drowski, S. Jeneke, H. Ishida, *J. Phys. (Paris)* **C3**, 677 (1983); S. E. Tunney, J. Suenaga, J. K. Stille, *Macromolecules* **16**, 1398 (1983).
55. P. M. Grant, *Phys. Rev. B* **27**, 3934 (1983); *ibid.* **26**, 6888 (1982); F. Herman, *Phys. Scr.* **16**, 303 (1977); F. Herman, D. R. Salahub, R. P. Messmer, *Phys. Rev. B* **16**, 2453 (1977).
56. M.-Y. Whangbo, in (*3*), vol. 2, pp. 127–158; C. L. Honeybourne, *J. Chem. Soc. Chem. Commun.* (1982), p. 744; M. C. Böhm, *Solid State Commun.* **45**, 117 (1983); M.-H. Whangbo and K. R. Stewart, *Isr. J. Chem.* **23**, 133 (1983); S. Alvarez and E. Canadell, *Solid State Commun.* **50**, 141 (1984); E. Canadell and S. Alvarez, *Inorg. Chem.* **23**, 573 (1984).
57. K. A. Doris, M. A. Ratner, D. E. Ellis, B. Delley, T. J. Marks, *Bull. Am. Phys. Soc.* **28**, 245 (1983); E. Ciliberto *et al.*, *J. Am. Chem. Soc.* **106**, 7748 (1984); N. S. Hush and A. S. Cheung, *Chem. Phys. Lett.* **47** (1977).
58. W. J. Pietro, D. E. Ellis, T. J. Marks, M. A. Ratner, *Mol. Cryst. Liq. Cryst.* **105**, 273 (1984).
59. E. J. Baerends, D. E. Ellis, P. Ros, *Chem. Phys.* **2**, 41 (1973); Z. Berkovitch-Yellin, D. E. Ellis, M. A. Ratner, *ibid.* **62**, 21 (1981); B. Delley and D. E. Ellis, *J. Chem. Phys.* **76**, 1949 (1982); A. Rosen *et al.*, *ibid.* **65**, 3269 (1975).
60. K. A. Doris, M. A. Ratner, D. E. Ellis, T. J. Marks, *J. Phys. Chem.* **88**, 3157 (1984); K. A. Doris, D. E. Ellis, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **106**, 2491 (1984).
61. J. M. Williams *et al.*, *J. Am. Chem. Soc.* **105**, 643 (1983).
62. W. J. Pietro, M. A. Ratner, T. J. Marks, in preparation.
63. P. J. Flory, *Proc. R. Soc. London* **234**, 73 (1956); *J. Polym. Sci.* **49**, 105 (1961).
64. J. R. Schaefgen *et al.*, in *Ultra-High Modulus Polymers*, A. Cifferi and I. M. Ward, Eds. (Applied Science, London, 1979), pp. 173–201; E. E. Magat and R. E. Morrison, *ChemTech* **6**, 702 (1976); G. B. Carter and V. T. J. Schenk, in *Structure and Properties of Oriented Polymers*, I. M. Ward, Ed. (Wiley, New York, 1976), chapter 13; M. G. Dobb and J. D. McIntyre, *Adv. Polym. Sci.* **60–61**, 61 (1984).
65. T. Inabe, J. W. Lyding, M. K. Moguel, T. J. Marks, *J. Phys. (Paris)* **C3**, 625 (1983); T. Inabe, J. W. Lyding, T. J. Marks, *J. Chem. Soc. Chem. Comun.* (1983), p. 1084.
66. T. Inabe, J. F. Lomax, J. W. Lyding, C. R. Kannewurf, T. J. Marks, *Synth. Met.* **9**, 303 (1984); T. Inabe *et al.*, *Macromolecules* **17**, 262 (1984).
67. T. Inabe and T. J. Marks, in preparation.
68. K. J. Wynne, A. E. Zachariades, T. Inabe, T. J. Marks, in preparation.
69. W.-B. Liang and T. J. Marks, unpublished results.
70. This research on conductive polymers was supported by the National Science Foundation through the Northwestern Materials Research Center (grant DMR82-16972) and by the Office of Naval Research. It is a sincere pleasure to acknowledge the invaluable contributions of R. L. Burton, S. H. Carr, C. W. Dirk, K. A. Doris, D. E. Ellis, I. L. Fragalà, F. H. Herbstein, T. Inabe, C. R. Kannewurf, W.-B. Liang, J. W. Lyding, W. J. McCarthy, M. K. Moguel, W. J. Pietro, M. A. Ratner, G. M. Reisner, K. F. Schoch, Jr., K. J. Wynne, and X. Zhou to this work.

Laser Probing of Chemical Reaction Dynamics

Stephen R. Leone

The advent of lasers has heralded revolutions in almost all fields of technical endeavor (*1*). In chemistry, much of the original excitement centered on the possibilities for laser-driven, bond-selective synthesis and isotope separation (*2*). While a few such schemes for laser-selective chemistry do appear promising, an even greater number of remarkable side benefits have arisen from the intense activity in this field. Tremendous progress in molecular spectroscopy has been made possible by the availability of highly developed tunable laser sources. Another area of rapid progress is in the sophisticated understanding of chemical reaction dynamics which has been obtained through laser studies of state-selective reactions. It is the latter field which is the subject of this article.

Chemical reaction dynamics is a relatively new field (*3, 4*). It is, in essence, a modern-day approach to the study of chemical kinetics, or the rates at which reactions proceed. Rather than merely measuring the rates of chemical reactions under various conditions, chemists are now accustomed to achieving a much finer level of detail. With the availability of laser sources for selective excitation and detection, it is possible to infer many things about the dynamics, that is, the particular motions, that the molecules are likely to undergo in the chemical reaction. It is possible to interrogate, or probe, the specific forms of excitation that best lead to chemical reaction, for example, vibrational, rotational or translational motion, or electronic excitation. Thus, the study of gas-phase, state-resolved dynamics offers many answers to questions of fundamental interest in chemical reactivity.

