

ULTRAFAST REACTION DYNAMICS

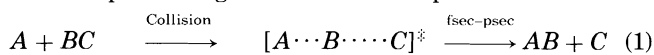
Martin Gruebele
and Ahmed H. Zewail

With new laser techniques and with gas phase and molecular beam experiments, it is now possible to determine the ultrafast motion in isolated chemical reactions—chemistry on the 10^{-13} -second time scale.

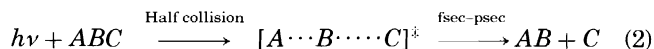
A decade ago this magazine devoted a special issue to laser chemistry (see *PHYSICS TODAY*, November 1980). One of the articles emphasized the importance of time scales in chemical reactions and the possible use of ultrashort laser pulses to induce chemistry. Over the past 10 years new laser techniques, and gas-phase and molecular-beam experiments, have revealed much about the fundamental steps of elementary chemical reactions. These approaches and the tremendous detail they have exposed about the dynamics of chemical reactions are the subject of the present article.

The most elementary steps into which any sequence of chemical reactions can be broken have a common time scale dictated by the rapidity of nuclear rearrangement. This fundamental chemical time scale ranges from 10 femtoseconds to 10 picoseconds. Research in gas phase-molecular beam chemical dynamics uses either indirect or direct time-resolved methods to study such chemical motions free of external perturbations, the goal being an understanding of what happens in these $10\text{--}10^4$ femtoseconds.

In general, one can write an elementary chemical reaction proceeding from reactants to products as follows:



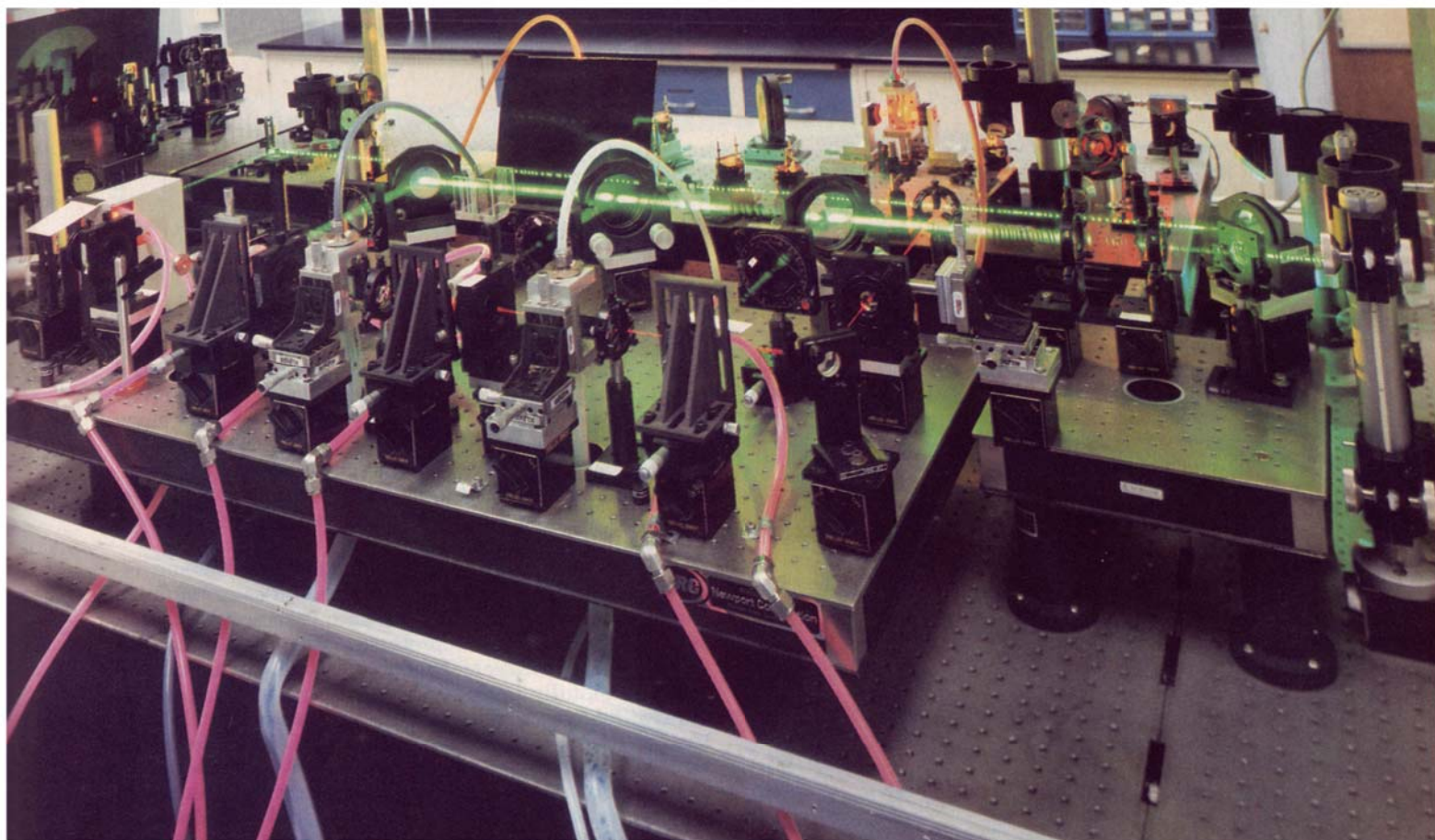
Reactants Transition state Products



The division between the two sides is provided by very-short-lived (fsec-psec) transition states, which have characteristics between those of the reactants and those of the products. (The symbol \ddagger indicates a transition state.) There is a unique transition state that defines reaction rates in some theories, but it is the continuum of transition configurations along the reaction path that determines the dynamics. We use the term “transition state” in its broadest sense to include all of these possibilities.

As depicted in the above equations, the transition

Martin Gruebele is a postdoctoral research fellow and **Ahmed Zewail** is Linus Pauling Professor of Chemical Physics at the California Institute of Technology.



