FEATURE ARTICLE

Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond[†]

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This anthology, which is adapted from the Nobel Lecture, gives an overview of the field of *Femtochemistry* from a personal perspective, encompassing our research at Caltech and focusing on the evolution of techniques, concepts, and new discoveries. In developing femtochemistry—the study of molecular motions in the ephemeral *transition states* of physical, chemical, and biological changes—we have harnessed the powerful concept of molecular *coherence* and developed *ultrafast-laser techniques* for observing these motions. Femtosecond resolution (1 fs = 10^{-15} s) is the ultimate achievement for studies of the dynamics of the chemical bond at the atomic level. On this time scale, matter wave packets (particle-type) can be created and their coherent evolution as a *single-molecule trajectory* can be observed. The field began with simple systems of a few atoms and has reached the realm of the very complex in isolated, mesoscopic, and condensed phases and in biological systems such as proteins and DNA. It also offers new possibilities for the control of reactivity and for structural femtochemistry and femtobiology.

I. Introduction

Over many millennia, humankind has thought to explore phenomena on an ever shorter time scale. As early as 3100 BC, the “Astronomical Calendar” was introduced in ancient Egypt to time the passage of days in a year through observations of the event of the heliacal rising of the brilliant star Sothis (or Sirius). Since then, and with the development of Sundials in ca. 1500 BC, time periods of year, month, day, and hour have been known. About 1300 AD, the mechanical clock was advanced in Europe, ushering in a revolution in precision and miniaturization. The present time standard is the cesium atomic clock, which provides precision of about 1:10^{13}; i.e., the clock loses or gains one second every 1.6 million years.

Until 1800 AD, the ability to record the timing of individual steps in any process was essentially limited to time scales amenable to direct sensory perception—for example, the eye’s ability to see the movement of a clock or the ear’s ability to recognize a tone. Anything more fleeting than the blink of an eye (∼0.1 s) or the response of the ear (∼0.1 ms) was simply beyond the realm of inquiry. In the nineteenth century, the technology was to change drastically, resolving time intervals into the subsecond domain. The famous motion pictures by Eadweard Muybridge (1878) of a galloping horse, by Etienne-Jules Marey (1894) of a righting cat, and by Harold Edgerton (mid-1900s) of a bullet passing through an apple and other objects are examples of these developments, with millisecond to microsecond time resolution, using snapshot photography, chronophotography, and stroboscopy, respectively. By the 1980s, this resolution became 10 orders of magnitude better (see section II2), reaching the femtosecond scale, the scale for atoms and molecules in motion.

The actual atomic motions involved in chemical reactions had never been observed in real time despite the rich history of chemistry over two millennia. Chemical bonds break, form, or geometrically change with awesome rapidity. Whether in isolation or in any other phase, this ultrafast transformation is a dynamic process involving the mechanical motion of electrons and atomic nuclei. The speed of atomic motion is ∼1 km/s, and hence, to record atomic-scale dynamics over a distance of an angström, the average time required is ∼100 fs. The very act of such atomic motions as reactions unfold and pass through their transition states is the focus of the field of femtochemistry. With femtosecond time resolution we can “freeze” structures far from equilibrium and prior to their vibrational and rotational motions, or reactivity.

The pertinent questions about the dynamics of the chemical bond are the following: How does the energy put into a reactant molecule redistribute among the different degrees of freedom, and how fast does this happen? What are the speeds of the chemical changes connecting individual quantum states in the reactants and products? What are the detailed nuclear motions that chart the reaction through its transition states, and how rapid are these motions? As pointed out by Jim Baggott, “*the entire history of chemical reaction dynamics and kinetics has been about providing some approximate answers to these three questions*.”

Ultrafast pulsed laser techniques have made direct exploration of this temporal realm a reality (sections II and III). Spectroscopy, mass spectrometry, and diffraction play the role of “ultrahigh-speed photography” in the investigation of molecular processes. A femtosecond laser *probe* pulse provides the shutter speed for freezing nuclear motion with the necessary spatial resolution. The pulse probes the motion by stroboscopy, i.e., by pulsed illumination of the molecule in motion and recording

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the particular snapshot. A full sequence of the motion is achieved by using an accurately timed series of these probe pulses, defining the number of frames per second.

For molecules there exist three additional requirements in order to study the motion. First, we need to *clock* the motion by defining its zero of time, also accurate to tens of femtoseconds. Second, the motion must be *synchronized* since millions of molecules are typically used in the recording of molecular motion. Third, molecular *coherence* (see below) must be induced to localize the nuclei. These requirements are satisfied by using a femtosecond *pump* (*initiating*) laser pulse, in what is referred to as a *pump*−*probe* configuration. For femtosecond studies, where femtosecond control of relative timing is needed, the laser pump and probe pulses are produced in synchrony, then the probe pulse is diverted through an adjustable optical path length (Figure 1). The finite speed of light translates the difference in path length into a difference in arrival time of the two pulses at the sample; 1μ corresponds to 3.3 fs. The individual snapshots combine to produce a complete record of the continuous time evolution—a motion picture, or a movie—in what may be termed femtoscopy.

In femtochemistry, studies of physical, chemical, or biological changes are at the fundamental time scale of molecular vibrations: the actual nuclear motions (Figure 2). The ephemeral transition states, denoted in the past by a bracket $[TS]^{\ddagger}$ for their elusiveness, can now be clocked as a molecular species $TS^{\ddagger}$. Moreover, the femtosecond time scale is unique for the creation of coherent molecular wave packets on the atomic scale of length, a basic problem rooted in the development of quantum mechanics and the duality of matter. Molecular wave functions are spatially diffuse and exhibit no motion. Superposition of a number of separate wave functions of appropriately chosen phases can produce the spatially localized and moving coherent wave packet (Figure 3). The packet has a well-defined (group) velocity and position, which now makes it analogous to a moving classical marble, but at atomic resolution, and without violation of the uncertainty principle. As long as the wave packet (typical width ∼0.05 Å) is sufficiently localized on the scale of all accessible space (∼0.5 Å or more), as in the figure, a description in terms of the classical concepts of particle position and momentum is entirely appropriate. In this way, localization in time and in space are simultaneously achievable for reactive and nonreactive systems (section III4).

The observation of motion in real systems requires not only the formation of localized wave packets in each molecule but also a small spread in position among wave packets formed in the typically millions of molecules on which the measurement is performed. The key to achieving this condition is generally provided by (a) the well-defined *initial*, equilibrium configuration of the studied molecules before excitation and (b) by the *"instantaneous"* femtosecond launching of the packet. The spatial confinement (in this case ∼0.05 Å) of the initial ground state of the system ensures that all molecules, each with its own coherence among the states that form its wave packet, begin their motion in a bond-distance range much smaller than that executed by the motion. The femtosecond launching ensures that this narrow range of bond distance is maintained during the entire process of preparation, as shown below. Unless molecular and ensemble coherences are destroyed by intra- and/or intermolecular perturbations, the motion is that of a *single-molecule trajectory*.

This powerful concept of *coherence* lies at the core of femtochemistry and was a key advance in observing the dynamics. The realization of its importance and its detection by selectivity in both preparation and probing were essential in all studies, initially of states and orientations, and culminating in atomic motions in reactions. With these concepts in mind, the marriage of ultrafast lasers with molecular beams (Figure 1A,B) proved to be essential for the initial development. Laser-induced fluorescence was the first probe used, but later we invoked mass spectrometry and nonlinear optical techniques. Now numerous methods of probing are known and used in laboratories around the world; Coulomb explosion is the most recent powerful probe developed by Will Castleman for arresting reactive intermediates.

Applications of femtochemistry have spanned the different types of chemical bonds—covalent, ionic, dative, and metallic, and the weaker ones, hydrogen and van der Waals bonds. The studies have continued to address the varying complexity of molecular systems, from diatomics to proteins and DNA. Studies have also been made in the different phases of matter: gases and molecular beams; mesoscopic phases of clusters, nanostructures, particles, and droplets; condensed phases of dense fluids, liquids, solids, surfaces, and interfaces; and in sibling fields of femtoscience such as femtobiology.

II. Dynamics and Arrow of Time

(1) From Kinetics to Dynamics: The Transition State. At the turn of the 20th century, the study of reactivity was dominated by the question: *How do reactions proceed and what are their kinetic rates?* Svante Arrhenius[1] gave the seminal description of the change in rates of chemical reactions with temperature and formulated in 1889 the familiar expression for the rate constant,

$$k = A \exp(-E_a/RT) \qquad (1)$$

which, as Arrhenius acknowledged, had its roots in van't Hoff's (1884) equations.[1]

The rate constant, $k(T)$, does not provide a detailed molecular picture of the reaction. This is because $k(T)$, which was obtained from an analogy with van't Hoff's description of the change with T of the equilibrium constant K (thermodynamics), is an average of the microscopic, reagent-state to product-state rate coefficients over all possible encounters. These might include different relative velocities, mutual orientations, vibrational and rotational phases, and impact parameters. A new way was needed to describe, by some quantitative measure, the process of the chemical reaction itself: How reagent molecules approach, collide, exchange energy, sometimes break bonds and make new ones, and finally separate into products. Such a description is the goal of molecular reaction dynamics.[2]

For some time, theory was ahead of experiment in studies of *microscopic* molecular reaction dynamics. The effort started shortly after the publication of the Heitler−London quantum-mechanical treatment (1927) of the hydrogen molecule.[3] One year later (1928), for Sommerfeld's Festschrift (60th birthday), London[3] presented an approximate expression for the potential energy of triatomic systems, e.g., H_3, in terms of the Coulombic and exchange energies of the "diatomic" pairs. In 1931 Henry Eyring and Michael Polanyi,[3] using the London equation, provided a semiempirical calculation of a potential energy surface (PES) of the $H + H_2$ reaction describing the journey of nuclei from the reactant state of the system to the product state, passing through the crucial transition state of activated complexes. The birth of "reaction dynamics" resulted from this pioneering effort and, for the first time, one could think of the PES and the trajectories of dynamics on it—*in those days, often,*

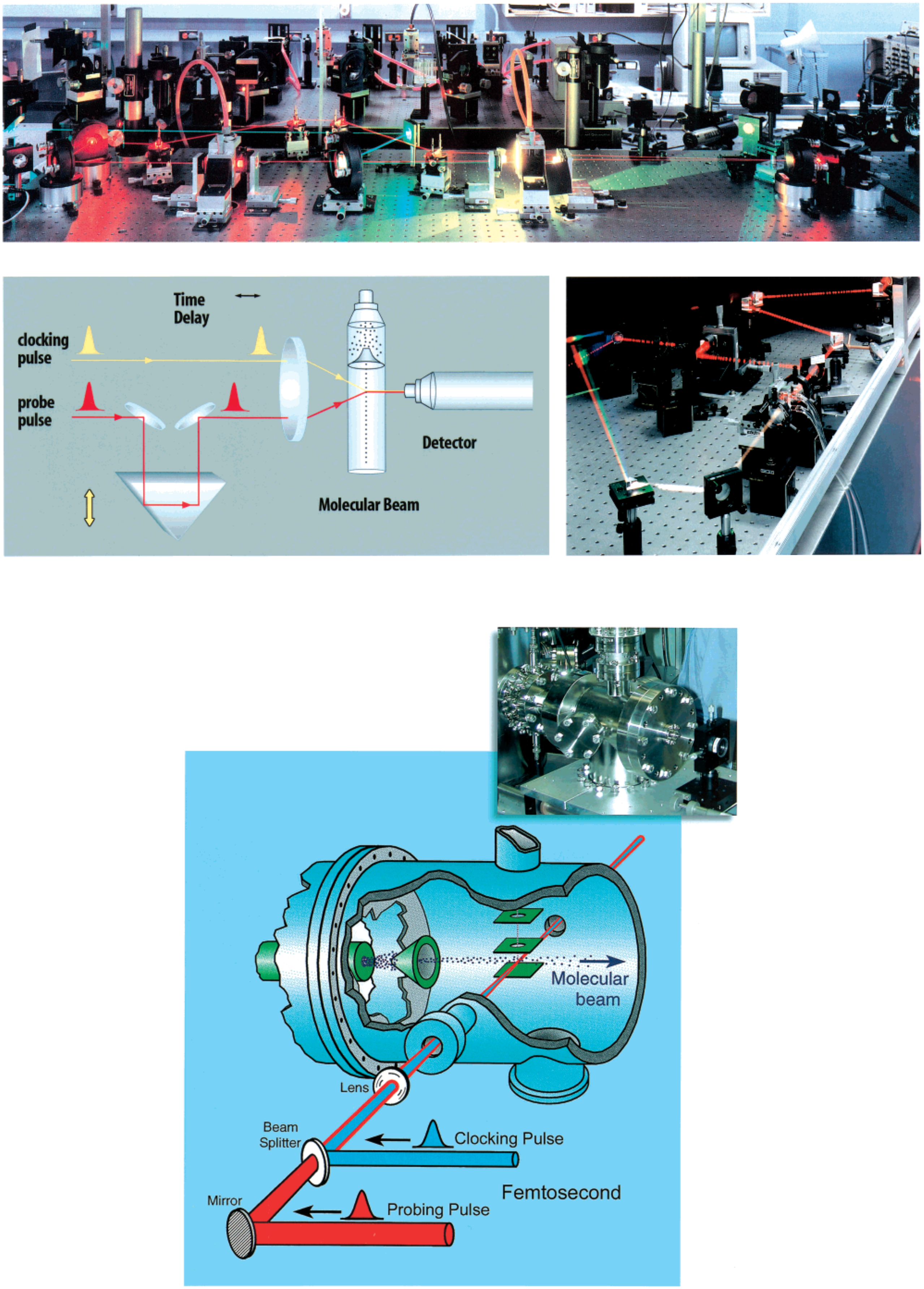


Figure 1. Femtochemistry apparatus, typical of early Femtolands. Laser system: (top) the first CPM oscillator used in Femtoland I; (bottom) the continuum generation to the right and the experimental layout for clocking, to the left. Molecular beam apparatus of Femtoland III, together with a view of the beam/laser arrangement.

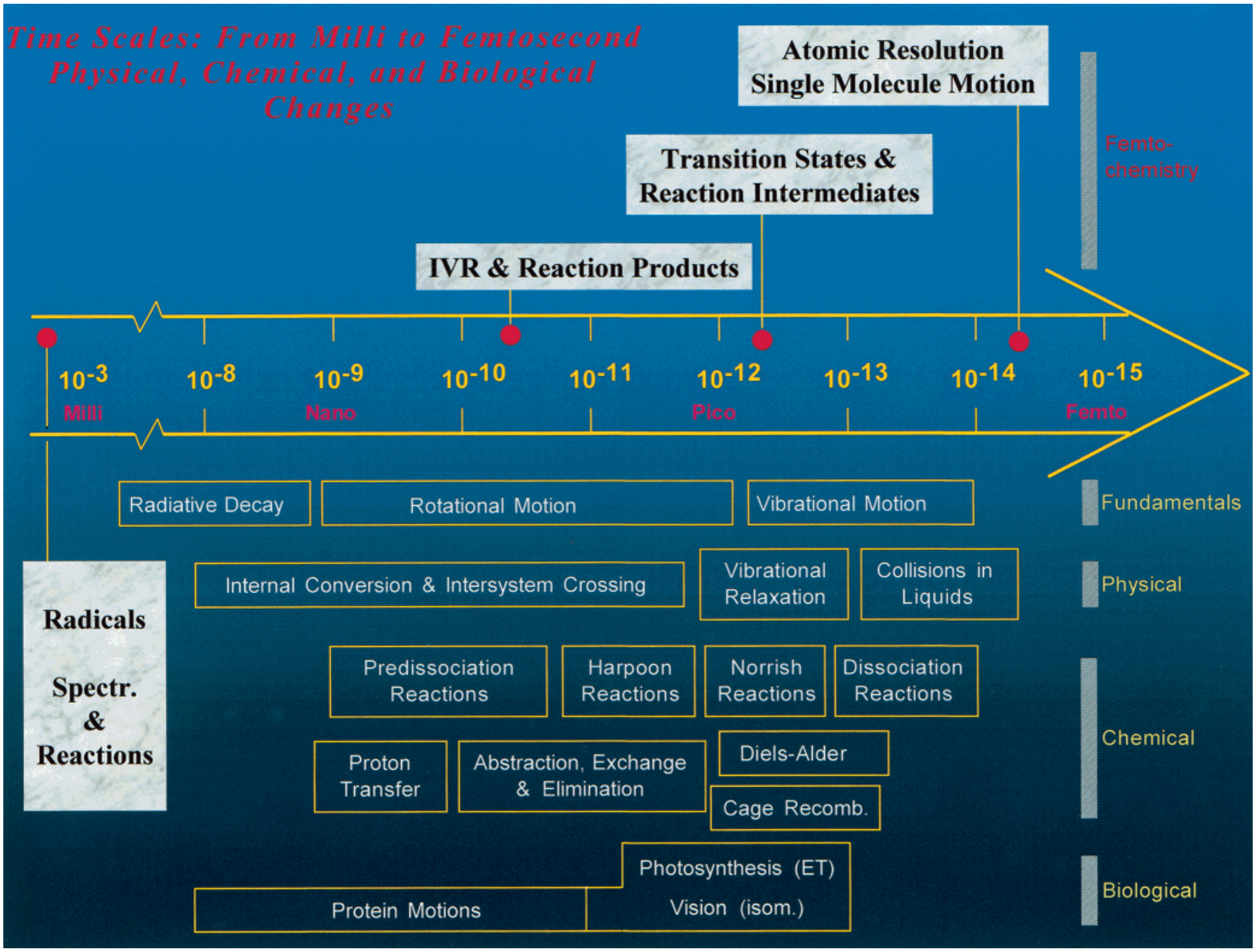


Figure 2. Time scales. The relevance to physical, chemical, and biological changes. The fundamental limit of the vibrational motion defines the regime for femtochemistry. Examples are given for each change and scale.

expressed in atomic units of time! But no one could have dreamed in the 1930s of observing the transient molecular structures of a chemical reaction, since the time scale for those *far from equilibrium* activated complexes in the transition state was estimated to be less than 1 ps.

The time scale was rooted in the theory developed for the description of reaction rates. Building on Arrhenius' work and the work of Polanyi and Wigner (1928),[4] in 1935, Eyring, and independently Evans and Polanyi, formulated *transition-state theory*, which gave an explicit expression for Arrhenius' preexponential factor:[4]

$$k = \frac{\mathbf{k}T}{h}K^{\ddagger} = \frac{\mathbf{k}T}{h}\frac{Q^{\ddagger}}{Q_A Q_B}\exp(-E_0/\mathbf{k}T) \qquad (2)$$

where $\mathbf{k}$ is Boltzmann's constant, h is Planck's constant, and Q is the partition function; E_o and E_a are related. According to transition-state theory, the fastest reaction is given by $\mathbf{k}T/h$, which is basically the "frequency" for the passage through the transition state (eq 2). At room temperature this value is 6×10^{12} s^{-1}, corresponding to ~170 fs; the time scale of molecular vibrations is typically 10−100 fs. In 1936 the first classical trajectory from Hirschfelder−Eyring−Topley molecular dynamics simulations of the $H + H_2$ reaction showed the femtosecond steps needed to follow the reaction profile, albeit on the wrong PES. Later, Martin Karplus, Don Bunker, and others showed a range for the time scales, picosecond to femtosecond, depending on the reaction and using more realistic PES's (see ref 5 and references therein).

In general, for an elementary reaction of the type

$$A + BC \rightarrow [ABC]^{\ddagger} \rightarrow AB + C \qquad (3)$$

the whole journey from reagents to products involves changes in internuclear separation totaling ~10 Å. If the atoms moved at 10^4−10^5 cm/s, then the entire 10 Å trip would take 10^{-12}−10^{-11} s. If the "transition state", $[ABC]^{\ddagger}$, is defined to encompass *all configurations of ABC significantly perturbed from the potential-energy of the reagents A + BC or the products AB + C*, then this period of 1−10 ps is the time available for its observation. To achieve a resolution of ~0.1 Å, the probe time window must be 10−100 fs.

