Ultrafast laser spectroscopy has extended reaction-dynamic studies into the picosecond and femtosecond time domain, allowing for experimental observations of transitory fragments that occur during collision or half-collision. This ability to observe molecular reactions allows real-time viewing of energy redistributions, measurements of state-to-state rates, and tests of microscopic statistical theories as prescribed by potential energy surface (PES) considerations. In this article, the focus is on unimolecular reactions. Recent advances in the studies of "oriented" bimolecular reactions and "transition states" of elementary reactions are also briefly considered.

A major goal of chemical physics is to understand how chemical reactions complete their journey from reactants to products. A wealth of information is already available on the thermodynamics and energetics of reactions (1). Over the past two decades, emphasis has been directed toward developing a more complete understanding of the "microscopic picture" of reaction dynamics. This picture is essential to our knowledge of the multidimensional potential energy surface (PES) and to the detailed quantum description of chemistry on a state-to-state level.

For bimolecular reactions, studies of both reactive and nonreactive collisions in crossed molecular beams have provided valuable information on PES and have inferred the time scale for the activated collision complex (2). For unimolecular reactions, the approach has been to study the "half-collision" photofragment spectroscopy of the reaction (3). Product-state distributions, which result from the dissociation, have been probed (very sensitively) by a variety of laser spectroscopic techniques and have revealed the translational-, rotational-, vibrational-, and electronic-state distributions of the products — in some cases for all the possible product fragments. In these half-collision studies, one starts with the parent molecule, preferably in some well-defined initial state, and deposits a known amount of energy via a photon to dissociate the molecule.

Both molecular beam scattering and photofragment product-state distributions yield information that is the time-integrated result of fragments' interaction on the PES. As pointed out by Smith (4), this approach concentrates on the "before" and "after" of chemical events at the molecular level. The making of new bonds (and the breaking of old ones) in elementary chemical reactions occurs in a very short time (picoseconds–femtoseconds), and it requires new techniques with ultrashort laser pulses to investigate chemical dynamics "during" the actual molecular processes that lead to chemistry.

Over the past eight years, such techniques have been developed in molecular beams to study the ultrafast chemistry of unimolecular and "oriented" bimolecular reactions (5–8). These studies have resulted in real-time viewing of energy redistribution, measurements of state-to-state rates, and tests of microscopic statistical theories as prescribed by the PES (5–11). More recently, the technique has been extended to the femtosecond time domain (12,13) to view the "transition state" of simple elementary reactions. The time scale for this femtochemistry (14) currently allows for the observation of fragments during the collision or half-collision of a chemical reaction. Because fragments' recoil speed is typically 1 km s⁻¹, the femtosecond time resolution is probing dynamics at fragments' separation of <0.5 Å.

In this article, we will highlight some of the recent studies in ultrafast spectroscopy of chemical reactions and illustrate the applications to different classes of reactions.

EXPERIMENTAL METHODOLOGY

The general ultrafast spectroscopic technique utilizes two ultrashort laser pulses (picosecond or femtosecond) in a pump–probe configuration in a molecular beam (or, in some cases, in low-pressure gases). In essence, one laser pulse is used to excite the molecule of interest and initiate the reaction. The second pulse is then used to probe for the formation of products (or perturbed fragments) — or the depletion of the reactant — at some later time. As is the advantage in all pump–probe experiments, the limit of the time resolution is determined solely by the width of the laser pulses used. In the examples presented here, this varies from 40 fs to approximately 10 ps. In Figure 1, the experimental setup is shown schematically for one of our picosecond systems, emphasizing the lasers involved and the molecular beam apparatus. The details of the ps/fs laser systems used in the different studies are described elsewhere (5–13). The incorporation of two independently tunable dye lasers has broadened the scope of possible experiments. Two independently tunable lasers are required for the large number of systems where state-to-state reaction rates are measured. In these cases one can excite a well-defined reactant state and then selectively monitor the formation of particular product states by appropriate tuning of the probe pulses. For femtosecond experiments, the tunability of the probe is essential for observing spectra of perturbed fragments.

