

This paper is a summary of a session presented at the first Japanese-American Frontiers of Science symposium, held August 21–23, 1998, at the Arnold and Mabel Beckman Center of the National Academies of Sciences and Engineering in Irvine, CA.

Femtochemistry

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ABSTRACT The topic of femtochemistry is surveyed from both theoretical and experimental points of view. A time-dependent wave packet description of the photodissociation of the O—C—S molecule reveals vibrational motion in the transition-state region and suggests targets for direct experimental observation. Theoretical approaches for treating femtosecond chemical phenomena in condensed phases are featured along with prospects for laser-controlled chemical reactions by using tailored ultrashort chirped pulses. An experimental study of the photoisomerization of retinal in the protein bacteriorhodopsin is discussed with an aim to gain insight into the potential energy surfaces on which this remarkably efficient and selective reactions proceeds. Finally, a prospective view of new frontiers in femtochemistry is given.

The essence of the chemical industry and indeed of life is the making and breaking of molecular bonds. The elementary steps in bond making and breaking occur on the time scale of molecular vibrations and rotations, the fastest period of which is ≈ 10 femtoseconds (10^{-14} s). Chemical reactions are, therefore, ultrafast processes, and the study of these elementary chemical steps has been termed “femtochemistry” (1). A primary aim of this field is to develop an understanding of chemical reaction pathways at a molecular level. Given this information, one can better conceive of new methods to control the outcome of a chemical reaction. Because chemical reaction pathways for all but the simplest of reactions are complex, this field poses challenges both theoretically and experimentally. Nevertheless, much progress is being made, and systems as complex as biomolecules can now be investigated in great detail. In the following, we will present results from theoretical and experimental efforts to probe deeply into the nature of chemical reactions in complex systems.

Theory. Ultrafast dynamics of molecules have long been studied theoretically by integrating a relevant equation of motion. The time-dependent wave packet approach has proven to be particularly promising for following femtosecond chemical reactions in real time. Briefly, a molecular system can be characterized by electronic potential energy surfaces on which wave packets propagate. For example, an electronic excited-state potential of the O—C—S molecule is depicted in Fig. 1 as a function of interatomic separation between C and O (R_{CO}) and C and S (R_{CS}). The time evolution of the wave packet has been investigated by integrating the Schrödinger equation as the wave packet propagates on this potential energy surface. The initial wave packet ($t = 0$) was prepared on the excited electronic state surface by photoexcitation from the ground electronic state (2). It is apparent from wave packet evolution that one portion of the wave packet propagates along the dissociation coordinate fairly rapidly, whereas another portion

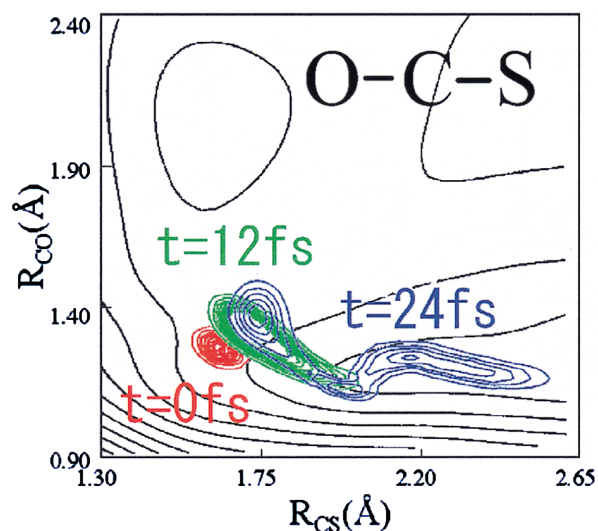


FIG. 1. Time evolution of a dissociating wave packet on an electronically excited state of O—C—S. The initial wave packet at (a) $t = 0$ (red) and its snapshots at (b) $t = 12$ fs (green) and (c) $t = 24$ fs (blue).

remains localized near the Franck–Condon region. The localized portion moves along the in-phase-stretching coordinate with comparable vibrational amplitudes for both CO and CS stretching motions. This oscillatory wave packet motion can be regarded as motion along an unstable periodic orbit on the excited state potential energy surface, which would give rise to prominent spectral peaks in the experimental UV absorption spectrum of O—C—S. A wave packet calculation on the *ab initio* potential energy surface reproduces the qualitative features of the autocorrelation function that has been experimentally extracted from photofragment excitation spectroscopy (2). A recurrence period of 48 fs was predicted theoretically, which is comparable to the experimental value of 42 fs (2). This agreement between experimental and theoretical vibrational periods in the transition-state region highlights the power of recent theoretical approaches.

