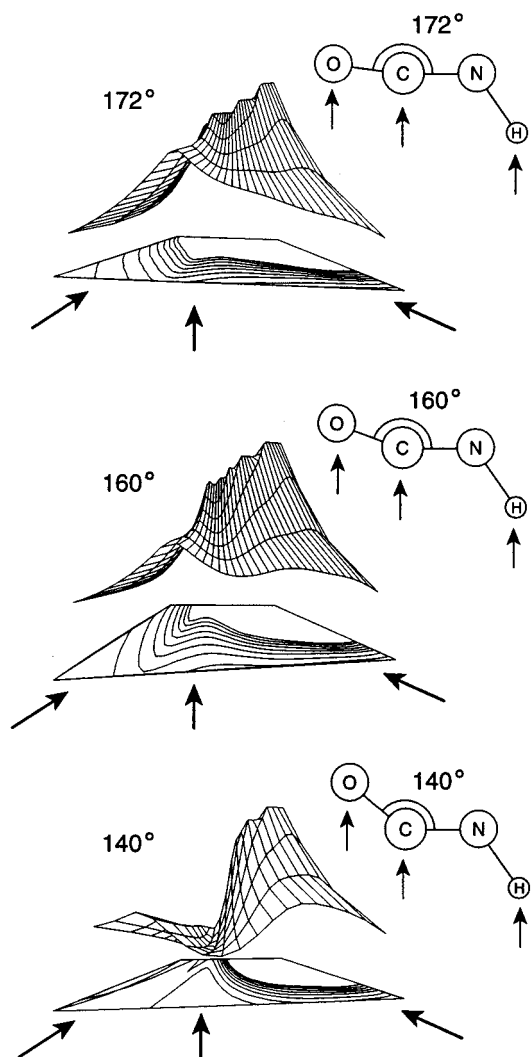
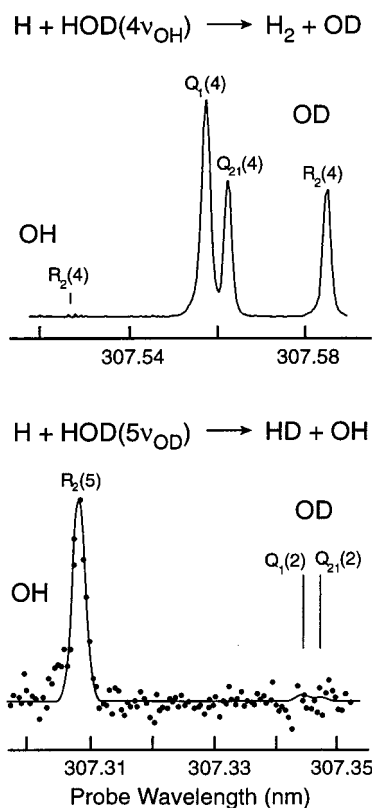


FIGURE 5. Interaction potential for Cl with HNCO molecules having different N–C–O bending angles.

with CH<sub>4</sub> to form HCl and CH<sub>3</sub>.<sup>31</sup> Kandel et al. concluded from measurements of the differential reaction cross section that thermally populated bending vibrations accelerated the reaction. Both the inhibition of H atom abstraction by Cl for HNCO and its acceleration for CH<sub>4</sub> share a common origin in the dependence of the interaction potential on the bending angle. In the reaction with HNCO, bending carries the reactant molecule into non-reactive configurations, while with CH<sub>4</sub>, bending carries it into reactive ones.