Most of the experiments presented in this article were performed on samples cooled in seeded supersonic expansions. The beam apparatus consisted of two differentially pumped chambers. One chamber housed a home-built supersonic valve that was pulsed at the laser-repetition rate and was capable of heating samples to ~200 °C. Either the beam was interrogated in this chamber, where laser-induced fluorescence (LIF) detection of the products is performed, or the beam was skimmed and allowed to enter the second chamber, where
multiphoton ionization product-state detection is performed. This supersonic cooling prepares the molecules in a few well-defined states of internal energy so that the total energy available for dissociation is determined solely by the photolysis photon energy, and not by any distribution of internal energy. The importance of this is demonstrated in the photodissociation rates of the molecule NCNO, which will be discussed later.

**DIRECT BOND BREAKING**

**ICN: Bond breaking rate and the “transition state.”** For the reaction shown below, we first used subpicosecond pulses (13), and more recently ~100-fs pulses (12), to probe the process of bond breaking.

\[
\text{ICN} \rightarrow [\text{ICN}]^* \rightarrow \text{I} + \text{CN}
\]  

[1]

The ICN molecule was chosen for these studies because it offers several advantages. The excitation is to a repulsive state of the C-I coordinate, and the CN product can be detected using laser-induced fluorescence with very high sensitivity. There is a large and ever-growing body of literature on the dynamics of the dissociation of ICN (15), including product-state distributions, measurements of the anisotropy of product recoil, fragment alignment effects, and other topics.
Figure 2: Figure shows (a) the plot of CN LIF signal resulting from the photolysis of ICN as a function of pump-probe pulse delay. The top trace shows the appearance of the free CN radical by probing exactly on resonance. The lower two traces probe CN in the transition state by probing the perturbed CN B-X electronic transition; (b) a schematic of the energy levels involved.

The laser system used in these first experiments was modified for subpicosecond operation by pulse-compressing the output of a cavity-dumped dye laser. These pulses were then amplified in a pulsed-dye amplifier as before with the addition of a saturable absorber dye jet to minimize the broadening effects of the amplification process. The 306-nm pump pulse was obtained simply by frequency doubling, while the 388-nm probe pulse was generated by mixing the 612-nm dye-laser fundamental with the 1.06-μm output of the amplifying Nd:YAG laser. The cross correlation of the 306-nm and 388-nm pulses was ∼400 fs. The pump excitation was to the ICN repulsive A state on the red edge of the broad room-temperature absorption spectrum. Probing was achieved by performing LIF on the one-photon transition in the CN radical.

This particular experiment was performed in a room-temperature cell because the small amount of thermal energy was expected to have little effect on the repulsive-state dissociation. Furthermore, doing so allowed for an easy and accurate determination of the system-response function by performing I + 1 photoionization on N,N-diethylaniline in a separate photoionization cell. This procedure allowed the experimental transient and response function to be obtained merely by interchanging the two cells and making no further modifications to the optical arrangement. This is an important consideration for ultrafast measurements where broadening and shifting effects from experimental changes must be carefully considered at all times.

From the rise of the CN LIF signal, we have measured the dissociation rate on the repulsive surface. To interpret these results, dissociation must be defined more precisely because the reaction is a continuous transition from reactant to products. The question is: When in this transition does one consider the reaction to be over? The answer, for the experimental observations reported, is that the reaction is over when the CN is spectroscopically identifiable as the free CN radical, not as a CN radical perturbed by the close proximity of an I atom. Because the probe can be tuned to the free or perturbed CN transitions, one can answer such a question.

In more recent experiments with femtosecond time resolution (12), the rate of formation of free and perturbed CN has been measured (Figure 2). These rates provided the time for the CN and I fragments of ICN to separate completely from each other, and the transit time for the CN fragment in the process of separating from the I fragment (transition states). Such measurements of transition-state temporal behavior give direct information on the PES (16).

Alkyl iodides: direct and secondary dissociation. The general energy-level structure for this class of molecules is shown in Figure 3, and the reaction is described as follows:

\[ \text{R} + \text{I} \rightarrow \text{RI} \rightarrow \text{R} + \text{I} \]  

[2]

The important feature is that the first excited state is repulsive with respect to the C-I bond, and excitation to this state leads to very rapid dissociation. These systems, particularly methyl iodide and ICN, have been studied extensively by a number of techniques in an attempt to understand the nature and number of excited-state surfaces involved in the dissociation. Of particular interest in the present context are experiments that indirectly determine the time scale for dissociation. For example, Wilson and co-workers (17) estimated these lifetimes by observing the angular dependent product distribution that resulted from photodissociation induced by a polarized laser beam. Dissociation processes that occur rapidly in relation to the rotational period of the parent molecule lead to anisotropic angular distributions in the laboratory frame. The excited-state lifetime can be inferred from the degree of anisotropy.