The above definition of the transition state follows the general description given by John Polanyi and the author,[6] namely the full family of configurations through which the reacting particles evolve en route from reagents to products. This description may seem broad to those accustomed to seeing the TS symbol, ‡, displayed at the crest of the energy barrier to a reaction. As stated in ref 6, even if one restricts one's interest to the overall rates of chemical reactions, one requires a knowledge of the family of intermediates sampled by reagent collisions of different collision energy, angle, and impact parameters. The variational theory of reaction rates further extends the range of TS of interest, quantum considerations extend the range yet further,

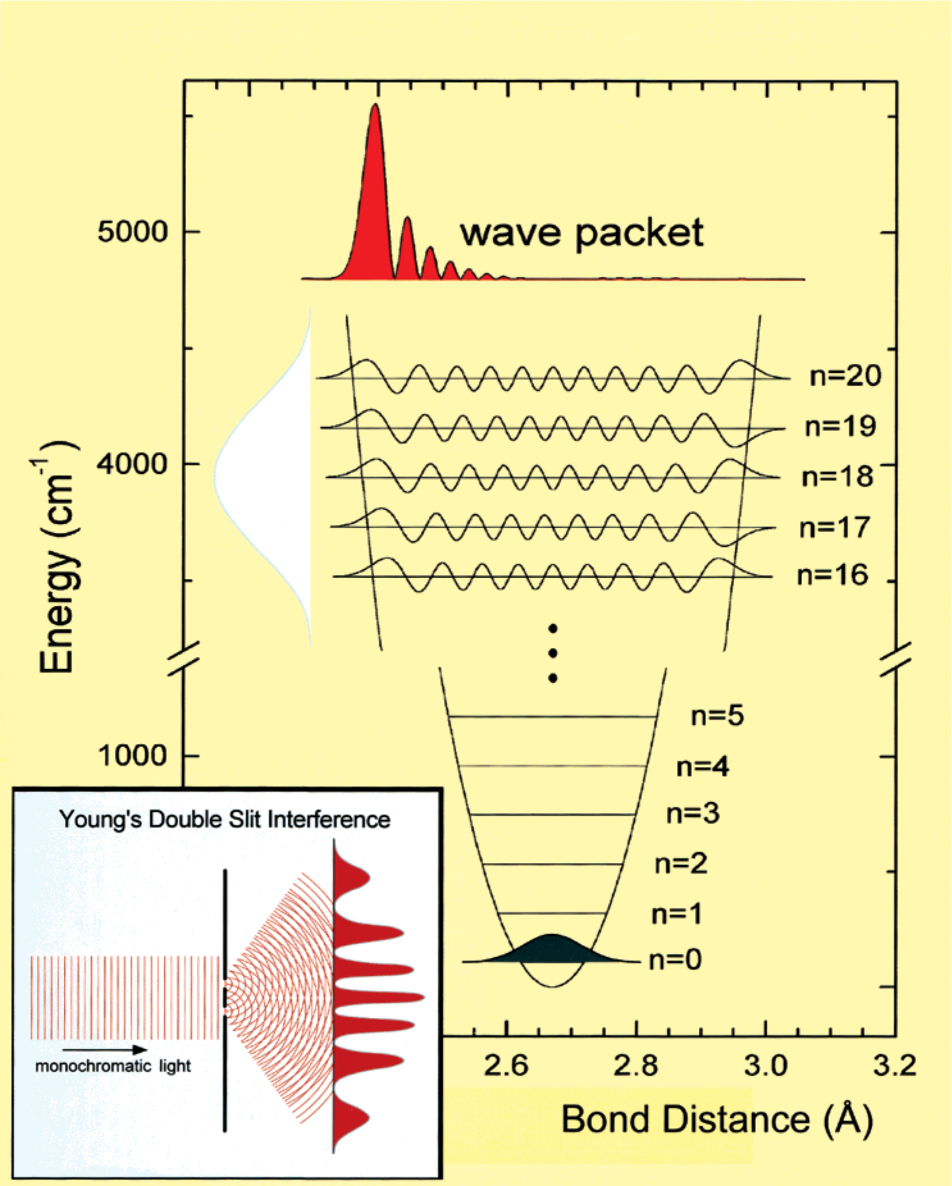


Figure 3. Coherent, localized wave packet (de Broglie length ~0.04 Å) calculated for a diatomic molecule (iodine) for a 20 fs pulse. The contrast with the diffuse wave function limit (quantum number *n*) is clear. The inset shows Thomas Young's experiment (1801) with the interference which is useful for analogy with light. Reference 39.

and the concern with rates to yield products in specified quantum states and angles extends the requirements most of all. A definition of the TS that embraces the entire process of bond breaking and bond making is therefore likely to prove the most enduring; the saddle point may be referred to as the transition structure or activated complex. This point is especially important as we address the energy landscape of complex reactions, as discussed below.

Various techniques have been advanced to probe transition states more directly, especially for elementary reactions. Polanyi's analogy[7] of transition-state spectroscopy, from "spectral wing emission", to (Lorentz) collisional line broadening studies, made earlier by A. Gallagher and others (see ref 6), set the stage for the use of CW spectroscopic methods as a probe. (In this way, only about one part in a million of the population is available for detection.) Emission, absorption, scattering, and electron photodetachment are some of the novel methods presented for such time-integrated spectroscopies. The groups of Jim Kinsey, Philip Brooks and Bob Curl, Benoit Soep and Curt Wittig, Dan Neumark, and others, have made important contributions to this area of research. The key idea was to obtain, as Kinsey[8] puts it, *short-time dynamics from long-time experiments.* The time-domain dynamics from CW spectroscopy, pioneered by Rick Heller, can describe such transformation and will be highlighted in sections III4 and III6.[9] Recently, this subject has been reviewed by Polanyi and the author and details of these contributions are given therein,[6] and also in ref 5.

(2) Arrow of Time: A Century of Development. In over a century of development, time resolution in chemistry and biology has witnessed major strides, which are highlighted in Figure 4.[10] As mentioned above, the Arrhenius equation (1889) for the speed of a chemical reaction gave information about the time scale of rates, and the Eyring and Michael Polanyi's (1931) microscopic theoretical description made chemists think of the atomic motions through the transition state and on the vibrational time scale. But the focus naturally had to be on what could be measured in those days, namely the slow rates of reactions. Systematic studies of reaction velocities were hardly undertaken before the middle of the 19th century; in 1850 Ludwig Wilhelmy reported the first quantitative rate measure-

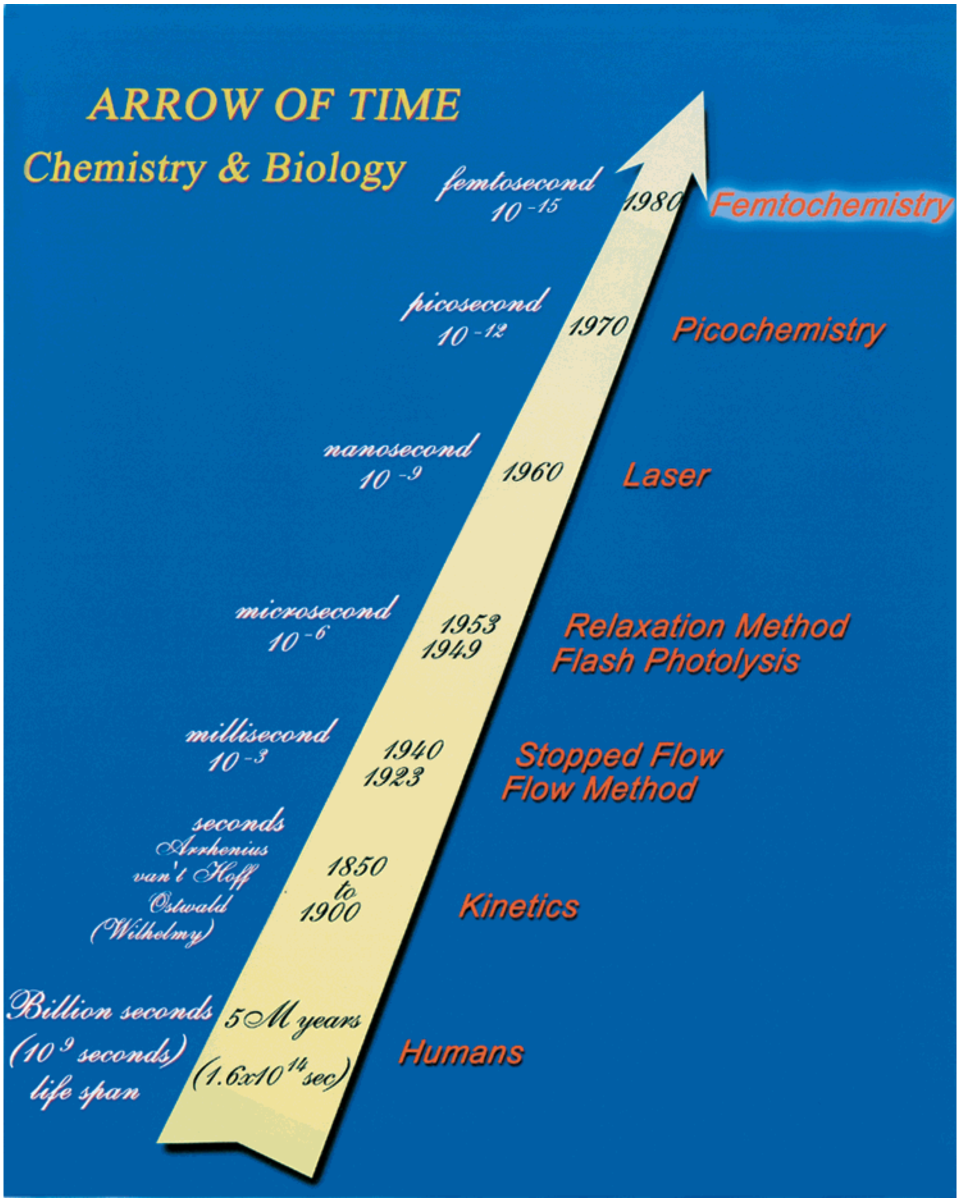


Figure 4. Arrow of time in chemistry and biology, some steps over a century of development.

ment, the hydrolysis of a solution of sucrose to glucose and fructose.[11] In 1901, the first Nobel Prize for chemistry was awarded to van't Hoff for, among other contributions, the theoretical expressions (chemical dynamics) that were precursors to the important work of Arrhenius on rates. Arrhenius too received the Prize in 1903 for his work on electrolytic theory of dissociation.

A major advance in experiments involving subsecond time resolution was made with flow tubes in 1923 by H. Hartridge and F. J. W. Roughton for solution reactions. Two reactants were mixed in a flow tube, and the reaction products were observed at different distances. Knowing the speed of the flow, one could translate this into time, on a scale of tens of milliseconds. Such measurements of nonradiative processes were a real advance in view of the fact that they were probing the "invisible", in contrast with radiative glows seen by the naked eye and measured using phosphoroscopes. Then came the stopped-flow method (B. Chance, 1940) that reached the millisecond scale. The stopped-flow method is still used today in biological kinetics.

Around 1950, a stride forward for time resolution in chemistry came about when Manfred Eigen in Germany and R. G. W. Norrish and George Porter in England developed techniques reaching the microsecond time scale.[12] For this contribution, Eigen and Norrish and Porter shared the 1967 Nobel Prize. The method of flash photolysis was developed by Norrish and Porter a few years after World War II, using electronics developed at the time. They produced an intense burst of light and created radicals in the sample, and, using other light, they recorded the spectra of these radicals. They achieved kinetics on this time scale and observed some relatively stable intermediates.

Before the turn of the 20th century, it was known that electrical sparks and Kerr cell shutters could have response times as short as 10 ns. In an ingenious experiment, Abraham and Lemoine (1899)[13] in France demonstrated that the Kerr response of carbon disulfide was faster than 10 ns; it has now been measured to be about 2 ps (with femtosecond response). They used an electrical pulse that produced a spark and simultaneously activated a Kerr shutter. Light from the spark was collimated through a variable-delay path and through the Kerr cell (polarizer, CS_2 cell, and analyzer). The rotation of the analyzer indicated the presence of birefringence in the cell for short optical delays; this birefringence disappeared for path lengths greater than several meters, reflecting the total optical/electrical response time of 2.5 ns. They demonstrated in 1899 the importance of synchronization in a pump−probe configuration. The setting of time delays was achieved by varying the light path. Bloembergen has recently given a historical perspective of short-pulse generation.[14] Flash photolysis utilized the above approach,[14] but one of the flashes was made very strong to generate high concentrations of free radicals and hence their utility in chemical and spectroscopic applications.

Eigen developed "the relaxation method", which reached the microsecond and close to the nanosecond scale. By disturbing the equilibrium of a solution by either a heat jump, a pressure jump, or an electric field, the system shifts from equilibrium. This is the point of time zero. Then the system equilibrates, and its kinetics can be followed. (At about the same time, shock-tube methods were used to provide kinetics on similar time scales.) Eigen called these reactions "immeasurably fast" in his Nobel lecture. There was a feeling that this time resolution was the fastest that could be measured or that needed to be measured for relevance to chemistry (section IV). The invention of the laser has changed the picture.

Shortly after the realization of the first (ruby) laser by Maiman (1960), the generation of giant and short pulses became possible: nanoseconds by Q-switching (Hellwarth, 1961) and picoseconds (De Maria et al., 1966) by mode-locking (1964). Subpicosecond pulses from dye lasers (Schäfer and Sorokin, 1966) were obtained in 1974 by Chuck Shank and Eric Ippen at Bell Labs, and in 1987 a 6 fs pulse was achieved.[15] In 1991, with the generation of femtosecond pulses from solid-state Ti-sapphire lasers by Sibbett and colleagues,[15] dye lasers were rapidly replaced and femtosecond pulse generation became a standard laboratory tool; the state-of-the-art,[15] once 8 fs, is currently ∼4 fs and made it into the Guinness Book of World Records (Douwe Wiersma's group[15]). The tunability is mastered using continuum generation (Alfano and Shapiro) and optical parametric amplification.[15]

In the late sixties and in the seventies, picosecond resolution made it possible to study *nonradiative* processes, a major detour from the studies of conventional *radiative* processes to infer the nonradiative ones. As a beginning student, I recall the exciting reports of the photophysical rates of internal conversion and biological studies by Peter Rentzepis;[16] the first picosecond study of chemical reactions (and orientational relaxations) in solutions by Ken Eisensthal;[17] the direct measurement of the rates of intersystem crossing by Robin Hochstrasser;[18] and the novel approach for measurement of picosecond vibrational relaxations (in the ground state of molecules) in liquids by Wolfgang Kaiser and colleagues.[19] The groups of Shank and Ippen have made important contributions to the development of dye lasers and their applications in the picosecond and into the femtosecond regime.[15] Other studies of chemical and biological nonradiative processes followed on the picosecond time scale, the scale coined by G. N. Lewis as the "jiffy"—the time needed for a photon to travel 1 cm, or 33 ps.[20]

At about the same time in the sixties, molecular-beam studies of reactions were being developed, and although I was not initially a member of this community, beams later became part of our effort in femtochemistry. Molecular collisions occur on a shorter time scale than a picosecond, and real time studies were not possible at the time. Crossed molecular beams and chemiluminescence techniques provided new approaches for examining the dynamics of single collisions using the post-attributes of the event, the reaction products. The contributions by Dudley Herschbach, Yuan Lee, and John Polanyi[7,21] were acknowledged by the 1986 Nobel Prize. Crossed molecular beam-laser studies have probed dynamics via careful analyses of product internal energy (vibrational and rotational) distributions and steady-state alignment and orientation of products. The contributions to this area are highlighted in the article by Dick Zare and Dick Bernstein[21] and in the book by Raphy Levine and Bernstein.[2] An overview of femtochemistry (as of 1988) in connection with these other areas is given in a feature article[5] by Zewail and Bernstein.

III. Femtochemistry: Development of the Field

In this section, the development of the field is highlighted, from the early years of studying coherence to the birth of femtochemistry and the explosion of research. On the way, there were conceptual and experimental problems to overcome and many members of our Caltech group have made the successful evolution possible. The review article published in *The Journal of Physical Chemistry* (**1993**, *97*, 12427) names their contributions in the early stages of development. The original publications are given here in the figure captions and in the book chapter in Les Prix Nobel (2000).

(1) The Early Years of Coherence. When I arrived in the U.S. as a graduate student in 1969, nine years after the invention of the first laser, I had no idea of what lasers were about. When appointed to the Caltech faculty as an assistant professor in 1976, I was not thinking or dreaming of femtosecond time resolution. But we had the desire to explore *coherence* as a new concept in dynamics, intra- and intermolecular. This proved to be vital and fruitful. The initial effort was focused on two directions: (i) studies of coherence in disordered solids and (ii) the development of a new laser program for the studies of the phenomena of (optical) coherence.

With the theoretical knowledge acquired in handling coherence effects, which requires expertise with density matrix formalism and its manipulation in geometrical frames, we had a novel idea: we should be able to detect *coherence* on the *incoherent* emission at optical frequencies. Indeed, we were able to observe the photon echo on the spontaneous emission of a molecule using *three* optical pulses. This work was followed by a variety of extensions to studies in gases and solids and also in a homemade (from glass) effusive molecular beam. To generate laser pulses, we used switching methods developed at JILA and IBM. The work at IBM by Dick Brewer's group triggered our interest in using electro-optic switching methods. Our studies of coherence in different systems were summarized in a review I wrote in *Accounts of Chemical Research*, published in 1980, with the title "Optical Molecular Dephasing: Principles of and Probings by Coherent Laser Spectroscopy".

From these studies of optical transients, we learned that molecular coherence can be probed directly in real time in gases (and solids) and that incoherent decay (e.g., fluorescence) can be used to monitor such coherences provided that the laser pulse(s) is(are) capable of forming a superposition of states. For two stationary states of a transition (say ψ_a and ψ_b), the coherent superposition of states can be written as

$$\Psi_{\text{coherent}}(t) = a(t)\psi_a + b(t)\psi_b \tag{4}$$

where the coefficients, $a(t)$ and $b(t)$, contain in them the familiar quantum-mechanical phase factors, $\exp(-iE_a t/\hbar)$ and $\exp(-iE_b t/\hbar)$, respectively. With pulse sequences, we could

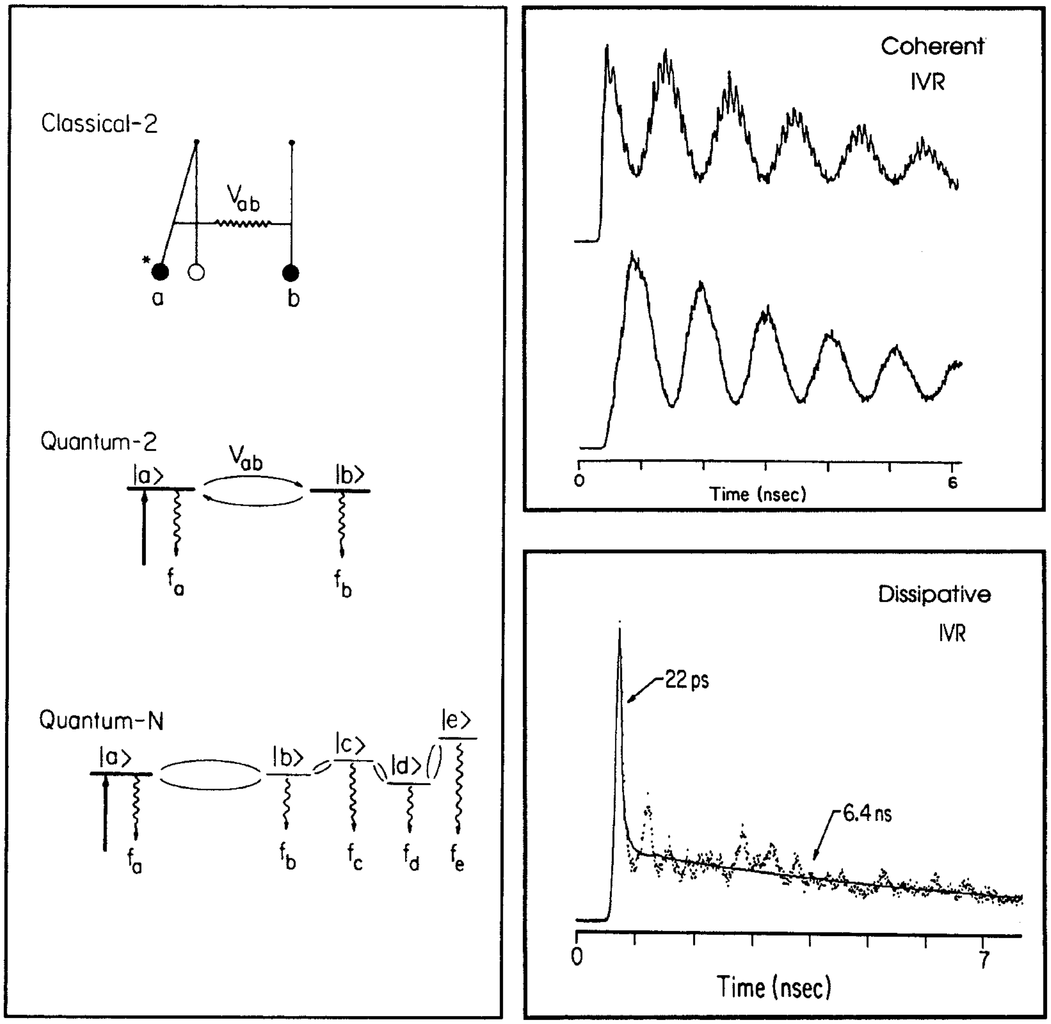


Figure 5. Dynamics of IVR, intramolecular vibrational-energy redistribution. The coherent, restricted, and dissipative regimes. Note the exact *in-phase* and *out-of-phase* oscillatory behavior between the vibrational states of the system (anthracene in a molecular beam). The theory for classical and quantum pictures (to the left) has been discussed in detail in the references given. Reference 40.

monitor the behavior of the ensemble-averaged coefficients of $\Psi \cdot \Psi^*$, $\langle a(t)\ b^*(t) \rangle$, which contain information on the coherence decay time (optical T_2); they are the off-diagonal elements of a density matrix, ρ_{ab}. The term $\langle a(t)\ a^*(t) \rangle$ is the population of state ψ_a and represents the diagonal density-matrix element, ρ_{aa}; $\langle a(t)\ a^*(t) \rangle$ decays with optical T_1.

One feature of this work that later helped us in the study of molecular reaction dynamics was the realization of the importance of the *pulse phase (shape)* in studies of coherence. With the acousto-optic modulation techniques we developed earlier, it became possible to make optical pulse sequences with well-defined phases. This development took us into the domain of selective and prescribed pulse sequences that could then be used to enhance coherences or suppress them—*the optical analogue of NMR multiple pulse spectroscopy*. We published several papers on phase control (section III6) and extended the applications to include photon locking. We were eager to extend these techniques to the picosecond time domain in order to study solids, but for several reasons, our attention was diverted to gas-phase molecular dynamics.

(2) The Marriage with Molecular Beams. Stimulated by the work on coherence, and now with the availability of picosecond pulses, we thought of an interesting problem relating to the question of intramolecular vs intermolecular dephasing. In large, isolated molecules (as opposed to diatomics), there are the so-called heat bath modes that can be a sink for the energy. The question arose: Could these bath modes in *isolated* large molecules dephase the optically excited initial state in the same way that phonons of a crystal (or collisions in gases) do? This problem has some roots in the question of state preparation in radiationless transitions (see below). Moreover, part of the total dephasing rate is due to intramolecular vibrational-energy redistribution (IVR), and at the time, IVR was deduced from spectral broadenings (Rick Smalley and colleagues) or collisional timing (Charlie Parmenter). We decided on a new direction for the studies of coherence (T_1 and T_2) in a supersonic molecular beam.

Our goal in the beginning was to directly measure the rate of IVR, expecting to see a decrease with time (exponential decay) in the population of the initially excited vibrational state and to possibly see a rise in population in the state after the redistribution, thus obtaining T_1 directly. What we saw in the large system (anthracene) was contrary to the popular wisdom and unexpected. The population during IVR was oscillating coherently back and forth (Figure 5) with well-defined period(s) and phases! We were very excited because the results revealed the significance of coherence at its best in a complex molecular system (with many degrees of freedom), now *isolated* in a molecular beam. I knew this would receive attention and skepticism. We had to be extra cautious in our experimental tests of the observation, since earlier observations by another group of such a “quantum coherence effect” in large molecules turned out to be due to an artifact. We published a Communication in *The Journal of Chemical Physics* (1981). Some scientists in the field were skeptical of our new observation, and theorists argued that the molecule is too big to see such quantum coherence effects among the *vibrational* states. Furthermore, it was argued that rotational effects should wash out such an observation. Looking back, this novel and unexpected observation was a *paradigm shift* of critical importance, for a number of reasons.