The laser has played a central role in the development of these studies of chemical reaction dynamics. However, laser sources are not the sole means of studying chemical processes with state-selected detail. For many years, complementary techniques of spectrally resolved infrared and visible chemiluminescence and molecular beam reactive scattering have also provided exceedingly detailed results on reaction dynamics (*5, 6*). Lasers have, however, provided some of the most sensitive methods for detection of molecular states, as well as the means to select specific reagent states with high resolution. Through the inherent polarization of their light, lasers can be used to study numerous chemical reactions as a function of the geometric alignment of reagents or products. With the high resolution of lasers, it is even possible to probe the differences in reactivity of closely spaced spin-orbit states. Lasers even provide the capability to probe the exceedingly short-lived transition states of simple reactions.

Data from experiments on state-selected chemical dynamics now comprise a large body of knowledge from which it is possible to infer many things about the dynamics. It is important to emphasize, though, that even a series of the most cleverly designed experiments together with appropriate theoretical interpretation (*7*) can only lead to powerful inferences concerning the specific motions that the molecules undergo. Nearly all experiments interrogate the system at a time that is either well before the reaction, by specific reagent state preparation, or well after the transition state of the reaction, by probing the final product states. Most of our simple pictures of the dynamical motions have been derived from this powerful combination of experimental facts, inference, and theory. Experimentalists would like to obtain even more concrete information, rather than rely so heavily on inference. This is why the possibility of more directly probing the transition states of reactions has intrigued so many investigators.

General Methods of Laser Probing

An apparatus for studying chemical reaction dynamics through either selective laser excitation of reagents or laser detection of product states can have many variations (*4, 8*). However, a num-

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Summary. Lasers are used in increasingly sophisticated ways to carry out reactions between molecules in selected vibrational, rotational, and electronic states and to probe the product states of chemical reactions. Such investigations are providing unprecedented insights into chemical reaction dynamics, the study of the detailed motions that molecules undergo in simple chemical reactions. In many cases it is possible to describe the influence that specific types of molecular excitation have on reactive events. Experiments are also being carried out to learn about chemical reactivity as a function of the alignment of reagents. There is increasing excitement concerning the potential of laser methods to interrogate the transition states of molecular reactions.

ber of key features common to all these devices can be outlined. Figure 1 shows an apparatus that could be used for many types of investigations in reaction dynamics. It consists of a low-pressure reaction chamber, a laser for excitation or dissociation to produce the initial reagent states, a laser for interrogation of product states, and detectors for molecular fluorescence or laser absorption. In some cases the second laser is replaced by a detector for time- and wavelength-resolved emission in either the infrared or visible. Provision can be made to rotate the planes of polarization of the exciting and analyzing lasers. The reagents themselves may be stable molecules or short-lived atomic, radical, or ion species. Thus, many different gas sources are employed to generate the reagents of interest.

In ideal circumstances the reactions are carried out under "single-collision" conditions. These conditions typically require low pressures, so that a product molecule which is born in a particular state is not modified by subsequent collisions during the time of interrogation. Since very short laser pulses are frequently used, the time between excitation and interrogation can be less than 10^{-8} second. In this case, pressures as high as hundreds of pascals (1 Pa = 7.5×10^{-3} torr) can be used with virtually no collisions occurring between the formation of a product and its detection.

It should be immediately apparent that collisional relaxation, which is itself an active area of investigation called molecular energy transfer, is of central importance in the issue of obtaining nascent, or newly born, product state distributions. Moreover, collisional energy transfer pathways can play an underlying role in the dynamics of the reactive event. There are numerous examples of competition between reactive and energy transfer pathways, and the flow of energy between various degrees of freedom during the lifetime of the active transition state can be important in the final outcome of product states. Thus, the field of reaction dynamics requires an implicit understanding of the role that molecular energy transfer plays and the magnitudes of the rates of both energy transfer and reaction.

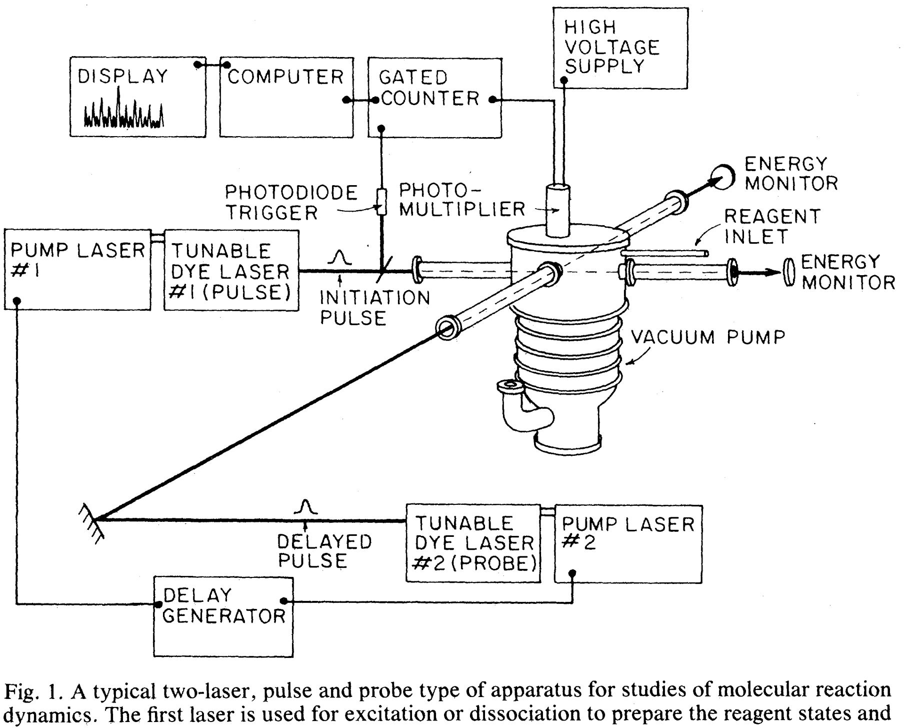


Fig. 1. A typical two-laser, pulse and probe type of apparatus for studies of molecular reaction dynamics. The first laser is used for excitation or dissociation to prepare the reagent states and the second laser is used to interrogate the product states a short time later.

