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# Laser Control of Chemical Reactions

Richard N. Zare

Experiments show how product pathways can be controlled by irradiation with one or more laser beams during individual bimolecular collisions or during unimolecular decompositions. For bimolecular collisions, control has been achieved by selective excitation of reagent vibrational modes, by control of reagent approach geometry, and by control of orbital alignment. For unimolecular reactions, control has been achieved by quantum interference between different reaction pathways connecting the same initial and final states and by adjusting the temporal shape and spectral content of ultrashort, chirped pulses of radiation. These collision-control experiments deeply enrich the understanding of how chemical reactions occur.

One of the intriguing aspects of reaction dynamics is the possibility that what we learn might allow us to control the outcome of chemical reactions (1). The practical reasons for seeking such control range from suppressing unwanted side products to synthesizing new structures and new materials. Control of chemical reactions is a well-established concept. Successful control is commonly practiced by a variety of means, such as varying the external conditions of the reaction mixture by changing, for example, the temperature or the pressure, or finding a suitable catalyst that selectively lowers the activation barrier to the desired reaction products.

Here, I explore a different approach to reaction control where we, as chemists, "guide" the reaction process during a single reactive encounter. This guidance usually takes one of two forms. First, we may select one or more internal energy states of the reagent before collision. State preparation has a long history of successful applications. Some preparations depend simply on increasing the energy available to the reactants. Others involve more subtle effects such as control by promoting internal motions that aid or hinder various reaction pathways and stereodynamic control in which the three-dimensional geometry of the activated complex is selected. Second, we may actively intervene during the course of the reaction and guide the reactants by controlling the phase of their motions. This active control may cause the reactants to follow preferentially one of many different reaction routes. This second procedure is less well established, but in some cases, very promising results have been recently obtained. In what follows, I present a few examples of collision control along with an assessment of what has been accomplished to date and what likely lies ahead.

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## Mode-Selective Chemistry

In 1972, Polanyi (2) proposed that vibrational excitation along the reaction coordinate would be more efficacious than translational motion in promoting endoergic (uphill) reactions with a "late" reaction barrier, that is, reactions in which the transition-state region occurs late in the passage from reactants to products. Since then, a number of atom-plus-diatom reaction studies confirmed this conjecture (3), but extension of the idea to reactions involving polyatomic molecules was rather slow in coming. In 1984, Schatz and co-workers (4) carried out quasi-classical trajectory calculations on the  $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}$  reaction, which is estimated to have a reaction barrier of  $7580 \text{ cm}^{-1}$  (5). Schatz *et al.* (4) clearly demonstrated that the reaction rate should be enhanced by excitation of the H-OH stretching vibration of water, because the transition-state geometry shows a marked preference for extension of one of the O-H bonds in water.

An isotopic variant of water, HOD, has proven to be an excellent candidate system for demonstrating the power of vibrational control of polyatomic reagents to influence the outcome of a chemical reaction. The H-OD and HO-D stretching frequencies are approximately at  $3800 \text{ cm}^{-1}$  and  $2800 \text{ cm}^{-1}$ , respectively. Consequently, these two stretches are quite distinct and represent nearly pure stretching modes. The first example of the power of reagent vibrational excitation in controlling the outcome of a bimolecular reaction with a polyatomic reagent was achieved by Crim and co-workers (6), who found that reaction of thermal H atoms with HOD prepared with four quanta in the H-OD stretch produces almost exclusively  $\text{H}_2 + \text{OD}$ , whereas reaction of thermal H atoms with HOD prepared with five quanta in the HO-D stretch produces almost exclusively  $\text{HD} + \text{OH}$ . In this experimental study, the H atoms were generated

with a microwave discharge, and the HOD molecule was prepared in a selected overtone stretch by laser irradiation in the visible wavelengths. Zare and co-workers (7) showed that the product-branching ratio selectivity was reduced but still survived for reactions of fast H atoms with HOD prepared in either the H-OD or HO-D stretching fundamental. Here, fast H atoms were generated by photolysis of HI, and the HOD stretching fundamental was excited by laser irradiation in the infrared. Bronikowski *et al.* (8) went on to examine the reaction of fast H atoms with  $\text{D}_2\text{O}$ , in which the  $\text{D}_2\text{O}$  was prepared in either the asymmetric stretching fundamental or in a combination band consisting of the asymmetric stretch and one quantum of the bend. The bending motion was found to be ineffective in promoting reaction, as expected. Other examples of vibrational-state control on polyatomic reactions are  $\text{Cl} + \text{HOD}$  (9) and  $\text{Cl} + \text{HCN}$  (10). All these studies definitively demonstrate what is called mode-selective chemistry, which means for the same internal energy content, the mode of internal excitation controls the reaction outcome.