First, the observation was the first to clearly demonstrate the presence of "quantum coherence effect" in an isolated complex system and only among selected vibrational states of a single electronic potential. *Second*, the observation indicated that coherence had not previously been detected in complex systems, not because of its absence but due to the inability to devise a selective probe, the correlation of time and frequency. *Third*, observation of phase coherent dynamics gave us a new dimension. The phase shift indicates a true transfer of population, in contrast with conventional quantum beats, and by analyzing the phases we could understand the nature of IVR: *"concerted"*, i.e., going at the same time to all states, or *"nonconcerted"*, i.e., going in a sequential redistribution of vibrational energy. *Fourth*, the observation illustrated the importance of the preparation of nonstationary states in molecules.

Some concepts regarding the nature of IVR and its regions were advanced. We divided the regions of IVR into three basic ones: *no IVR*, *restricted IVR*, and *dissipative IVR*. We also showed that the IVR picture of one vibrational state coupled to a continuum of vibrational levels is not adequate. Instead, it is a multitier coupling among vibrational states. These studies, theory and experiment, were published in two series of papers and reviewed in two book chapters. The laboratory known as 036 was in the sub-basement of Noyes, and in this laboratory, the initial work on IVR was followed by fruitful applications spanning (i) studies of IVR in other systems, (ii) radiationless transitions, and (iii) energy-selective reaction rates of a variety of processes, including isomerization, proton and electron transfer, and solvation.

The success with the anthracene experiment made us ask a similar question, but now regarding the coherent *rotational motion* of isolated, complex molecules. There were some theories that discarded its possibility because of the belief that Coriolis interactions, anharmonicity, and other interactions would destroy the coherence. We treated the problem theoretically, and the results suggested possibly another surprise: If we could align the molecules with a *polarized* picosecond pulse and probe (polarization-selective) the rotating molecules, we should be able to observe rotational recurrences that would give the full period of rotations of the isolated (large) molecule. Classically, it is as if the molecule rotated back to its initial configuration. This rotation period gives the moment of inertia and, since the masses of the atoms are known, we can deduce distances, and hence obtain information on molecular structures of very large molecules.

Indeed, the recurrences in stilbene were observed with high precision, and its molecular structure was deduced. Coherence in rotational motion was clearly evident and could be probed in a manner similar to what we had done with vibrational coherence. Initially, there was a question regarding the generality of the approach as a molecular structure technique. However, it is now accepted as a powerful Doppler-free technique; more than 120 structures have been studied this way. The method is termed "Rotational Coherence Spectroscopy (RCS)" and is used in other laboratories. Some book chapters and review articles have been published on the subject.

Out of this first marriage between ultrafast lasers and molecular beams came the developments and concepts discussed above. We were now poised to study molecules and reactions with even shorter time resolution. We could study their vibrational and rotational dynamics and align ("orient") them by controlling time.

(3) The Transition to the Subpicosecond Regime. For this time regime, we decided to build a second generation beam apparatus to house a time-of-flight mass spectrometer. The same beam machine was equipped with optics for laser-induced fluorescence detection. The new beam machine was integrated with two independently tunable dye lasers. We had to be concerned with density, clocking, and the temporal resolution. For example, the two picosecond (and later femtosecond) pulses should be propagated in the *same* direction; otherwise we would lose the ultrashort time resolution! In this same laboratory, we studied with a resolution of a few picoseconds: (1) dissociation reactions; (2) ground-state, overtone-initiated reactions; (3) van der Waals reactions and others. We wrote a series of papers on *state-to-state microcanonical rates*, $k(E)$, and addressed the theoretical consequences and deviations from the statistical regime.

It was in two of these systems (reactions of NCNO and ketene) that we found that the statistical phase-space theory, although successful in describing product-state distributions, failed in describing the microcanonical rates $k(E)$ as a function of energy. Moreover, we made careful studies of the effect of rotational population on $k(E)$, and the effect was dramatic near the threshold. Rudy Marcus, stimulated by these studies of $k(E)$, applied variational RRKM theory, and we published some papers in a collaborative effort. The key point here is that the TS "moves" to different (shorter) distances along the reaction coordinate at different energies; the cardinal definition is relaxed (see above, section II). In another system (H_2O_2), we studied the *ground-state* ("thermal") reaction for the first time in real time by initiating the reaction with direct excitation of the overtones of the OH stretch ($v = 5, 6$) vibration. The coupling between theory and experiment stimulated my interest in the nature of transition states that generally live for less than a picosecond. The thirst for even shorter time resolution became real!

In the early 1980s, the technology of pulse compression, a fiber optic arrangement to reduce the laser pulse width to subpicosecond, became available and we incorporated one into our laser system. The experiment was intended to *directly* monitor the elementary bond breakage in a molecule. The triatomic molecule ICN was chosen because the CN radical could be conveniently monitored by laser-induced fluorescence; we had been encouraged by the positive experience we had had with CN from NCNO and with earlier picosecond results on ICN. Also, ICN had been central to studies of dissociation reactions and to photofragment spectroscopy. Previous work, without time resolution, had provided a measurement of the so-called anisotropy parameter β and, hence, inference of the time scale.

All that we needed was a factor of 10−100 improvement in time resolution from what we currently had in the group. We used pulses of ∼400 fs and observed the first ICN *subpicosecond* transient, thus establishing the new methodology. In the same year, we wrote a paper that was accepted and published (December 1985) in *The Journal of Physical Chemistry*. We did not resolve the transition states of this reaction, but only detected the rise of the product. The last paragraph in this paper summarized what it would be possible to do if the time resolution could be improved by a further order of magnitude: *"Since the recoil velocity is* $\sim 2 \times 10^5$ *cm/s, the fragment separation is* $\sim$*10 Å on the time scale of the experiment (*$\sim$*500 fs). With this time resolution, we must, therefore, consider the proximity of fragments at the time of probing, i.e., the evolution of the transition state to final products."* I wrote this sentence having in mind that the femtosecond resolution is the ideal one and that our next step in research should be in this direction.

(4) The Femtosecond Dream. To achieve the femtosecond time resolution, we needed a new laser system. A piece of good fortune came our way at a time when funding was limited and when the marriage of femtosecond lasers and molecular beam technologies required a "quantum jump" in support. After my lecture at a workshop in Rochester (October 1985) on intramolecular vibrational redistribution and quantum chaos, two program directors from the Air Force Office of Scientific Research requested a preliminary proposal immediately. I sent one in October, followed by a complete proposal in January of 1986, and it was funded in the same year. We focused again on the ICN reaction, but this time on the femtosecond time scale in FEMTOLAND I.

(A) Dynamics of Bond Breakage. The goal of the ICN experiment was to resolve in time the transition-state configurations en route to dissociation:

$$\mathrm{ICN}^* \rightarrow \mathrm{I}\cdots\mathrm{CN}^{*\ddagger} \rightarrow \mathrm{I} + \mathrm{CN} \tag{5}$$

Not only did we wish to monitor the final CN, free of the force field of iodine (which we did in 1985), but also the transitory species $\mathrm{I}\cdots\mathrm{CN}^{*\ddagger}$ (Figure 6). Numerous control experiments had to be done. We submitted our first communication to *The Journal of Chemical Physics* (received June 3, 1987), and it was accepted on June 15, 1987. The referee of this paper was not only prompt, but also, in retrospect, visionary. His report was ultrashort: *"It (the manuscript) has the smell that the authors are onto some very exciting new stuff.... This manuscript meets all requirements for a communication. It may turn out to be a classic. Publish with all dispatch."*

Our thinking about the process of bond breakage was intuitive and relied on classical concepts. The basic observations made (Figure 6) in the ICN experiment could be related to the femtosecond nuclear dynamics; the delayed appearance of the CN (on-resonance) and the rise and decay of transition configurations (off-resonance) was understood using simple classical mechanics and even a helpful kinetic picture of A → B → C, describing the "elementary" steps of the reaction. Two papers (I and II of a series), published in *The Journal of Chemical Physics*, outlined the methodology of "femtosecond transition-state spectroscopy (FTS)" with applications to the ICN dissociation reaction. From these first experiments, we expressed the change in internuclear separation with time, i.e., the reaction trajectory, and the time of bond breakage:

$$\tau = \int_{R_0}^{R} \frac{\mathrm{d}R'}{v(R')} \qquad \tau^{\ddagger} = \frac{\Delta V(R^{\ddagger})}{v(R^{\ddagger})|F(R^{\ddagger})|} \tag{6}$$

For a given potential of interaction V, the velocity is v and the force is $F = -\partial V/\partial R$.

We obtained the time of the motion to final products (τ) and during the transition state ($\tau^{\ddagger}$), as well as the distance of separation $R(t)$. Thus, for a given total energy E, we expressed the distance of separation between I and CN and the time of bond breakage and compared these with experimental results, hitherto unmeasured directly. Significantly, we were able, for the first time, to observe the passage through the transition state, potential energy window $\Delta V(R^{\ddagger})$, and measure its "lifetime" or transit time $\tau^{\ddagger}$ with femtosecond resolution. This experiment on the dynamics of bond breaking and another one on the dynamics of bond making ($\mathrm{H} + \mathrm{CO_2} \rightarrow \mathrm{OH} + \mathrm{CO}$) events were generally well received by colleagues in the scientific community worldwide, and we felt the excitement!

The quantum picture was intuitive too. On the basis of the experience outlined above, we could understand that coherent preparation can lead to nonstationary states that evolve with time (motion!) (section II). Extension to chemical reaction dynamics gives the following nonstationary wave packet:

$$\Psi(R,t) = \sum_i c_i \psi_i(R) \exp(-iE_i t/\hbar) \tag{7}$$

which evolves in time, similar to the two-level problem (eq 4), but now with spatial R localization because of the sum over many energy states. This principle of superposition holds because of the linearity of the time-dependent Schrödinger equation. The phases in eq 7 give rise to the interferences (quantum coherence) (Figure 3) and their fluctuations, due to intrinsic anharmonicities or interactions with the environment, lead to the delocalization. Since the packet can be synthesized easily when the sum criterion is satisfied, the femtosecond pulse becomes the ideal initiator of the motion of nuclei in a reaction.

The concept of describing quantum systems using wave packets is fundamental and goes back to the 1920s when the connection between quantum mechanics and classical phenomena was the subject of discussion and correspondence among many notable scientists such as Schrödinger, Lorentz, and others;[22] sections III4H and III6B highlight theoretical developments since then. The ICN results demonstrated the experimental observation of wave packets in molecular systems, and since then they have been synthesized in atoms, complex molecules, and biological systems, as well as in the different phases of gases, liquids, clusters, and solids. The behavior observed in ICN was found in other studies; the most recent is an elegant series of experiments of "bubbles in solids" by Majed Chergui's group in Lausanne.

The question then was, would quantum calculations reproduce the experimental results obtained for ICN? Dan Imre, being skeptical in the beginning, did the first of such calculations, and the results were important in showing the influence of the wave packet motion and spreading on the observed FTS transients. Horia Metiu addressed the role of rotations. We compared the quantum results with those obtained from the classical model of Bersohn and Zewail (Figure 6 and section III4H). The model described the experimental trends quite well, just as did the quantum calculation. This was followed by reports of trajectory calculations from Kent Wilson's group and a density-matrix description from Shaul Mukamel's group. The latter emphasized the different limits of dephasing and the time scale for nuclear motion. All theoretical results exhibited the general trends observed experimentally. In our early papers on ICN, we suggested that the "δ-function limit" of wave packet dynamics could be obtained if proper deconvolution was made, knowing the temporal response of the pulses. Very recently, Volker Engel and Niels Henriksen reported a quantum theoretical agreement with this simple picture and discussed its generality.

(B) The NaI Discovery: A Paradigm for the Field. There were two issues that needed to be established on firmer bases: the issue of the uncertainty principle and the influence of more complex potentials on the ability of the technique (FTS) to probe reactions. The *alkali halide reactions* were thought of as perfect prototypes because they involve two potentials (covalent and

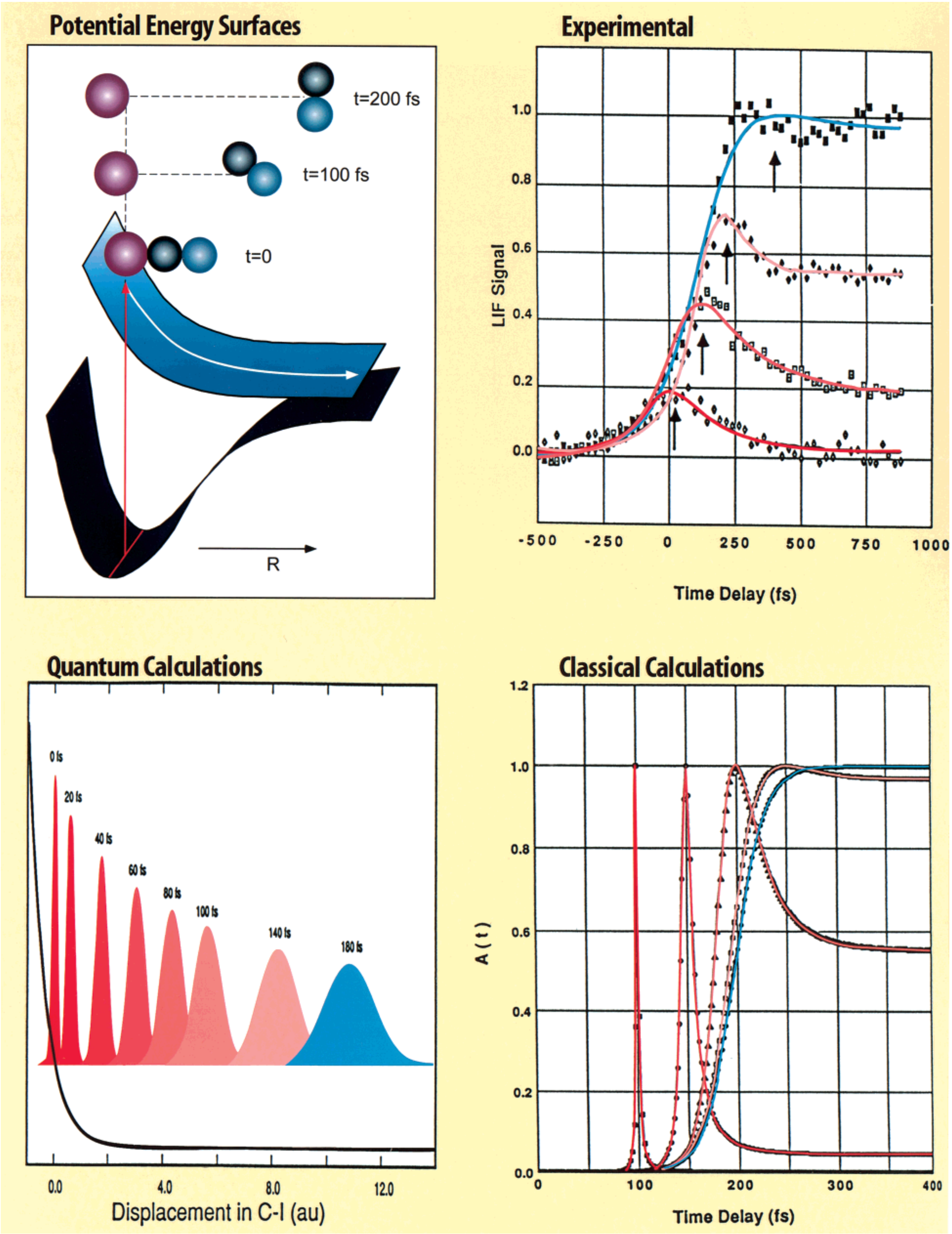
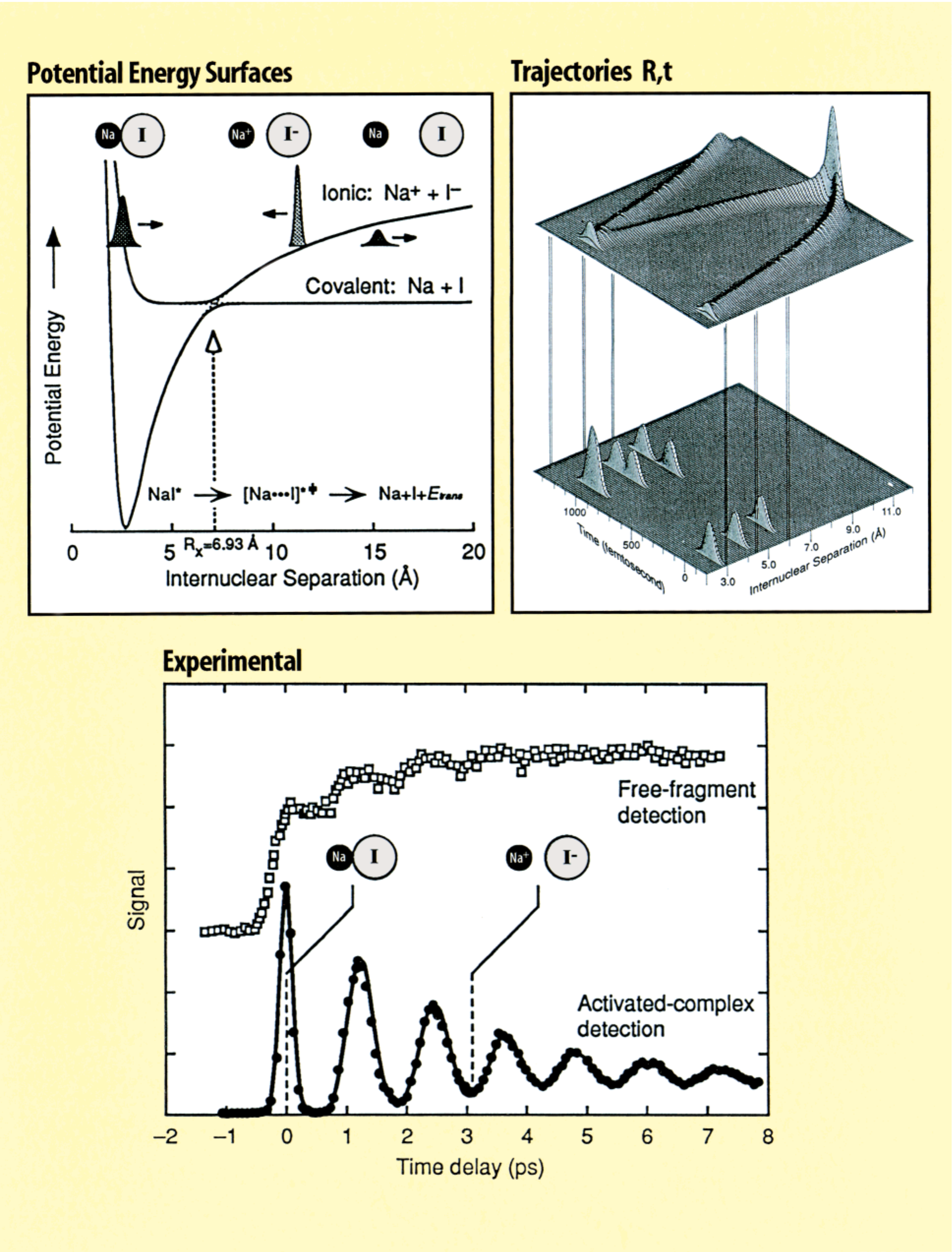


Figure 6. Femtochemistry of the ICN reaction, the first to be studied. The experimental results show the probing of the reaction in the transition-state region (rise and decay) and the final CN fragment (rise and leveling) with precise clocking of the process; the total time is 200 fs. The I fragment was also detected to elucidate the translational energy change with time. Classical and quantum calculations are shown. Reference 41.

ionic) along the reaction coordinate: the separation between Na and I. Moreover, their unique historical position in crossed molecular beam experiments (“The Alkali Age”) made them good candidates for the “femto age”. The resonance motion between covalent and ionic configurations is the key to the dynamics of bond breakage. *How could we probe such motion in real time?* We did the FTS experiments on NaI and NaBr, and the results, published in 1988, were thrilling (Figure 7) and made us feel very confident about the ability of FTS to probe transition states and final fragments. The NaI experiment was a watershed event leading to a new *paradigm* in the field of femtochemistry and establishing some new concepts for the dynamics.


Potential Energy Surfaces

Trajectories R,t

Experimental

Figure 7. Femtochemistry of the NaI reaction, the paradigm case. The experimental results show the resonance motion between the covalent and ionic structures of the bond, and the time scales for the reaction and for the spreading of the wave packet. Two transients are shown for the activated complexes in transition states and for final fragments. Note the “quantized” behavior of the signal, not simply an exponential rise or decay of the ensemble. The classical motion is simulated as trajectories in space and time. Reference 42.

First, we could show experimentally that the wave packet was highly localized in space, ∼0.1 Å, thus establishing the concept of dynamics at *atomic-scale resolution*. *Second*, the spreading of the wave packet was minimal up to a few picoseconds, thus establishing the concept of *single-molecule trajectory*; i.e., the ensemble coherence is *induced* effectively, as if the molecules are glued together, even though we start with a random and noncoherent ensemble—dynamics, *not* kinetics. *Third*, vibrational (rotational) coherence was observed during the entire course of the reaction (detecting products or transition states), thus establishing the concept of *coherent trajectories in reactions*, from reactants to products. *Fourth*, on the femtosecond time scale, the description of the dynamics follows an *intuitive classical picture* (marbles rolling on potential surfaces) since the spreading of the packet is minimal. Thus, a time-evolving profile of the reaction becomes parallel to our thinking of the evolution from reactants, to transition states, and then to products. The emerging picture is physically and chemically appealing.