Laser excitation of selected reagent states most frequently involves a direct absorption process. However, in some cases more subtle methods can be employed. For example, a high-power, polarized laser can be used to photodissociate a collection of molecules, leaving behind a small fraction of molecules with their planes of rotation very purely aligned (*9*). The laser photolysis method can be used to create high concentrations of reactive free radicals and atoms, and the fact that the laser power density can easily be varied is exploited to control those radical densities (*10*). Molecules can be prepared in states that are ordinarily inaccessible by pumping with two lasers, first through an intermediate state and then up or down into the state of interest. The latter method of down-pumping is called stimulated emission pumping and can be used to prepare molecules in very high vibrational levels of the ground electronic state (*11*).

Laser detection schemes are even more varied (*12*). One of the most common is laser-induced fluorescence, in which a molecule is excited to a fluorescing electronic level and photons are observed as a function of the wavelength of the laser (*12*). In this way, complete product state distributions can be mapped with vibrational and rotational resolution. Alternatively, the molecules can be ionized with one or more photons from a laser and the electrons or positive ions can be counted to obtain the state information. Transient measurements can be accomplished by absorption of a laser probe beam that is tuned to a particular transition. Various Raman processes, such as coherent anti-Stokes Raman spectroscopy (CARS), can be used as a quantitative probe of molecular-state information (*13*).

Perhaps the most significant reason for the tremendous variety of techniques now available for interrogating molecules is the extensive development of tunable laser sources that operate throughout the infrared, visible, ultraviolet, and vacuum ultraviolet regions of the spectrum. Techniques have been developed to probe almost any kind of atomic or molecular state, in many cases with sensitivities approaching number densities of 10^5 cm^{-3}, and in special circumstances with detection sensitivity even for single atoms (*14*). The types of lasers range from solid-state tunable diode lasers in the infrared to liquid-phase organic dye lasers in the visible. By elegant nonlinear optical techniques, the outputs from high-power, pulsed visible dye lasers can be summed and mixed to produce useful tunable ultraviolet and vacuum ultraviolet light, with wavelengths as short as 100 nm (*15*).

Examples of State-Specific Excitation and Detection

Lasers are frequently used to produce selective excitation of reagent states in an effort to learn about the specific mechanisms that will "drive" a chemical reaction (*16, 17*). In many cases tremendous enhancements in reactivity are attainable by excitation of certain reagent states. For example, the reactions of calcium and strontium with HF to form CaF and SrF are found to be enhanced by at least 10^4 upon excitation of the HF to the $v = 1$ vibrational state with a chemical laser (*18*). This rather large increase in the rate coefficient with vibrational excitation also facilitates probing the reactivity as a function of initial rotational state within the $v = 1$ manifold by the same selective laser excitation (*19*).

Reactions of the type M + HX, where M is a metal and X is a halogen, have many varied characteristics. However, in some of these reactions it is found that rotational excitation may slightly inhibit the reaction (*19*). Vibrational excitation is sometimes more effective than translational energy in promoting the reaction. The mechanism of these reactions is thought to involve an initial electron transfer from the metal atom to the electronegative halogen atom, forming a strong attractive force between the metal and the halogen. Increased vibrational excitation appears to overcome the barriers to this process in an effective way.

Reactions such as the ones described above may involve not only state-specific excitation of the reagents with lasers, but also interrogation of the product states by laser-induced fluorescence probing (*20*). In an elegant series of measurements on the Ca + HF system (*21*), the number of vibrational levels excited in the CaF product was found to increase monotonically with increasing rotational excitation (Fig. 2). The actual population distributions in the vibrational states were very nearly statistical, based on a comparison with calculations in which the total energy available to the products was statistically distributed among all the vibrational, rotational, and translational degrees of freedom. The latter result is suggestive of a long-lived reaction complex.

Insertion reactions. Reactions of electronically excited $O(^1D)$, $C(^1D)$, or $Mg(^1P_1)$ with hydrogen-containing compounds form OH, CH, or MgH as the product. These reactions have been exhaustively studied by laser-induced fluorescence probing of the OH, CH, or MgH product (*22, 23*). The atoms are produced selectively by direct laser excitation or ultraviolet laser photolysis of a molecule, such as ozone. One of the motivations for these extensive studies is that the reactions can take place through two very different types of chemical mechanisms. One involves direct abstraction of a hydrogen atom from an R–H type molecule, and the other involves insertion into the R–H bond followed by unimolecular decomposition of the highly excited species to form the product.

In principle, the insertion and abstraction mechanisms should be distinguishable by detailed measurements of the vibrational and rotational state distributions of the product. Typically, a direct abstraction reaction yields a very high degree of vibrational excitation (*7*). From 40 to 60 percent of the available reaction energy is channeled into vibration in the diatomic product, which represents a highly nonstatistical fraction of the available energy in vibration. An insertion reaction, on the other hand, may involve a long-lived complex intermediate, and the energy of the reaction may be partitioned in a more statistical manner between all the vibrational, rotational, and translational degrees of freedom. In a large polyatomic intermediate, this would mean that only a small fraction of the available energy would go into the diatomic vibration. However, if the insertion complex breaks up in a time short compared to the time scale for energy randomization, which might especially be the case for a complex with a small number of atoms, then highly nonstatistical distributions in both vibration and rotation can also be observed, making the interpretation ambiguous.

