Femtosecond pulses probe molecular events faster

Ultrafast investigations of molecular chemistry provide valuable insight into bulk-phase reaction dynamics.

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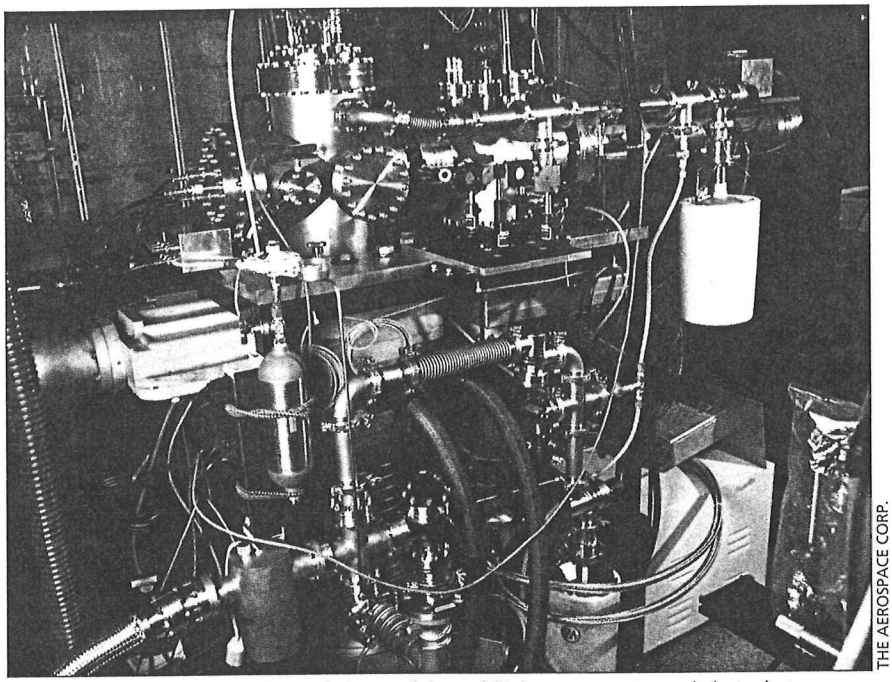

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Molecular-beam apparatus using techniques of time-of-flight spectrometry and photoelectron spectroscopy measures ultrafast and spectroscopic properties of isolated molecules and clusters.

The material properties of our world are governed by chemical bonds, and the transformation of these bonds is called chemistry. We often think about materials and chemistry as having macroscopic properties in space and time. We can see most of the devices we use, for example, and we must wait for most of the chemical reactions we need. Yet the spatial and temporal scales for forming and breaking bonds are angstroms and femtoseconds. Reconciling these vastly different yet intimately related microscopic and macroscopic scales requires a battery of sophisticated diagnostics covering the spatial and temporal scales for molecular-level to bulk-phase dynamics.

The development of ultrafast laser technology has been well documented.[1] Ultrafast lasers have been applied, mostly as research tools, to an enormous diversity of problems, particularly the study of chemical and material properties at the molecular level. One might ask, though, why study ultrafast processes on a molecular scale when practical devices occur on a human scale?

In fact, a surprising number of macroscopic phenomena occur directly on a molecular level. Vision is a good example for which sensitivity to a small number of photons has been demonstrated. There is also a practical need to separate the macroscopic or extended properties of a material or reaction from the underlying molecular properties. Thus, understanding the solvent contribution to solution-phase chemistry, for instance, requires a grasp of the chemical properties of the isolated molecule.

Furthermore, technology is driven by the continuous need to make devices smaller and faster. Miniaturization is pursued intensely in industries such as machining, etching, and optics. Nanotechnology is at the cutting edge of miniaturization, and, while most microdevices are engineered by linear scaling of bulk-phase properties, nanotechnology is fast approaching size scales at which these properties break down.

Femtosecond transition-state spectroscopy

Measurement techniques in ultrafast chemistry usually involve femtosecond pulses that are at different wavelengths and that are separated in time. While one pulse initiates the chemistry by excitation of a reactant molecule to a specific vibrational energy or dissociative state, a second pulse monitors the reaction by measuring changes in population of reactant, transition, or product states.[2,3] The measurement of transition-state dynamics is referred to as femtosecond transition-state spectroscopy.