There were a number of different approaches taken in applying the picosecond pump–probe technique to these systems. The initial experiments focused on alkyl iodides (18). Only one dye laser was used in these experiments, with the pump pulse being the second harmonic of the dye laser (at ∼2800 Å) and the probe pulse being generated by Raman shifting in methane (at ∼3040 Å). The experiments were performed in the molecular beam apparatus using multiphoton ionization (MPI) mass spectrometry to monitor the formation of the product I atoms. This observation was done in a state-selective way, with ei-
ther the $\Gamma P_v (3040 \text{ Å})$ or the $\Gamma P_v (3047 \text{ Å})$ states being detected by 2 + 1 photionization. The results indeed confirmed that the dissociation is direct, as the I-atom appearance time was $\tau < 0.4 \text{ ps}$. Moreover, the experiments demonstrated the sensitivity and selectivity of the method. In more recent experiments, the MPI method has been used to detect the spectra during the dissociation of methyl iodide (19). Femtosecond experiments, like those made for ICN, on these molecular species are in progress.

An interesting extension of this work was the study of diiodotetrafluoroethane, which was known to have the following photodissociation pathway:

$$\text{C}_2\text{F}_4\text{I}_2 \xrightarrow{h\nu} \text{C}_2\text{F}_4 + \text{I}^*(\Gamma P_v)$$  \hspace{1cm} [3]

and

$$\text{C}_2\text{F}_4\text{I} \xrightarrow{\text{spontaneous}} \text{C}_2\text{F}_4 + \text{I}^*(\Gamma P_v)$$  \hspace{1cm} [4]

The initial dissociation is expected to be fast, as in the case of methyl iodide. However, the $\text{C}_2\text{F}_4\text{I}$ radical product, if bound, should dissociate more slowly. The two reactions can be sorted out by virtue of the fact that perfluorinated alkyl iodides have been shown to dissociate from the excited repulsive surface to almost 100% iodine in the $\Gamma P_v$ state ($I^*$). The secondary reaction, which presumably occurs on its ground-state surface, should yield $\Gamma P_v$. The results are shown in Figure 4, where both the I and $I^*$ products have been monitored. The $I^*$ product shows an instantaneous rise, as in the case of methyl iodide. However, the $\Gamma P_v$ product shows a biexponential rise with the slow component measurement yielding a 30-ps rise. The interpretation is that the slow rise represents the unimolecular dissociation rate of the secondary reaction. This demonstrates that finite rates can be measured for the secondary reaction, but the result is a thermal average over all the possible internal states of the primary reaction product, the $\text{C}_2\text{F}_4\text{I}$ radical. In agreement with these findings, molecular beam results by Y.T. Lee's group (20,21) indicate the presence of a barrier ($\sim 8 \text{ kcal/mol}$).

**PREDISSOCIATION OF VAN DER WAALS' CLUSTERS**

Another area to which the general picosecond pump–probe technique has been applied is the photodissociation of van der Waals molecules. In this case, a quite different variant of the technique is used to monitor the course of a reaction. The particular systems studied by Kneel et al. (7) were phenol–benzene and cresol–benzene. The phenol and cresol were excited to vibrational states in their $I_s$ manifolds, where vibrational predissociation could proceed if the total vibrational energy exceeded the barrier to reaction. The excited-state populations were monitored by a probe-pulse photionization with mass resolution of the product ions. Thus, if no reaction is taking place, the population of the parent molecule (phenol–benzene complex) in the excited state would simply follow the bare-molecule intrinsic lifetime (radiative and nonradiative decay channels). However, if the vibrational energy is sufficient to break the van der Waals bond, then a vibrational predissociation channel will open:

$$\text{Phenol-phenol} \xrightarrow{h\nu} \text{phenol}^* + \text{benzene}$$ \hspace{1cm} [5]

It should be noted that the product phenol is still electronically excited and can be ionized by the probe as well. Thus, it is imperative to have mass resolution so that one can follow the evolution of the parent species selectively. The experiment consists, then, of monitoring the parent complex as a function of pump–probe delay time, with photodissociation now being measured as a decrease in reactant population rather than the former examples, where the rise of products was monitored.