Femtosecond laser system for investigating transition states of chemical reactions. The apparatus at Caltech generates and amplifies ultrashort laser pulses for real-time studies of the reactions. Another part of the apparatus, not shown, houses a molecular-beam system for studies under isolated conditions. **Figure 1**

state can be reached in two different ways, depending on the reaction. In case 1, the transition state $[ABC]^{\ddagger}$ results from a collision of two reaction partners. The products then separate in the second half of the collision process, and the two halves comprise a full collision—a bimolecular reaction. In case 2, $[ABC]^{\ddagger}$ is formed by depositing sufficient energy in a stable molecule. This is followed by the second half of the collision process leading to products, and is described as a half-collision—a unimolecular dissociation reaction. In many cases, the latter method of preparing the transition state allows one to select its properties more simply, which may be useful in understanding the dynamics.

The nuclear and electronic motions in the transition state, which lives for only 10 picoseconds or less, fully determine the outcome of the reaction, although the reactants encounter each other and the products are detected on a time scale 10^3 to 10^6 times slower than the reactive process of interest. Understanding the transition state therefore means understanding the chemical act.

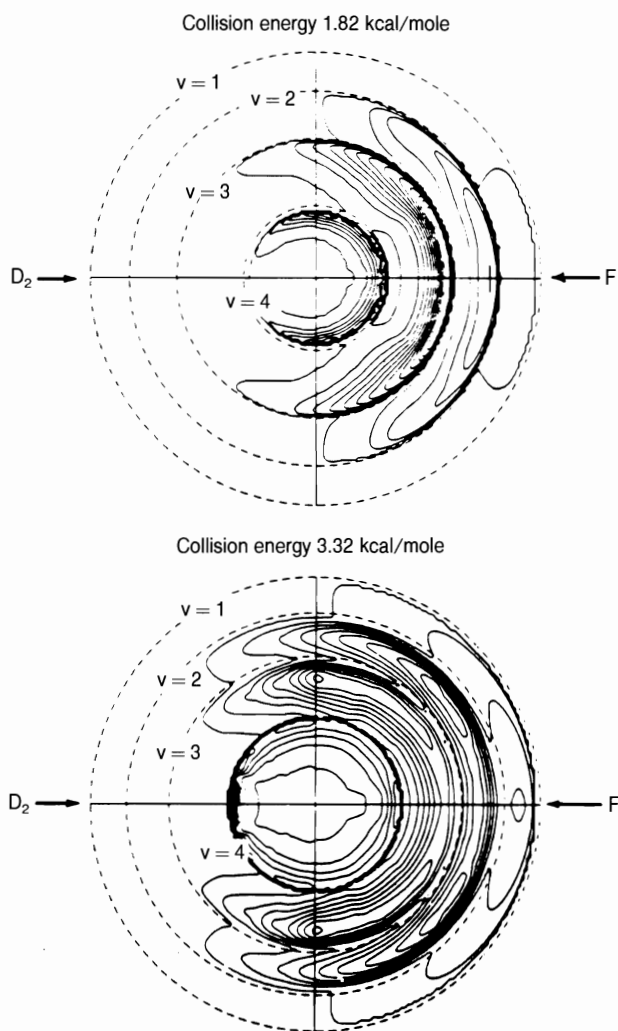
Theory has helped our understanding of this fundamental problem by addressing two main issues: the multidimensional potential energy surface governing nuclear motion during the reaction and the nature of the nuclear dynamics itself under a variety of initial conditions of energy and angular momentum. On the experimental side, there has been great progress in developing new methods using molecular beams, lasers and other tools, and in probing chemical reactions in the gas phase.

Until recently, the experimentally achievable time resolution was insufficient for direct studies of the transition state in either full or half collisions, and research concentrated on “before” (reactants) and “after” (products) the collision or half-collision.¹ With ultrashort laser pulses (figure 1) and gas phase-molecular beam experiments, it is now possible to observe the various stages of the reaction. These approaches provide a complementary study of chemical reactions, one concentrating on the asymptotic properties of the reaction, such as the state distribution of products, the other focusing on a direct view of the transition state in real time.

The remainder of this article comprises three main sections. The first describes spectroscopic and molecular beam experiments that study products and reactants in equations 1 and 2; it explains what these experiments allow us to say about a reaction. The second section describes novel steady state (that is, no time resolution) methods that indirectly probe the transition region. The final section describes work at Caltech on real-time ultrafast reaction dynamics and the transition state. The discussion is not meant to be exhaustive, but rather to point out a few typical examples of what can be done and to show how the various approaches can interact to give us a full picture of chemical reactions on a fundamental level.

Reactants and products

The studies of chemical reactions by molecular beams and lasers have led to important advances in reaction dynam-



Velocity contour maps of deuterium fluoride produced in the reaction $F + D_2 \rightarrow DF + D$. The results of the molecular beam experiment are shown for two different collision energies. At lower energy (top) DF is mostly back scattered, while at high energy (bottom) forward scattering is also observed for the vibrational state $v = 4$. The presence of forward and backward scattering for $v = 4$ indicates a long-lived collision complex. The dotted circles represent maximum velocity limits for the given vibrational states, as dictated by energy conservation. (Adapted from D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, J. Shobatake, R. K. Sparks, T. P. Schafer, Y. T. Lee, *J. Chem. Phys.* **82**, 3067, 1985.) **Figure 2**