Experimental efforts in the field of femtochemistry have exploited the pump-probe technique, where a “pump” laser pulse initiates a chemical reaction and a “probe” laser pulse records a “snapshot” of the chemical reaction at a time controlled by the temporal delay between the pump and probe pulses. By recording snapshots as a function of the temporal delay, one can follow the time evolution of a chemical reaction with time resolution limited only by the duration of the laser pulses. Beyond monitoring the outcome of a normal photo-reaction, the phase and frequency of a femtosecond “pump”

pulse can be tailored, as prescribed by theory, to drive a molecular state to a target location on its potential energy surface and then steer it toward a channel that favors a particular photochemical outcome. For example, the excitation pulse might be a femtosecond linear chirped laser pulse, which can interact with the wave packet through a so-called intra-pulse pump-dump process. A negatively chirped pulse (frequency components shift in time from blue to red) might be tailored to maintain resonance with the wave packet as it evolves along the excited state surface. In contrast, a positively chirped pulse might quickly go off resonance with the wave packet, and the photoexcitation would be nonselective. This intra-pulse pump-dump effect, first proposed theoretically (3), has been demonstrated experimentally quite recently (4). It was also shown that ultrashort chirped laser pulses can be used for laser-controlling photodissociation processes of NaI and CO (5).

When molecules are studied in the gas phase, interactions between neighboring molecules can be neglected. However, a vast range of chemical phenomena occurs preferentially or even exclusively in a liquid environment. When a reaction occurs in a condensed phase, the theoretical problem becomes significantly more complex. This difficulty is because motion of the surrounding molecules leads to fluctuations in the structures and energy levels of neighboring molecules, thereby promoting or hindering thermally activated processes in these systems. Understanding molecular motions and how they couple to the reaction coordinate is, therefore, crucial for a comprehensive description of the underlying microscopic processes. This problem is particularly challenging because molecules exhibit strong mutual interactions, and these interactions evolve on the femtosecond time scale because of random thermal motion of the molecules. In essence, understanding the dynamics of a molecular system in the condensed phase boils down to a problem of nonequilibrium statistical physics. Combined with an impressive increase in computational capacity, recent developments in theoretical methodology such as molecular dynamics (6), path integral approaches (7), and kinetic equation approaches for dissipative systems (8) have enlarged dramatically the scope of what is now theoretically tractable.

Experiment. Whereas ultrafast spectroscopic methods used to be confined to a handful of research labs, recent advances in femtosecond laser technology have led to the introduction of commercial lasers that generate optical pulses shorter than 100 fs. The widespread availability of such short pulses has, in turn, led to the study of a diverse range of molecular systems as they transform from "reactants" to "products." Systems of ever-increasing complexity have now been investigated, including small-molecule reactions in the condensed phase and photo-induced reactions in biological systems. Here, we focus our attention on the photoisomerization of retinal in the protein bacteriorhodopsin with an aim to gain further insight into the potential energy surfaces on which this photoisomerization reaction proceeds.

Bacteriorhodopsin is a trans-membrane protein found in a simple archaeobacterium, *Halobacterium halobium*. This protein has a photosynthetic function and converts light energy to chemical energy by pumping protons across a cell membrane. The chromophore responsible for light absorption is a retinal that is covalently bound within the interior of a seven-helix protein in the form of a protonated Schiff base (9, 10). On absorbing a photon, the retinal isomerizes from its all-trans form to its 13-*cis* form (11–14) with a quantum efficiency of about 64% (15–17). This primary process triggers a cascade of events, which ultimately leads to the translocation of a proton across the cell membrane and the return of the retinal to its all-trans form (18, 19). The pathway of the primary photoisomerization is the focus of this experimental work. Time-resolved spectra recorded over a broad spectral range suggest

a reaction pathway that involves three electronic states whose surfaces cross in two regions along the photoisomerization pathway (20, 21). Theoretical support for this notion has also been presented (22–24). The three-state model provides a compelling explanation for the origins of selectivity and efficiency demonstrated by this biological reaction. Not all aspects of this reaction are fully understood, however. The measured dynamics for the isomerization reaction evolve biexponentially with 200-fs and 700-fs components in a 2:1 ratio. Although the origin of this nonexponential process is yet to be explained (25), ongoing efforts to model the kinetics in finer detail appear promising.

New Frontiers. To extend beyond the view afforded by ultrafast spectroscopy, ultrafast structural techniques are being developed. For example, time-resolved x-ray crystal structures of photolyzed carbon monoxymyoglobin (MbCO + $h\nu^*$ Mb + CO) have been acquired at the European Synchrotron and Radiation Facility in Grenoble, France, with 7.5-ns time resolution (26). For these experiments, the "probe" is an x-ray pulse, not a laser pulse, and the sample x-ray diffraction is recorded instead of its absorbance spectrum. Further experiments by Wulff and collaborators are being carried out with about 150-ps time resolution. In addition to x-ray approaches, ultrafast electron diffraction is also being developed (27, 28). Because of the current pace of new technological developments, the opportunities to directly monitor the motion of nuclei throughout the course of chemical reactions are becoming ever more numerous. Furthermore, by monitoring nuclear motion on a time scale that is accessible to theory, comparisons can be made that test directly the validity of various theoretical approaches. Such detailed comparisons can then serve to guide the design of laser-controlled chemical reactions. Femtochemistry, therefore, affords the opportunity to relate the formal study of nonequilibrium statistical physics to the real world of molecular science.

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