Finally, the NaI case was the first to demonstrate the *resonance behavior*, in real time, of a bond converting from being covalent to being ionic along the reaction coordinate. From the results, we obtained the key parameters of the dynamics such as the time of bond breakage, the covalent/ionic coupling magnitude, the branching of trajectories, etc. In the 1930s, Linus Pauling's description of this bond was static at equilibrium; now we can describe the dynamics in real time by preparing structures far from equilibrium. I still reflect on the beauty of these NaI experiments and the rich number of concepts they brought to dynamics. Some of the concepts were not as clear when we first made the observations as they are now. The paradigm shift in our thinking is linked and similar in value to the work on IVR (section III2), but the difference is major—for IVR we studied coherence of states, but for reactions we observed coherence of the nuclear motion with atomic resolution.

After the initial set of experiments, we continued on this system for some time, exploring other phenomena of interest. The studies included: (1) direct observation of the reaction trajectory in R and t, and the resolution of the motion *into* and *from* the transition state (this work was first published in *Nature*); (2) direct observation of recurrences (echo-type), reflecting rephasing at long times ($t = 20-40$ ps) (this work was published in *Chemical Physics Letters*); (3) studies of the effect of the velocity of the nuclei on the probability of crossing to products, providing the interaction matrix element for the coupling between the covalent and ionic potentials; and (4) treatment of classical and quantum dynamics (these studies were published in *The Journal of Physical Chemistry* and *The Journal of Chemical Physics*).

Numerous theoretical and experimental papers have been published by colleagues, and the system enjoys a central role in femtodynamics. From the beginning we understood major features of the dynamics from the point of view of classical mechanics. The "exact" quantum calculations were first made by Volker Engel and Horia Metiu, and these were important in identifying the sensitivity of the observations to details of the motion and the potential. The agreement with the experimental results was remarkable. The same agreement was found for later theoretical studies involving classical, quantum, and semiclassical approaches.

(C) The Saddle-Point Transition State. Our next goal was to examine reactions governed by multidimensional (nuclear) potentials, starting with "barrier reactions" that define a saddle-point transition state, the classic case of chemistry textbooks. If the reaction dynamics involve more than one nuclear coordinate, an interesting question arises: *can one observe in real time the reactive evolution from the TS at the saddle point to final products on the global PES?* The question was addressed by performing femtochemistry on ABA systems. Stunning observations were made on the IHgI system—the product HgI was *coherently* formed from the transition state (Figure 8). Also, the transition state, which absorbs a probe femtosecond pulse in the red, as opposed to the HgI product, which absorbs in the UV, was found to leave the initial configuration in only ~200 fs, and this state produces different coherent product states (different periods of vibrational oscillation). It was also in this system that we studied the coherence of rotational motion (real-time alignment) and learned about the geometry of the (initially prepared) transition-state, activated complex $IHgI^{*\ddagger}$.

With simple theoretical PES's and molecular dynamics simulations we examined details of the motion, but the major features were evident in the experimental observations. Originally, we studied the TS and the evolution to HgI products by using laser-induced fluorescence. Later, we used mass spectrometry to also detect the I atoms and the translational energy; this effort triggered a great deal of theoretical work (Figure 8) in our group addressing in depth the actual meaning of classical TS structure, as discussed below. Features of this reaction were later found in other classes of reactions, including those in condensed phases and biological systems.

The studies of this ABA system were published with an emphasis on the following points: *First*, the observation of coherent nuclear motion on *multidimensional surfaces* involving multiple-bond breakage (or formation). *Second*, the survival of coherence in the entire reaction journey, even in multidimensional systems, and the selective *coherence-in-products*. *Third*, the evolution, observed for the first time, for a *saddle-point TS* into two- and three-body fragmentation. *Fourth*, the alignment of the *TS* (zero time) and the evolution into rotations of the diatom (AB) and the translation of the A and AB (or A, B, and A) fragments—the vibrational (scalar) and rotational (vectorial) motions.

(D) The Uncertainty Principle Paradox. At the time, some were raising a question about the "energy resolution" of the femtosecond experiments: *How can a broad-energy pulse probe a sharp resonance*? In the conventional teaching on spectroscopy of "eigenstates", one thinks of stationary states and their populations, but now we must think of coherent states (Figure 3). All information pertinent to eigenstates is in the wave packet structure. This point was elucidated by our experiments on a *bound nonreactive* system—the iodine system (Figure 9). The oscillations directly gave the periods of the nuclear (vibration) motion, and the data could be related to the change with time of the I−I separation and the rotation of I_2; the time scales were separated (femtoseconds vs picoseconds) and the vibrational (scalar) and rotational (vectorial) motions were clearly seen.

We used classical mechanical inversion methods and the RKR and quantum inversion methods to characterize the potential. This was followed by a study of the ICl system. It became evident that (1) *the uncertainty in energy for short pulses works in our favor*, and the femtosecond pulses provide better localization of the wave packet, and (2) we could now observe *the vibrations and rotations of molecules in real time*, not from energy spectra. This work was first published in *Nature* and detailed later in *The Journal of Chemical Physics*. The real message of this I_2 experiment was in its conceptual elucidation of the role of the uncertainty principle and the robustness of time, space, and energy resolutions because of *coherence*: Because $\Delta x \Delta p \sim \hbar$ and $\Delta t \Delta E \sim \hbar$, we can achieve localization with a very small de Broglie wavelength (Figure 3).

(E) Bimolecular Reactions, Bond Making and Breaking. For bimolecular reactions, the problem was that the transit time for reactants to undergo a collision is generally nanoseconds to microseconds. By using van der Waals complexes, an idea introduced for the studies of product-state distributions by Benoit Soep and Curt Wittig, we could expand the reactants, HI and CO_2, in a single molecular beam. But now, with the two reagents

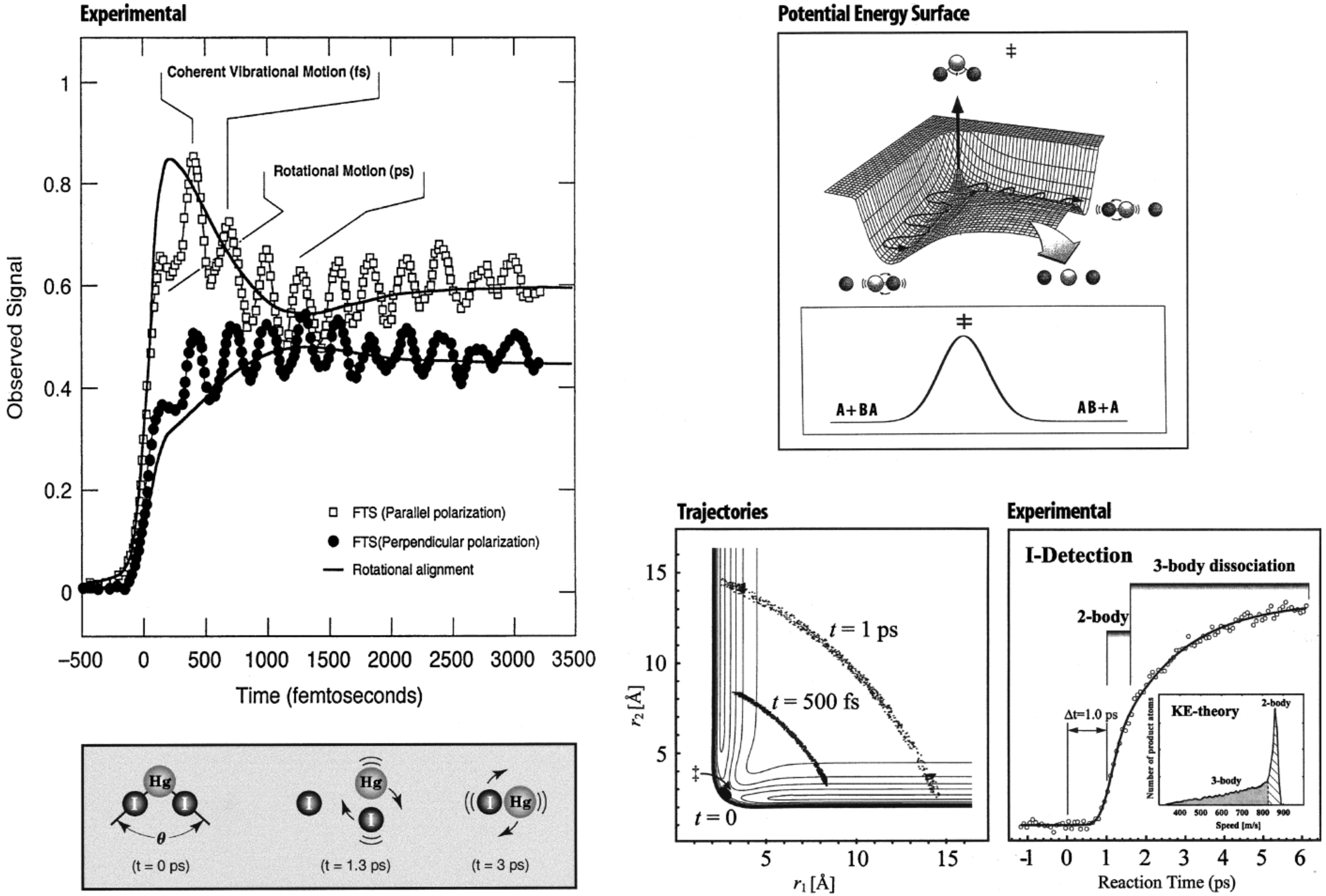


Figure 8. Femtochemistry of the IHgI reaction, the saddle-point transition state (barrier reactions). The experimental results show both the coherent vibrational and rotational motions of the reaction (left). The transition state $IHgI^{*\ddagger}$ and final fragment HgI were probed. We also probed the I fragment and the change of translational energy with time. The classical trajectory calculations are shown (right), together with experimental results for I detection; both theory and experiment illustrate the family of reaction trajectories on the global PES, in time and in kinetic energy distribution. Quantum calculations were also made (not shown). This ABA system is a prototype for saddle-point transition states. Reference 43.

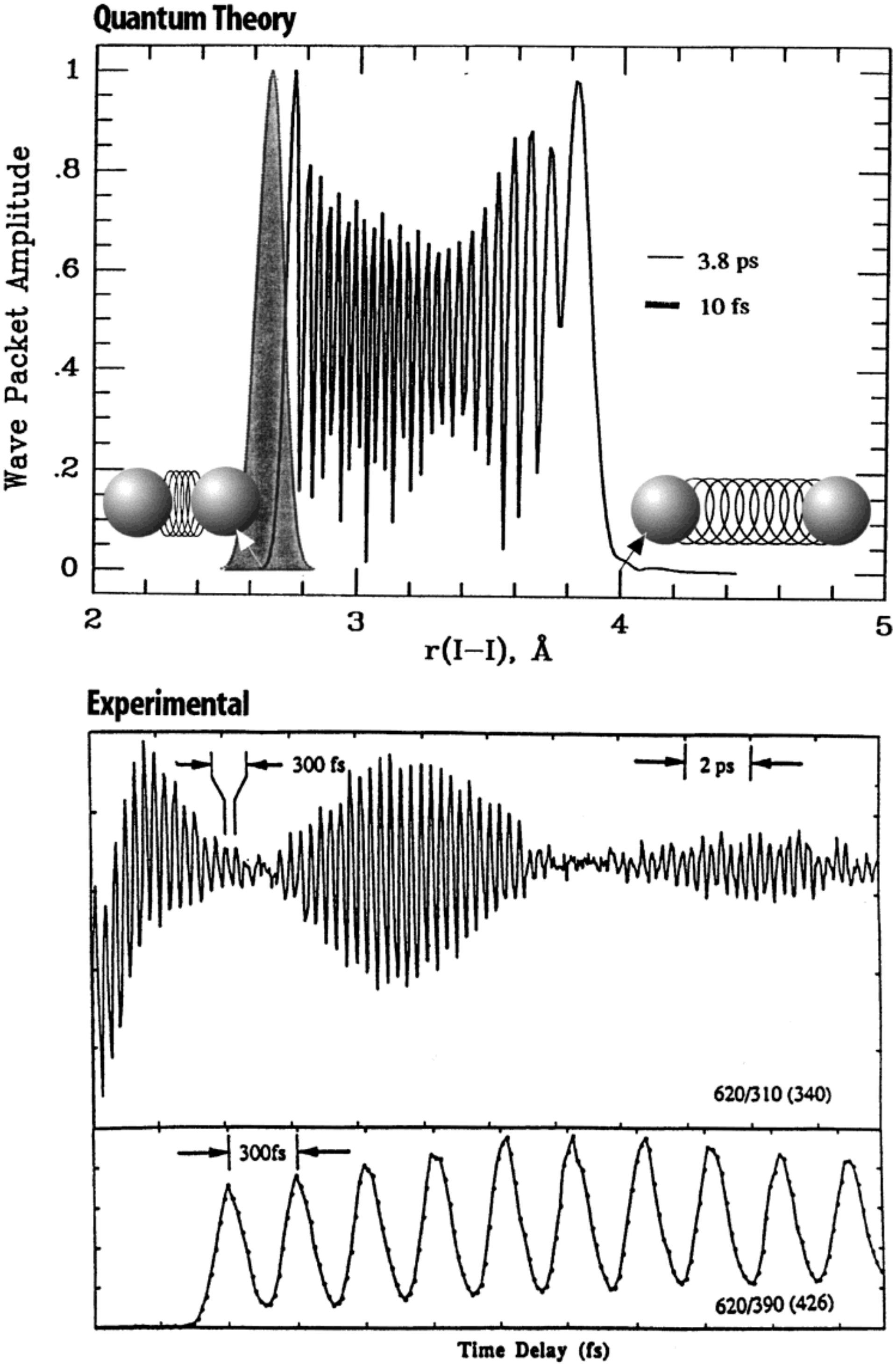


Figure 9. Femtosecond, real time observation of the vibrational (and rotational) motion of iodine. The experiments show the anharmonic nature of the bound motion. Quantum theory indicates the limit for creating a localized wave packet on the femtosecond time scale. The localized wave packet describes the classical spring motion. Reference 44.

within angstroms of each other, we could examine the dynamics of the single collision. We used the first pulse to liberate the H atom with a known translational energy and a second pulse to probe the nascent OH product—the *zero of time* became well-defined and the collision was that of a limited impact parameter. The results were exciting and, in our joint paper, Dick Bernstein termed this the "birth of OH from H + CO_2"—the "simultaneous" processes of bonds being broken and formed. Wittig's group improved the time resolution and studied, among other things, the energy dependence of the rates. Figure 10 gives a summary for this system.

The H + CO_2 *ground-state* reaction proved to be important for a number of reasons. *First,* it showed how *Reactive Scattering Resonances* can be probed in real time during the collision and for a system of a complex number of degrees of freedom. *Second,* the experiments established that the *intermediate* $HOCO^{‡}$ lives for $\tau \sim 1$ ps and that for this reaction the OH bond making and the CO bond breaking are made in a *nonconcerted* pathway. The nuclear motions of HOCO thus determine the reaction mechanism. If τ was found to be 10−100 fs, the picture would have been entirely different; bond making and breaking would occur as a result of the electron

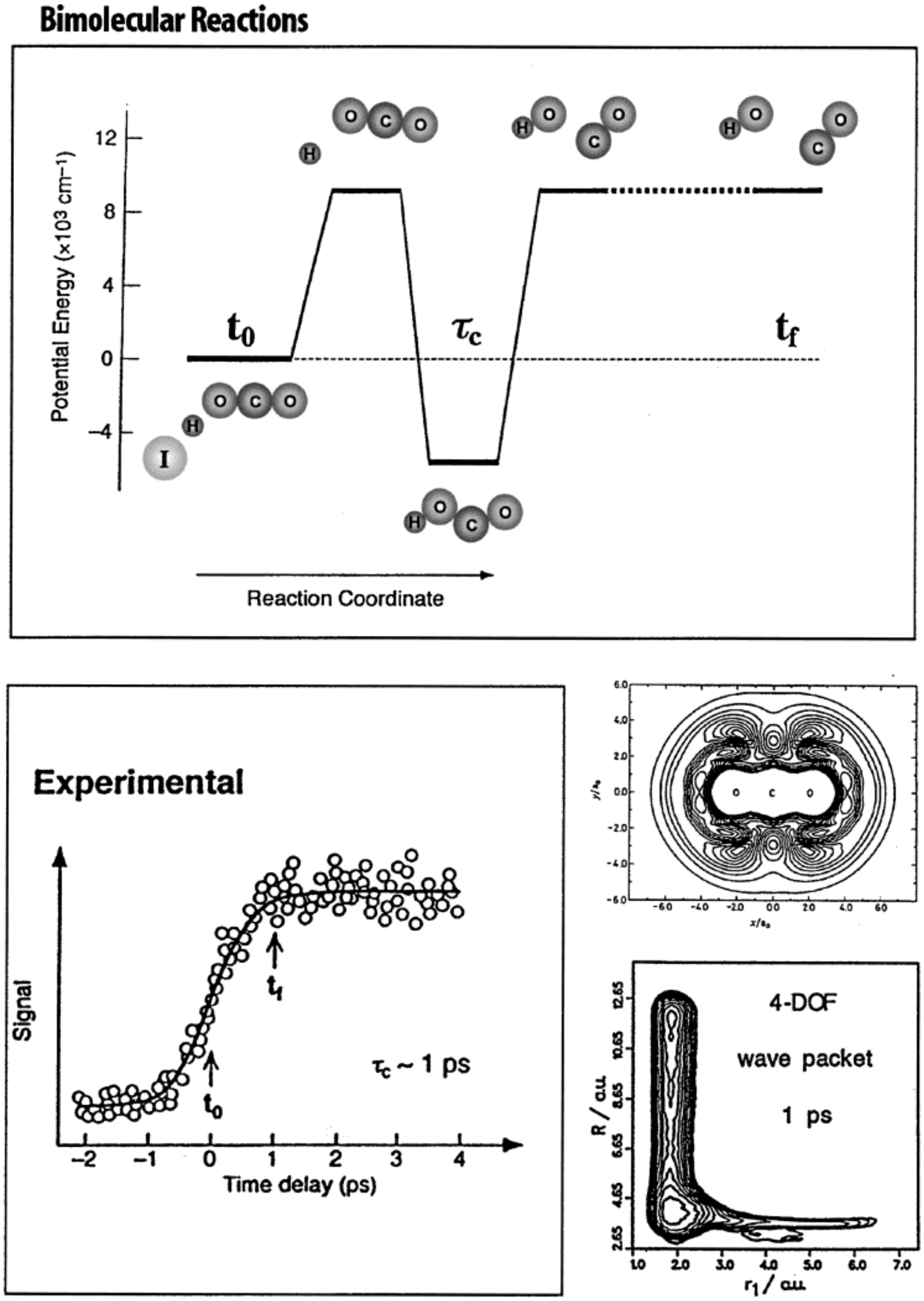


Figure 10. Femtochemistry of the bimolecular H + CO_2 reaction. The precursor in this molecular beam experiment is HI/CO_2 in a van der Waals complex. The initial experiments utilized picosecond pulses, but later subpicosecond pulses were used (see text). Theoretical ab initio calculations of the PES and the dynamics (classical, semiclassical and quantum wave packet) have all been reported (see text). The transit species $HOCO^‡$ lives for ~1 ps. Similar studies were made of reactive Br + I_2, of the inelastic collision between I and CH_3I, and of other bimolecular reactions. Reference 45.

redistribution with the nuclei essentially "frozen" in configuration. Obtaining τ directly is critical for the nature of the *transition state/intermediate*. This is particularly true when τ is much longer than the vibrational and rotational periods, and all other methods will fail in deducing τ. *Third*, direct comparison with *theory* at the ab initio level can be made. High-quality ab initio calculations of the PES and dynamics (Figure 10) were made available by David Clary, George Schatz, John Zhang, and others, and theory compares favorably with experiments showing that vibrations (resonances) of HOCO bottleneck the trajectories. The reaction OH + CO → CO_2 + H is one of the key reactions in both combustion and atmospheric chemistry and represents the most studied four-atom reaction, both theoretically and experimentally (see refs 23 and 24).

We constructed FEMTOLAND II and began to examine other bimolecular reactions. Precursors, of which the H−Br/I−I system is a prototype, were chosen to study bimolecular halogen atom + halogen molecule reactions. When the HBr bond breaks, the hydrogen goes many angstroms away from the field of the reaction (in femtoseconds) and we are left with the Br + I_2 collision. This halogen reaction had a history in crossed molecular beam experiments. We measured the evolution of BrI + I and found it to occur through a sticky (~50 ps) collision complex. It is a stable intermediate of BrII, and there is no other way we know of to determine its lifetime and dynamics. We examined classical trajectories of motion and compared them with the experimental results. In more recent work, Doug McDonald's group obtained similar times and discussed the possibility of the involvement of ground and excited halogen surfaces. In this study of an atom + diatom collision, we learned the effect of impact parameters, the influence of translational energy, and the interplay between bonding and dynamics. Studies of bimolecular collisions in complex systems have continued in our and other laboratories; the most recent came from NIST (John Stephenson and colleagues) on the studies of $CH_4 + O \rightarrow CH_3 + OH$, using $CH_4{\cdot}O_3$ as a precursor, and from our work on bimolecular charge transfer and acid−base reactions (see below).

(F) Ultrafast Electron Diffraction (UED). FEMTOLAND III was the home of our next effort, ultrafast electron diffraction (UED). Our goal was to complement the detection schemes of spectroscopy and mass spectrometry and to use diffraction to follow structural changes, especially for large systems. The idea was suggested in 1991 in a *Faraday Discussion* paper (see bibliography), and we had our first success in 1992. We were able to record structures with an electron pulse duration of a few picoseconds, but with no time scan. This was followed by other studies, on both the theoretical and experimental fronts. In our group, rumor had it that UED was a “NO to the power 10 experiment!” We now have the third generation of UED machines. In a *Nature* paper in 1997, we reported our state-of-the-art experimental development of the methodology. We also developed a “difference-method” that allows us to record the structure of radicals, carbenes, and intermediates, and with higher sensitivity, as discussed below.