Examples of mode-selective chemistry are not limited to bimolecular neutral reactions. For example, the  $\text{NH}_3^+ + \text{ND}_3$  reaction shows clear distinctions among the three product branches [ $\text{NH}_3 + \text{ND}_3^+$  (charge transfer),  $\text{NH}_2 + \text{ND}_3\text{H}^+$  (proton transfer), and  $\text{NH}_3\text{D}^+ + \text{ND}_2$  (D-atom abstraction)], depending on whether the  $\text{NH}_3^+$  was selectively prepared with excitation of its umbrella inversion mode or its all-symmetric stretching mode (11). Charge transfer is enhanced with umbrella inversion motion, and this effect has been rationalized by the preference of the neutral molecule to take on a pyramidal geometry. This argument is analogous to the Franck-Condon principle (12). The more energetic all-symmetric stretch is found to be essentially inactive. Theoretical calculations are able to model this behavior well (13).

Another example of how the selection of nuclear motion of the reagent can influence reaction outcome has been provided by Anderson and co-workers (14) who studied the ion-molecule reaction  $\text{C}_2\text{H}_2^+ + \text{CH}_4$  in which the acetylene cation was prepared with vibrational excitation in either the C-C stretch or the *cis*-bend. The reaction proceeds by two mechanisms. At low collision energies, the dominant reaction is mediated by a strongly bound  $\text{C}_3\text{H}_6^+$

complex that breaks apart to produce either  $C_3H_5^+ + H$  or  $C_3H_4^+ + H_2$ . This complex is sufficiently long-lived that the H atoms in an isotopically labeled experiment are scrambled. The complex-mediated mechanism decreases in importance with increasing collision energy and with C-C stretch vibration to a similar extent, but *cis*-bending excitation enhances the reactivity via this mechanism by 50 to 100%, depending on collision energy. A direct H-atom abstraction mechanism competes with this mechanism, yielding  $C_2H_3^+ + CH_3$ . This slightly endoergic channel is enhanced by nearly a factor of 30 by *cis*-bending excitation. At low collision energies, this bending excitation favors the direct over the complex reaction channel by a factor of 40. Collision energy and C-C stretching also enhance the direct mechanism at low collision energies, but much less markedly than bending excitation. Recoil velocity measurements reveal that direct H-atom abstraction proceeds through a weakly bound complex with a lifetime of about 1 ps. Anderson and co-workers proposed that two different bent transition-state geometries control the direct and complex-mediated reaction channels. Subsequent theoretical studies by Klippenstein (15) are consistent with this model.

Just as mode-selective chemistry can be achieved by localizing vibrational energy in a bond or a motion along the reaction coordinate, so can selectivity also be achieved by localized electronic excitation. Examples are the selective breaking of the C-I or C-Br bonds in  $CH_2IBr$  and the C-S and S-H bonds in  $CH_3SH$  by Butler, Lee, and co-workers (16).

How effectively mode-selective chemistry can be applied to collisions between large polyatomic molecules remains an unsettled

issue. It seems that three conditions must be met to achieve mode-selective chemistry: First, it must be possible to excite a state of the reagent (an eigenstate or a superposition of eigenstates) that localizes energy in some part of the molecule; second, this energy must remain relatively localized during the reaction; and third, this prepared state must promote or hinder reactivity of that portion of the molecule to cause a change in the product-branching ratio. Fast, direct reactions fulfill these criteria best because it is necessary for the reaction to occur before the excitation energy becomes statistically distributed among the degrees of freedom available, in which case vibrational excitation is no more effective than heat.