In some cases the ambiguity can be resolved by careful measurements of the rotational state distributions. Bimodal distributions in rotation, in which very different populations and degrees of excitation occur for groupings of low and high rotational states, are typically indicative of multiple pathways or mechanisms. One of the clearest examples of such a bimodal character in rotation comes from the reaction of $Mg(^1P_1)$ with H_2 (*23*). This reaction is simple enough and the fractions of the insertion and

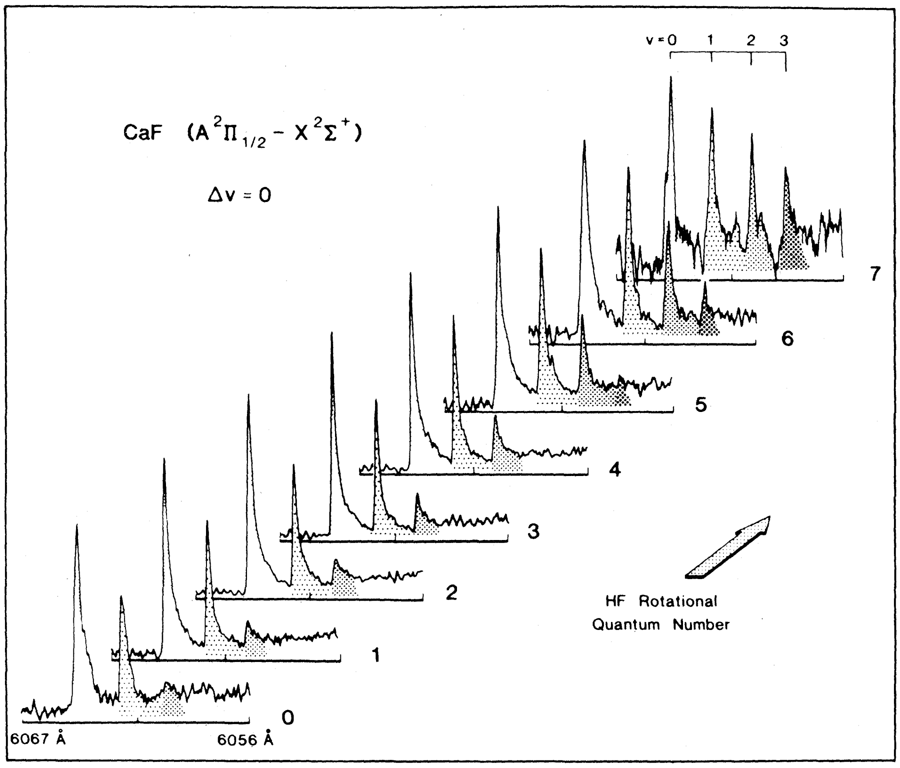


Fig. 2. Laser-induced fluorescence spectra of the CaF product formed in the Ca + HF($v = 1$) reaction as a function of rotational level in the HF reagent. Band heads corresponding to different CaF vibrational levels are shaded differently to indicate the increase in CaF vibrational excitation with reagent rotational excitation. [From (*21*), courtesy of *Chemical Physics Letters*]

abstraction channels are both large enough that the two pathways are apparent in the rotational data (Fig. 3). There is substantial evidence in this reaction that the abstraction component is responsible for the low rotational levels and the insertion mechanism is responsible for the high rotational levels.

Several examples of $O(^1D)$ reactions further demonstrate the exceptional level of detail that can be obtained from this type of study but are also illustrative of the frequent ambiguities and uncertainties that occur in the interpretation of data to describe the dynamics. Much of the experimental evidence indicates that both insertion and abstraction mechanisms are important in the reactions of $O(^1D)$. For example, in the reactions with hydrocarbons, highly nonstatistical distributions in OH vibration and bimodal distributions in rotation of the OH product are interpreted as meaning that both abstraction and insertion are occurring (*24*). From these measurements it has been possible to estimate the fractions of the abstraction and insertion components, to determine the different extents of vibrational excitation for each component, and to relate these to the statistical and nonstatistical partitioning. Several of these results are shown in Table 1 for the reactions of $O(^1D)$ with H_2, CH_4, C_2H_6, C_3H_8, and $C(CH_3)_4$.

Unfortunately, not all the results are so clear-cut concerning the interpretation of $O(^1D)$ mechanisms. For example, in one of the most elegant experimental studies to date, the complete vibrational and rotational partitioning in the ^{16}OD and ^{18}OD products of the reaction between $^{16}O(^1D)$ and $D_2{}^{18}O$ has been measured (*25*). The ^{16}OD product, which is the result of a newly formed bond, is found to have 40 percent of the available energy in its vibration. The ^{18}OD molecule, in contrast, has a negligible 2 percent of the energy in its vibration. The rotational excitations in both products are similar, but they also exhibit the typical bimodal pattern, with a very cold component in the low rotational levels and a very hot fraction in the higher rotational levels. In this case, however, the authors suggest that this reaction must be direct, and they favor an abstraction type of mechanism in which the ^{18}O–D bond is a spectator. The interpretation is ambiguous because a very short-lived insertion intermediate might also explain the large difference in vibrational excitation between the two products and still account for the bimodal distributions in rotation.

Table 1. Properties of the abstraction and insertion components of $O(^1D)$ + RH reactions (*24*).

RH	F_A* ($v = 0$)	$\left(\frac{v=1}{v=0}\right)_I$†	$\left(\frac{v=1}{v=0}\right)_A$‡
H_2	0.0	0.9	
CH_4	0.05	1.0	1.0
C_2H_6	0.2	0.65	0.3
C_3H_8	0.7	0.55	0.08
$C(CH_3)_4$	0.9		≤0.05

*Fraction of the abstraction component for the OH($v = 0$) channel. †Ratio ($v = 1$)/($v = 0$) for the insertion component. ‡Ratio ($v = 1$)/($v = 0$) for the abstraction component.

Reactions of fast hydrogen atoms. High-power, pulsed laser outputs at short ultraviolet wavelengths have become available with the advent of excimer lasers. These lasers make it possible to generate high densities of translationally energetic atoms, such as hydrogen atoms, by photolysis of simple precursor molecules such as H_2S, HI, and HBr. The energy of each 193- or 248-nm laser photon in excess of the bond energy is partitioned almost entirely into kinetic energy of the atom of lower mass, due to simple conservation of energy and momentum. This has made possible a number of new and basic studies on the dynamics of reactive and inelastic energy transfer pathways in the collisions of hydrogen atoms with simple molecules.