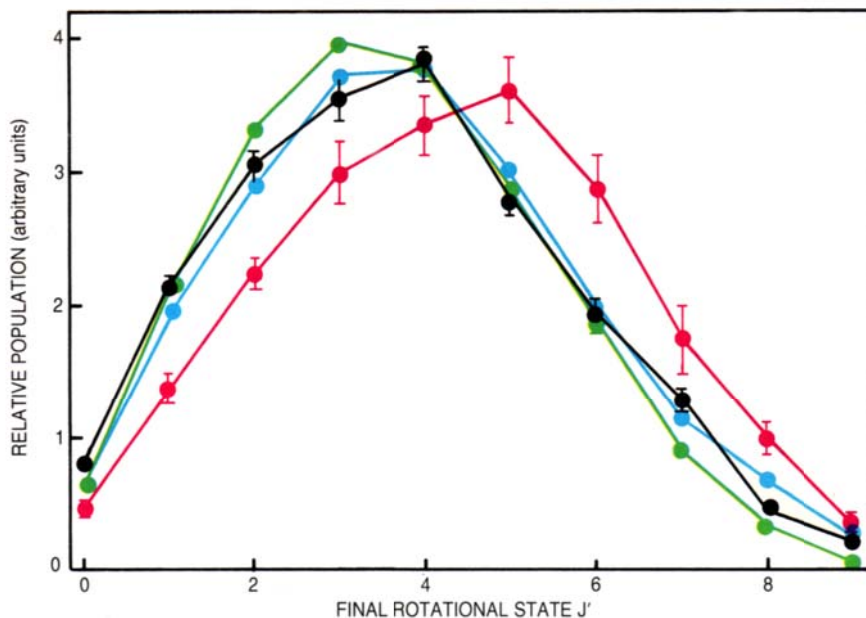
ics. These tools afford energy and spatial (or orientational) resolution, and have been integrated into a variety of experimental techniques.¹

Molecular beams allow one to determine the spatial and translational energy distribution of the product of two colliding beams of molecules. Furthermore, one can use these beams to cool reactant molecules to low vibrational and rotational temperatures.

Lasers are used to deposit a well-defined amount of energy in a molecule, to dissociate molecules or to probe for the presence of products and reactants through spectroscopically known processes, such as absorption, emission and ionization. Product-state distributions have been successfully probed in many reactions using laser-induced fluorescence² and chemiluminescence.³ Today's laser sources cover energy regimes from molecular rotations (0.001 eV) and vibrations (0.1 eV) to electronic transitions (1–10 eV), and molecular beams have become a major tool for studying the angular and translational energy distributions of chemical reaction products.⁴

Orientation⁵ and alignment⁶ techniques are also important methods for probing the “before” and “after” in reactions.¹ In an orientation experiment, the “heads and tails” of reactants are identified. For example, in one experiment, the polar “symmetric top” molecule CH_3I is oriented in the laboratory reference frame and then excited by a polarized laser beam to a dissociative electronic state. The atomic iodine produced is ejected primarily in one direction, indicating that the excited molecule dissociated before rotation. This observation sets an upper limit of 1 psec on the reaction time, in agreement with real-time measurements.¹ Using alignment with polarized lasers, one learns about reaction anisotropies or vector properties, such as the recoil direction relative to the initial polarization direction of the laser. When a polarized laser pulse excites a molecule to a dissociative electronic state, the degree of alignment in the products can, as in the orientation experiments, give a limit on the time scale for dissociation relative to the rotational period. Recently, many laboratories have studied the vector properties—or “stereodynamics”—of alignment experiments to learn about the dynamics of reactions.⁶

Some approaches to the study of chemical reactivity⁷ in bimolecular and unimolecular reactions—equations 1 and 2—are illustrated in two examples: the hydrogen exchange reaction and the ketene dissociation reaction. In the bimolecular reaction, two cold beams of reactants collide with a distribution of orientations and impact parameters. The resulting products, ejected from the interaction volume with varying degrees of internal excitation, are then analyzed. One can control the reactant internal energy by laser excitation and the translational energy by the crossing angle and the beam velocities.



Product-state distribution for the reaction $D + H_2(v = 0, J) \rightarrow HD(v' = 1, J') + H$, as determined in recent experiments at a center-of-mass collision energy of 1.05 eV. The quantum number J represents angular momentum, and v denotes the vibrational quantum number. Theoretical quantum mechanical calculations (blue and green curves) and a quasiclassical trajectory calculation (red) are shown for comparison with experiment (black). Both theory and experiment have contributed to our understanding of this class of reactions.²³ (Adapted from D. A. V. Kliner, K.-D. Rimmen, R. N. Zare, *Chem. Phys. Lett.* **166**, 107, 1990.) **Figure 3**

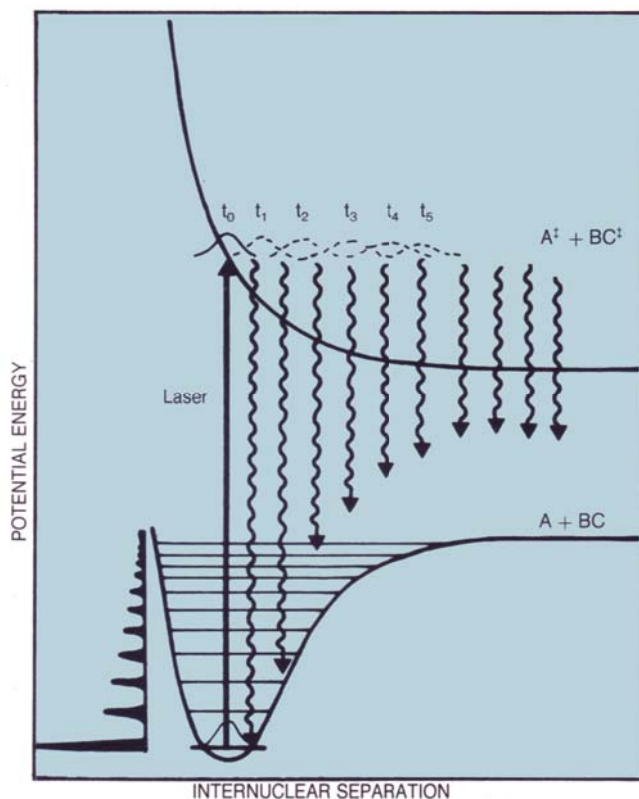
For the reaction of $F + D_2 \rightarrow D + DF$, the DF product is scattered primarily backward in the center-of-mass frame of the reactants, indicating the formation of a short-lived reaction intermediate (figure 2). The analogous exchange reaction of $H + H_2 \rightarrow H_2 + H$ is one of the simplest of all chemical reactions, but also one of the most difficult to study experimentally. It offers the best hope for a detailed comparison between theory and experiment because rigorous quantum mechanical calculations of the product excitation as a function of impact parameter and energy, as well as all other important properties, are possible. Gas phase-crossed beam experiments by many groups around the world are uncovering a wealth of information on reactive scattering cross sections and product-state distributions (figure 3). Comparison of these results with several theoretical calculations indicates that work remains to be done before even this simplest chemical reaction is fully understood.