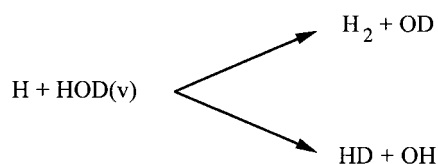
## Bond-Selected Bimolecular Reactions

The observation that an atom reacts with only one vibrationally excited bond in water points to a means of using laser excitation to break a selected bond in a bimolecular reaction. Replacing one of the H atoms with a D atom differentiates the bonds so that we can investigate their selective reaction.<sup>5,6</sup> Exciting rovibrational transitions belonging to only HOD allows us to prepare its vibrations selectively in a gaseous mixture of HOD, H<sub>2</sub>O, and D<sub>2</sub>O. We excite O–H and O–D stretches and use laser-induced fluorescence to observe the relative



**FIGURE 6.** Laser-induced fluorescence spectra showing the relative production of OH and OD in the reactions of HOD( $4\nu_{\text{OH}}$ ) and HOD( $5\nu_{\text{OD}}$ ) with H atoms. The spectra show that the reaction of HOD( $4\nu_{\text{OH}}$ ) preferentially breaks the O–H bond to yield OD radicals and that the reaction of HOD( $5\nu_{\text{OD}}$ ) does the opposite. The line in the lower trace is a fit through the points.

yields of OD, left behind after the abstraction of a H atom, and OH, which remains after removal of a D atom, Figure



6 shows laser-induced fluorescence excitation spectra of products formed when H atoms react with HOD molecules excited to either a molecular eigenstate that is primarily four quanta of O–H stretch ( $4\nu_{\text{OH}}$ ) or one that is primarily five quanta of O–D stretch ( $5\nu_{\text{OD}}$ ). The energies of the two states lie within 12 kJ/mol ( $1000 \text{ cm}^{-1}$ ) of each other, but their reaction products are very different. The upper trace, taken after excitation of four quanta of O–H stretch, shows that HOD( $4\nu_{\text{OH}}$ ) reacts to form OD in at least a 200-fold excess over OH, and the lower trace, taken after excitation of five quanta of O–D stretch, shows the opposite. These two measurements demonstrate that, in HOD, the vibrationally excited bond indeed reacts preferentially. Reactions with both Cl and O atoms behave the same way.<sup>5,6</sup>

Driving the reaction in one direction with vibrational excitation does not require that all the energy come from vibration. Bronikowski et al.<sup>11</sup> excited the fundamental

O–H or O–D stretching vibrations and used translationally energetic H atoms to provide the remainder of the energy. They also observed a preferential reaction of the vibrationally excited bond, albeit with less selectivity. The difference in selectivity for the two experiments again points to an essential element of driving bond-selected bimolecular reactions. The excitation needs to be in a motion that preferentially carries the system along the reaction coordinate for cleaving the target bond. The HOD molecule is almost ideal for demonstrating bond-selected bimolecular reactions because its two stretching eigenstates closely resemble vibrations of individual bonds and its atom abstraction reaction proceeds by a direct, spectator mechanism.

## Challenges and Directions

Laser-driven, bond-selective bimolecular chemistry is a reality. Preparing a molecular eigenstate with motion along the reaction coordinate for abstraction of an atom accelerates the reaction. The natural limit that eigenstate-driven bimolecular chemistry must encounter comes from the requirement that the eigenstate contain a significant amount of motion along the reaction coordinate. For sufficiently large and strongly coupled molecules, the individual eigenstates may well be mixtures of so many different zero-order states that they contain little of the zero-order state that projects onto the reaction coordinate. In particular, the reactive zero-order state might be diluted among so many eigenstates that none of them contains enough excitation of one bond over another to produce selective reaction. One of the challenges for studies of eigenstate-controlled bond-selective chemistry is discovering the limits of using stationary states to control reactions in larger molecules. Clearly, studies of the vibrational spectroscopy of molecules containing enough energy to react are closely related to controlling reactions in larger molecules since spectroscopy reveals the intramolecular couplings that determine the nature of the eigenstates.