The most elementary reaction is the breaking of a bond in a diatomic molecule. An example of the dynamics for such a simple system is a study of NaI dissociation by A. H. Zewail and coworkers at the California Institute of Technology (Pasadena, CA).[4] The reaction coordinate consists of potential energy crossing between the bound ion-pair ground-state Na^+I^- and a dissociative covalent excited state (see Fig. 1).

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These results show the critical reactive configuration at the surface crossing and measure the probability of the molecule reverting back to reactant or going forward as product.

Zewail's group has pioneered the use of ultrafast lasers in studies of femtosecond transition-state dynamics.[2,3] Using techniques similar to those for the NaI reaction, the group has achieved transition-state probing of several reaction classes involving three or more atoms. C. Wittig and coworkers at the University of Southern California (Los Angeles, CA) and B. Soep's group at CNRS (Orsay, France) are using aligned bimolecular reactions induced by complex photodissociation to extend these studies into the femtosecond regime. Other researchers employing novel ultrafast techniques for probing gas-phase reaction dynamics include P. Sorokin at IBM (Yorktown Heights, NY), Y. R. Chen at the University of California (Berkeley, CA), and G. Gerber at the University of Freiburg (Freiburg, Germany).

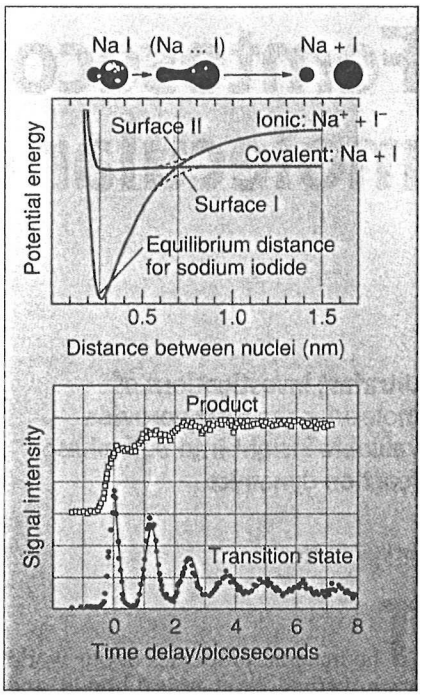

FIGURE 1. Femtosecond laser excitation of the neutral excited state of sodium iodide (NaI) leads to a repulsive interaction of the two atoms shown in the potential energy curves of the transition-state spectra for the reaction (top). The molecule tries to dissociate, but is bound in the dissociative limit by the surface crossing with the ionic state, which sets up a vibrational coherence that is clearly evident in the oscillatory behavior of the NaI signal in the transients, showing discrete transitions to product at the curve crossing (bottom).

The transition-state signal decays because each time the vibrating Na-I molecule encounters the outer crossing there is a small probability of penetration to the product channel Na + I—hence, the time dependence for product Na, which shows an increasing yield with time that occurs in steps corresponding to the moment of encounter with the surface crossing.

How short must a laser pulse be to probe transition states in chemical reactions? Approximately the time that it takes for two atoms to move from an average bond distance to some minimum separation that we can call bond breaking. Assuming a change in distance of about an angstrom and a typical recoil velocity of 10^5 cm/s, then

pulses of about 100 fs or less are necessary to resolve temporally the bond reorganizations of the transition state.

Gas-phase to condensed-phase chemistry

Early ultrafast chemical dynamics involved understanding a solvent's role in condensed-phase chemistry. Chemical rates at comparable energies were compared with and without solvent—in the gas phase and in solution. A benchmark unimolecular reaction, studied by numerous groups for many decades, is photoisomerization of *cis*- and *trans*-stilbene (1,2-diphenyl ethylene).

Some of the first time-resolved measurements of this system were reported by R. M. Hochstrasser's group at the University of Pennsylvania (Philadelphia, PA), which described a series of isomerization-rate measurements in solution and gas phase at thermal energies.[5] Isomerization rates in isolated *trans*-stilbene molecules were subsequently measured by picosecond molecular-beam spectroscopy, which permits laser excitation of gas-phase molecules to specific vibronic states because the molecules are cooled to near absolute zero.[6] Following rapid intramolecular vibrational redistribution, the excited molecule can isomerize.

A key reason for studying ultrafast dynamics on a molecular level is to understand real-world processes.