For unimolecular reactions, on the other hand, the situation is different. A laser pulse excites the precursor above the dissociation energy, and the motions of nuclei on the potential-energy surface eventually lead to dissociation, as in equation 2. As an example, consider the dissociation of ketene ($H_2C = C = O$) to triplet or singlet (electronically excited) methylene (H_2C) and carbon monoxide (CO). One can use the fact that the carbon monoxide and methylene states appear abruptly as a function of energy to determine the reaction threshold for the singlet and triplet channels. Product-state distributions, and reactant-state to product-state rates have been measured.⁸

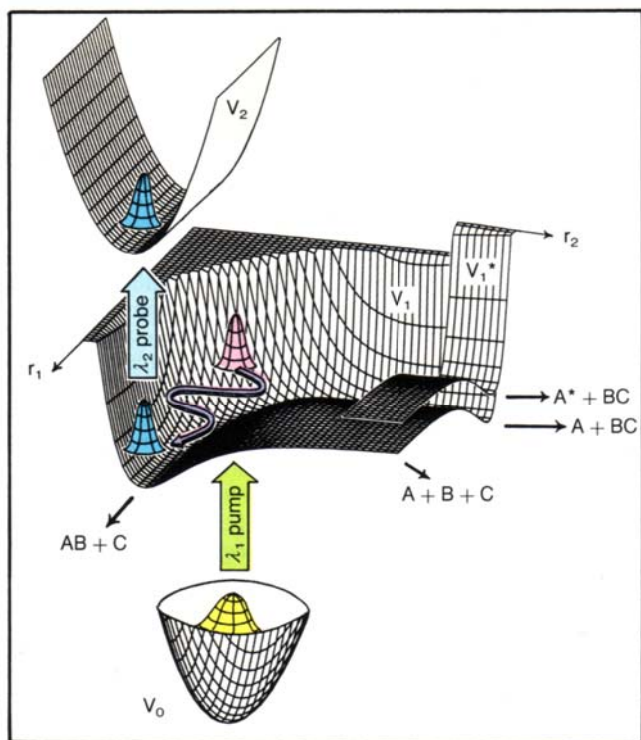
For many unimolecular reactions, one can compare the distribution of the product's rotational and vibrational states as a function of excess energy (energy above dissociation) with the various theories, such as the statistical RRKM theory, the statistical adiabatic channel theory or phase space theory. There are many vibrational and rotational degrees of freedom involved, and theory and experiment must address both the energy flow and the bond breaking. Indeed, much theoretical and experimental work has advanced this important area of half-collision dynamics.⁹ The time scale of the experiments, however, does not allow for direct study of the transition state.

The transition region

For closer examination of the potential energy surface near nonequilibrium configurations—that is, away from



Scheme for time-integrated studies of transition states, showing how Raman spectroscopy can be used to probe a dissociation reaction. A molecule of the form $A-BC$ (such as $I-CH_3$) is excited to a dissociative electronic state. As the wave packet moves to dissociation, a very weak emission to the ground-state vibrational levels can be measured, recording the behavior of the wave packet in the experimental intensities (represented by the peaks at the lower left). The bell-shaped curves labeled t_0 through t_5 are theoretical wave packets.²⁴ (Adapted from D. Imre, J. L. Kinsey, A. Sinha, J. Krenos, *J. Phys. Chem.* **88**, 3956, 1984.) **Figure 4**



Two-dimensional representation of a real-time femtosecond transition-state spectroscopy experiment. In this schematic diagram an ultrafast light pulse pumps the molecule ABC to the reactive surface V_1 . (In the bimolecular case, $A + BC$ is activated.) The molecular wave packet propagates to products $AB + C$. On its way, after a delay Δt , it is probed by a second femtosecond laser pulse, which takes it to the surface V_2 , from which a fluorescence, ion count or other suitable signal is detected. The motion of the dissociating wave packet can thus be imaged as a function of time. V_1^* indicates a second reactive surface, which in the case of $I-Hg-I$ corresponds to spin-orbit excited iodine. (Adapted from M. Gruebele, G. Roberts, A. H. Zewail, *Phil. Trans. Roy. Soc.*, to appear August 1990; see also ref. 16.) **Figure 5**

reactants and products—investigators have devised a number of novel schemes to probe the transition region more directly. These are steady-state experiments; the time resolution is much longer than the reaction time.

Studies of the dissociation of the alkali halide NaI have found “wing emission” around the sodium D line. This emission about the line is attributable in part to the reactive transition state—that is, to the sodium atom perturbed by the proximity of the iodine atom in the course of the reaction.¹⁰ Because the reaction time of about 10^{-13} sec is much shorter than the free-sodium emission lifetime of about 10^{-8} sec, the wing emission is weaker by five orders of magnitude compared to the sodium transition. However, this wing emission can, with the help of theory, project into the frequency domain features of the dynamics. Similarly, instead of transition-state emission, transition-state absorption¹¹ can be achieved by tuning the laser away from reactant and product absorption frequencies, but the signal is very weak.