### Stereodynamic Control

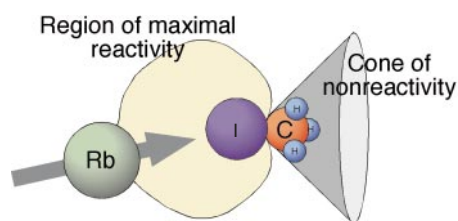
Another type of state preparation is control of the reagent approach geometry, which also may be called stereodynamic control (17). The orientation of one reagent with respect to the other is usually achieved by colliding two beams of reagents in which one reagent is oriented or aligned by the application of an external electric field, such as a strong homogeneous electric field (18) or an inhomogeneous field created by a hexapole. Alternatively, the rotational angular momentum direction of one reagent is controlled by the absorption of linearly polarized light (19). For example, Brooks and co-workers (20) and Bernstein and co-workers (21, 22) reacted alkali atoms M with  $CH_3I$  molecules oriented by a hexapole field to give  $MI + CH_3$  and showed that reaction preferentially occurred when M collided with the I end of the molecule (Fig. 1). Loesch and co-workers (23) reacted Sr and K atoms with vibrationally excited HF molecules aligned with linearly polarized light to give  $SrF + H$  and  $KF + H$ , respectively. At low collision energies, reactivity of Sr with HF is favored by the HF bond being perpendicular to the Sr approach direction, whereas reactivity of K with HF is favored by the HF bond being parallel to the K approach direction. In contrast, at higher collision energies, reactivity of Sr with HF reverses so that the HF bond prefers to be parallel to the Sr approach direction, whereas reactivity of K with HF becomes insensitive to the alignment of the HF bond. These studies show that by controlling the plane of rotation of HF with respect to the incoming atom, the HF reagent presents distinctly different chemical shapes in the reaction with a monovalent K atom or with a divalent Sr atom as a function of collision energy.

Not only is it possible to control the nuclear framework in a reactive encounter, but it is also possible to control the direc-

tion of the electronic charge distribution for open-shell reagents, as was first demonstrated by Rettner and Zare (24) on the reactions of electronically excited calcium atoms ( $Ca\ 3s3p\ ^1P$ ) with various halogen-containing compounds. Since then, many related studies have been carried out. Lee and co-workers (25) investigated the electron transfer rates for the collisions of aligned, electronically excited Ba atoms with  $NO_2$  to yield  $Ba^+$ . The rate of electron transfer varied by more than a factor of 2 as the orientation of the p orbital occupied by the electron was changed. Leone and co-workers (26) performed an extensive set of inelastic scattering studies using orbitally aligned, excited alkaline earth atoms. Ding *et al.* (27) showed that orbital alignment of  $Ca(^1P)$  colliding with  $CH_3I$  can influence the  $CaI$  product vibrational distributions. Although orientation and alignment studies have shown that reaction rates can only be changed by less than an order of magnitude, these studies do provide an impressive probe of the three-dimensional geometries of reaction pathways.

Reagent approach geometry may also be controlled, to some extent, by starting with a loosely bound (van der Waals) complex of the form AB attached to CD and photolyzing the CD moiety to liberate C and D. Then the reaction of  $AB + C$  can be investigated, in which the approach geometry is set by the structure of the complex. Quite interesting experiments of this type have been carried out by the research groups of Soep (28), Wittig (29), and Zewail (30), among others. A related approach, advocated by Polanyi (31), is to photolyze molecules adsorbed on a surface. The difficulty with interpreting this type of experiment is that the spatial relations between AB and CD in the loose complex or on the surface may be poorly known or poorly constrained, or both. Moreover, the spectator D may not get out of the way soon enough, thus becoming an "unwanted participant," that interferes with the reaction.

Stereodynamic control is also possible for gas-surface scattering reactions. For example, Jacobs and co-workers (32) studied collisions of fast  $NO^+$  with the (111) face of single-crystal silver. In this gas-surface scattering system, both  $NO^-$  and  $O^-$  are detected, although the yield of negative ions is less than  $10^{-4}$ . The  $NO^+$  is prepared from the NO neutral precursor via resonance enhanced multiphoton ionization, and the polarization of the radiation is used to select whether the ion collides end-on or side-on with the surface. Jacobs and co-workers found that end-on collisions enhance  $O^-$  production by a factor of two compared to side-on collisions, but hardly affect  $NO^-$  production. They interpret their