(G) Clusters, Dense Fluids and Liquids, and New Femtolands. With the above-mentioned spectroscopy, mass spectrometry, and diffraction techniques, it was becoming possible to study many new systems. In addition to FEMTOLANDS I−III, PICOLANDS I and II were still operational in order to cover the different time scales of reaction dynamics. We are now up to FEMTOLAND VI. Two additional beam machines, equipped with mass spectrometry and spectroscopic detectors, were added. These new FEMTOLANDS were built to accommodate the expanding scope of research, from gas phase to clusters, to liquids and dense fluids, to the world of complex organic and inorganic chemistry, and to the very complex biological systems. Complex reactions are fascinating and we have devoted significant effort to this area, studying both uni- and bimolecular reactions. We also maintain strong theoretical efforts on *molecular structures* and *molecular dynamics* to compare theory with experiment on the relevant time scale.

(H) Theoretical Femtochemistry. Our involvement had roots in the study of coherence and dephasing. This line of research was initiated by using pulsed lasers to form a coherent state (eq 4). The evolution was followed in time to obtain the pure dephasing time (T_2'), which reflects the extent of phase interruptions, and the population or energy decay time (T_1). We invoked theoretical techniques such as density matrix formalism, Kubo relaxation theory, and the Bloch equations to describe the optical analogue of NMR experiments. The 1956 Feynman, Vernon, and Hellwarth paper was an important contribution, as it pointed out the linkage between “spin” and “optical” coherence experiments. All of this was known at the time. Our interest in theory was to relate T_1 and T_2 to molecular processes and to learn about their formal limits of applicability. We wrote a book chapter on the subject and published a number of papers relating these relaxation times to the anharmonicity of molecular vibrations, the phonon structure of solids, and collision dynamics in gases.

For collisionless, large molecules, the issue of intramolecular electronic-states coupling was, by the 1970s, well developed theoretically and heavily imbedded in theories of radiationless transitions formulated to explain the origin of nonradiative decays. Wilse Robinson, Joshua Jortner, Stuart Rice, and others were involved in the early stages of this development. The Bixon−Jortner model gave the description for such inter-electronic-states coupling and the important role of a doorway state that “dephases” and “relaxes” depending on electronic coupling matrix elements, Franck−Condon factors, and the density of states.[25]

For IVR (section III2), we developed a theoretical description for the coherent preparation of a set of vibrational eigenstates on a *single* potential surface, defining the preparation of a nonstationary *vibrational* packet, with the role of rotations and vibrational couplings explicitly expressed. The probability of being in the initial state ψ_0 is

$$P(t) = |\langle\psi_0|\Psi(t)\rangle|^2 = \sum_{i,j}\alpha(i,j)\exp[-(i\omega_{ij} + \Gamma)t] \tag{8}$$

where the sum is over a product of coefficients α and displays the interference of states *i* and *j*, together with their damping rate Γ. This treatment was useful because (1) it gives a direct view of IVR, from the initial nonstationary state and as a function of time, (2) it indicates the critical role of selective probing (if all states were monitored, coherence would be obscured), and (3) it shows that $P(t)$ is a measure of vibrational chaos, defining what we called restricted or nonchaotic IVR. Similarly, we considered the theory for rotational coherence using polarization-analyzed probes with focus on the phenomenon of pure rotational coherence and its utility for molecular structural determination, and for obtaining the rotational dephasing time.

The first femtochemistry experiments elucidated the nature of the coherent packet, with the atomic scale for the de Broglie wavelength. Accordingly, we could invoke a simple classical picture of the motion. The first of such models was published after we considered the theoretical treatment of absorption of fragments *during* reactions. We derived the following expression:

$$A(t;R) = C\{\delta^2 + W^2(t,t^{\ddagger})\}^{-1} \tag{9a}$$

where C is a constant and $W = V(t) - V(t^{\ddagger})$ is the potential (or more generally, the difference of the two potentials probed); δ is a half-width of the pulse (and damping). For exponential repulsion, $V = E\,\mathrm{sech}^2(\upsilon t/2L)$, with L defining the length scale and υ being the speed at the total energy E. The time for bond breakage can thus be related to FTS observables:

$$\tau_{BB} = (L/\upsilon)\ln(4E/\delta) \tag{9b}$$

The model describes the reaction trajectory $R(t)$ or $\tau(R)$ and provides a simple picture of the dynamics: the dissociation time (when V drops to δ), transition-state lifetime, and acting forces (see eq 6 and Figure 6). Rich Bersohn and I wrote a short paper on the subject, and while Dick Bernstein was at Caltech, we extended the model to obtain the potential using an inversion approach. Peter Sorokin and colleagues at IBM have addressed different limits of the classical regime in connection with their original studies of femtosecond transient absorption of dissociation.

Next, we considered the treatment of the effect of alignment and orientation on femtochemical reaction dynamics. The time evolution of alignment and coherence were considered for a single rotational angular momentum and then averaged over the different trajectories to define the coherence time; τ_c (in picoseconds) becomes simple and equal to $2.2[B\langle E_R\rangle]^{-1/2}$, where B is the rotational constant and $\langle E_R\rangle$ is the average thermal rotational energy (cm^{-1}) produced in the reaction fragment(s). We applied this to reactions, and I wrote a paper on the subject, published in 1989. This was followed, in collaboration with Spencer Baskin, by a paper describing details of the approach and its applications.

In quantum treatments, we have benefited greatly from the advances made in theoretical formalism and computation. A major step forward was made when Rick Heller[9] reformulated the time-dependent picture for applications in spectroscopy, and Jim Kinsey and Dan Imre[9] described their novel dynamical Raman experiments in terms of wave packet theory. Progress was significantly helped by advances made in the theoretical execution and speed of computation by Ronnie Kosloff[9] and, subsequently, by many others. In section III6, we discuss the contributions made in the 1980s in connection with quantum control.

As mentioned above, the groups of Imre and Metiu did the first "exact" quantum calculations of femtochemical dynamics (ICN and NaI). The literature is now rich with numerous theoretical studies with applications to experiments. This is summarized in the (1996 Nobel Symposium) book edited by Villy Sundström on *Femtochemistry and Femtobiology*.[24] Jörn Manz, who has played a significant role in this field, gave an overview of developments since Schrödinger's 1926 paper, with 1500 references. Jörn classifies the field into periods of *origins, sleeping beauty, renaissance, and revolution*. In this Nobel Symposium book (and another one[25]) Jortner provides a unifying overview of molecular dynamics in femtochemistry and femtobiology, and Mukamel gives an exposition of a general approach using the density matrix formalism.

For complex systems, our theoretical effort has taken on the following approach. With the help of molecular dynamics (MD) simulations, we compare theory with experiments. Then we use the MD simulations as a tool and vary parameters until we reduce the problem to identify the important key forces of dynamics. At this point, we can provide a microscopic dynamical picture with focus on the relative vibrational coordinates, time scales, or system parameters. Two examples illustrate the point. The first was our study of the dynamics of a guest molecule in dense fluids with focus on the density dependence of microscopic friction, T_1 and T_2, and of bond breaking/remaking dynamics. The second is the study of numerous organic reaction mechanisms. For the latter, we also use advanced computational methods, such as density functional theory (DFT), ab initio, and CASSCF computations. For ground-state reactions, the theory can be compared in a critical way with experiment, while for excited states the situation is more challenging.[26]

(I) Experimental Femtochemistry. The generation, amplification, and characterization of ultrashort pulses are a major part of femtochemistry experiments. Another is the reaction chamber: molecular-beam machine, gas cell, ultrahigh-vacuum (UHV) surface apparatus, or the high-pressure/liquid cell. Here, we mention only the different systems designed for the studies presented in this anthology; further details can be found in refs 10 and 27. At Caltech, over the years, we have constructed different types of lasers depending on the particular development and the resolution needed, picosecond to femtosecond; one apparatus is shown in Figure 1.

Since 1976, our research has involved thirteen laser systems: Passive mode-locked, and cavity-dumped, dye laser; Synchronously pumped, mode-locked dye laser system; Mode-locked argon ion laser; Synchronously pumped, cavity-dumped dye laser; Mode-locked (CW) Nd:YAG laser which synchronously pumps two dye lasers, with two amplifiers; Dye lasers as described in the latter case, but with an extra-cavity pulse compressor (using a fiber-grating optics arrangement) to obtain ∼0.4 ps pulses; Colliding-pulse mode-locked (CPM) ring dye laser, amplified in a four-stage dye amplifier (a compression at the output of the amplifier was also used); Synchronously pumped, cavity-dumped dye lasers (two); Passively mode-locked, dispersion-compensated tunable dye laser (synchronously pumped by a frequency-doubled, CW, mode-locked Nd:YAG laser), amplified in a four-stage dye amplifier. The compression is after the amplifier; CPM laser-amplifier system, used for ultrashort electron pulse generation; Ti:sapphire laser system, argon-ion pumped (Ti:sapphire amplifier pumped by Nd:YAG laser, one OPA system); Ti:sapphire laser system, oscillator, diode pumped and amplifier (Ti:sapphire) Nd:YLF (2) pumped—all solid state, with two optical parametric amplifiers (OPA); Ti:sapphire laser system, same as the latter, but pulse width 120 fs and energy 3 mJ, 1 kHz repetition rate.

For recording and clocking in any study, the resolution must be determined accurately, as must the zero-of-time ($t = 0$). The pulses were characterized using autocorrelation and cross-correlation techniques, typically by scanning the time delay between the two pulses (of the same or different colors) in an interferometer arrangement and observing the sum- or difference-frequency generation in a nonlinear crystal. In this way, we can obtain the duration of the pulse. The central frequency of the pulse can be determined by passing the pulse through a calibrated spectrometer, while the shape of the pulse can be obtained from frequency-resolved-optical-gating (FROG) measurements, where the time and frequency components of the pulse are correlated and displayed as a 2D image. In clocking experiments, the zero-of-time was precisely determined by an in situ measurement, typically using ionization techniques in beam experiments, lensing techniques in diffraction experiments, or the solvent response in condensed phase experiments.

The detection probes are numerous. Initially, we used laser-induced fluorescence, and there we had a *frequency−time correlation*. Later, we invoked mass spectrometry (multiphoton ionization) for *mass−time 2D correlations*. This was followed by *speed−time* and *angle−time correlations.* All these correlations proved important in the studies of complex systems; a prime example was the application of the latter two correlations to the study of charge transfer in isolated bimolecular reactions and in clusters (see below). For absorption-type measurements, we used nonlinear techniques such as degenerate-four-wave mixing. In a recent collaboration with the groups of Wolfgang Kiefer and Arnulf Materny, we also used CARS, with frequency−time correlations to study the dynamics of ground-state systems, in this case polymers. Other advances include Coulomb explosion, energy-resolved and ZEKE photoelectron spectroscopy, ion−electron coincidence ionization techniques, and absorption and photodetachment spectroscopy.[24,28] The range of wavelength is from the IR to the far UV.

(5) Applications—Examples from Caltech. The range of applications to different systems and phases in many laboratories around the world is extensive and beyond the purpose of this

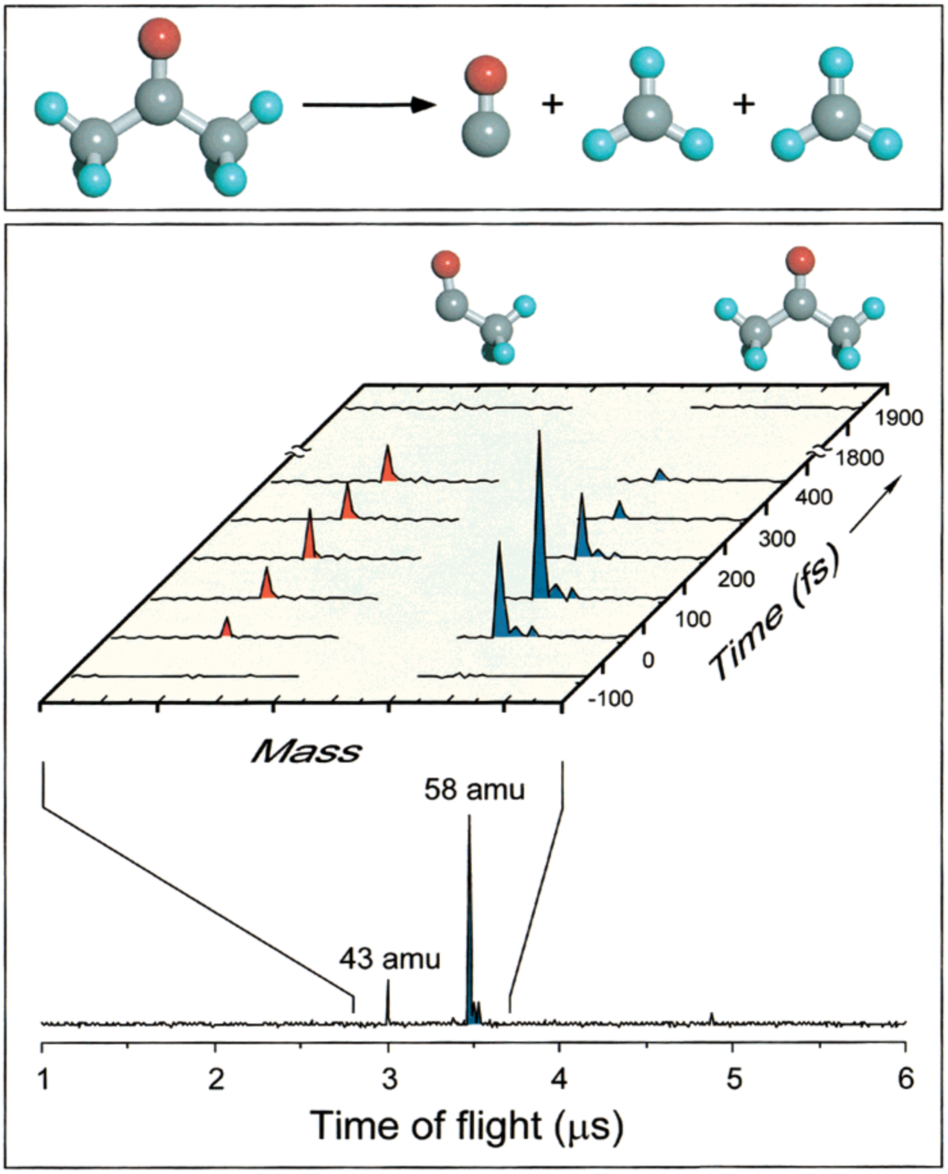


Figure 11. Femtosecond mass spectrometry, a 2D correlation important in the studies of reactive intermediates. The example given here is for the reaction of acetone (Norrish-type I) and its nonconcerted behavior. Reference 46.

report. In this section we limit ourselves to the examples studied by the Caltech group. The details are given in the original publications and are summarized in the reviews and books mentioned here.

(A) Elementary Reactions and Transition States. The focus here was on the studies of elementary reactions. Some of these have already been discussed above. The dynamics are generally of three classes:

(i) dynamics of bond breakage
(ii) dynamics of the (saddle-point) transition state
(iii) dynamics of (bimolecular) bond breakage−bond formation

(B) Organic Chemistry. With the integration of mass spectrometry into femtochemistry experiments, the field of organic reaction mechanisms became open to investigations of *multiple* transition states and reaction intermediates (Figure 11). The technique of femtosecond-resolved kinetic-energy-time-of-flight (KETOF) provided a new dimension to the experiment—correlations of *time*, *speed*, and *orientation* that elucidate the *scalar* and *vectorial* dynamics. The examples of reactions include (Figures 11−14)

(i) isomerization reactions
(ii) pericyclic addition and cleavage reactions
(iii) Diels−Alder/sigmatropic reactions
(iv) Norrish-type I and II reactions
(v) nucleophilic substitution (S_N) reactions
(vi) extrusion reactions
(vii) β-cleavage reactions
(viii) elimination reactions
(ix) valence structure isomerization
(x) reactive intermediates

(C) Electron and Proton Transfer. Here, we examined both bimolecular and intramolecular electron-transfer reactions, and these studies were the first to be made under solvent-free conditions. We also studied the transfer in clusters and in solutions (see Figures 12 and 13). For proton transfer, three classes of reactions were of interest, those of bimolecular and intramolecular reactions, and those involving double proton transfer (base-pair models):

(i) bimolecular electron-transfer reactions
(ii) intramolecular electron transfer and folding reactions

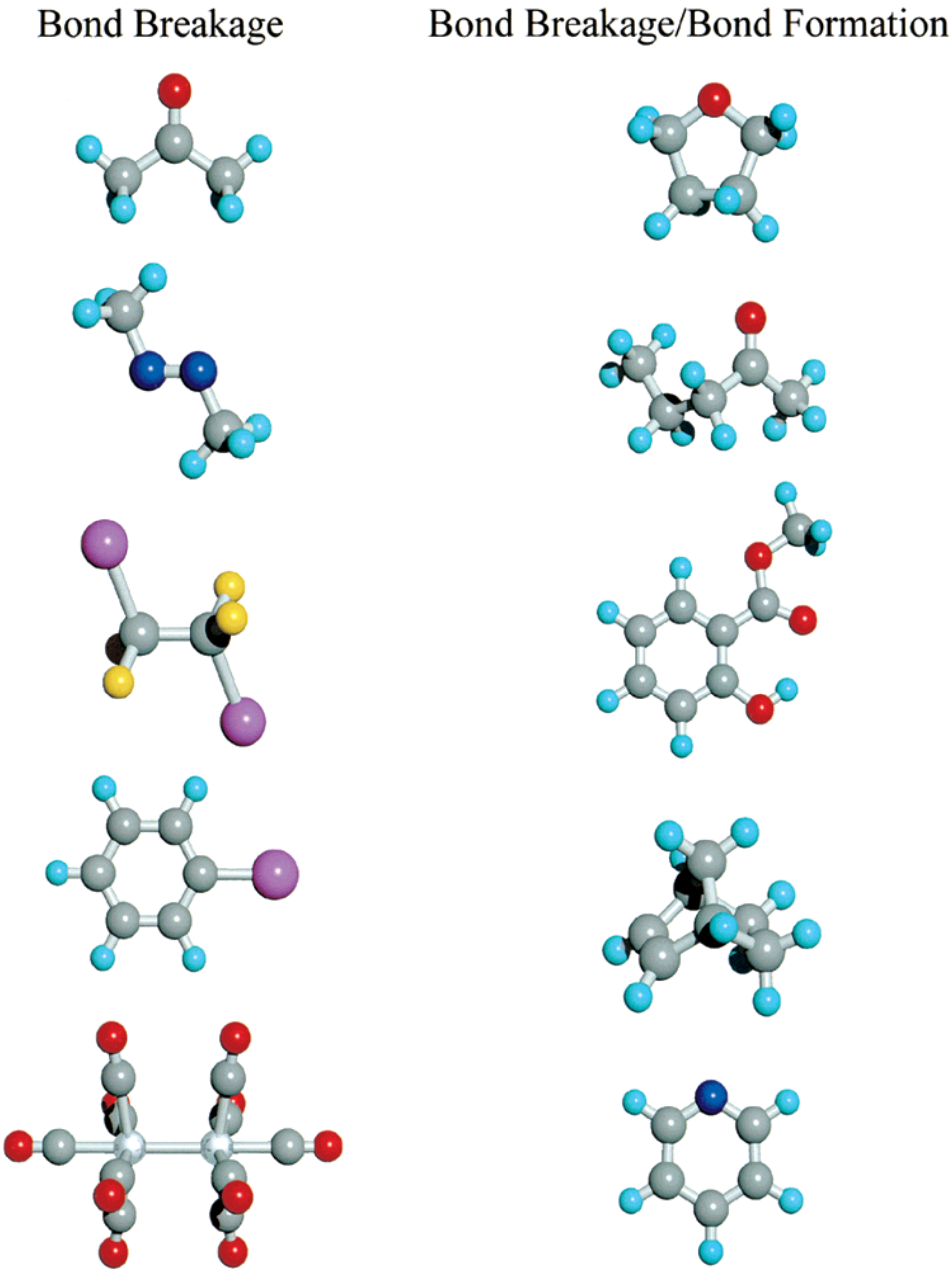


Figure 12. Molecular structures of different reactions studied, typical of the systems discussed in the text for organic and organometallic femtochemistry: acetone; azomethane; diiodoethane; iodobenzene; $Mn_2(CO)_{10}$; cyclic ethers; aliphatic ketones for Norrish-II reactions; methyl salicylate; one of the structures studied for addition and elimination reactions; pyridine for valence isomerization.

(iii) acid−base bimolecular reactions
(iv) intramolecular hydrogen-atom transfer
(v) tautomerization reactions: DNA base-pair models

(D) Inorganic and Atmospheric Chemistry. We extended the applications of femtochemistry to complex inorganic reactions of organometallics (Figure 12). Organometallic compounds have unique functions and properties that are determined by the dynamics of metal−metal (M−M) and metal−ligand (M−L) bonding. The time scales for cleavage of such bonds determine the product yield and the selectivity in product channels. They also establish the nature of the reactive surface: ground-state versus excited-state chemistry. Similarly, we studied the dynamics of chlorine atom production from OClO, a reaction of relevance to ozone depletion.