Raman spectroscopy has recently been cleverly used to image the motion of the wave packet on the potential-energy surface. This approach can be understood simply in terms of wave packet theory, or through more formal quantum treatments. Consider again the example of CH_3I . The molecule is excited to a dissociative state by a laser pulse that is long compared to the dissociation time (as in all the cases discussed in this section). The dissociation to CH_3 and iodine can be viewed in terms of a wave packet moving outward along a reaction coordinate on the repulsive potential-energy surface. A very small fraction of the wave packet goes into the ground-state vibrational levels as the fragments separate, and one can analyze the intensities of the emission to image the motion (figure 4).

A different version of Raman spectroscopy—coherent anti-Stokes Raman scattering—has been applied to the hydrogen exchange reaction to obtain the absolute (not relative) state-to-state cross section.¹² The experiments were performed at many different reactant collision

energies to obtain the change in cross section with energy. In a static gas cell, hydrogen atoms are produced by photolysis and then made to interact with isotopic H_2 molecules. Deconvoluting the signal gives rotationally and vibrationally resolved product-state distributions as a function of hydrogen atom velocity; this velocity is determined by the photolysis laser wavelength. In this case the energy dependence of the reaction cross section (about 0.03 \AA^2) displays structure, indirectly reflecting resonances of the transition region. Theory and experiment are not yet in full agreement for this simplest of reactions, and the transition state, which lives only a few femtoseconds, has yet to be observed in real time.

In a very different kind of experiment, the transition region has been studied through photoelectron spectroscopy.¹³ In a beam of a stable negative ion, such as $ClHCl^-$, the electron is photodetached to yield the species $ClHCl$. The photoelectron spectrum reveals vibrational structure and puts lower limits on the lifetime of the short-lived intermediate.

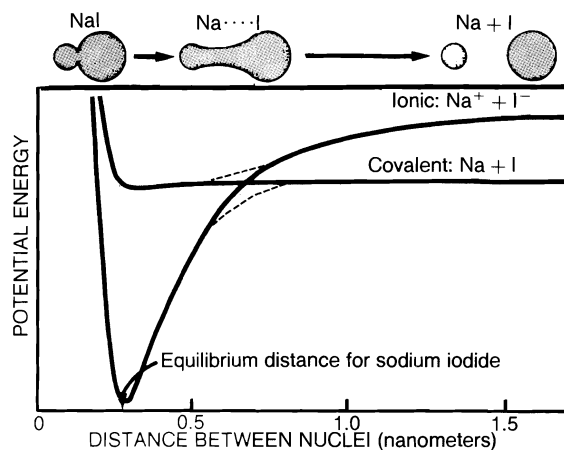
Theory has played an important role in all of these developments. Modern *ab initio* calculations of the potential energy surface for medium-sized reactive systems allow one to isolate transition states and other important features of the potential-energy surface. Classical and quantum scattering calculations can be performed on such a surface to extract important features of the dynamics for comparison with experiment. The most detailed potential-energy surface and dynamical calculations have been performed on the $H + H_2$ reaction. While experiment is generally ahead of theory for larger systems, theoretical calculations have provided valuable insights and approximations that guide our understanding of reaction dynamics.

Dynamics in real time

It took ultrafast laser technology over 20 years to reach the ultimate chemical time scale. The steps of progress¹⁴ were always large, and the current state¹⁵ of technology is reaching 8 fsec.

As discussed above, the main interest in chemical dynamics is the process of nuclear rearrangement on reactive potential-energy surfaces. The nuclear motions occur on the time scale of vibrations, or 10–1000 fsec; so 10–

Trapping of the wave packet on avoided-crossing surfaces of dissociation reactions. Top: In sodium iodide, the ionic potential curve and repulsive neutral curve intersect to form a quasibound potential well. Excitation of ground-state NaI to that potential produces a wave packet that vibrates back and forth, leaking a little (about 10%) to Na + I products every time it approaches the crossing region. Bottom: The experimental observations. The upper curve is the result of probing the sodium D line directly; it shows the growth of products in steps of about 1 psec. The lower curve is the result of probing the packet at longer wavelengths, in the transition region, to reveal its 1-psec periodic motion inside the potential well. (Intersecting surfaces adapted from J. Baggott, *New Scientist*, 17 June 1989, p. 58; experiments from T. Rose, M. J. Rosker, A. H. Zewail, *J. Chem. Phys.* **91**, 7415, 1989.) **Figure 8**



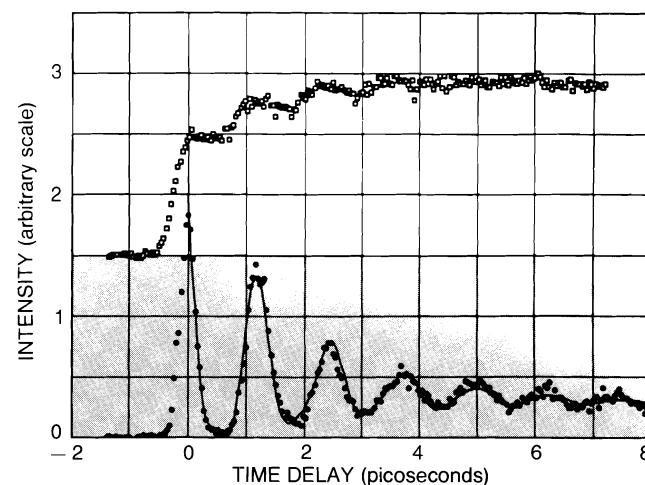
tional energy of HgI and the translational energy of the two recoiling fragments. As figure 5 shows, the excited-state surface has a saddle point near the vertical excitation limit from the ground state. Because of the large spin-orbit coupling in iodine (the energy difference between I and I* is 0.94 eV), there are two energy-displaced exit channels, and the laser pulse probes two energy regimes—the I and I* channels, shown as V_1 and V_1^* in figure 5.