**Fig. 1.** Observed steric effect for the  $Rb + CH_3I \rightarrow RbI + CH_3$  reaction. An oriented beam of  $CH_3I$  is crossed with an atomic beam of Rb; the RbI product is measured as a function of  $CH_3I$  orientation. Reactivity to produce back-scattered RbI is maximal for direct collisions of Rb with the I end of the C-I bond axis; reactivity decreases when the Rb impacts the side of the methyl iodide molecule and becomes vanishingly small in a region labeled as the "cone of nonreactivity." The Rb atom strikes the  $CH_3I$  molecule from any direction; the arrow shown is just an example. This figure is adapted from Parker and Bernstein (22).



data as involving fast neutralization of the ion on the surface followed by collision-induced dissociation and electron capture, the order of these two latter events being undetermined. This mechanism suggests that the end-on approach geometry is favored for  $O^-$  production because it leads to the lengthening of the N-O bond upon surface impact (Fig. 2). Classical trajectory calculations (32) support this explanation and suggest that vibrational excitation of the  $NO^+$  would enhance  $O^-$  production. Indeed, in subsequent studies of  $NO^+$  on the (110) face of gallium arsenide, it was shown that that  $NO^+$  ( $v = 6$ ) is 2.4 times more effective than  $NO^+$  ( $v = 0$ ) in production of  $O^-$ , whereas if the same energy of vibrational excitation is placed into  $NO^+$  ( $v = 0$ ) translation, the  $O^-$  yield increases only by a factor of 1.14 (33). Thus, both stereodynamic and vibrational control should be expected to be applicable for such processes.

## Quantum Control

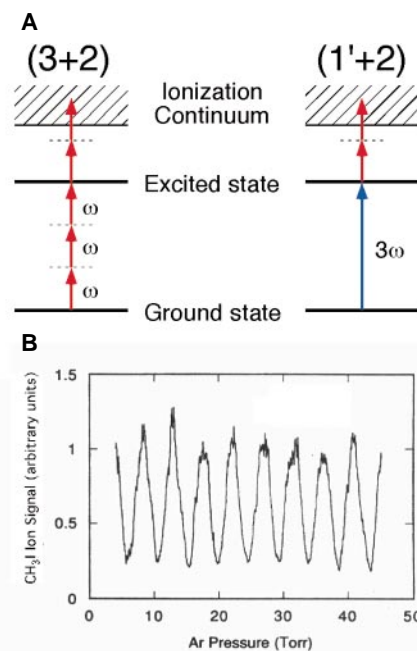
I turn next to phase control, which is most easily understood by reference to Young's celebrated two-slit experiment in optics. Here, a monochromatic plane wave is incident on two small circular apertures (slits). At each aperture, a new spherical wave emerges and travels to an observation screen at a distance large compared to the wavelength of the light. Each spherical wave has a fixed phase relation to the incident light wave and, hence, to each other. The observation screen shows an alternating pattern of bright and dark fringes. This interference pattern depends on whether the two waves are in or out of phase at any point on the observation screen, that is, whether they interfere constructively or destructively. Mathematically, the intensity of the screen

spot is proportional to the square of the total electric field  $E$  at that spot, that is,  $|E_1 + E_2|^2 = |E_1|^2 + |E_2|^2 + 2|E_1||E_2|\cos\phi$ , where  $\phi$  is the phase difference. The generalization to more than two slits is straightforward. Control of the phase difference  $\phi$  governs the intensity at any point.