(E) The Mesoscopic Phase: Clusters and Nanostructures. We have studied different types of reactions under microscopic solvation condition in clusters. These include (Figure 15)

(i) reactions of van der Waals complexes
(ii) unimolecular reactions
(iii) bimolecular reactions
(iv) recombination, caging reactions
(v) electron and proton-transfer reactions
(vi) isomerization reactions

(F) The Condensed Phase: Dense Fluids, Liquids, and Polymers. In this area of research, we have focused our efforts on the study of reactions in dense fluids and comparison with dynamics in liquids. By varying the solvent density, we could study the femtosecond dynamics from gas-phase conditions to the condensed phase of liquid-state density. Accordingly, we could observe the influence of solute−solvent collisions on reaction dynamics in real time. We also did studies in liquid solutions for some of the systems examined in the gas phase:

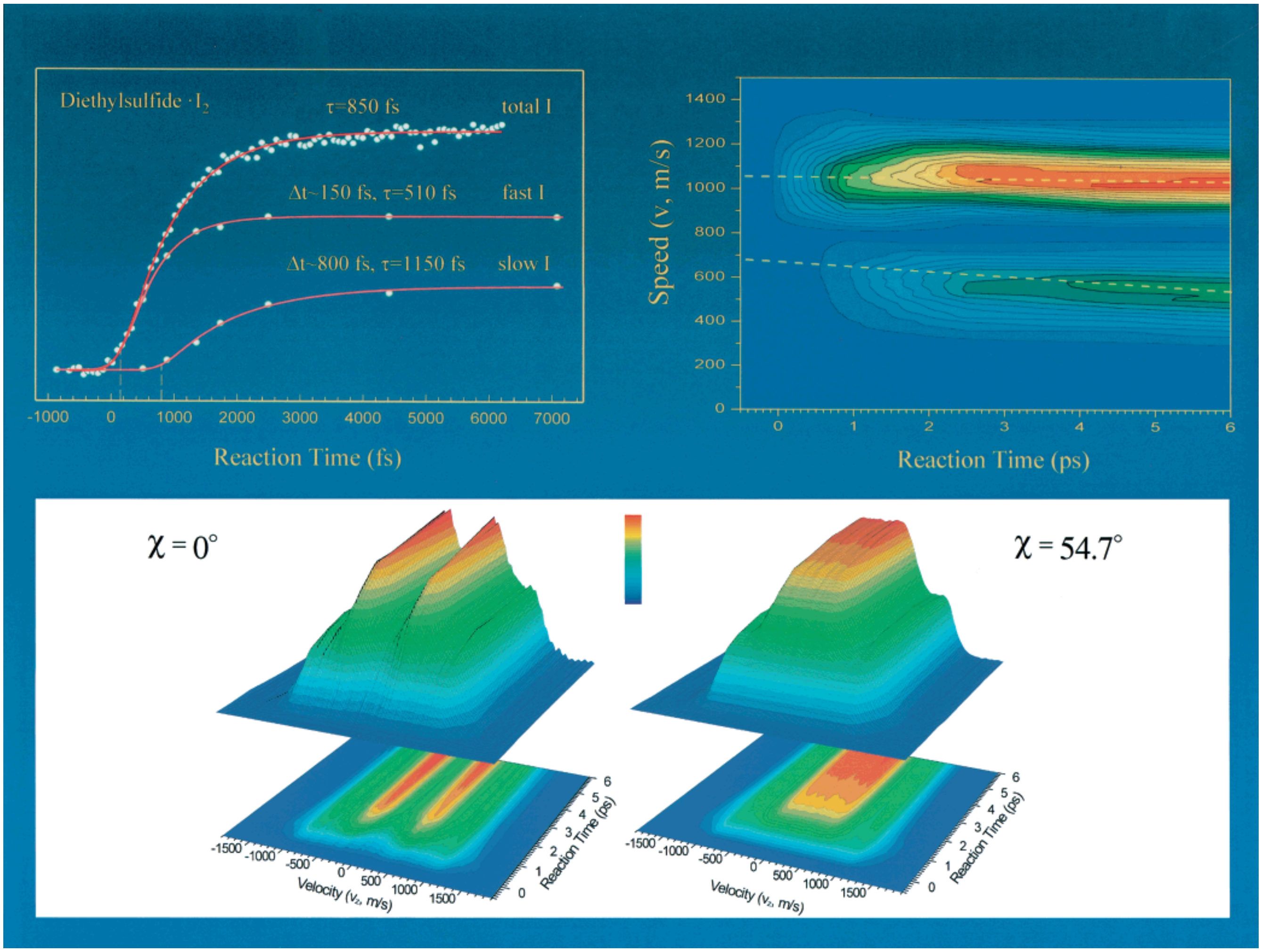


Figure 13. Femtochemistry of bimolecular electron-transfer reactions, the classic case of donors (e.g., benzene or diethyl sulfide) and acceptors (e.g., iodine or iodomonochloride). The experimental results clearly show the distinct velocity and time correlations, and thus the two-speed distributions and time scales of the reaction on the global PES. Reference 47.

bond breakage and caging; valence structure isomerization; double proton transfer. Similarly, we studied systems of nanocavities and polymers. Some highlights include (Figure 16)

(i) dynamics of the gas-to-liquid transition region (T_1 and T_2)
(ii) dynamics of bimolecular (one-atom) caging
(iii) dynamics of microscopic friction
(iv) dynamics in the liquid state
(v) dynamics of energy flow in polymers
(vi) dynamics of small and large molecules in cyclodextrins

(6) Opportunities for the Future. Three areas of study are discussed.

(A) Transient Structures from Ultrafast Electron Diffraction. Electron diffraction of molecules in their ground state has been a powerful tool over the past 50 years, and both electron and X-ray methods are now being advanced in several laboratories for the studies of structural changes. We have reported the latest advance in UED (Figure 17), by which major challenges were surmounted: the very low number densities of gas samples; the absence of the long-range order that is present in crystals, which enhances coherent interference; and the daunting task of determining in situ the zero-of-time when diffraction changes are on the picosecond and subpicosecond time scale.

With UED, we have been able to study molecular structures and branching ratios of final products on the picosecond time scale. The change in diffraction from before to after a chemical reaction was observed. However, the direct observation of transient structural changes in the course of a reaction was published only recently in PNAS (Figure 17). Specifically, we observed the transient intermediate in the elimination reaction of 1,2-diiodotetrafluoroethane ($C_2F_4I_2$) to produce the corresponding ethylene derivative by the breakage of two carbon−iodine bonds. The evolution of the ground-state intermediate (C_2F_4I radical) was revealed in the population change of a single chemical bond, namely, the second C−I bond. The elimination of two iodine atoms is nonconcerted, with the reaction time of the second C−I bond breakage being ~17 ps. The UED results on the short-lived C_2F_4I radical favor the classical structure over the bridged structure. Ab initio calculations were made to compare theory with experiments.

This leap in our ability to record structural changes on the picosecond and shorter time scales bodes well for many future applications to complex molecular systems, including biological systems. We have completed a new apparatus equipped with diffraction detection and also with mass spectrometry. This universal system is capable of studying complex systems in the gas and other phases. It holds great promise with opportunities for the future.

(B) Reaction Control. Our interest in this area goes back to the late 1970s when a number of research groups were reporting on the possibility of (vibrational) mode-selective chemistry with

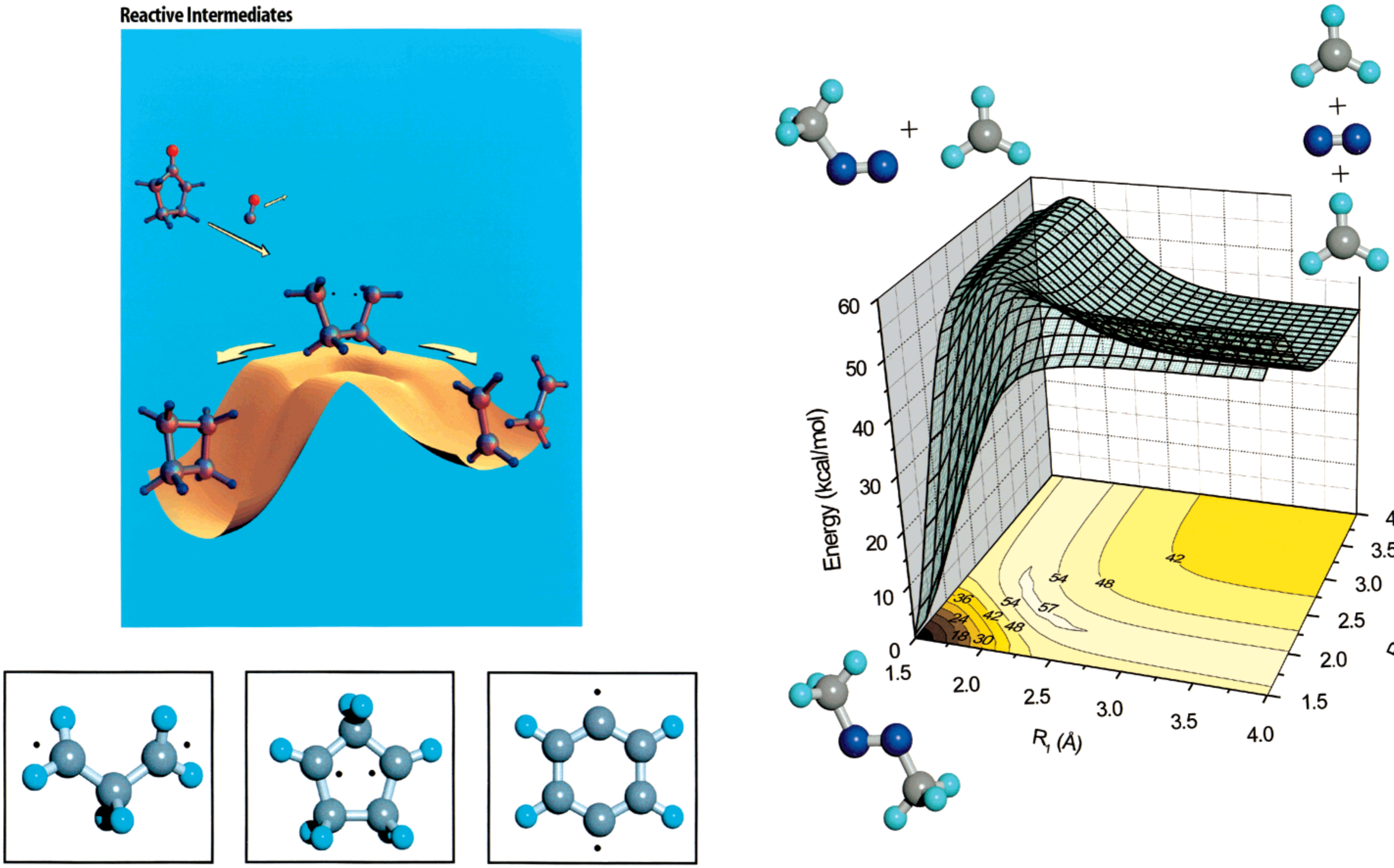


Figure 14. Reactive intermediates on the femtosecond time scale. (Left) Here, tetramethylene, trimethylene, bridged tetramethylene and benzyne are examples of species isolated on this time scale (see Figure 12 for others). (Right) Reaction dynamics of azomethane, based on the experimental, femtosecond studies. The ab initio PES was obtained from state-of-the-art calculations (E. Diau, this laboratory) which show the two reaction coordinates (C−N) relevant to the dynamics. A third coordinate, which involves a twisting motion, was also studied. Note the concerted and nonconcerted pathways. Reference 48.

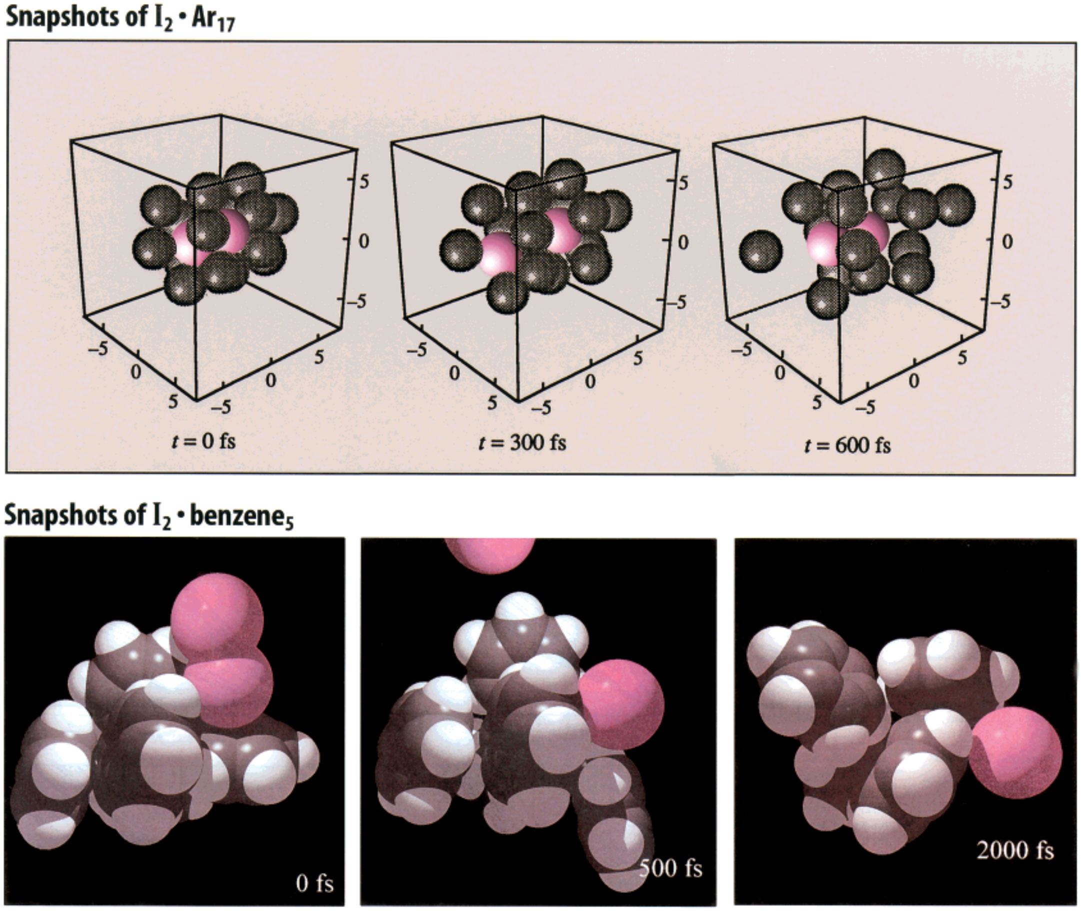


Figure 15. Femtosecond dynamics in the mesoscopic phase, reactions in solvent clusters. Two examples are given: The coherent nuclear dynamics of bond breakage and recombination of iodine in argon (the cage effect), and the dynamics of the same solute but in polyatomic solvents (benzene). It was for the former that the first *coherent* bond breakage in the cage was observed and separated from the effect of vibrational relaxation. For the latter, the two atoms experience different force fields and the time scales are determined by the degree of solvation. (We also studied van der Waals complexes.) Studies of acid−base reactions of naphthol with ammonia, changing the number of solvent molecules from 0 to 10, and the isomerization of stilbene (hexane as a solvent) were similarly made. Reference 49.

lasers. At the time, the thinking was directed along two avenues. One of these suggested that, by tuning a CW laser to a given state, it might be possible to induce selective chemistry. It turned out that its generalization could not be made without knowing and controlling the time scales of IVR in molecules. Moreover, state-selective chemistry is quite different from bond-selective chemistry. The second avenue was that of IR multiphoton chemistry. In this case, it was shown that the initial IR coherent pumping could be used for selective isotope separation. Such an approach has proven successful, even on the practical scale, and Letokhov has called the process "incoherent control".[29]

The discovery (section III2) of coherent and selective vibrational oscillations (in-phase and out-of-phase) in a large molecule such as anthracene triggered our interest in the possibility of temporally controlling the state of the system. The key idea was coherence among the vibrational degrees of freedom and its observation (published in 1981). In fact, Nico Bloembergen and I wrote a feature article (1984) emphasizing this point of coherent motion and its significance to mode-selective chemistry (see bibliography). Stuart Rice believed strongly in the concept of coherence and we even drafted a paper that was not finalized for publication.

Earlier, in 1980, I wrote a *Physics Today* article in a special issue on laser chemistry suggesting the use of ultrashort pulses (not continuous wave (CW) or long-time lasers) to control the outcome of a chemical reaction. The title of the paper was: Laser Selective Chemistry−Is it Possible? The subtitle stated the message, *"With sufficiently brief and intense radiation, properly tuned to specific resonances, we may be able to fulfill a chemist's dream, to break particular selected bonds in large molecules."* Ultrashort pulses should be used to control the system in the desired configuration by proper choice of the time duration and delay and the coherence time. Experimentally, we had already developed methods for the control of the phase of the field of optical pulses with the idea of using the *phase ("pulse shaping")* to control molecular processes−collisions, inhomogeneous broadenings, and even photon locking, which could inhibit relaxation; the time scale was nanoseconds and for the control of IVR, femtosecond pulses were needed.

Prior to this work, the optical pulse field,

$$E(t) = E_0\,A(t)\cos[\omega t + \phi(t)] \tag{10}$$

was simply defined by the envelope $A(t)$ and the frequency ω; the phase $\phi(t)$ was unknown. By controlling $\phi(t)$, we were able to make sequences of phase-coherent multiple pulses and to tailor a composite "single" pulse with a prescribed $\phi(t)$. We published a series of papers demonstrating the power of the approach, as mentioned above; see Figure 18. For example, with composite shaped pulses, a sequence of phase segments and tilt angles (in the rotating frame) of, e.g., $60_x - 300_{\bar{x}} - 60_x$, we showed experimentally that the emission of a molecule can be

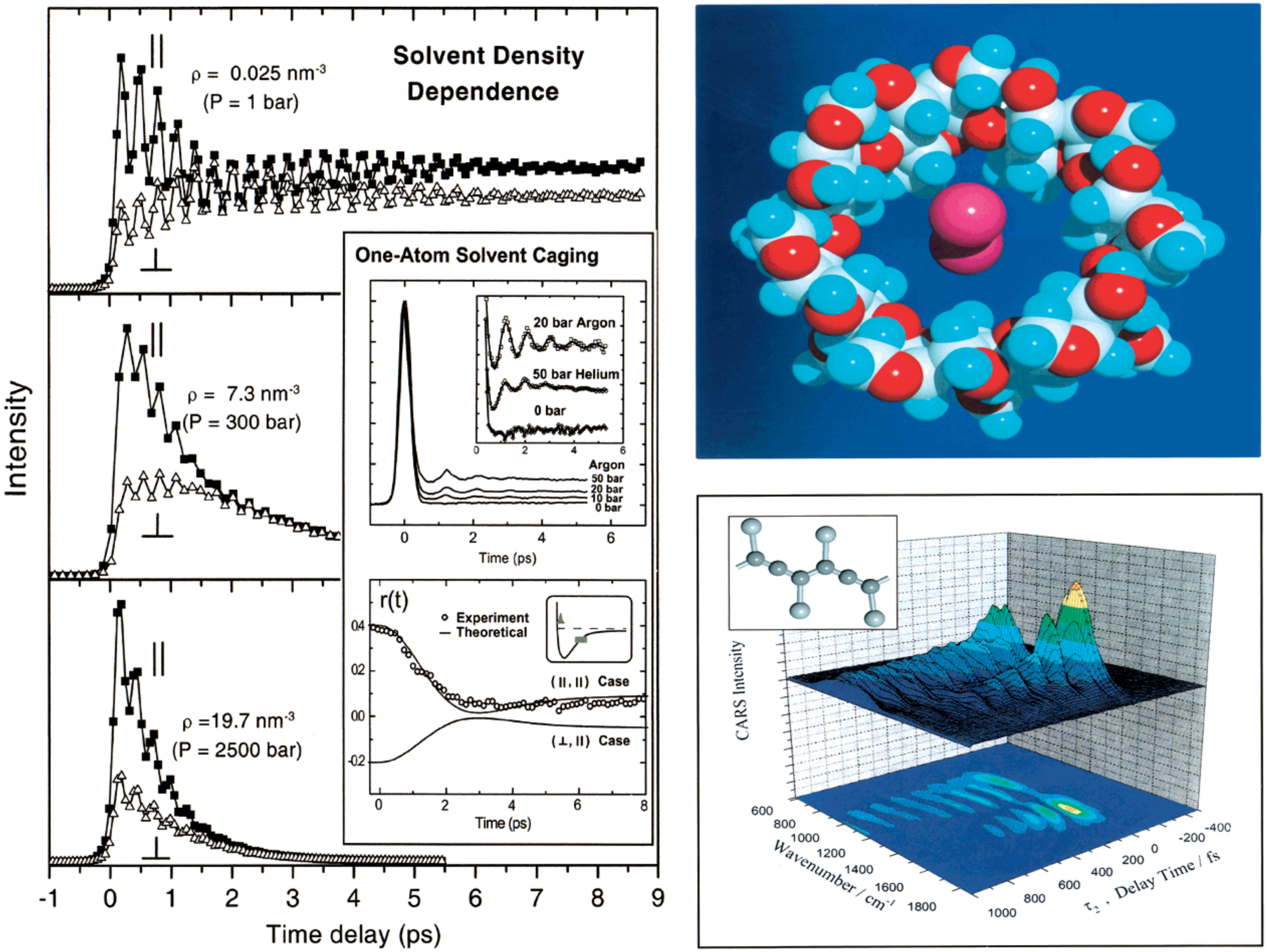


Figure 16. Femtosecond dynamics in the condensed phase: (left) coherent vibrational and rotational motions observed in dense fluids as a function of density and down to the one-atom collision with iodine; (right) nanocavities of cyclodextrins and polymers of polydiacetylenes; liquids (not shown, but references are given). Studies in these media include the one-atom coherent caging, J-coherence friction model, coherent IVR in polymer chains, and anomalous T_2 behavior in dense fluids. Reference 50.