One of the surprising results from the comparison is that *trans*-stilbene isomerization occurs more rapidly in solution than in gas phase at comparable energies. These results seemed at odds with conventional wisdom, which said that reactions involving large-amplitude motions, such as twisting around of bulky phenyl groups, should be slowed by solvent molecules. Some unforeseen solvent property is, therefore, changing the predicted dynamics.

Several research groups investigated this unusual effect. Leading the effort were the groups of J. Troe (Göttingen, Germany), G. R. Fleming at the University of Chicago (Chicago, IL), J. Jortner (Tel Aviv, Israel), and Hochstrasser. A definitive explanation is still elusive, although mounting evidence suggests that solvent molecules exert an unusually strong effect on the reactive potential energy surface and significantly lower the barrier, which would accelerate the isomerization rates.

Alternatively, the reaction barrier may be due to a surface crossing, and the crossing probability is strongly affected by solvent. In either case, predictions are that the solvent perturbation on the potential energy curve should be evident for no more than a few solvent molecules. If so, a definitive answer could be obtained by measuring isomerization rates in small molecular clusters of stilbene/solvent.

Detailed comparisons of a prototype

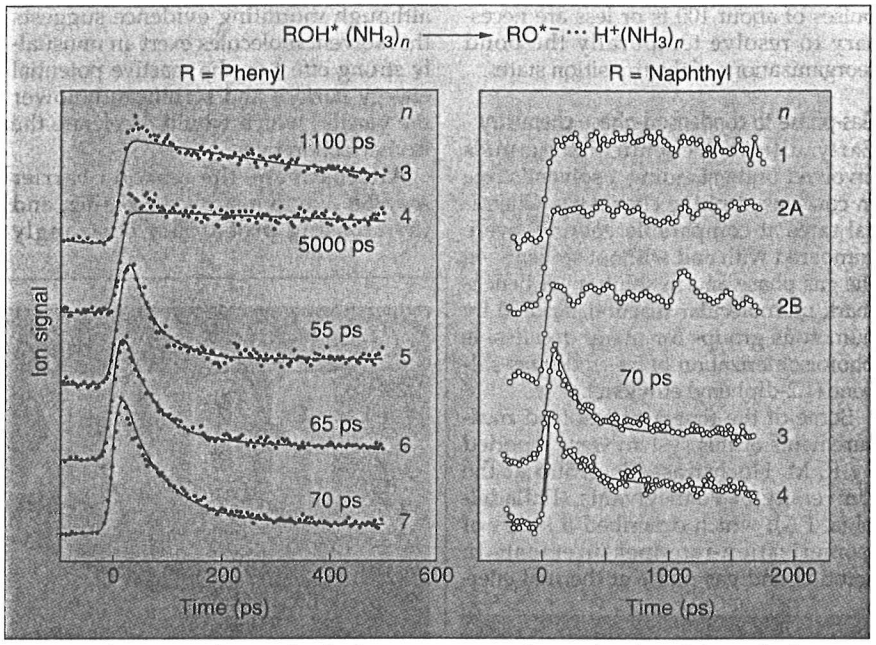

FIGURE 2. The measured rates of excited-state proton transfer as a function of cluster size for phenol and 1-naphthol in solvent clusters of ammonia show that addition of a single solvent molecule changes the reactant lifetime by two orders of magnitude. A distinct onset to fast chemistry occurs at $n = 3$ for 1-naphthol-$(NH_3)n$ clusters and at $n = 5$ for phenol-$(NH_3)n$ clusters. The cluster notation denotes a solute molecule embedded in a cluster of n solvent molecules; 2A and 2B refer to different geometries for $n = 2$ ammonia molecules.

reaction under gas- and condensed-phase conditions allow isolation of bulk solvation properties. Nonetheless, these studies represent two limiting phases of matter and do not directly connect molecular and bulk properties. One way to bridge this gap is to study clusters of molecules with increasing size such that, as molecular properties evolve to bulk properties they can be examined, literally, one molecule at a time.

Many research groups are involved in ultrafast measurements of chemistry in clusters; one compelling reason is to measure the interaction between individual solvent molecules. In an ultrafast experiment using mass spectrometry, reaction rates are measured as a function of cluster size. Chemical properties are compared as cluster size is changed by a single molecule so the role of individual solvent molecules can be discerned (see photo on p. 73).