The choice of these particular molecules was based on a number of experimental factors as well as the fact that phenol (22,23) and cresol (24,25) have been quite well characterized spectroscopically (particularly phenol). Also, Ito and co-workers (26–29) have performed spectroscopic experiments on phenol complexes and have characterized the hydrogen bonding interaction of the OH functional group with a number of binding partners. Benzene was chosen for studies of unimolecular dissociation rates because it has a relatively weak hydrogen-bonding interaction with phenol characterized as a $n$-hydrogen–bonding interaction. In this interaction, the phenol hydrogen bonds to the $n$ electrons above the plane of benzene. The weakness of this bond, $\approx 1400 \text{ cm}^{-1}$, allows dissociation to take place at relatively low excess energies on the $I_s$ surface, where there are still discrete optical transitions with sufficient intensity — even at significant energies above the dissociation threshold. Thus, a wide-ranging excess-energy study can be made, and a better opportunity to observe mode-specific effects is offered. Certainly similar or lower binding energies could be obtained by looking at rare gas adducts of phenol, as done recently for stilbene–rare gas complexes, which were studied by picosecond fluorescence (30,31). These hydrogen-bonding interactions, however, have the advantage that there is a single preferred binding site so that, in the supersonic expansion, the one-to-one species is formed more readily and there are fewer interferences from larger clusters.

An advantage of monitoring the parent population via the photodissociation–mass spectrometry technique is that the probe has no resonance requirements other than exceeding the ionization potential. Therefore, as mentioned, the pump and probe can be derived from a single visible dye-laser pulse. In this case, the probe is just the second harmonic of this visible pulse and the pump is obtained by anti-Stokes Raman shifting in methane (2914 cm$^{-1}$). As the pump is tuned to different excitation wavelengths, the probe also shifts in wavelength but remains above the ionization potential. Several experiments were performed with different wavelength-shifting schemes to measure the effect of the probe wavelength on the ob-
served decays. It was found that the form of the decay was invariant with respect to probe laser wavelength.

In Figure 5, the rates of dissociation of phenol-benzene are plotted as a function of excess energy above the barrier of 1400 cm\(^{-1}\). The position of this barrier, which was initially estimated by Ito and co-workers (26–29), was confirmed by the observation of no decay at 1275 cm\(^{-1}\) excitation and clearly visible dissociation at 1564 cm\(^{-1}\) (experimental parameters limited any finer definition of the limits of the barrier). The measurements all fit well to a single exponential decay and, as can be seen from the graph, increased more or less smoothly with excess energy. This trend can be taken as an indication that there are no important mode-specific effects, which in turn suggests that the process can be described statistically. The implication is that the energy deposited specifically in a particular mode is randomized rapidly compared with the time scale for dissociation. However, this could represent only a subset of the vibrational phase space (non-statistical). At the moment we do not know the extent of energy redistribution. More details are available elsewhere (7).

In order to have a system for comparison in which the relative rates would be the important consideration, cresol-benzene was also studied. It was reasoned that a small adjustment to the parent species—in this case, the addition of a methyl group—would not influence the electronic structure significantly, but would have an influence on the number of vibrational modes of the reactant and hence an influence on the rates. The results for cresol-benzene, however, were quite surprising in themselves. In the same experiment described for phenol-benzene and under very similar conditions, biexponential decay of the parent-ion mass signal was observed as a function of pump-probe delay, as shown in Figure 6. After a number of test experiments (7), it was concluded that the biexponential decay was indeed caused by the inherent properties of the dissociation process. The contributions of the fast versus slow component of the decay changed as a function of excess energy with the fast component becoming dominant at higher excess energies. A complete discussion is offered elsewhere (7), but the conclusion is that there must be a division of the vibrational phase space.