Recent studies of the reactive collisions of fast hydrogen atoms with D_2 molecules have received wide attention because of the fundamental nature of this simple chemical system and the large number of calculations that have already been carried out to generate accurate potential energy surfaces for the reaction. The vibrational and rotational states of the HD product molecules have been probed by both CARS (*13*) and laser multiphoton ionization (*26*). The hydrogen atoms are produced with high kinetic energy by laser photolysis of HI in the presence of D_2, and the interrogation takes place shortly after some reaction has occurred but before substantial relaxation has taken place. At a collision energy of 1.3 eV, newly born HD product molecules have been observed in the $v = 1$ and $v = 2$ vibrational states and over a range of rotational states from $J = 0$ to 9. The general agreement between experiment and theory for the vibrational and rotational state distributions formed in the reaction is very good (*26*). Further work will help to elucidate the origins of the small differences and will provide data on other channels, including direct excitation of the D_2 by energy transfer.

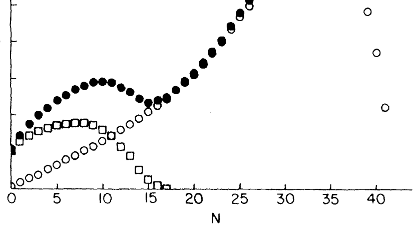
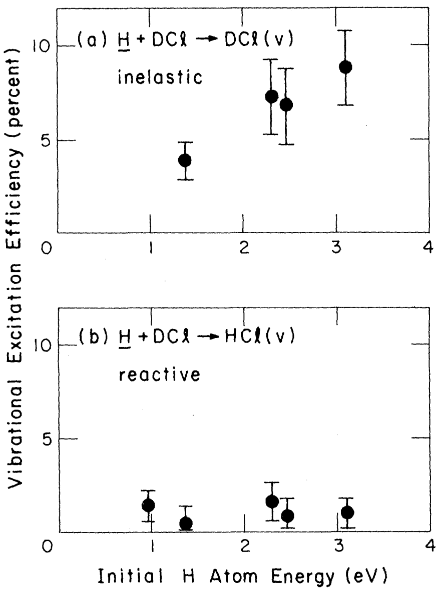


Fig. 3. A plot of the population $P(N)$ versus rotational state N, showing the deconvolution into the low and high rotational components in the reaction of $Mg(^1P_1)$ + H_2 to form MgH. A surprisal-type analysis (*5*), which compares the observed populations to a statistical predicted distribution, is used to estimate the populations of the high rotational components in the blended region. The low-N rotational levels are thought to occur by the direct abstraction mechanism and the high-N levels by insertion. [From (*23*), courtesy of the *Journal of Chemical Physics*]

Studies have also been made on the competition between vibrational excitation and atom exchange pathways in collisions of laser-generated fast hydrogen and deuterium atoms with HCl and DCl (*27*). Spectrally resolved infrared chemiluminescence is used to determine the amount of vibrational excitation in the HCl and DCl products of collisions between H and DCl. The vibrational population distributions show that the HCl product of the reactive exchange is substantially more excited than the DCl molecules which become vibrationally excited as a result of the direct, inelastic energy transfer process.

As further evidence that the atom exchange and energy transfer processes take place on fundamentally different chemical energy surfaces, the excitation efficiency as a function of the kinetic energy is found to exhibit strikingly different trends (Fig. 4). The efficiency of the pure energy transfer process increases sharply with kinetic energy, whereas the reactive exchange pathway has nearly a constant fraction of energy deposited into vibration over the range of collision energies investigated (1 to 3 eV). The results are interpreted as indicating that quantitatively more vibrational excitation results from the process of breaking and reforming the bond in the atom exchange process, but that once the kinetic energy is high enough to overcome the barrier to atom exchange, very little of the additional excess translational energy is deposited into the diatomic vibration.

Charge transfer reactions. The extremely high sensitivity of the laser-induced fluorescence method allows a number of new kinds of reactions to be studied for the first time. In particular, reactions of ions at near-thermal energies have been difficult to study with product state resolution. The problem of obtaining sufficiently high densities of ions to be able to probe the product states of such reactions under single-collision conditions has been solved by using high-velocity flows of helium to generate the ions (*28*). One of the most interesting and fundamental classes of reactions involves simple electron transfer, or charge transfer, from one molecule to another in the gas phase. Being free of the complications associated with solvent media, such studies have the potential of showing how the chemical energy of electron transformations can be channeled into the vibrational, rotational, and translational motions of the relatively heavy nuclei. At thermal collision energies the dynamics will be most sensitive to the strong attractive ion–induced dipole and ion-dipole forces.



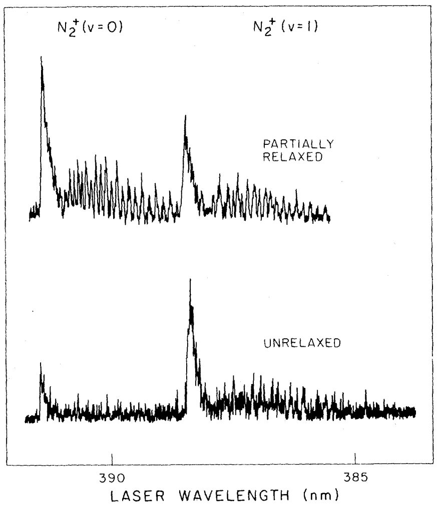


Fig. 4 (left). Plot showing the very different vibrational excitation efficiencies for direct energy transfer and reactive exchange pathways in collisions of H + DCl. Fig. 5 (right). Laser-induced fluorescence spectra of the N_2^+ product in the $Ar^+ + N_2$ charge transfer reaction, showing in the lower trace the nascent (unrelaxed) distribution in which $v = 1$ predominates and in the upper trace a partially relaxed result in which single-collision conditions are not achieved.

The mechanisms of charge transfer can be divided into two extreme models. A Franck-Condon electron transfer would obtain a vibrational distribution that is governed by isolated diatomic overlap factors for the vibrational wave functions of the ion and neutral species; this would look very much like a photoionization process. In contrast, an energy resonance picture would channel the reaction exothermicity as nearly as possible into the vibrational, rotational, or electronic internal degrees of freedom.