The pump laser prepares a wave packet near the saddle point, and the wave packet initially moves out along the symmetric stretching coordinate. At high energies, this motion continues essentially unperturbed, on to full dissociation into three fragments, as represented by the bottom part of equation 3. As the energy is decreased, the wave packet leaks into the two HgI channels, and HgI at lower vibrational excitation is formed, as represented by the top part of equation 3.

Depending on the energy of the probe laser (figure 9), one can obtain two types of femtosecond transients in a given channel. Near 2 eV, one probes the fragments at a very early time during dissociation, and a femtosecond transition-state spectroscopy signal is observed as the fragments briefly become resonant with the probe laser. Near 3.2 eV, one probes transitions in essentially free HgI, and coherent oscillations due to vibrational excitation in the HgI product are observed. The higher the vibrational excitation in HgI, the longer the observed vibrational period, due to the anharmonicity of the potential curve. These observations give us a detailed “photographic” picture of the dissociation reaction, both near the transition state and after the products have formed (figure 9).

One question of interest is the alignment of the product relative to the reactant as a function of time. On the 400-fsec time scale of fragment separation, the HgI₂ bending motion, which is transformed into HgI rotational angular momentum and relative I/HgI angular momentum, should not be very important. At longer times, however, the alignment gives us information on the nature of the torque imposed on the HgI and hence the distribution of angular momentum in the product. This has been studied theoretically and experimentally to get information on possible crossings of potential-energy surfaces and on the effect of bending vibrational motions. Simple ABA systems are a fascinating source of insight into fundamental chemical dynamics, and much will be learned from them in coming years.

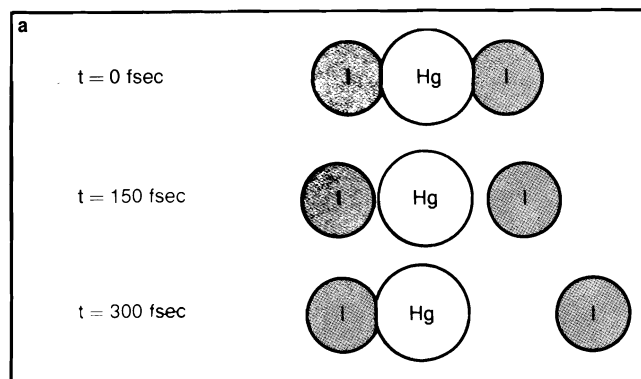
Full collisions. The final level of complexity is the



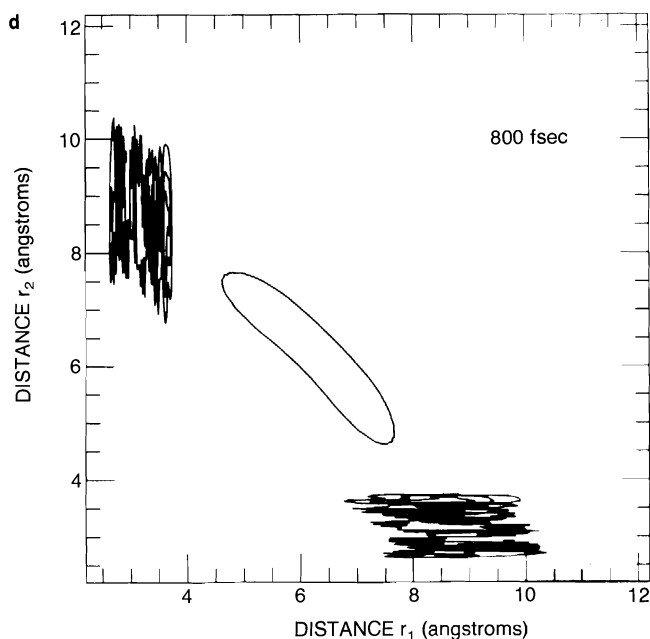
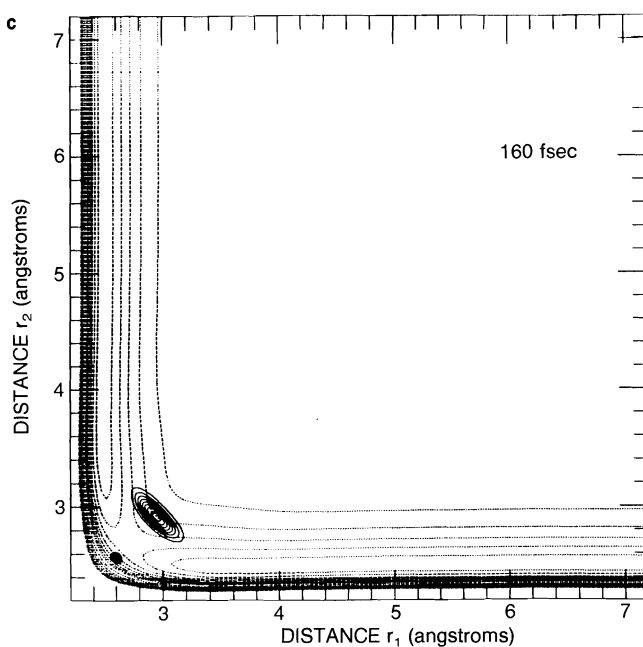
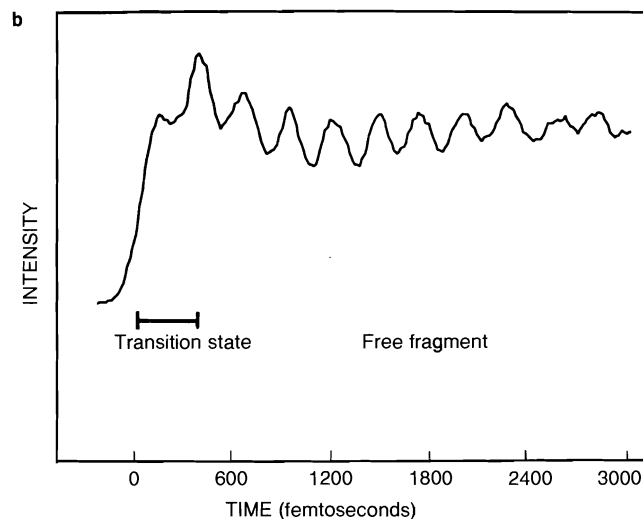
bimolecular or full chemical reaction, and the culmination of ultrafast chemical studies is the investigation of the nuclear motions in such reactions. At first it seems that this goal might lie outside the reach of ultrafast experiments: In crossed molecular beams, two reactant molecules travel for nanoseconds or microseconds before colliding in the interaction region. This long time utterly destroys the sensitive femtosecond timing required to resolve the molecular motions.