As the above findings suggest, the study of just these two systems has revealed much information and a number of unexpected results. The pump-probe technique described should be very generally applicable (particularly because of the nonresonant requirement of the probe) to a number of weakly bound systems. As more systems are studied we can expect to understand in more detail the dynamic factors at work, specifically the question of how the rate and extent of intramolecular vibrational-energy redistribution (IVR) influence the observed dissociation behavior. Recent experiments from this group

![Figure 5: Rates of phenol-benzene unimolecular dissociation as a function of excess vibrational energy above the reaction threshold. Also displayed are calculated RRKM rates. See text for details.](image)

![Figure 6: Cresol-benzene multiphoton ionization signal as a function of pump-probe delay time. The signal is mass gated to detect the parent ion, and thus dissociation in the neutral intermediate state leads to a decay in ion signal. The varying degree of biexponential behavior as a function of excess vibrational energy is clearly evident.](image)
have sorted out these dynamical channels, and mode selectivity, that is non-RRKM (Rice-Ramsperger-Kassel-Marcus) theory behavior, has been observed (31).

STATE-TO-STATE UNIMOLECULAR REACTION RATES
One of the most important developments made possible by these picosecond pump–probe experiments is the ability to measure state-to-state unimolecular reaction rates. By having independently tunable pump and probe pulses, one can optically prepare a well-defined excited state and then probe the time evolution of the appearance of the products, by monitoring not only the total number formed but also their internal energy states. In the following examples, the rotational and vibrational product states will be considered:

\[ \text{NCNO} \xrightarrow{h\nu} \text{NCNO}^* \xrightarrow{K_{\text{obs}}} \text{CN} + \text{NO} \]  
and

\[ \text{H}_2\text{O}_3 \xrightarrow{h\nu} \text{H}_2\text{O}_3^* \xrightarrow{K_{\text{obs}}} 2 \text{OH} \]

The details of the expected experimental observables are now considered by first using a rate-equation approach, the validity of which will be discussed later. The case of NCNO will be used as an example, but it is a completely general treatment (Table I). Consider the number of reactant molecules to be given by \( N_{\text{NCNO}}(t) \) with the number initially created being \( N_{\text{NCNO}}(0) \). The overall decay rate of the reactant, \( K \), will simply be the sum of the individual channels that form all the possible product states, with \( k_{ij} \) being the rate of formation of the particular state, \( \text{CN}(u = i, N = j) \). Notice that the possible product states of the NO have not been enumerated. If this was done, each of the rate equations would be decomposed into a set where the product-state yields that determine the ratio \( k_{ij}/K \).

Substituting for the time-dependent NCNO population yields:

\[ \frac{d[N\text{CN}(i,j)]}{dt} = \{[\text{NCNO}(0)]e^{-kt}\}k_{ij} \]  

Solving for the \( \text{CN}(i,j) \) population gives:

\[ \text{CN}(i,j) = \frac{\text{NCNO}(0)}{K} \frac{k_{ij}}{1 - e^{-kt}} \]

Thus, we see that if this simple rate-equation treatment is valid, then all product states appear at the same absolute rate. \( K = \Sigma_{ij} k_{ij} \), but that the relative number of particular products formed is determined by the ratio \( k_{ij}/K \). Therefore, to obtain the microscopic rate constants, \( k_{ij} \), one needs to measure the absolute rate constant, \( K \), using the techniques described herein, as well as measuring the relative product-state yields that determine the ratio \( k_{ij}/K \).

The above kinetic-equations approach is adequate provided there are no phase-coherence effects. If there is a partitioning of the phase space that occurs in the reactant early in the process, then different product states may appear at different rates. In this context, the experimentally determined rates as a function of product state will have a direct bearing on this question. The findings of two studies on two different classes of reactions are provided in the following section.

The NCNO system: NCNO \( \rightarrow \) NC + NO. The impetus for undertaking the study of NCNO was the very complete set of information obtained by Wittig, Reisler, and co-workers (32) on the spectroscopy of this molecule, as well as the almost complete characterization of its product-state distributions. They were able to measure the product states of both the CN and NO fragments over a very large range of energies. The reaction scheme can be represented as:

\[ \text{NCNO}(E = S_o, u = 0, J = 0) \xrightarrow{h\nu} \text{NCNO}^*(E = S_o, u = i, J = 0) \rightarrow \text{CN}(u = j, N = k) + \text{NO}(u = m, J = n) \]