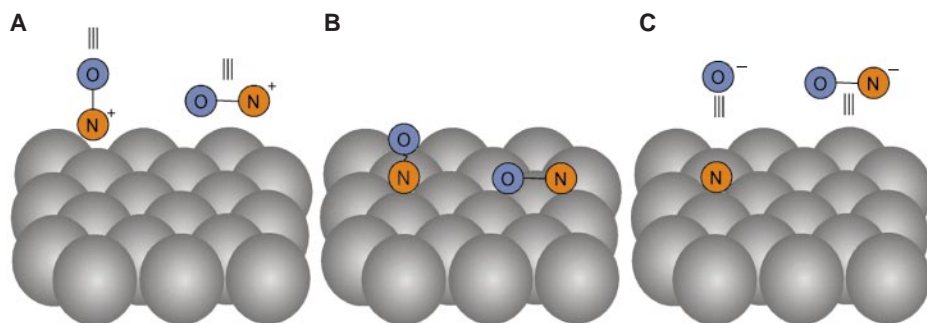
The molecular scattering equivalent to Young's two-slit experiment arises when an initial molecular state can follow two different paths, characterized by wave functions  $\Psi_1$  and  $\Psi_2$ , that lead to the same final scattering state. The probability of being in that final state is then proportional to the square of the total wave function. Once again, the two wave function amplitudes must be summed together before squaring, and the probability of the process contains a cross term involving the phase of the two wave functions. It follows that by altering the relative phases of a set of competing paths, it is possible to control the transition probability. This idea for phase control of a molecular scattering event was first put forward by Brumer and Shapiro (34) and was successfully demonstrated by Chen *et al.* (35) for atoms and by Park *et al.* (36) for molecules. The basic idea they use is to excite an atom or a molecule by two different optical pathways that lead to the same upper state from which various processes such as ionization or dissociation can occur by the absorption of a subsequent photon (37). In this manner, the upper state is created in a coherent superposition of (at least) two different product channels. The particular superposition depends on the optical pathway, that is, on how many photons are used to produce the excitation. It is to be expected that different optical pathways have different relative phases.

An example of the power of this type of

phase control is the study by Gordon and co-workers (38) who excited a beam of DI molecules with one photon at 118 nm and three photons at 354 nm. The experiment was begun with some phase relation between the two laser beams, and this phase relation was varied by passing both beams through a transparent gas medium. Because the refractive indices at the two different wavelengths vary, the phase can be controlled by changing the pressure inside the gas cell. The excited DI decays either by autoionization to produce  $DI^+ + e^-$  or by predissociation to produce a ground-state D atom and an excited  $I(^2P_{1/2})$  atom, which absorbs an additional photon to yield  $I^+$ . As the phase between the two laser beams is varied, the  $I^+$  and  $DI^+$  ion signals vary sinusoidally in and out of phase, and the depth of modulation typically reaches 15%. The relative yields are predicted to be a sinusoidal function of this phase difference and a function of the relative intensities of the fundamental and third harmonic of the light. Recently, Bersohn and co-workers (39, 40) studied the interference between the  $1' + 2$  and  $3 + 2$  multiphoton ionization of methyl iodide (Fig. 3), ammonia,



**Fig. 3.** Illustration of quantum control in the multiphoton ionization of  $CH_3I$ . **(A)** Three-photon and one-photon transitions from the ground state of methyl iodide to the same intermediate Rydberg state interfere in the  $(3 + 2)$  and  $(1' + 2)$  photoionization of methyl iodide. As the argon pressure is increased in a gas cell through which both the (one-photon) red and (three-photon) ultraviolet beams pass (red and blue arrows, respectively), the phase varies between them, which causes the observed modulation in the  $CH_3I$  ionization signal **(B)**. This figure is adapted from Bersohn and co-workers (39).



**Fig. 2.** Schematic drawing illustrating the effect of stereodynamic control in the production of  $O^-$  in collisions of aligned  $NO^+$  with a single-crystal silver surface: **(A)**  $NO^+$  approaches the  $Ag(111)$  surface either end-on or side-on, and in either case, the ion is rapidly neutralized; **(B)** the end-on collision causes a compression of the N-O bond, whereas the side-on collision does not compress the bond; **(C)** the compressed N-O bond is more likely to break, causing the formation and escape of  $O^-$  whereas the uncompressed molecule is less likely to rupture. The time ordering between N-O bond rupture and electron transfer from the surface is not known. This figure is based on the work of Jacobs and co-workers (32).

trimethylamine, triethylamine, cyclooctatetraene, and 1,1-dimethylhydrazine. [Here, the notation ( $n + m$ ) indicates that  $n$  photons are absorbed in the transition from the ground state to the intermediate state and  $m$  photons are absorbed in the transition from the intermediate state to the ionization continuum. A prime is added to a number to indicate a different frequency from the unprimed number.] In all experiments, interference was observed, which suggests that molecular size may be little obstacle to this type of phase control, provided that the molecule has sufficiently strong absorptions at the fundamental and at the frequency-tripled output of the laser beam to a bound intermediate state. One intriguing possibility for future work is the proposal (41) of controlling bimolecular reactions by preparing one of the reagents in a coherent superposition of its internal states.