Thus far, three reactions have been studied by laser probing of the diatomic product ion vibrational and rotational excitation: $Ar^+ + N_2$ (*29*), $Ar^+ + CO$ (*30*), and $N^+ + CO$ (*31*). In spite of the similarities between the atomic ions and the diatomic molecules in these cases, the reactions exhibit markedly different behaviors. The $Ar^+ + CO$ and N_2 reactions both show an exceptional preference for populating the highest vibrational levels accessible. For example, the N_2^+ is born with ten times as great a population in $v = 1$ as in $v = 0$. Figure 5 shows a spectral scan of the $v = 0$ and $v = 1$ levels of N_2^+ under conditions in which the N_2^+ is in a nascent distribution and partially relaxed by collisions. The CO^+ product of the Ar^+ reaction is born predominantly in the energetically near-resonant states $v = 5$ and $v = 6$. In contrast, the $N^+ + CO$ reaction produces 70 percent in $v = 0$, 28 percent in $v = 1$, and 2 percent in $v = 2$, which is in very close agreement with a Franck-Condon distribution of 96, 4, and 0 percent, respectively.

The rotational excitation in these charge transfer reactions further corroborates the differences in the mechanisms. In the $N^+ + CO$ reaction, only 2 percent of the energy goes into rotational excitation, indicating that a substantial fraction of the reactive events occur by long-range electron transfer, which would not impart any angular momentum to the diatomic ion product. In contrast, the reactions of Ar^+ with N_2 and CO both produce substantial rotational excitation of the diatomic ion product, indicating that a close encounter must occur, which would tend to impart angular momentum to the product. It is thought that such a close encounter is necessary to distort the diatomic bond length before the charge transfer transition state can be reached. Such studies will provide further insights into the geometric orientations and characteristic bond lengths that are necessary to allow the switching of an electron in simple systems.

Spin-orbit effects. The power of the laser to resolve even finer details of molecular reaction dynamics is demonstrated through recent studies of the reactivity of specific spin-orbit states. Spin-orbit states, which arise from the splitting of an atomic energy level by coupling of the nuclear spin with the orbital angular momentum, often involve only minute energy differences, but they can exhibit substantial differences in reactivity. A thorough series of studies has been carried out on the reactions of the $^2P_{1/2}$ and $^2P_{3/2}$ spin-orbit states of fluorine atoms with HBr by using a tunable vacuum ultraviolet laser to probe the corresponding $^2P_{1/2}$, $^2P_{3/2}$ spin-orbit states in the bromine atom product (*32*). The fluorine atom spin-orbit states could be populated to different extents by thermal heating. The fluorine atom ($^2P_{1/2}/^2P_{3/2}$) spin-orbit state ratio was varied over a factor of 6, while the product bromine atom spin-orbit ratio ($^2P_{1/2}/^2P_{3/2}$) remained constant at 6 percent. These results indicate that there is not a simple direct correlation between the reactant spin-orbit state and product spin-orbit state. Rather, it appears that only the ground $^2P_{3/2}$ electronic state is reactive in this case, most likely because of a high barrier in the potential surface for the excited spin-orbit state. The authors speculate that the constant fraction of bromine atom spin-orbit excitation may be the result of energy transfer in the transition state from the vibrationally excited HF product molecule to the bromine atoms before the products separate.

Despite the small splitting (160 cm^{-1}) of the Ca($^3P_{2,1,0}$) spin-orbit states, selective laser manipulation of the ratios of the three spin-orbit states has shown that they have substantially different reactivities with molecular chlorine to produce electronically excited CaCl products (*33*). The order of reactivity decreases by a factor of 3 to 4 in the series $^3P_2$, $^3P_1$, and $^3P_0$. This selectivity of the reactivity is remarkable in light of the ease with which these states are collisionally transferred from one to the other.

Alignment and orientation. The subject of atomic and molecular alignment and orientation is one of the exciting new areas of chemical reaction dynamics (*34, 35*). The laser allows a number of different effects to be studied by exciting atoms or molecules with polarized light or by probing specific product states which correspond to particular orbital configurations. In the chemical literature the meanings of alignment and orientation are characterized in the following way. Consider a linear molecule with two diffferent ends. Alignment means that the linear axis can be arranged either parallel or perpendicular to the collision partner. Orientation means that either of the two different ends of the molecule can be pointed toward the collision partner. Optical state preparation with lasers can only provide alignment. In a few cases, hexapole electric fields have been used to provide orientation.

In spite of the fact that the degree of alignment cannot always be perfectly controlled, several substantial effects of alignment or reactivity have already been demonstrated. Most remarkable are the reactions of the excited *P* state of calcium with Cl_2, HCl, and CCl_4, which are probed as a function of the *p*-orbital alignment (*36*). The reaction with Cl_2 shows a marked preference for perpendicular alignment of the calcium *p* orbital with the incoming reaction partner (Fig. 6). The reaction with HCl shows a variation of the CaCl A and B electronic product states with the orbital alignment, while the reaction with CCl_4 shows almost no preferential characteristics associated with alignment.

For molecular reagents, the degree of alignment that can be achieved in a simple absorption process cannot be very great. Even so, a polarized laser has been used to align the HF(v = 1) reagent in the reaction with strontium atoms (*37*). A weak enhancement of the v = 2 SrF product state is observed for the broadside collision geometry. If a powerful pulsed laser is used to photodissociate molecules rather than to excite them directly, the remaining undissociated molecules can be prepared with a very high degree of alignment. This method has been used to select the plane of rotation of IBr molecules and to find that the reaction of excited xenon atoms with IBr is preferentially enhanced when the geometry of reagent approach is parallel to the plane of rotation of the IBr molecules (*9*).