The barrier for the reaction has been determined to be 17,085 cm\(^{-1}\), which is 5686 cm\(^{-1}\) above the \( S_o \) origin. One of the positive features of NCNO is that its \( S_o \) spectrum has appreciable intensity from the origin all the way up to \( \sim10,000 \text{ cm}^{-1} \) of excess energy due to the distorted excited-state geometry. Thus, one can pump the photodissociation reaction well above threshold. The time-resolved experiments discussed later were performed in a supersonic molecular beam so that individual features in the NCNO spectrum could be selectively excited. It should be noted here that the reaction proceeds first by internal conversion from \( S_o \) to the \( S_1 \) surface with subsequent reaction on the \( S_1 \) surface (5,32). It is presumed that vibrational redistribution takes place during and immediately after internal conversion. All experimental (indirect) evidence indicates that this internal conversion process is quite fast (< 10 ps) and that measurements are for the dissociation from \( S_0 \), which is the bottleneck in the \( S_1 \rightarrow S_0 \) reaction scheme.

As mentioned previously, a second dye laser has been incorporated into these particular experiments so that the pump and probe wavelengths could be tuned independently. The second color pulses originate in a dye laser that is synchronously pumped by approximately half the output of a mode-locked Nd:YAG laser, the other half of which pumps the original dye laser. In this way, the outputs of the two dye lasers are synchronized yet independently tunable, and show a cross correlation of 8-10 ps. The output of the dye laser is amplified in a pulsed-dye amplifier. The visible output of one dye laser is used directly to pump the NCNO \( S_1 \) vibrational states. The CN product of the reaction is monitored by the probe pulse using LIE. The probe pulse is obtained by mixing the second dye laser output with the 1.06-\( \mu \)m fundamental of the amplifying Nd:YAG dye laser. The probe, \( \sim388 \text{ nm} \), is tuned to the one-photon transition of CN and can select individual rotational levels in the 0-0 vibronic transition.
transient showing the rise of CN population is shown in Figure 7.

It was observed by Khundkar et al. (5) that for a given pump wavelength, all the product CN rotational states showed identical appearance rates. This was rigorously true at all pump wavelengths, provided the molecular beam was cooling the molecules properly (in other words, so there was no thermal distribution of reactants). Because the appearance of all product rotational states occurs at the same rate, the dimensionality of the problem is drastically reduced and the data can be represented as a simple graph of rate versus excess energy. This is shown in Figure 8, in which the excess energy dependence is measured up to \( \approx 700 \text{ cm}^{-1} \) above the barrier. At this point, a time resolution of \( \approx 10 \text{ ps} \) was reached. Overall, the rates increase rather smoothly with excess energy, but there is a plateau at \( 17,420 \text{ cm}^{-1} \) (\( \approx 320 \text{ cm}^{-1} \) above threshold) after which the rates rise again. This was investigated throughout and all the points were found to be reproducible with a high degree of accuracy.

The above results give the microcanonical rates of the reaction \( K(E, J) \). Also, from these rate measurements and the product-state distributions obtained by Wittig, Reisler, and co-workers (32) (which could be reproduced by the picosecond system described here) one can obtain the state-to-state rate constants:

\[
k_{ij} = \frac{N_{ij}}{N_{i}} K
\]  

where \( N_{ij} \) is the number of internal energy levels in the transition state with energy less than \( E \) and \( \varphi \) is the density of reactant states at that energy. The density of reactant states is a tractable quantity because all the modes of the stable molecule in its equilibrium geometry can be determined. The transition state is of course a less well-defined configuration and considerable approximations are needed to
specify the number of states, $N^\dagger$. Phase-space theory statistically allocates the excess energy available from the reaction to the products and defines $N^\dagger$ as the number of possible product states. The only other constraint on the allocation of the energy is that angular momentum be conserved throughout the reaction. In a general sense, one expects this estimate of $N^\dagger$ to be too high because we are placing the barrier to reaction — where $N^\dagger$ should be calculated — in the region of product formation, a so-called loose transition state. Indeed, it was found that the phase-space calculations did overestimate the rates even though they reproduced product-state distributions. Phase-space-calculated rates do not, of course, show any behavior that could reproduce the plateau observed at 320 cm$^{-1}$ above the barrier. RRKM calculations were also performed. In this case, $N^\dagger$ is calculated from the normal modes of the molecule, minus vibration of the reaction coordinate. If the normal modes are not modified, particularly the bending modes containing the reaction coordinate, then the transition state obtained is clearly too tight and the calculated rates will be too slow.