A prototype reaction for cluster studies is the excited-state proton transfer (ESPT) of aromatic acids, such as phenol and naphthol, bound to clusters of base-like solvent molecules (see Fig. 2). In these cases, adding a single solvent molecule changes the reactant lifetime by two orders of magnitude.[8–10] The reason that ESPT occurs with fewer solvent molecules in 1-naphthol relative to phenol is that the former molecule is a slightly stronger acid. We are pursuing ultrafast measurements of proton transfer in clusters, as are Zewail, D. F. Kelley and E. R. Bernstein at Colorado State University (Fort Collins, CO), and A. W. Castleman at Pennsylvania State University (University Park, PA). These studies are providing detailed information about the effects of solvent molecules on the potential energy surface and on the mechanism of proton tunneling.

Another prototype system for measuring solvent caging of a photodissociation is molecular iodine surrounded by a solvent (I_2-Mn). Clusters offer a unique way to probe the microscopic solvent shell structure and the influence on dynamics.

Two very exciting results relating neutral I_2 dissociation/recombination in clusters and solids have recently been reported using rare-gas atoms as the solvent cage.[11,12] In these studies, the solvent or matrix potential barrier is directly probed and the extent of lattice excitation measured. When I_2 is dissociated in an argon cluster[11] or frozen krypton solvent cage,[12] the recombination and subsequent vibrational oscillations and relaxation are readily observable (see Fig. 3).

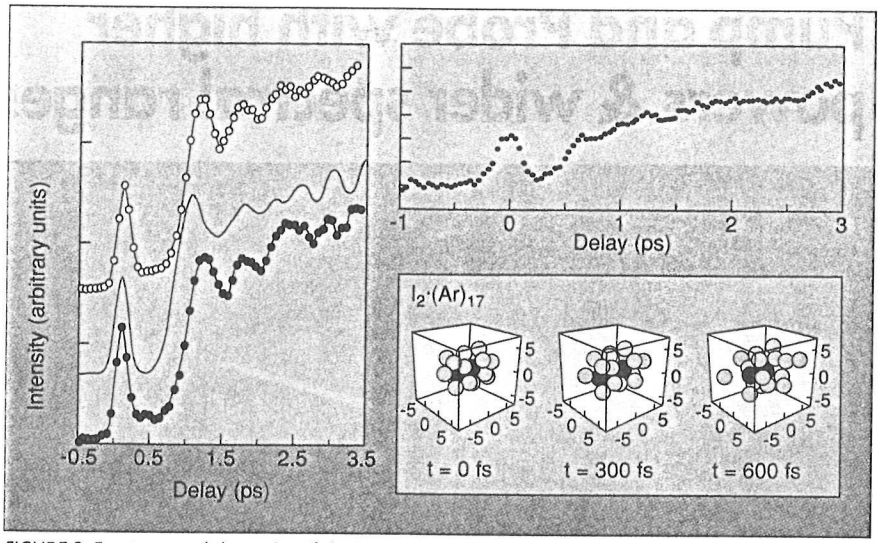

FIGURE 3. Femtosecond dynamics of the I_2 => 2I reaction show the recombination and subsequent vibrational oscillations and relaxation with I_2 in a krypton matrix (left) and in an argon solvent cage (upper right). The open and solid symbols are experimental data for 15 K and 35 K, respectively, and the solid line is a molecular dynamics calculation. A calculation (lower right) shows the dissociation and recombination of I_2 in a solvent cluster.

Excitation of I_2 was via the *A* state at 704 nm and 614 nm, respectively. The signal is due to laser-induced fluorescence of I_2 from an ultraviolet probe pulse. The lower right diagram represents the dissociation of I_2 in a solvent cluster.

W. C. Lineberger's group at the University of Colorado (Boulder, CO) carried out elegant caging experiments on I_2-$(CO_2)n$.[13] The cluster ions are size-selected in a mass analyzer, then measured by time-resolved spectroscopy. Nearly complete caging was observed for $n \geq 16$ and an interesting recurrence occurred at 2 ps. For smaller cluster sizes, the cage probability decreased nearly monotonically with decreasing n.

Molecular biology

A key reason for studying ultrafast dynamics on a molecular level is to understand real-world processes. Vision provides an excellent example of the connection between the microscopic and macroscopic realms. The process begins with the absorption of a photon by the protein rhodopsin, which initiates an 11-*cis* to 11-*trans* isomerization of the retinal chromophore of rhodopsin (see Fig. 4).