Information about the alignment of molecular orbitals in the transition states of chemical reactions can also be obtained by the analysis of certain lambda doublet components in the laser-induced fluorescence product spectra (*22*). This has been particularly applied to the OH products of numerous oxygen atom and hydrogen atom reactions. For high rotational states in the OH product, the lambda doublet components can be uniquely associated with the direction of the orbital containing the lone electron. For example, in the reaction of translationally fast hydrogen atoms with O_2, the energetically lower lambda doublet component is populated by 6:1 preferentially over the energetically higher component (*38*). The preferred component corresponds to the case where the singly occupied orbital lies in the plane of the OH rotation. A similar type of preferential population is observed for many other reactions that produce OH. It is taken to indicate that the OH is released with its plane of rotation rigorously in the plane of the transition state and that the bond that is broken has the lone electron in an orbital within this plane.

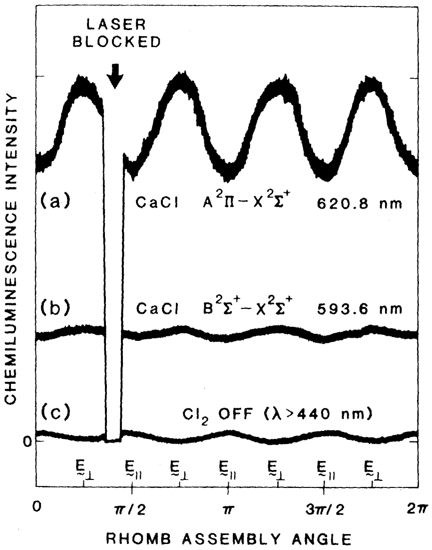


Fig. 6. Variation of the alignment angle between the Ca($^1P_1$) orbital and incoming Cl_2 showing the variation of product chemiluminescence for (a) the CaCl (A) state, (b) the CaCl (B) state, and (c) the result with the reagent Cl_2 turned off. The latter signal is due to variaton of the laser scattered light with rotation of the laser polarization. [From (*36*), courtesy of the *Journal of Chemical Physics*]

Probing the transition state. The laser has been crucial to recent investigations that have brought experimentalists closer to being able to probe the details of the actual transition states of chemical reactions. The high power densities of the light from lasers facilitate the manipulation of even the shortest-lived species, by forcing a competition between the natural rates of the reaction process and the rates of some light absorption or emission processes that can be driven by the laser. There are several reports of the successful manipulation of reactions by absorption of laser light during the lifetime of a transient collision intermediate (*39*). Substantial success has also been achieved in a study of the transition states of chemical reactions by direct emission (*40*). Several of the experiments involve reactions of xenon with Cl_2 to form electronically excited XeCl. Other definitive experiments have been carried out on the laser-assisted associative ionization of two sodium atoms during a collision. In a novel experiment a cluster of Hg with Cl_2 was formed and then excited with a laser, and the prompt formation of electronically excited HgCl product was observed (*41*). As more reports come forth, it will be possible to say much more about the potential of these laser manipulation methods for increasing our understanding of the dynamics of transition states.

Conclusions

The laser provides the means not only to investigate the reactivity of well-specified initial reagent states, but also to quantitatively probe product vibrational, rotational, and electronic states. In several cases, through more subtle features of molecular spectroscopy and optical pumping, it is possible to interrogate the reactivity associated with specific geometries. As new techniques for state detection with lasers become available, the number of possibilities for further detailed study will increase dramatically. Thus the potential of laser methods for the study of chemical reactivity and reaction dynamics is perhaps still largely untapped. The initial goal of many investigations, to demonstrate the possibility of laser isotope separation and bond-selective chemistry, has been partially successful. Far greater rewards have been achieved from the ensuing fundamental studies of the dynamical behavior in state-selected chemical reactions.

References and Notes

1. A. A. Boraiko, *Natl. Geogr.* **165**, 335 (1984).
2. J. Jortner, R. D. Levine, S. A. Rice, Eds., *Photoselective Chemistry* (Wiley, New York, 1981), parts 1 and 2.
3. R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics* (Oxford Univ. Press, New York, 1974).
4. M. R. Levy, *Prog. React. Kinet.* **10**, 1 (1979).
5. R. B. Bernstein, *Chemical Dynamics via Molecular Beam and Laser Techniques* (Oxford Univ. Press, New York, 1982).
6. I. W. M. Smith, *Kinetics and Dynamics of Elementary Gas Reactions* (Butterworths, London, 1980).
7. D. Henderson, Ed., *Theoretical Chemistry. Theory of Scattering: Papers in Honor of Henry Eyring* (Academic Press, New York, 1981), vols. 6A and 6B.
8. For an introduction to laser sources, see S. R. Leone and C. B. Moore, in *Chemical and Biochemical Applications of Lasers*, C. B. Moore, Ed. (Academic Press, New York, 1974), pp. 1–27.
9. M. S. deVries, V. I. Srdanov, C. P. Hanrahan, R. P. Martin, *J. Chem. Phys.* **78**, 5582 (1983).
10. D. J. Nesbitt and S. R. Leone, *ibid.* **72**, 1722 (1980).
11. D. E. Reisner, R. W. Field, J. L. Kinsey, H.-L. Dai, *ibid.* **80**, 5968 (1984).