The rates thus calculated are indeed too small, but this method permits one to obtain a better fit to the data by adjusting the frequencies of one or more modes. When this adjustment is made for NCNO, one finds that the form of the rates versus excess energy can be approximated either below or above the plateau region, but no fit approximates both regions. To model data as complete as those presented for NCNO, one needs to consider the detailed nature of the potential energy surface in the region of the barrier. In this area, efforts are currently underway using modified statistical theories to attempt to locate the exact position of the barrier on the potential surface.

The fact that the product-state distributions are predicted accurately by phase-space theory but the rates cannot be similarly calculated (even in the form of rates versus excess energy, if not in magnitude) reflects the complementary nature of the information obtained. The rates have contributions from any possible bottleneck (barrier) on the potential energy surface on the way to products. The product-state distribution is an integration of all the influences of the potential on the way to products. If there is a region of the potential close to the formation of products that allows for a statistical distribution of energy into all possible product states, then any influences of the potential early in the reaction will be lost. The rates are sensitive to the passage through the transition state and, together with product-state distributions, give us the trajectory of the reaction on the PES. Both sets of information are now available for NCNO.

In summary, these picosecond pump–probe experiments provide the absolute rates, $k$ (obtained from the transients); the product-state distributions and state-to-state rates, $k$ (obtained from the asymptotic values of the probe signals, that is, long-delay-time experiments); and the dissociation energy (obtained from the threshold behavior), all of which will hopefully allow us to test critically the different theories of chemical reactions.

The HOOH system: overtone excitation. Consider the following reaction:

$$\text{H}_2\text{O}_2 \xrightleftharpoons{hv} \text{H}_2\text{O} \cdot (v = 5) \xrightarrow{\text{diss}} 2\text{OH}$$  \[19\]

The photodissociation studies of hydrogen peroxide are fundamentally different from those outlined above because the photolysis pump is to a well-defined vibrational overtone excitation. In this case, the entire reaction takes place on the ground-state surface, eliminating any possible complication of the dynamics from electronic-state coupling effects. The specific transition is to the fourth overtone of the O-H stretching mode. Clearly, this is an attractive system on which to have results. From a theoretical point of view, peroxide is a small molecule, and detailed vibrational-coupling interactions may be treated with some rigor. The questions to address are the initial dephasing of the optically prepared state, the extent of the energy redistribution, and the actual rate of dissociation.

Dynamics of overtone states have been addressed previously by measuring the line width of absorption transitions. Inhomogeneous broadening is a major obstacle in such cases and is always a concern in trying to identify the purely homogeneous contribution. Furthermore, for the case considered here, the line width will show contributions from both the dissociation rate and from the initial vibrational dephasing that must serve as a precursor to dissociation. Therefore, one expects the line width (if homogeneous) and direct-rate measurements to yield complementary information on the dynamics of the reaction.

Experimentally, this system is a challenge because of the weak transition dipole moment associated with the overtone transition (6). The experiments of Scherer et al. (6) were done at room temperature to help increase the number density and, hence, the sensitivity. The thermal distribution of molecules makes it difficult to prepare excited-state reactants with well-defined energies such as those achieved in the NCNO experiments. As was the case for NCNO, two lasers were used so that for a given pump energy, a distribution of products from the reaction could be monitored. The pump laser for the overtone excitation is the visible output from the amplified dye laser (∼6011–6163 Å). The reaction was probed using laser-induced fluorescence with the frequency-doubled output of the second dye laser resonant with the product OH radical electronic transition. This laser could be tuned to permit the selective excitation of particular product rotational states (designated by quantum number $N$). As mentioned, sensitivity was a problem because the overtone nature of the pump transition yielded a very small number of product OH radicals for each laser shot. This was aggravated by the fact that the OH emission was strongly dominated by resonance fluorescence, and so detection had to include the laser wavelength. Thus, extensive baffling was incorporated to separate the weak fluorescence from the laser scatter. Single-photon counting was employed, with the number of photons counted being monitored as a function of pump– probe delay time to measure the photodissociation reaction rate.

The question of the thermal distribution of the initial states will now be addressed. In the case of O–H fourth-overtone excitation, it is actually vital to have thermal excitation of rotational and vibrational modes because the photon energy of this transition is insufficient, by 1100 cm$^{-1}$, to exceed the O–O bond strength of 49.6 kcal/mol. Therefore, only “hot” transitions of the $v = 0\rightarrow 4$ excitation, or highly excited rotational states, can contribute to the formation of OH products. This is illustrated by the photodissociation spectrum of peroxide (38). These photodissociation spectra and associated product-state distributions obtained first by Crim’s group are an invaluable aid for the time-resolved experiments. Both types of measurements (rates and product-state distributions) can now be used to test the theory carefully, as discussed for the NCNO experiments.