Experiments in which the bright zero-order state projects well onto the reaction coordinate are particularly convenient because the bright zero-order state leaves a clear spectroscopic signature on the eigenstates. Excitation with a short laser pulse whose bandwidth spans all of the molecular eigenstates that contain some of the bright state, such as those illustrated in Figure 2, initially prepares the bright zero-order state rather than an eigenstate. This nonstationary state then evolves, transferring energy into other states in the molecule, in a time determined by the couplings among the states. While the zero-order state remains, one can react it selectively. However, such a prompt encounter is a very stringent demand for a bimolecular reaction since the reactive collision must occur while the zero-order state survives. This requirement is less of a problem for a photodissociation, where one can use another short pulse soon after the preparation of the nonstationary state to dissociate the vibrationally excited molecule. In fact, we have prepared the zero-order

state consisting of two quanta of O–H stretching excitation in nitric acid (HONO<sub>2</sub>) and followed the flow of energy from it using photodissociation to observe the arrival of energy in other parts of the molecule. These measurements show that the initially excited zero-order state survives for less than 12 ps.<sup>32</sup>

A great deal of chemistry occurs not in low-density gases, where molecules interact rarely, but in liquids, where molecules interact continuously. Thus, another major challenge is to accelerate and control chemical reactions in liquids by selective vibrational excitation. At the density of a liquid, molecules collide every 100 fs, a time interval accessible with current laser technology. There are already examples of using short laser pulses to probe the vibrational states of the products populated by the reaction of an atom with a solvent.<sup>33</sup> The stage is set to drive bimolecular reactions in solutions with processes analogous to those used in the gas phase. There are challenges in two broad categories to those attempting to accelerate and control reactions with vibrational energy. One is to use stationary vibrational states prepared in low-pressure gases to control bimolecular chemistry in larger molecules. The other is to use nonstationary states to drive reactions in liquids.

*The National Science Foundation supports the work described in this Account. A group of able and enthusiastic graduate students and postdoctoral associates, many of whose names appear in the references, have conducted our research on the dynamics of bimolecular reactions.*