The most general scheme for controlling the evolution of a molecule undergoing some dynamical process is to control the interaction of the molecule and an electromagnetic field whose spectral and temporal characteristics are continuously tuned (chirped) throughout the evolution of the molecular system in such a manner as to favor a particular outcome of the time evolution of the molecular state. One implementation of this general scheme has been put forward by Tannor and Rice (42), who proposed to vary the interval between an initial pump pulse of radiation that transfers amplitude from the ground state of the molecule to the excited state and a dump pulse of radiation that transfers amplitude in the opposite direction. As has been pointed out by Rabitz and co-workers (43) and by Kosloff, Rice, and co-workers (44), optimal control theory may be used to find the pulse shape and spectral content of the pulse that maximizes the yield of the specified product.

So far, experimental examples of this type of control are rather sparse, but quite recently, Wilson and co-workers (45) investigated the effect of chirped femtosecond pulses on the three-photon absorption of  $I_2$ . They demonstrated a significant enhancement compared to transform-limited zero-chirped pulses. For a positively chirped pulse, the low-frequency components arrive before the high-frequency components, whereas the order is reversed for a negatively chirped pulse. An ultrashort pulse with its concomitantly broad spectral character prepares a coherent superposition of excited molecular states, and the corresponding wave packet evolves in time. In this experiment, the absorption process is resonantly enhanced and corresponds to the sequence  $X \rightarrow B \rightarrow$

$C \rightarrow D$ , where the capital letters denote different electronic states of the  $I_2$  molecule. A fluorescence signal at 340 nm from collisionally relaxed  $D \rightarrow A$  emission is detected. Wilson and co-workers found that at 570 nm, a positively chirped pulse yields an increase by a factor of 3 in the  $D \rightarrow A$  fluorescence signal compared to the shortest, transform-limited pulse. They suggest that the three-photon absorption enhancement involves several factors. These include a time-delay resonance mechanism, in which the high-frequency components of the positively chirped pulse arrive as the moving wave packet comes into resonance with the  $B \rightarrow C$  transition; a wave packet-following mechanism, in which the change in pulse frequency follows in time the change in the wave packet's electronic transition energy; and a sequential resonance mechanism, in which the chirp provides frequencies that are first resonant with  $X \rightarrow B$ , then with  $B \rightarrow C$ , and finally with the  $C \rightarrow D$  transitions.

The extension of this type of quantum control to large molecules in solution, which is the medium in which most chemistry is done, is a challenging task both because of the complexity and because of the lack of detailed understanding about such a system. It should be possible, however, to use the behavior of the molecular system in an iterative manner (feedback control) to "teach" the experimenter how to tailor the radiation guidance (46). The first preliminary but promising report of such a success has just been made by Wilson, Warren, and co-workers (47) who tailored femtosecond pulses by a computer-controlled acousto-optic pulse shaper to excite fluorescence from an infrared laser dye in solution.

## Concluding Remarks

Collision control is presently a topic of intense research activity. The increasing versatility of laser sources and laser techniques underpins almost all advances. Until the cost of performing photon-induced chemical reactions is greatly reduced, however, no practical applications can be anticipated for this type of chemical reaction control. Moreover, in many cases the effects are too small to be useful. Nevertheless, the real gain in pursuing laser-based collision control is likely to be the increased understanding of how chemical reactions occur, which in time will no doubt lead to important applications.

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# Quantum Theory of Chemical Reaction Dynamics

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It is now possible to use rigorous quantum scattering theory to perform accurate calculations on the detailed state-to-state dynamics of chemical reactions in the gas phase. Calculations on simple reactions, such as  $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$  and  $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ , compete with experiment in their accuracy. Recent advances in theory promise to extend such accurate predictions to more complicated reactions, such as  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ , and even to reactions of molecules on solid surfaces. New experimental techniques for probing reaction transition states, such as negative-ion photodetachment spectroscopy and pump-probe femtosecond spectroscopy, are stimulating the development of new theories.