A solution to this zero-of-time problem uses ultrashort pulses.²⁰ It relies on the van der Waals forces to hold the reactants in close proximity before the initiation of the reaction.²¹ Figure 10 illustrates the principle for the reaction $H + CO_2 \rightarrow HO + CO$, which was studied at Caltech. A pump pulse dissociates the HI molecule in the approximately T-shaped HI·CO₂ system, providing a well-defined zero of time. The H atom then forms a collision complex with the CO₂, which breaks into HO and CO.

Experiments show that the lifetime of the [HOCO][‡] complex is about 5 psec. These experiments also indicate an induction period for complex formation: Although the H atom, at the dissociation energies used, could travel the 2 Å to the CO₂ molecule in a matter of 0.1 psec or less, it appears to take longer to form the complex. Better temporal resolution should reveal interesting motional structure and should show the detailed nature of the induction period. A unique feature of this class of bimolecular reactions is that one can change the precursor—by using HBr instead of HI, for example—and thus change the initial condition of the reaction. However, the intermolecular vibrational amplitude of the van der Waals bond is large, and thus a large span of impact angles between the two reactant molecules will be covered. Such changes also



Evolution of *ABA*-type reactions on a potential surface with a saddle point. **a:** The *AB* molecule (Hgl in this case) comes out vibrationally hot. **b:** The experimental spectra show the corresponding oscillatory motion from the transition-state region to final fragments. **c,d:** Snapshots of a quantum wave packet calculation, at an energy 1350 cm^{-1} above the total $\text{Hg} + \text{I} + \text{I}^*$ dissociation energy. The two coordinates correspond to the two Hg-I bonds in dissociating IHgl. The small oval at $(3\text{ \AA}, 3\text{ \AA})$ in frame **c** is the wave packet at $t = 160\text{ fsec}$, while the initial packet is at $(2.6\text{ \AA}, 2.6\text{ \AA})$; the other lines are potential energy contours. At 800 fsec, the wave packet has spread into the free fragment channels of $\text{I} + \text{Hgl}$ and $\text{I} + \text{Hg} + \text{I}$. (Experimental results adapted from M. Dantus, R. M. Bowman, M. Gruebele, A. H. Zewail, *J. Chem. Phys.* **91**, 7437, 1989; quantum calculation adapted from M. Gruebele, G. Roberts, A. H. Zewail, *Philos. Trans. R. Soc.*, to appear August 1990.) **Figure 9**



allow one to study the effect of the “spectator” halogen on the dynamics. We have now reached a stage where the time resolution is sufficient to observe the dynamics in this class of reactions. Such studies, together with time-integrated experiments in which the products are selected in their vibrational and rotational states, will yield a much more detailed picture of the dynamics in systems with many degrees of freedom.

Perspectives

Ten years ago, we would not have predicted many of the developments outlined above. Since 1980 the techniques described here have allowed much progress toward the central issues of chemical reactivity: energy redistribution in molecules, reactant-to-product reaction rates and the nature of the transition states. However, much remains to be studied in gas phase-molecular beam reaction dynamics, and the new energy- and time-resolved tools are opening new windows through which we can view and understand the elementary chemical act.

Future directions include both very simple and more complex reactions, reactions in clusters and on surfaces, autoionization²² and ion-molecule reactions. Theoretical work must address the increased need for accurate potential-energy surfaces and the methodology for obtaining the dynamics on them.

Reaction dynamics, one of the most fundamental areas of chemical physics, is reaching an exciting stage.

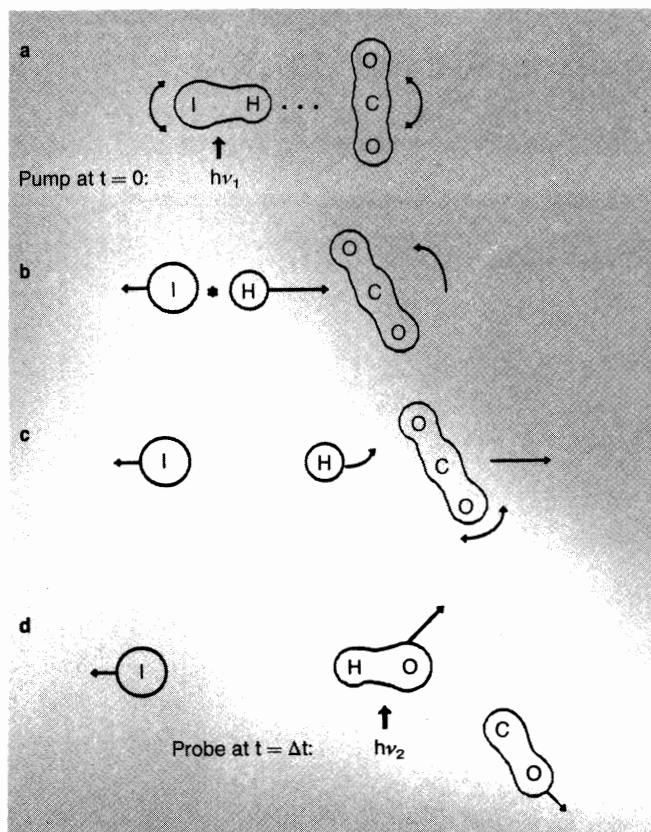
Experiment and theory are joining forces to learn at last about the heart of chemistry, the ephemeral transition state.