## References

- (1) Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity*; Oxford University Press: New York, 1987.
- (2) Hawthorne, G.; Sharkey, P.; Smith, I. W. M. Rate Coefficients for the Reaction and Relaxation of Vibrationally Excited H<sub>2</sub>O(|04<sup>-</sup>) with H atoms and H<sub>2</sub>O. *J. Chem. Phys.* **1998**, *108*, 4693–4696.
- (3) Crim, F. F. Bond-Selected Chemistry: Vibrational State Control of Photodissociation and Bimolecular Reaction. *J. Phys. Chem.* **1996**, *100*, 12725–12734.
- (4) Zare, R. N. Laser control of chemical reactions. *Science* **1998**, *279*, 1875–1879.
- (5) Sinha, A.; Hsiao, M. C.; Crim, F. F. Bond-Selected Bimolecular Chemistry: H + HOD(4ν<sub>OH</sub>) → OD + H<sub>2</sub>. *J. Chem. Phys.* **1990**, *92*, 6333.
- (6) Metz, R. B.; Thoemke, J. D.; Pfeiffer, J. M.; Crim, F. F. Selectively Breaking Either Bond in the Bimolecular Reaction of HOD with Hydrogen Atoms. *J. Chem. Phys.* **1993**, *99*, 1744–1751.
- (7) Sinha, A.; Hsiao, M. C.; Crim, F. F. Controlling Bimolecular Reactions: Mode and Bond Selected Reaction of Water with Hydrogen Atoms. *J. Chem. Phys.* **1991**, *94*, 4928.
- (8) Sinha, A.; Thoemke, J. D.; Crim, F. F. Controlling Bimolecular Reactions: Mode and Bond Selected Reaction of Water with Translationally Energetic Chlorine Atoms. *J. Chem. Phys.* **1992**, *96*, 372.
- (9) Thoemke, J. D.; Pfeiffer, J. M.; Metz, R. B.; Crim, F. F. Mode- and Bond-Selective Reactions of Chlorine Atoms with Highly Vibrationally Excited H<sub>2</sub>O and HOD. *J. Phys. Chem.* **1995**, *99*, 13748–13754.
- (10) Hsiao, M. C.; Sinha, A.; Crim, F. F. Energy Disposal in the Vibrational State- and Bond-Selected Reaction of Water with Hydrogen Atoms. *J. Phys. Chem.* **1991**, *95*, 8263.
- (11) Bronikowski, M. J.; Simpson, W. R.; Girard, B.; Zare, R. N. Bond-Specific Chemistry—OD-OH Product Ratios for the Reactions H+HOD(100) and H+HOD-(001). *J. Chem. Phys.* **1991**, *95*, 8647–8648. Bronikowski, M. J.; Simpson, W. R.; Zare, R. N. Effect of Reagent Vibration on the H+HOD Reaction—An Example of Bond-Specific Chemistry. *J. Phys. Chem.* **1993**, *97*, 2194–2203.
- (12) Simpson, W. R.; Rakitzis, T. P.; Kandel, S. A.; Orrewing, A. J.; Zare, R. N. Reaction of Cl With Vibrationally Excited CH<sub>4</sub> and CHD<sub>3</sub>—State- to-State Differential Cross-Sections and Steric Effects For the HCl Product. *J. Chem. Phys.* **1995**, *103*, 7313–7335.
- (13) Pfeiffer, J. M.; Metz, R. B.; Thoemke, J. D.; Woods, E.; Crim, F. F. Reactions of O, H, and Cl atoms with Highly Vibrationally Excited HCN: Using Product States to Determine Mechanisms. *J. Chem. Phys.* **1996**, *104*, 4490–4501.
- (14) Kreher, C.; Rinnenthal, J. L.; Gericke, K. H. Vibrational State Control of Bimolecular Reactions. *J. Chem. Phys.* **1998**, *108*, 3154–3167; Kreher, C.; Theinl, R.; Gericke, K. H. State-To-State Reaction Dynamics of R+HCN (ν<sub>1</sub>ν<sub>2</sub><sup>l</sup>ν<sub>3</sub>) → RH+CN(v,J) with R = Cl, H. *J. Chem. Phys.* **1996**, *104*, 4481–4489.
- (15) Ravichandran, K.; Williams, R.; Fletcher, R. Atmospheric Reactions of Vibrationally Excited Greenhouse Gases—SH+N<sub>2</sub>O (N, 0, 0). *Chem. Phys. Lett.* **1994**, *217*, 375–380.
- (16) Woods, E.; Cheatum, C. M.; Crim, F. F. Using Stretching and Bending Vibrations to Direct the Reaction of Cl Atoms with Isocyanic Acid (HNCO). *J. Chem. Phys.*, in press.
- (17) Anderson, S. L. Mode-Selective Differential Scattering as a Probe of Polyatomic Ion Reaction Mechanisms. *Acc. Chem. Res.* **1997**, *30*, 28–36.
- (18) For example, see: Fu, H. S.; Qian, J.; Green, R. J.; Anderson, S. L. Vibrational Mode-selected Differential Scattering of NH<sub>3</sub><sup>+</sup> + Methanol (d<sub>1</sub>, d<sub>3</sub>, d<sub>4</sub>): Control of Product Branching by Hydrogen-bonded Complex Formation. *J. Chem. Phys.* **1998**, *108*, 2395–2407.
- (19) For example, see: Guettler, R. D.; Jones, G. C.; Posey, L. A.; Zare, R. N. Partial Control of an Ion–Molecule Reaction by Selection of the Internal Motion of the Polyatomic Reagent Ion. *Science* **1994**, *266*, 259–261.
- (20) Rosencwaig, A. *Photoacoustics and Photacoustic Spectroscopy*; Academic Press: New York, 1981.
- (21) The two identical bonds in water require the identification of the state as either a symmetric or an antisymmetric combination of the states with different amounts of stretching excitation in each bond. The states we excite are the antisymmetric combinations. For example, the antisymmetric combination of four quanta in one bond and none in the other is |04<sup>-</sup>, and the antisymmetric combination having three quanta in one bond and one in the other is |13<sup>-</sup>.
- (22) Child, M. S.; Halonen, L. Overtone Frequencies and Intensities in the Local Mode Picture. *Adv. Chem. Phys.* **1984**, *57*, 1–58.
- (23) Schatz, G.; Colton, M.; Grant, J. A Quasiclassical Trajectory Study of the State-to-State Dynamics of H + H<sub>2</sub>O → OH + H<sub>2</sub>. *J. Phys. Chem.* **1984**, *88*, 2971–2977.