Experiments and theory on chemical reaction dynamics aim to study the details of reactions beyond just simple rate constants at room temperature (1). Reactant and product molecules can have different translational energies, varying angles of orientation and different internal quantum states. Developing experiments and theory to study such microscopic aspects of chemical reactions, and to probe directly the structure and lifetimes of reaction transition states (2, 3), has become a major field. The results provide the most detailed insight into the mechanisms of chemical reactions and are useful also in a variety of other contexts. For example, an understanding of both atmospheric (4) and combustion processes (5) can require data on the chemical reactions of molecules in selected vibrational quantum states, and modeling of the nonequilibrium environments of interstellar clouds (6) needs information on the reaction rates of molecules in selected rotational states for low collision energies.

Theory has a special role to play in chemical reaction dynamics as it is often essential for extracting useful information from experimental results. Furthermore, reaction dynamics theory can now provide detailed predictions with an accuracy that can rival experiment on simple reactions in the gas phase (7), and the theory has been extended, albeit more approximately, to

more complex problems such as reactions of polyatomic molecules (8) and reactions on solid surfaces (9) and in solution (10).

## Quantum Reaction Dynamics

The best theory of chemical reactions uses quantum mechanics. The Born-Oppenheimer approximation is usually invoked, allowing electronic and nuclear motion to be separated, so that a calculation reduces to two separate steps: solution of the Schrödinger equation for the electrons with fixed positions of the nuclei to obtain a potential energy surface, followed by solution of the “quantum scattering” Schrödinger equation for the nuclei moving on this potential energy surface.

Significant advances in ab initio quantum chemistry techniques are enabling potential energy surfaces to be calculated to a high accuracy for simple reactions (11). However, one problem is that reaction rate constants  $k(T)$  often depend exponentially on the height  $E_a$  of the barrier in a potential energy surface according to the Arrhenius expression  $k(T) = A \exp(-E_a/RT)$ , where  $A$  is a constant,  $R$  is the gas constant, and  $T$  is temperature. This exponential dependence shows that  $E_a$  needs to be calculated extremely accurately. This constraint presents a major problem for quantum chemistry calculations on reactions involving molecules with several electrons.

In a quantum scattering calculation on a chemical reaction  $\text{A} + \text{BC}(v, j) \rightarrow \text{AB}(v',$

$j') + \text{C}$  in the gas phase, it is necessary to use coordinates that go smoothly from reactants to products and can describe the initial  $(v, j)$  and final  $(v', j')$  vibration-rotation molecular states accurately. Devising the most appropriate coordinates has not been straightforward. A useful “hyper-spherical coordinate” approach is to take the bonds being broken and formed in the reaction and transform them into polar coordinates  $(\rho, \theta)$  (12). The “hyper-radius”  $\rho$  has the advantage that it can be used as a common scattering coordinate for both the entrance and exit channels of the reaction. The time-independent Schrödinger equation  $H\Psi = E\Psi$  can then be solved, and scattering boundary conditions can be applied to calculate reaction probabilities selected in all of the vibration-rotation states of reactants and products and with well-defined collision energy. This method has been used quite widely on reactions involving three atoms (13) and has also recently been applied to four-atom reactions (8).

A different approach is to solve the time-dependent Schrödinger equation for the nuclear motion. This method has the computational advantage that reaction out of individual reactant quantum states can be computed efficiently (14). However, it has been difficult until recently to extend this “wave packet” technique to calculate state-to-state reaction probabilities. Therefore, total reaction probabilities summed over all product states are often computed.

The large number of coupled vibrational and rotational states of molecules that can be involved in chemical reactions has made the solution of the nuclear Schrödinger equation computationally expensive. Therefore, the field of theoretical reaction dynamics has had to wait for the modern generation of fast computers with large memory capabilities before reliable calculations have been possible. This is why the field of quantum reaction dynamics is now suddenly blossoming.

## Simple Reactions

How well does the best theory do when compared with the best experiments? One of the simplest chemical reactions is  $\text{H} + \text{D}_2(v = 0, j = 0) \rightarrow \text{HD}(v', j') + \text{D}$ . This reaction has been studied in one of the most detailed experiments that can be performed, crossed-molecular beam experi-

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