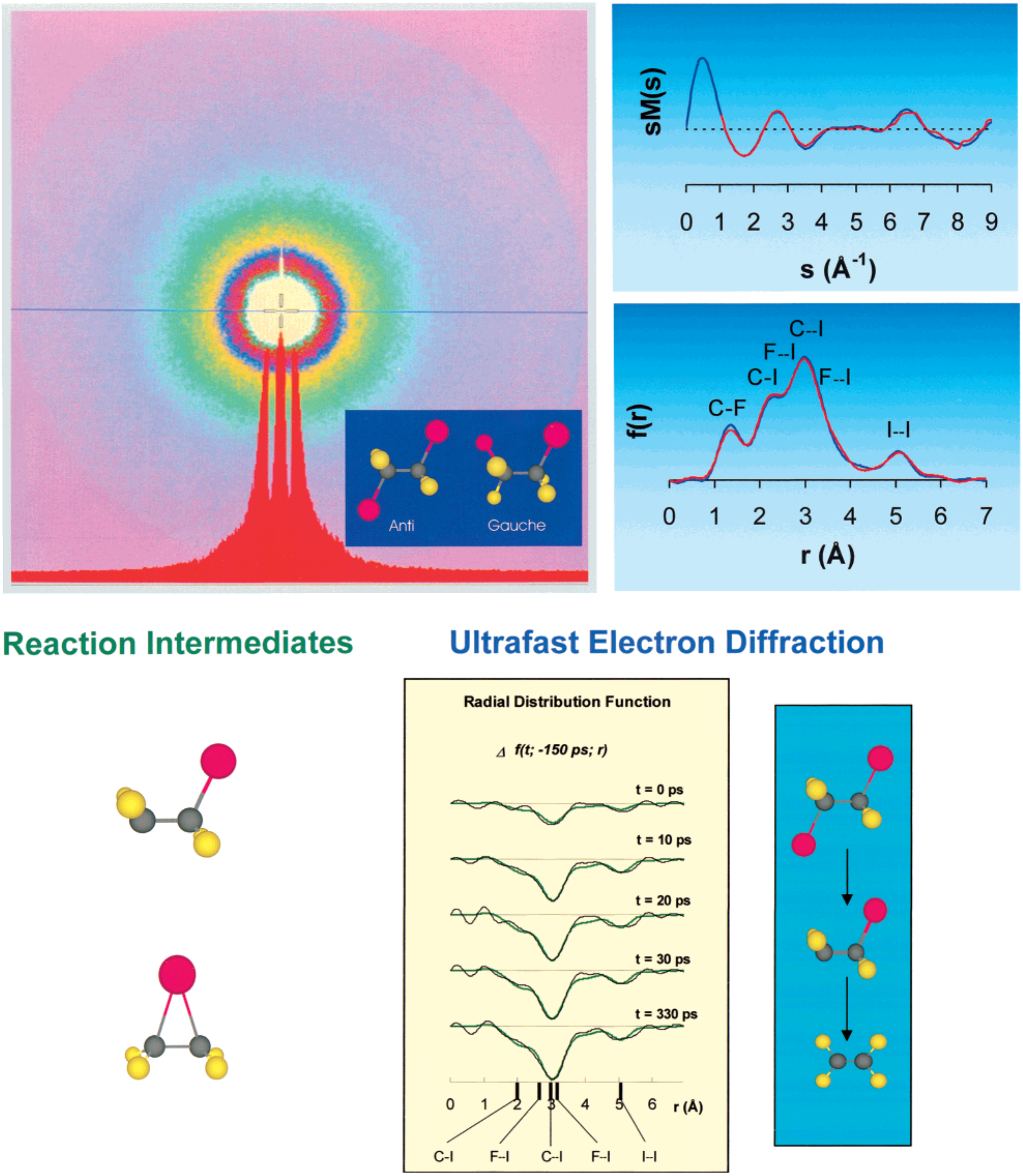


Figure 17. Ultrafast electron diffraction (UED). (Top) 2D image (CCD) and the obtained molecular scattering sM(s) and radial distribution *f*(*r*) functions: (red) experimental, (blue) theory. (Bottom) The temporal change observed on a bond population elucidates the structure of the reaction intermediate (shown above as two possibilities). Reference 51.

made twice that as when a normal single pulse was used (Figure 18). Similarly, by choosing pulse sequences such as $x-y-x(\bar{x})$, we experimentally locked the system and thus lengthened its relaxation time considerably. In theoretical papers, we examined the use of the approach for selectivity and control of molecular relaxations; in recent reviews,[30] Warren has discussed pulse shaping and its relevance to quantum control.

On the femtosecond time scale, the theoretical work of Heller[9] stimulated the use of the time-dependent wave packet picture for absorption and emission. In 1985, David Tannor and Stuart Rice, using the wave packet picture, provided a two-photon scheme for the control of selectivity with pulse-sequence coherence being an important part of the evolution. This scheme was extended, and in their review article of 1988,[31] they described phase sensitive experiments such as the ones we reported earlier. An important realization was the desire to optimize the yield of a given channel. With femtosecond resolution, we began testing the idea of timing of pulses on small molecular systems (Figure 18). We first studied the control of population in bound states (iodine). Then we reported results

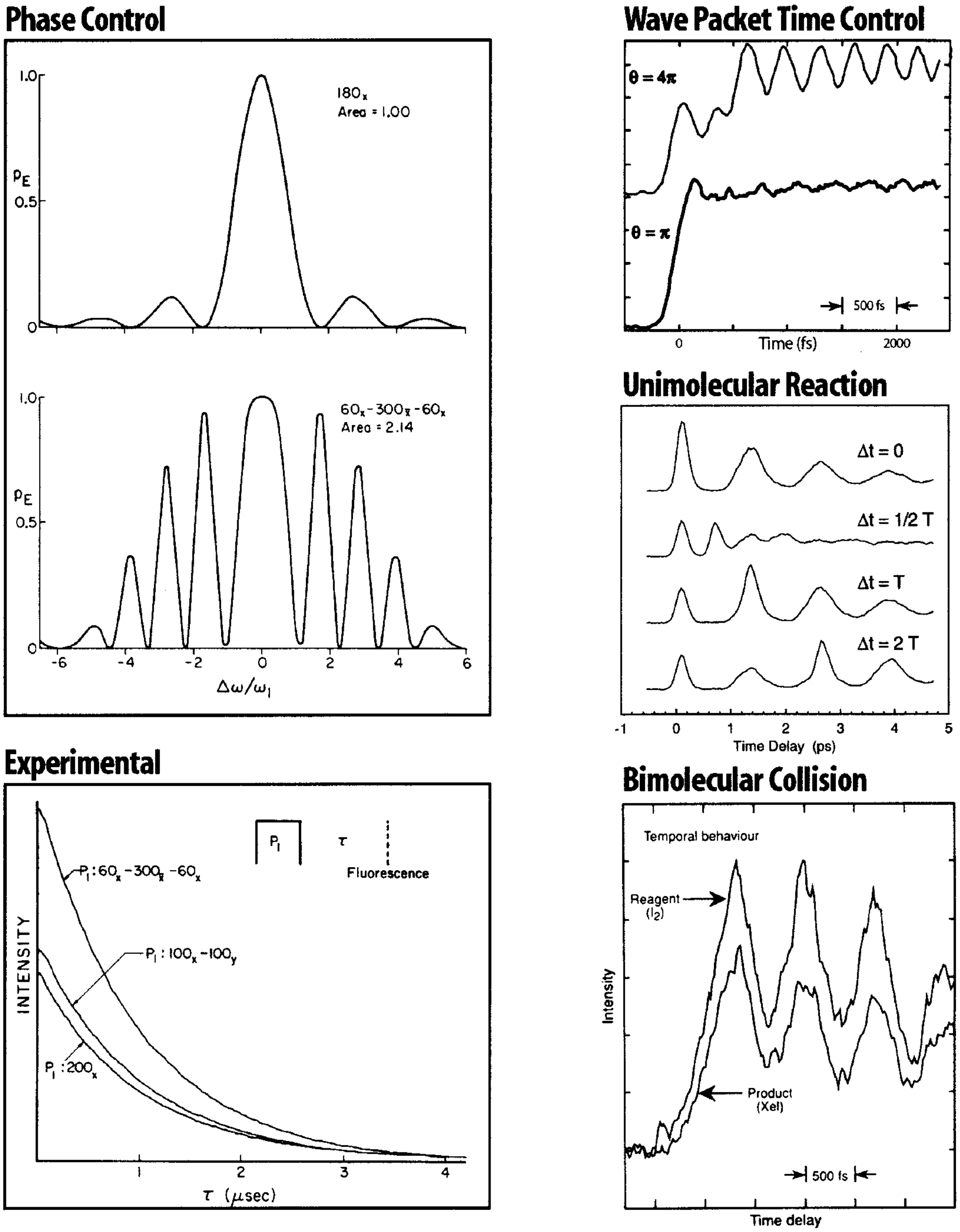


Figure 18. Control by the phase and/or the delay, or the duration of optical pulses. (Left) effect of a designed composite pulse on the fluorescence of a molecule (iodine), showing the large experimental enhancement for the labeled phase-controlled sequence. (Right) control of the population (I_2), of unimolecular reactions (NaI), and of a bimolecular collision (Xe + I_2); see text. Reference 52.

on the control of the yield in the reaction Xe + I_2 + $h\nu \rightarrow$ XeI + I as a function of the delay time between pump and control. Although the mechanism is not fully resolved, the important point is that the yield of product *XeI* followed the temporal motion of the iodine wave packet. In a third experiment, we used pump-control-probe femtosecond pulses to control the branching of the NaI reaction; these, together with the experiment by Gustav Gerber's group on $Na_2(Na_2^+ + e\ vs\ Na + Na^+ + e)$, are prototypes for the Tannor–Rice–Kosloff scheme. Phase-locked pulses were extended to the femtosecond resolution by Norbert Scherer and Graham Fleming in elegant studies of iodine.

Recently, we turned our attention to complex molecular systems, but this time using femtosecond pulses to implement the 1980 idea. In a series of molecules of increasing complexity, but retaining the same reaction coordinate, we studied selectivity control (IVR and entering near the transition state); the rate of reaction was 2–3 orders of magnitude larger than the expected *statistical* limit. This work was published in *Science* (Figure 19) and promises to be significant for achieving nonstatistical chemistry at high energies. The concept suggests that control at high energies (chemical energies) is more realistic, in contrast with the conventional wisdom that asserts the need for low energies—time is of the essence! Further studies should explore other systems. Another example of nonstatistical femtochemistry comes from the work on surfaces.[32] Recently, the group in Berlin (Ertl and Wolf[32]) demonstrated, in an elegant experiment, the critical role of femtosecond resolution in inducing oxidation (vs desorption) of CO on Ru surfaces—the femtosecond nonequilibrated electron distribution of the surface gives a selective

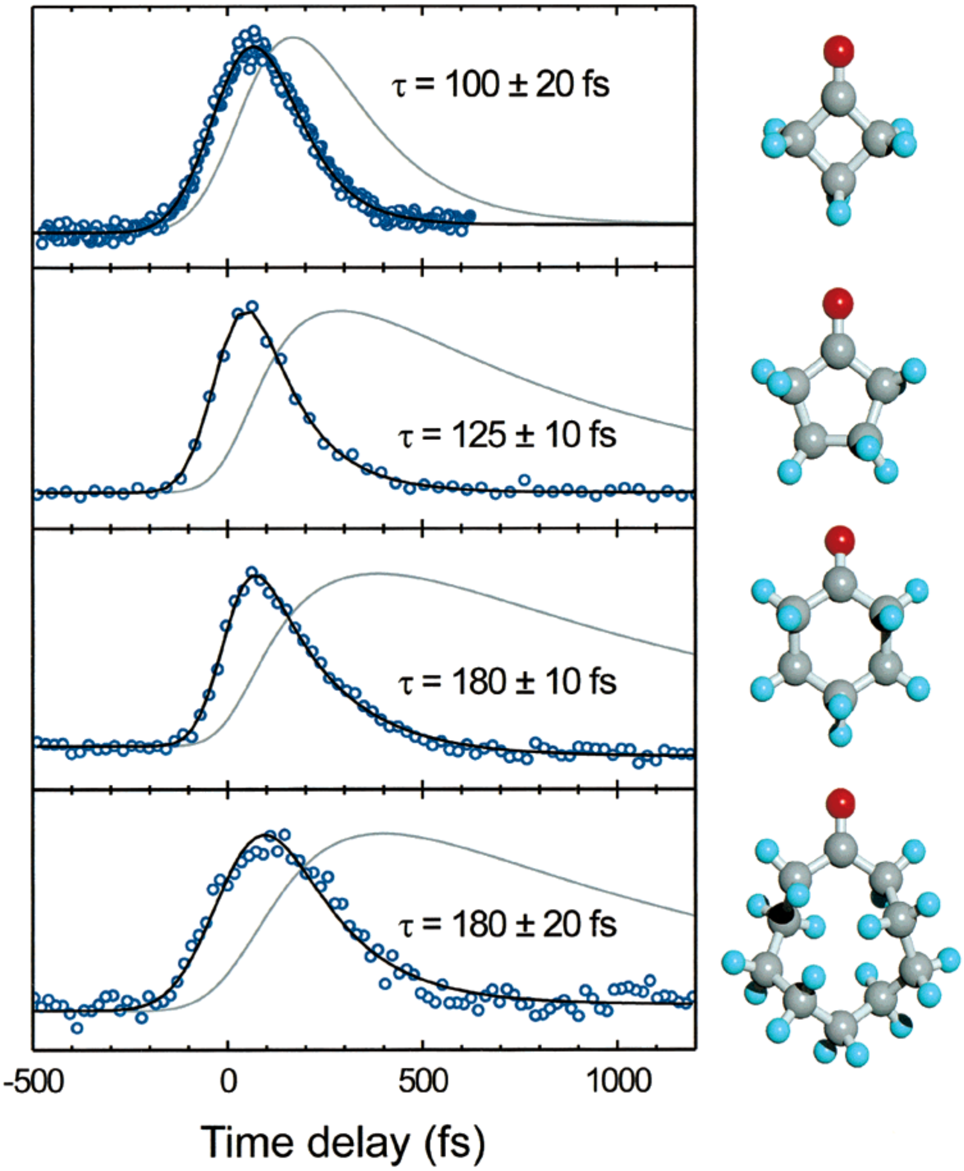


Figure 19. Localized control by femtosecond wave packet preparation at high energies, beating IVR. The series has the same reaction coordinate (C−C bond), but the molecular size has increased in complexity. Reference 53.

chemistry different from that of equilibrated phonon distribution, or thermal heating.

In the future, there will be extensions and new directions in femtosecond light-matter control based on the temporal coherence of light and its interference with matter waves. One area that holds promise is the use of femtosecond pulses to induce selectivity by utilizing the three parameters of the pulse, the central frequency, the width, and the chirp, in an iterative algorithm; the chirp is, in a way, similar to a composite pulse of the type described above. The technique of liquid-crystal display developed by Andy Weiner for femtosecond pulse shaping, combined with the evolutionary feedback idea of Herschel Rabitz, makes possible the generation of the desired complex $E(t)$ field to achieve (combinatorial) control. This optimal control has been demonstrated for a targeted second harmonic generation or a yield of chemical reaction as reported by Gerber's group in Würzburg.[33] Kent Wilson[33] showed the importance of chirped pulses in focusing and reflecting wave packets and, in a more recent contribution, he, with Warren Warren, used the evolutionary feedback approach to optimize the fluorescence of a molecule in solution.

It should be noted that all of the above schemes change the coherent composition of the initial packet and hence the evolution in different channels—but we have not changed the evolution dictated by the natural forces of the atoms! Intense fields may do so. Paul Corkum, Thomas Baumert, and other colleagues have provided novel observations with intense fields. Clearly, these areas of control by ultrafast pulse timing (t), phase (ϕ) (shape), spatial localization (R), and intensity to alter the potential (V) offer new opportunities for the future. Theoretical efforts have already been advanced ahead of current experiments, and Manz' group is providing new possibilities using timed and shaped pulses (see his review, in ref 24, of 1500 references to all work). We did not discuss here the CW control scheme advanced by Paul Brumer and Moshe Shapiro, nor could we be complete in referencing all work done in this area.

(C) Biological Dynamics. There have been important contributions to femtobiology and these include studies of the elementary steps of vision, photosynthesis, protein dynamics, and electron and proton transport in DNA. In proteins such as those of photosynthetic reaction centers and antennas, hemoglobins, cytochromes, and rhodopsin, a femtosecond event, bond

breaking, twisting, or electron transfer, occurs. There exist global and coherent nuclear motions, observed in these complex systems, and it is possible that the complexity is not as complicated as we think (see below).

Our efforts in this direction have so far focused on DNA twisting dynamics, electron transfer in DNA assemblies, DNA base-pair models, and protein-ligand dynamics. The work on the torsional rigidity of DNA was published in 1980−1982, while that relating to proton transfer in model base pairs was reported in the past few years. With donors (D) and acceptors (A) covalently bonded to DNA, studies of ET on more well-defined assemblies were made possible, and the effect of distance could be addressed. With femtosecond resolution, we obtained the actual time scale of ET and related the rates to the distance between D and A. In collaboration with Jackie Barton's group, we published this work in PNAS. The time scale of orientational coherence and solvation was also examined, allowing us to elucidate the role of molecular motions, including the effect of DNA rigidity. The results reveal the nature of ultrafast ET and its mechanism: in DNA, ET cannot be described as in proteins simply by a phenomenological parameter, β. Instead, the local involvement of the base pairs controls the time scale and the degree of coherent transport. Molecular dynamics are critical to the description of the transport. The measured rates and the distance range (Figure 20) of the transfer suggest that DNA is not an efficient molecular wire.

For proteins, our current interest is in the studies of the hydrophobic forces and ET, and oxygen reduction in models of metallo-enzymes (Figure 20). For the former, we have studied, with femtosecond resolution, the protein Human Serum Albumin (HSA), probed with the small (ligand) molecule hydroxyphenyl methyloxazole (HPMO); this work is in collaboration with Abderrazzak Douhal. We also studied ET in hyperthermophilic proteins. For model enzymes, we examined novel picket-fence structures that bind oxygen to the central metal with ~85% efficiency at room temperature. In this system (Figure 21), we observed the release of O_2 in 1.9 ps and the recombination was found to occur on a much longer time scale. These are fruitful areas for future research, especially in that they provide prototype systems for O_2 reduction in the transition state (similar to the smaller systems of benzenes/halogens (discussed in Figure 13) but at room temperature. We published our first report recently in *Angewandte Chemie* in collaboration with Fred Anson's group at Caltech.

IV. Impact and Concepts—A Retrospective

In retrospect, the key to the explosion of research can perhaps be traced to three pillars of femtochemistry.

(1) Time Resolution—Reaching the Transition-State Limit. Three points are relevant: (i) The improvement of nearly 10 orders of magnitude in time resolution, from the (milli) microsecond time scale (Eigen, Norrish, and Porter) to present femtosecond resolution, opened the door to studies of new phenomena and to new discoveries. (ii) The transition state, the cornerstone of reactivity, could be clocked as a molecular species $TS^{\ddagger}$, providing a real foundation to the hypothesis of Arrhenius, Eyring, and Polanyi for ephemeral species $[TS]^{\ddagger}$, and leading the way to numerous new studies. Extensions will be made to study transition state dynamics in complex systems, but the previous virtual status of the transition state has now given way to experimental reality. (iii) Inferences deduced from "rotational periods" as clocks in uni- and bimolecular reactions can now be replaced by the actual clocking of the nuclear (vibrational) motion. This is particularly important when a chemical phenomenon such as "concertedness" is involved or the time scale of complexes or intermediates is many vibrational periods. In the 1960s, there was some thought[34] that the relevant time scale for chemistry was the microsecond regime. Moreover, the uncertainty principle was thought to represent a severe limit of the utility of shorter time resolution; coherence was not part of the thinking in deciphering femtosecond nuclear motion, as discussed in section III (development of femtochemistry) and below.

(2) Atomic-Scale Resolution. Two points are relevant: (i) The transition from *kinetics* to *dynamics*. On the femtosecond time scale, one can see the coherent nuclear motion of atoms—*oscillatory* or *quantized steps* instead of *exponential decays* or *rises*. This was proved to be the case for bound, quasi-bound, or unbound systems and in simple (diatomics) and in complex systems (proteins). (ii) The issue of *the uncertainty principle*. The thought was that the pulse was too short in time, thus broad in energy by the uncertainty principle $\Delta t \Delta E \sim \hbar$, but as discussed above, localization is consistent with the two uncertainty relationships (Figure 3) and coherence is the key. The energy uncertainty ΔE should be compared with bond energies: ΔE is 0.7 kcal/mol for a 60 fs pulse. At the 1972 Welch Conference, in a lively exchange between Eugene Wigner and Edward Teller, even picosecond time resolution was of concern because of the perceived fundamental limitation imposed on time and energy by Heisenberg's uncertainty principle.

(3) Generality of the Approach. Three points are relevant: (i) In retrospect, the femtosecond time scale was just right for observing the "earliest dynamics" at the actual vibrational time scale of the chemical bond. (ii) The time resolution offers unique opportunities when compared with other methods. Processes often appear complex because we look at them on an extended time scale, during which many steps in the process are integrated. (iii) The methodology is versatile and general, as evidenced by the scope of applications in different phases and of different systems. It is worth noting that both *excited*- and *ground-state* reactions can be studied. It has been known for some time that the use of multiple pulses can populate the ground state of the system, and, therefore, the population and coherence of the system can be monitored. The use of CARS, DFWM, SRS, π-pulses, or direct IR excitation are some of the approaches possible. Two recent examples demonstrate this point: one invokes the use of IR femtosecond pulses to study reactions involving hydrogen (bond) motions in liquid water, work done in France and Germany, and the other utilizes CARS for the study of polymers in their ground state, as discussed above. Ground-state dynamics have also been studied by novel femtosecond photodetachment of negative ions, and the subfield of femtosecond dynamics of ions is now active in a number of laboratories.[35]

(4) Some Concepts. The concepts and phenomena have been discussed in the original publications and reviews. Below, only a few will be highlighted.