- (24) Kudla, K.; Schatz, G. C. A Quasi-Classical Trajectory Study of Mode-Specific Reaction Dynamics in the  $\text{Cl}+\text{HOD}$  and  $\text{H}+\text{HOD}$  Reactions. *Chem. Phys.* **1993**, *175*, 71–82.
- (25) Schatz, G.; Wu, G.; Lendvay, G.; Fang, D.; Harding, L. Reaction of H with Highly Vibrationally Excited Water: Activated or Not? *Faraday Discuss.*, in press.
- (26) Nyman, G.; Clary, D. C. Quantum Scattering Calculations on  $\text{H}_2\text{O}+\text{H} \rightarrow \text{H}_2+\text{OH}$  and Isotopes—Rotational Distributions and Cross Sections. *J. Chem. Phys.* **1993**, *99*, 7774–7786. Clary, D. C. Four-atom Reaction Dynamics. *J. Phys. Chem.* **1994**, *98*, 10678–10688. Nyman, G.; Clary, D. C. Vibrational and Rotational Effects in the  $\text{Cl}+\text{HOD} \rightarrow \text{HCl}+\text{OD}$  Reaction. *J. Chem. Phys.* **1994**, *100*, 3556–3567.
- (27) Bowman, J.; Wang, D. Mode Selectivity in Reactions of H with  $\text{HOD}(100)$ ,  $\text{HOD}(001)$ , and  $\text{HOD}(002)$ . *J. Chem. Phys.* **1992**, *96*, 7852. Wang, D. S.; Bowman, J. M. Quantum Calculations of Mode Specificity in Reactions of H with  $\text{HOD}$  and  $\text{H}_2\text{O}$ . *J. Chem. Phys.* **1993**, *98*, 6235–6247.
- (28) The three quantum numbers designate the C–N stretch, the H–C–N bend, and the C–H stretch, respectively.
- (29) Harding, L. B. A theoretical study of reactions on the  $\text{ClHCN}$  surface. *J. Phys. Chem.* **1996**, *100*, 10123–10130.
- (30) Coffey, M.; Berghout, H.; Woods, E., III; Crim, F. Vibrational Spectroscopy and Intramolecular Energy Transfer In Isocyanic Acid ( $\text{HNCO}$ ). *J. Chem. Phys.* **1999**, *110*, 10850–10862.
- (31) Kandel, S. A.; Zare, R. N. Reaction Dynamics of Atomic Chlorine with Methane: Importance of Methane Bending and Torsional Excitation in Controlling Reactivity. *J. Chem. Phys.* **1998**, *109*, 9719–9727.
- (32) Bingemann, D.; Gorman, M. P.; King, A. M.; Crim, F. F. Time-Resolved Vibrationally Mediated Photodissociation of  $\text{HNO}_3$ : Watching Vibrational Energy Flow. *J. Chem. Phys.* **1997**, *107*, 661–664.
- (33) Raftery, D.; Iannone, M.; Phillips, C. M.; Hochstrasser, R. M. Hydrogen Abstraction Dynamics in Solution Studied By Picosecond Infrared-Spectroscopy. *Chem. Phys. Lett.* **1993**, *201*, 513–520. Raftery, D.; Gooding, E.; Romanovsky, A.; Hochstrasser, R. M. Vibrational Product State Dynamics in Solution-Phase Bimolecular Reactions—Transient Infrared Study of  $\text{CN}$  Radical Reactions. *J. Chem. Phys.* **1994**, *101*, 8572–8579.

AR950046A