12. W. Demtröder, *Laser Spectroscopy: Basic Concepts and Instrumentation* (Springer-Verlag, New York, 1982).
13. D. P. Gerrity and J. J. Valentini, *J. Chem. Phys.* **79**, 5202 (1983).
14. G. S. Hurst, M. H. Nayfeh, J. P. Young, M. G. Payne, L. W. Grossman, in *Laser Spectroscopy III*, J. L. Hall and J. L. Carlsten, Eds. (Springer-Verlag, New York, 1977), p. 44.
15. R. Hilbig and R. Wallenstein, *Appl. Opt.* **21**, 913 (1982).
16. M. Kneba and J. Wolfrum, *Annu. Rev. Phys. Chem.* **31**, 47 (1980).
17. I. W. M. Smith, in *Physical Chemistry of Fast Reactions*, I. W. M. Smith, Ed. (Plenum, New York, 1980), vol. 2, pp. 1–82.
18. Z. Karny and R. N. Zare, *J. Chem. Phys.* **68**, 3360 (1980).
19. C.-K. Man and R. C. Estler, *ibid.* **75**, 2779 (1981).
20. B. E. Holmes and D. W. Setser, in *Physical Chemistry of Fast Reactions*, I. W. M. Smith, Ed. (Plenum, New York, 1980), vol. 2, pp. 83–214.
21. R. Altcorn, F. E. Bartoszek, J. DeHaven, G. Hancock, D. S. Perry, R. N. Zare, *Chem. Phys. Lett.* **98**, 212 (1983).
22. S. R. Leone, *Annu. Rev. Phys. Chem.* **35**, 109 (1984).
23. W. H. Breckenridge and H. Umemoto, *J. Chem. Phys.* **80**, 4168 (1984).
24. A. C. Luntz, *ibid.* **73**, 1143 (1980).
25. W. A. Guillory, K. H. Gericke, F. J. Comes, *ibid.* **78**, 5993 (1983).
26. E. E. Marinero, C. T. Rettner, R. N. Zare, *ibid.* **80**, 4142 (1984).
27. C. A. Wight, F. Magnotta, S. R. Leone, *ibid.* **81**, 3951 (1984).
28. E. E. Ferguson, F. C. Fehsenfeld, A. L. Schmeltekopf, *Adv. At. Mol. Phys.* **5**, 1 (1969).
29. L. Hüwel, D. R. Guyer, G. H. Lin, S. R. Leone, *J. Chem. Phys.* **81**, 3520 (1984).
30. C. E. Hamilton, G. H. Lin, J. Maier, V. M. Bierbaum, S. R. Leone, in preparation.
31. D. R. Guyer, L. Hüwel, S. R. Leone, *J. Chem. Phys.* **79**, 1259 (1983); C. E. Hamilton, V. M. Bierbaum, S. R. Leone, in preparation.
32. J. W. Hepburn, K. Liu, R. G. Macdonald, F. J. Northrup, J. C. Polanyi, *J. Chem. Phys.* **75**, 3353 (1981).
33. H.-J. Yuh and P. J. Dagdigian, *ibid.* **79**, 2086 (1983).
34. R. N. Zare, *Ber. Bunsenges. Phys. Chem.* **86**, 422 (1982).
35. S. Stolte, *ibid.*, p. 413.
36. T. Rettner and R. N. Zare, *J. Chem. Phys.* **77**, 2416 (1982).
37. Z. Karny, R. C. Estler, R. N. Zare, *ibid.* **69**, 5199 (1978).
38. K. Kleinermanns and J. Wolfrum, *ibid.* **80**, 1446 (1984).
39. P. R. Brooks, R. F. Curl, T. C. Maguire, *Ber. Bunsenges. Phys. Chem.* **86**, 401 (1982).
40. P. Arrowsmith, S. H. P. Bly, P. E. Charters, J. C. Polanyi, *J. Chem. Phys.* **79**, 283 (1983).
41. C. Jouvet and B. Soep, *Chem. Phys. Lett.* **96** 426 (1983).
42. I am grateful for support from the National Bureau of Standards, National Science Foundation, Air Force Office of Scientific Research, Department of Energy, and Army Research Office.

Understanding Molecular Dynamics Quantum-State by Quantum-State

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Summary. It is now possible to resolve completely the initial and final quantum states in chemical processes. Spectra of reactive intermediates, of highly vibrationally excited molecules, and even of molecules in the process of falling apart have been recorded. This information has led to greater understanding of the molecular structure and dynamics of small gas-phase molecules. Many of the concepts and spectroscopic techniques that have been developed will be valuable throughout chemistry.

The process of energy transfer within a molecule or group of molecules is closely related to the making and breaking of chemical bonds. Although it is not possible to photograph step-by-step motions of individual atoms and molecules, it is possible to resolve individual quantum states in the observation of molecular spectra, in the preparation of reactant molecules, and in the analysis of reaction products.

Such information, in combination with theory, reveals a great deal about the dynamics of atomic and molecular motions and about the potential energy surfaces that govern them. In an article in this issue, Leone (*1*) discusses bimolecular reactions in the gas phase. Our article deals with unimolecular processes, including the nature of excited states and reaction intermediates as revealed by their spectra, the dynamics of intramolecular vibrational energy redistribution as probed by spectroscopy, and the dynamics of photofragmentation as resolved quantum-state by quantum-state. We have selected a few examples to illustrate the power of some of the new types of experiments and of the tools now available, but much equally important and interesting work is not discussed.

Spectroscopy of Transient Molecules

Lasers have made it possible to observe the spectra and study the dynamics and chemical kinetics of many free radicals (*2*, *3*), ions (*2*, *4*), molecular excited states, and other transient species (*2*). Frequency resolution as high as 1 part in 10^8 is possible. Lasers with pulses as brief as 10^{-14} to 10^{-13} second access the shortest chemically significant time scales, for which the energy uncertainty, $\Delta E \sim \hbar/\Delta t$, is comparable to chemical bond energies (*3*, *5*). Sensitivities sufficient to detect single molecules have been demonstrated for more modest limits of spectral and temporal resolution (*6*).

Methylene (CH_2), the prototype for divalent carbon intermediates, has been the focus of many experimental and theoretical studies aimed at determining the structure and the energy separation of the two low-lying electronic states, the "metastable" singlet ($^1CH_2$) and the ground triplet ($^3CH_2$) states. Spectroscopic detection of methylene eluded experimentalists for many years during which the only evidence for the theoretically postulated electronic structure of methylene was the vastly different chemistry exhibited by the two electronic spin states (*3*). In an article in this issue, Goddard (*7*) discusses the interaction between experiment and theory that produced accurate determinations of both the singlet and triplet structures, as well as the value of 9 kcal/mol for the energy separation between the singlet and triplet states (Δ_{s-t}).

The pioneering flash-kinetic spectroscopy work of Herzberg provided the first spectra and structure for triplet methylene and showed that it is the ground state (*8*). Laser magnetic resonance, a technique whereby rotational or

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