Some of the earliest ultrafast measurements were carried out on rhodopsin by P. M. Rentzepis and coworkers at AT&T Bell Laboratories

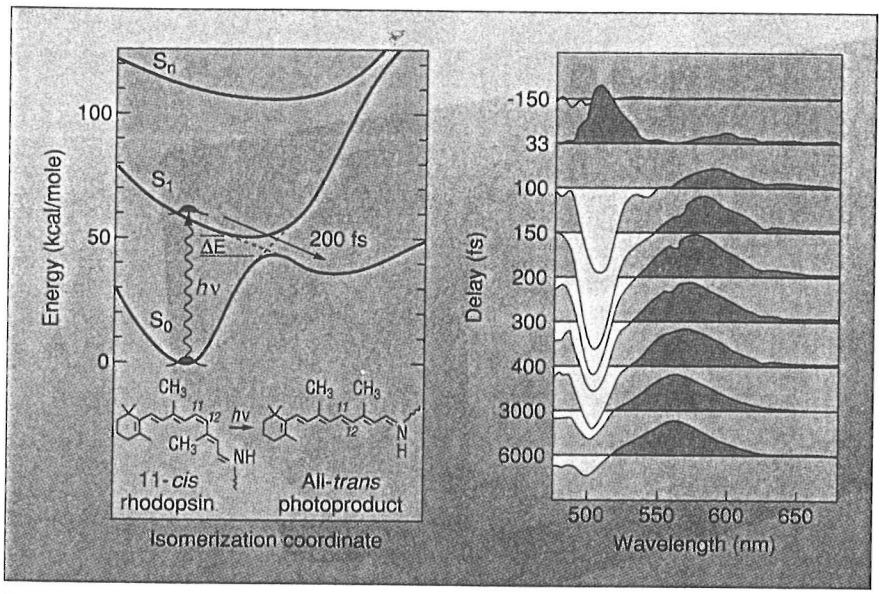

FIGURE 4. Human vision begins with the absorption of a photon by the protein rhodopsin, which initiates an 11-*cis* to 11-*trans* isomerization of the retinal chromophore of rhodopsin (left). Measuring the time-resolved absorption spectrum from the photoexcited state showed that the 200-fs event encompasses bond twisting on the excited state surface and conversion to the ground state photoproduct along a nonadiabatic potential. Previous studies at lower time resolution indicated that the two processes were separated in time, the former occurring in about 200 ps and the latter in a few picoseconds.

A series of transient absorption spectra using a 500-nm pump pulse and a continuum probe pulse were recorded by subtracting pump-only from pump-and-probe absorption spectra (right). The band at 510 nm represents absorption from the initially prepared reactant excited state and decays concurrent with the formation of the photoproduct band at 570 nm with a time constant of 200 fs. The reactant signal decays to a negative value due to bleaching of the ground state absorption by the pump excitation at 500 nm.

(Murray Hill, NJ). The primary event was found to be faster than the laser time resolution, which was then 6 ps. Recently, R. A. Mathies, E. V. Shank, and coworkers at the University of California (Berkeley, CA) used 35-fs pulses to measure a barrierless isomerization time of 200 fs.[14]

These measurements are intriguing because they indicate that the primary step in vision occurs on a vibrational time scale. This implies that vibrational redistribution of the initial excited state may not be an important mechanism for

reaction. Instead, the dynamics of isomerization involve a coherent vibrational motion. Such observations are normally found in small molecules, where the density of vibrational states available for energy redistribution is small. It is, therefore, important to discover and understand phenomena in large molecules and biological molecules that exhibit truly elementary chemical behavior.

Other applications

If technology is moving toward smaller and faster, then ultrafast lasers will play a key role in our understanding of properties of matter and molecular-level chemistry. Ultrafast studies of clusters help unravel the correspondence between bulk-phase and gas-phase properties.

In computing, technology is driven by memory storage and logic switching. One can imagine individual molecules serving as binary devices that can be optically flipped as in *cis/trans* isomerization, for example, or an optical switch consisting of a donor/acceptor pair of molecules involving transfer of an electron or proton to form an ion-pair state.

Basic research yields information of direct importance to the real world, whether it be photoisomerization relating to vision or memory devices, proton transfer relating to acid catalysis or optical switching, or cluster studies relating to nanotechnology. □

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