A typical transient measurement is shown in Figure 9. In all cases, the data are clearly nonexponential in form and can be fit to a biexponential rise in signal level. Although the data may not be rigorously biexponential in nature, the fits to this form were satisfactory within the limits of the signal-to-noise ratio. More details can be found in the paper of Scherer et al. (6). The time-resolved results indicate that the overtone transition is inhomogeneously broadened and put a limit on the total dephasing rate. But what about the dissociation rates? Can the theory predict the observed OH build-up rate? Because of the thermal energy available, the rates can be modeled using statistical or nonstatistical treatment (6). Experiments in a molecular beam are needed before addressing the mechanism. However, it is clear that the dissociation is slow (∼60 ps or longer) and cannot be the major contributor to the apparent inhomogeneous line width. Comparison between experiments and theory for HOOH will be most illuminating for aforementioned reasons. There is a hope here to use this system to test both the nonstatistical (39) and statistical (33–37) models of vibrational energy flow on ground-state surfaces.

OTHER STUDIES

More recently we have applied the techniques to studies of the following reactions:

- Reactions involving the predissociation of van der Waals molecules (stilbene with He, Ne, and Ar). Product rotational coherence and direct-rate measurements were found (30,31) (Figure 10).

- Bimolecular reactions involving van der Waals molecules (in collaboration with R.B. Bernstein (40)). The product-state distribution of the system studied is known from the elegant
CONCLUSIONS

In this article, we hope that the examples given show the diversity of possibilities for the applications of ultrafast laser spectroscopy to chemical reactions. The focus here was made on the techniques and on studies involving unimolecular reactions, although we discussed two new directions that have been initiated recently, namely applications to "oriented" bimolecular reactions and the "transition-state" spectroscopy of elementary reactions.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation (endowments DMR-8521191 and CHE-8512887) and by the Air Force Office of Scientific Research (Grant No. 87-0071). The majority of the work presented in this review on unimolecular reactions has been published in collaboration with Norbert Scherer and Lutfur Khundkar. Without their efforts and dedication to the development of the techniques, this article could not have been written. We wish to thank professors C.B. Moore and R.N. Zare for stimulating discussions and for communicating unpublished work. We also thank M. Dantus for his efforts on Figure 1.

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Joseph L. Knee is an assistant professor in the department of chemistry at Wesleyan University, Middletown, Connecticut 06457. He received his BA in chemistry from the State University of New York at Binghamton in 1979 and his PhD in chemistry from the State University of New York at Stony Brook in 1983. His postdoctoral work was at the California Institute of Technology from 1984 to 1986.

Ahmed H. Zewail has worked since 1982 as a professor of chemical physics at the California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, California 91125. He received his BS and MS degrees from Alexandria University and his PhD from the University of Pennsylvania. After completing his postdoctoral work as an IBM Research Fellow at the University of California at Berkeley, Zewail joined the California Institute of Technology in 1976 as an assistant professor. Zewail is the author and coauthor of more than 180 scientific papers; he is also the editor of four books on laser chemistry and spectroscopy. Among the honors and awards he has received are: the Alfred P. Sloan Fellowship; the Camille & Henry Dreyfus Foundation Teacher–Scholar Award; distinguished visiting lecturer at the University of Texas and at Xerox; the John van Geuns Stitching Visiting Professorship (Holland); and the Alexander von Humboldt Award for Senior United States Scientists (West Germany). He has been an invited speaker at many national and international conferences and seminars. Recently, he was awarded the 1985 ACS Buck–Whitney Medal and a 1987 John Simon Guggenheim Foundation Fellowship. Zewail’s broad research interests include the areas of laser chemistry, coherent nonlinear optical spectroscopy, and the study of ultrafast dynamics of chemical reactions. His pioneering work, which combines femtosecond lasers and coherent nonlinear optical techniques with supersonic beams to study molecular dynamics, energy transfer, electronic and vibrational relaxation, and photochemistry, has opened new frontiers in the understanding of chemical dynamical processes.