* * *

The work at Caltech is supported by the Air Force Office of Scientific Research and the National Science Foundation. We are grateful that Richard B. Bernstein is with us at Caltech at the writing of this article; his contribution to the manuscript was invaluable. We thank many colleagues for their help and for their interest in reading the manuscript prior to publication.

References

1. A. H. Zewail, R. B. Bernstein, *Chem. Eng. News* **66**, 24 (1988), and references therein.
2. H. W. Cruse, P. J. Dagdigian, R. N. Zare, *Faraday Disc. Chem. Soc.* **55**, 277 (1973).
3. J. C. Polanyi, *Angew. Chem. Int. Ed. Engl.* **26**, 952 (1987).
4. D. R. Hershbach, *Angew. Chem. Int. Ed. Engl.* **26**, 1221 (1987). Y. T. Lee, *Angew. Chem. Int. Ed. Engl.* **26**, 939 (1987).
5. R. B. Bernstein, S. E. Choi, S. Stolte, *J. Chem. Soc., Faraday Trans. 2*, **85**, 1097 (1989).
6. C. H. Greene, R. N. Zare, *Annu. Rev. Phys. Chem.* **33**, 119 (1982). R. Bersohn, *J. Phys. Chem.* **88**, 5145 (1984). M. Brouard, M. T. Martinez, C. J. Milne, J. P. Simons, J. X. Wang, *Chem. Phys. Lett.* **165**, 423 (1990). G. E. Hall, P. L. Houston, *Annu. Rev. Phys. Chem.* **40**, 375 (1989).
7. R. D. Levine, R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford U. P., New York (1987).
8. For further discussion of product-state distributions, see I.-C. Chen, W. H. Green Jr, C. B. Moore, *J. Chem. Phys.* **89**, 314 (1988). For further discussion of state-to-state reaction rates, see E. D. Potter, M. Gruebele, L. Khundkar, A. H. Zewail, *Chem. Phys. Lett.* **164**, 463 (1989).
9. For more on experiment, see the work of F. Crim, R. Huber, S. Leone, H. Reisler and C. Wittig, reviewed in ref. 1. For more on theory, see the work of K. Freed, R. Marcus, W. Miller, M. Quack, R. Schinke, M. Shapiro, J. Troe and others, reviewed in ref. 1.
10. H.-J. Foth, J. C. Polanyi, H. H. Telle, *J. Phys. Chem.* **86**, 5027 (1982).
11. T. C. Maguire, P. R. Brooks, R. F. Curl, J. H. Spence, S. Ulvick, *J. Chem. Phys.* **85**, 844 (1986).
12. J.-C. Nieh, J. Valentini, *Phys. Rev. Lett.* **60**, 519 (1988).
13. R. B. Metz, A. Weaver, S. E. Bradforth, T. N. Kitsopoulos, D. M. Neumark, *J. Phys. Chem.* **94**, 1377 (1990).
14. W. Kaiser, ed., *Ultrashort Laser Pulses*, Topics in Applied Physics 60, Springer-Verlag, New York (1988), and references therein. S. L. Shapiro, ed., *Ultrashort Light Pulses*, Topics in Applied Physics 18, Springer-Verlag, New York (1977).
15. C. V. Shank, *Science* **233**, 1276 (1986), and references therein.
16. A. H. Zewail, *Science* **242**, 1645 (1988), and references therein. L. Khundkar, A. H. Zewail, *Annu. Rev. Phys. Chem.* **41** (1990), in press.
17. I. W. M. Smith, *Nature* **343**, 691 (1990).
18. M. Dantus, R. Bowman, A. H. Zewail, *Nature* **343**, 737 (1990). M. Gruebele, G. Roberts, M. Dantus, R. M. Bowman, A. H. Zewail, *Chem. Phys. Lett.* **166**, 459 (1990).
19. J. H. Glowina, J. A. Misewich, P. P. Sorokin, *J. Chem. Phys.* **92**, 3335 (1990).
20. N. F. Scherer, L. R. Khundkar, R. B. Bernstein, A. H. Zewail, *J. Chem. Phys.* **87**, 1451 (1987). N. F. Scherer, C. Sipes, R. B. Bernstein, A. H. Zewail, *J. Chem. Phys.* **92**, 5239 (1990).
21. S. Buelow, G. Radhakrishnan, J. Catanzarite, C. Wittig, *J. Chem. Phys.* **83**, 444 (1985). C. Jouviet, B. Soep, *J. Chem. Phys.* **80**, 2229 (1984).
22. T. Baumert, B. Buehler, R. Thalweiser, G. Gerber, *Phys. Rev. Lett.* **64**, 733 (1990).
23. For more on experiment, see the work of R. Bersohn, R. Gentry, Y. T. Lee, P. Toennies, J. Valentini and R. N. Zare, reviewed in ref. 1. For more on potential energy surfaces, see the work of C. Horowitz, B. Liu, P. Siegbahn, D. Truhlar, reviewed in ref. 1. For more on theory, see the work of D. Kouri, A. Kuppermann, J. Light, H. Mayne, W. Miller, D. Truhlar, R. Wyatt and others, reviewed in ref. 1.
24. E. J. Heller, *Acc. Chem. Res.* **14**, 368 (1981). R. Kosloff, S. A. Rice, D. J. Tannor, *Chem. Phys.* **139**, 201 (1989). ■



Probing scheme for the bimolecular reaction $H + CO_2$. A short laser pulse dissociates the HI molecule in the approximately T-shaped precursor (a). The hot H atom attacks the CO_2 molecule (b), forming an $HOCO$ collision complex (c), which decays to products (d). The course of the reaction²⁰ is monitored by a probe pulse at time Δt . Experiments indicate that the collision complex lives for about 5 psec. **Figure 10**