(A) Resonance (Nonequilibrium Dynamics). The concept of resonance in the structure of the chemical bond goes back to the era of Linus Pauling and the idea of interconversion between different electronic structures. The interconversion was a hypothesis, not an observable fact. Quantum mechanically, chemists usually speak of eigenstates of the system, which are stationary with no time evolution. Resonance in dynamics is a concept that is not a stationary-state picture. With coherent preparation of molecules, it is possible to prepare a nonstationary *(nonequilibrium)* state of a given nuclear structure and for the system to evolve in time. In our studies this was shown for

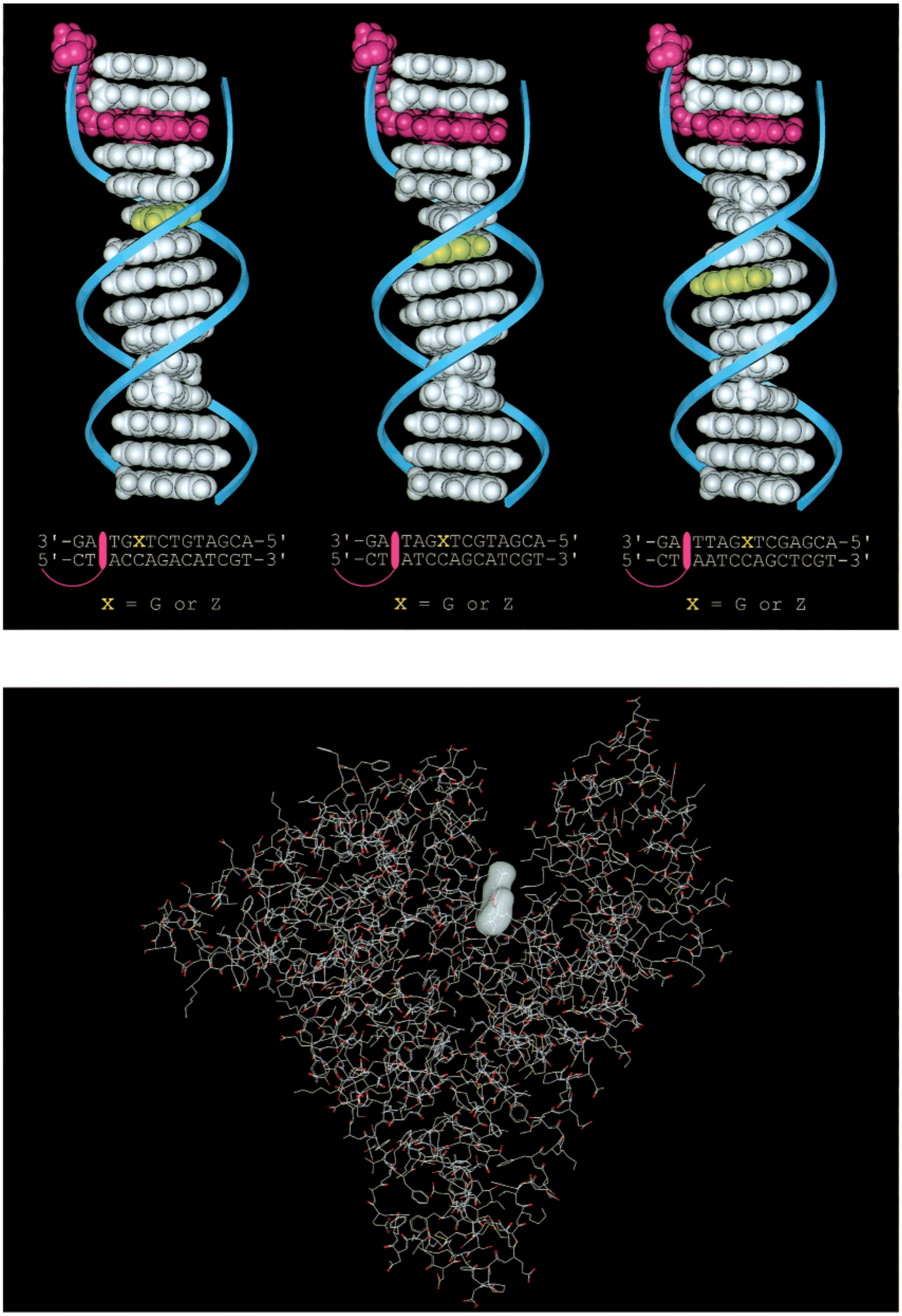


Figure 20. DNA assemblies and protein complexes studied on the femtosecond time scale. Shown are two examples: DNA with donors and acceptors at fixed distances (top) and protein HSA with the molecule HPMO shown in the interior. The focus of research is on electron transfer and molecular dynamics for the former and on probing ligand-recognition effects for the latter. References 54 and 55.

vibrational redistribution, for rotational orientation, and for wave packet nuclear motions. Such nonstationary evolution does not violate the uncertainty principle and is fundamental to chemical dynamics.

(B) Coherence (Single-Molecule-Type Dynamics). Perhaps one of the most powerful concepts in femtochemistry is coherence of the *molecule*, of the *ensemble*, and of the *trajectory*. First, the coherence created by a femtosecond pulse is reflected in the motion of the wave packet; for a force-free motion the group velocity is that of a free particle (p/m), a classical motion. Second is the ability to "transform" the ensemble's incoherent behavior to a coherent molecular trajectory. This is achieved

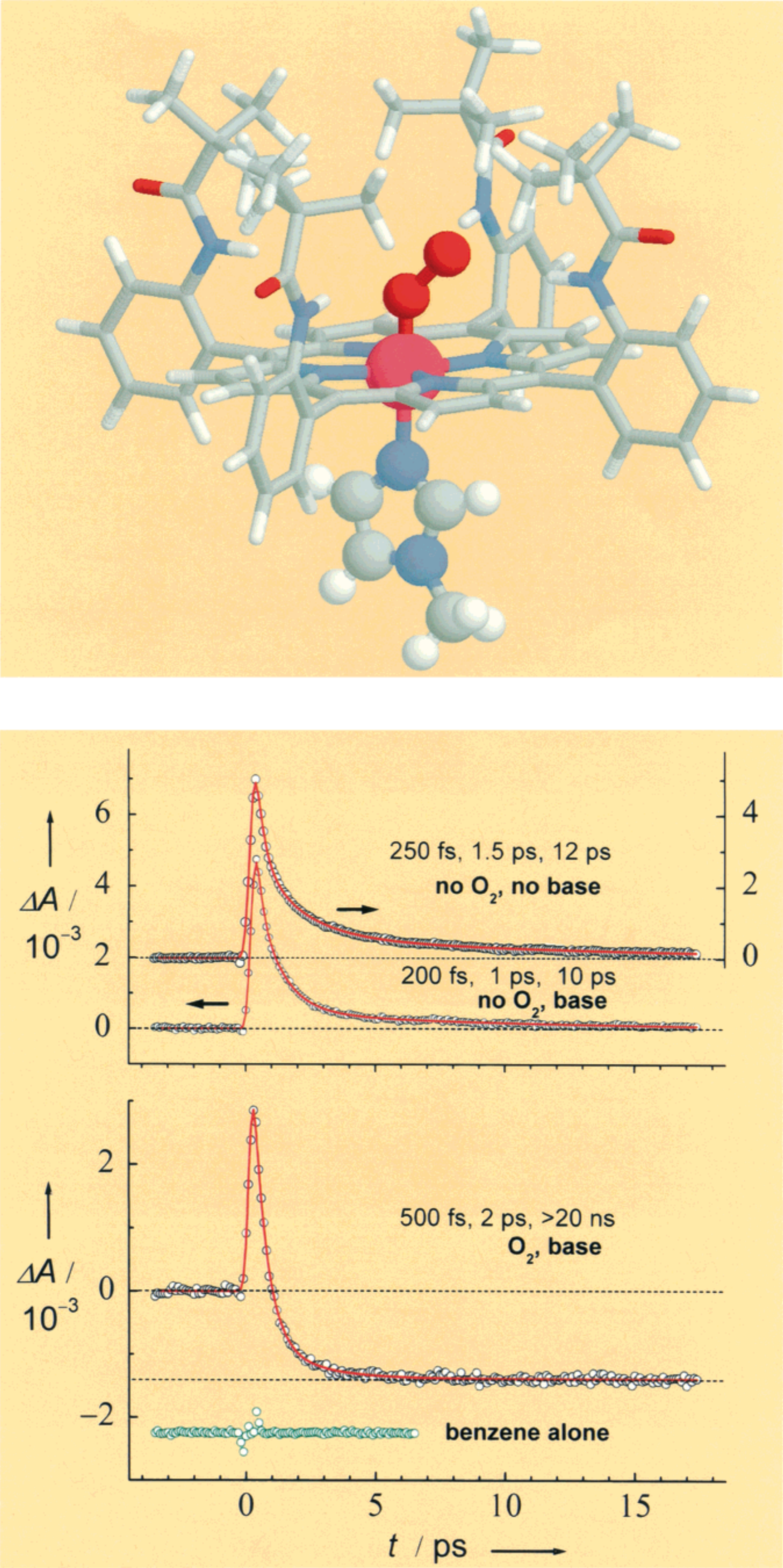


Figure 21. Femtosecond dynamics of model biological systems. Shown here is the structure of dioxygen-picket fence cobalt porphyrin and the femtosecond transients that show the time scales involved and the release of O_2 in 1.9 ps at room temperature. The studies on this and the other model systems (not shown) are part of the continued effort in this area. Reference 56.

because on the femtosecond time scale the system can be promoted and localized in space with a localization length (ΔR) only limited by the uncertainty of the initial system, typically ~0.05 Å; all molecules that do not interact span this range.

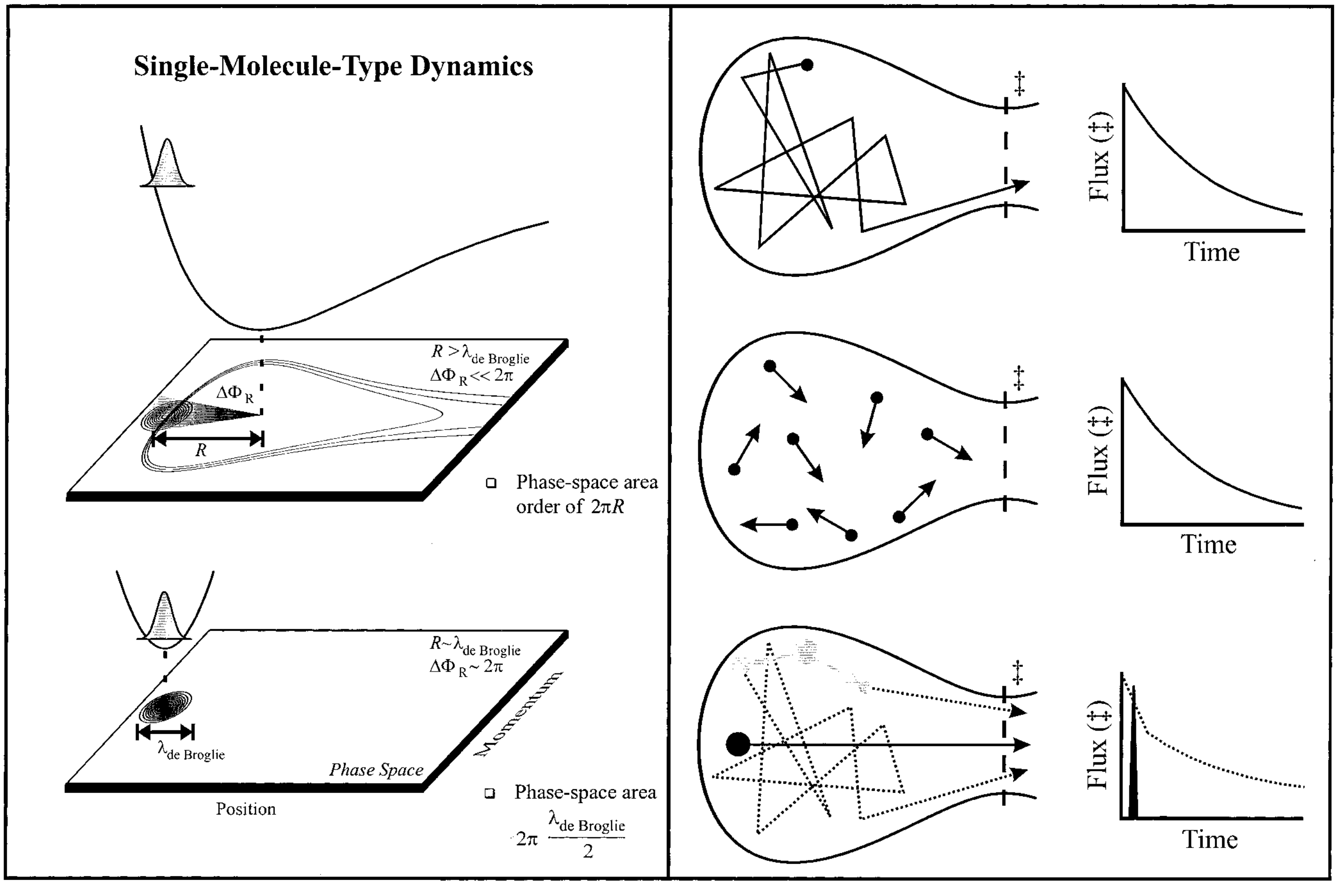


Figure 22. Concept of coherence, both in the dynamics at the atomic scale and in the control of nonstatistical behavior. Shown is the phase space picture, describing the robustness of coherence (left); note the phase-space area of the initial state relative to that of the reaction. (Right) We present, for simplicity, a schematic of a configuration space made of the reactive coordinate and all nonreactive coordinates perpendicular to it (an equivalent phase-space picture can be made). Shown are three cases of interest: (top) the ergodic dynamics, (middle) the incoherent preparation, and (bottom) the coherent wave packet preparation, showing the initial *localization*, spatially and temporally, and the *bifurcation* into direct and indirect reaction trajectories. Recent theoretical work (K. Møller, this laboratory) of the corresponding temporal behavior has elucidated the different regimes for the influence of the initial preparation, from a wave packet to a microcanonical limit.

The chemical length scale (R) of interest is several angströms and this is why the system behaves as a single-molecule trajectory. Because the initial state is promoted nearly intact on the femtosecond time scale, the only dispersion is that which causes the different trajectories to spread under the influence of the new forces of the energy landscape or by external perturbations, such as solvation. If longer time pulses are used for the preparation, then ΔR is on the scale of R, and kinetics of the states are recovered. Put in time-domain language, the inhomogeneous dephasing time of the ensemble is relatively long for femtosecond preparation *and* the homogeneous dynamics and the actual coherence of the packet become dominant, as amply demonstrated here and elsewhere. Third, the concept of coherence is crucial for achieving a coherent trajectory of reactions. Such control projects the nonstatistical behavior through the preparation of a localized configuration, as opposed to incoherently prepared space by, e.g., chemical activation, or spatially-diffuse long-time methods (Figure 22).

(C) Transition Structures (Landscape Dynamics). This concept became clear to us after studies of the elementary dynamics in simple reactions of three atoms and in complex reactions of organic systems. Traditionally, one uses a reaction path and makes a distinction between a TS and a reactive intermediate by the absence or presence of a potential well—if there is no well, bonds are not formed and thus we do not speak of a “real” structure. On the femtosecond time scale, we can isolate a continuous trajectory of transition structures; none are in a potential well. Such structures are defined by the change in bond order and lead to a *family of trajectories* of reaction products. Thus, the two classical pathways of either a “concerted” or “sequential” process represent a very crude approximation for the actual landscape dynamics, even in a three-atom system. There is a whole distribution of reaction times and kinetic energy releases. The problem becomes even more severe if the landscape is complex and has near-flat energy regions or entropic changes, as for the case of complex organic reactions and protein folding. The concept of transition structures and landscape dynamics is significant to issues addressing stereochemistry, product branching, and selectivity, and to the real distinction between TS and intermediates in many reactions. Finally, the presence of such a family of trajectories on the energy landscape makes the restricted definition of TS—as only the saddle point—less clear. Concerted reactions, in the strict synchronous sense, essentially do not exist.

(D) Reduced Space (Directed Dynamics). Another important concept in dynamics is the reduction of nuclear space to the subspace critical to reactivity and nonradiative behavior in complex systems. Here, the femtosecond time scale allows one to project the *primary events* out of all processes possible. In complex systems with many degrees of freedom, the reduced space becomes the focus and the remaining space becomes a “continuum”, thus moving the description from a multidimensional ($3N - 6$) PES to a few coordinates plus a weakly coupled continuum. This idea was central to our description of the

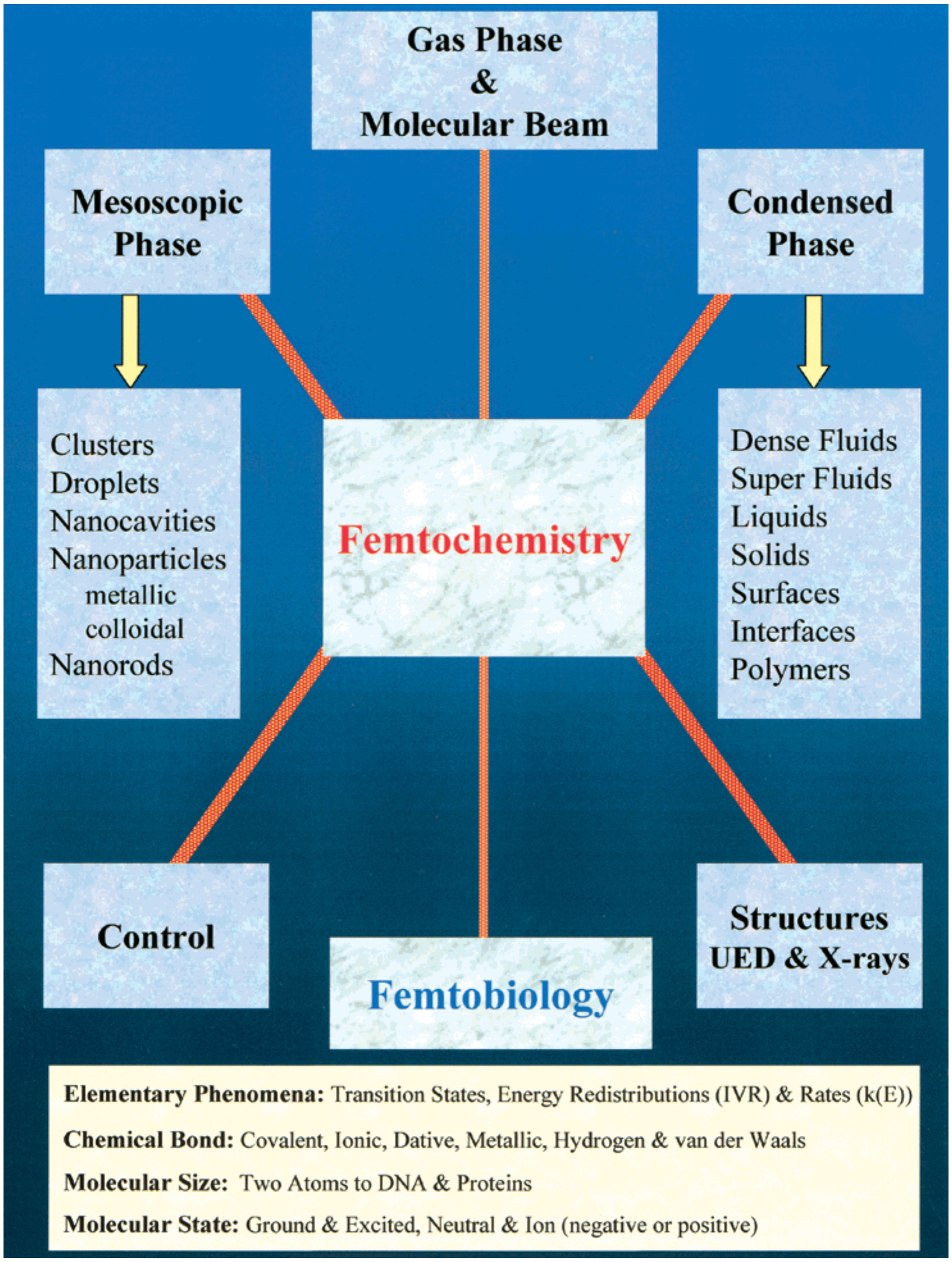


Figure 23. Areas of study in femtochemistry.

dynamical isotope effect in elementary reactions, bifurcation to chemical and photophysical channels by conical intersections, concertedness and stereochemistry in organic reactions, nonstatistical behavior, and reaction control in large systems at high energies. The consequences to photochemistry are significant: Reactions from high-energy states ($\pi\pi^*$, Rydberg, etc.) usually result in ground-state chemistry, and bifurcation into conical intersections is the key; for transitions involving σ^* orbitals, the time scale of rupture becomes comparable to that of the funneling through conical intersections, resulting in competitive chemical channels. It is possible that this same concept of reduced space is significant to biological dynamics. By reducing the space for dynamics, events occur efficiently and without "wasting" energy to all degrees of freedom possible. In addition, such designed local activity makes the system robust and immune to transferring "damage" over long distances. The ultrafast time scale is important because on it the system separates the important from the unimportant events—DNA bases quench their energy (nonradiatively) very rapidly, ET in DNA is locally ultrafast, and the first event of vision is very efficient and occurs in 200 fs.

V. Epilogue

As the ability to explore shorter and shorter time scales has progressed from the millisecond to the present stage of widely exploited femtosecond capabilities, each step along the way has provided surprising discoveries, new understanding, and new mysteries. In their editorial on the 10th anniversary of Femtochemistry, Will Castleman and Villy Sundström put this advance in a historical perspective.[28] The report in ref 36 addresses with details the field and its position in over a century of developments. Figure 23 summarizes areas of study and the scope of applications. Developments will continue and new directions of research will be pursued. Surely, studies of transition states and their structures in chemistry and biology will remain active for exploration in new directions, from simple systems to complex enzymes and proteins, and from probing to controlling of matter.

Since the current femtosecond lasers (4.5 fs) are now providing the limit of time resolution for phenomena involving nuclear motion, one may ask: Is there another domain in which the race against time can continue to be pushed? Subfemtosecond or attosecond (10^{-18} s) resolution may one day allow for the direct observation of the electron's motion. I made this point in a 1991 *Faraday Discussion* review (see bibliography) and, since then, not much has been reported except for some progress in the generation of subfemtosecond pulses.[37] In the coming decades, this may change and we may view electron rearrangement, e.g., in the benzene molecule, in real time. Additionally, there will be studies involving the combination of the "three scales", namely time, length, and number. We should see extensions to studies of the femtosecond dynamics of *single molecules* and of *molecules on surfaces* (e.g., using STM). Combined time/length resolution will provide unique opportunities for making the important transition from molecular structures to dynamics and to functions (section III6). We may also see that all of femtochemistry can be done at micro-to-nano Kelvin temperatures, utilizing lasers and other cooling techniques.

It seems that on the femtosecond to attosecond time scale we are reaching the "inverse" of the big bang time, with the human heartbeat "enjoying" the geometric average of the two limits. The language of molecular dynamics is even similar to that of cosmos dynamics. Cosmologists are speaking of energy landscapes and transition states for the big bang and universe inflation.[38] Perhaps we are approaching a universal limit of time![57]

The future of femtoscience will surely witness many imaginative and unpredictable contributions. I hope that I will be able to enjoy the future as much as I have the past. Benjamin Franklin once wrote, "*The progress of human knowledge will be rapid and discoveries made of which we at present have no conception. I begin to be almost sorry I was born so soon since I cannot have the happiness of knowing what will be known in years hence.*"

Acknowledgment. Over the years, our research group at Caltech has had many outstanding students, postdoctoral fellows, and research associates; the International Roster is given below. Their contributions to the story told here are recognized in an earlier review (see section III) and in the book article published by Les Prix Nobel (ref 27); the figures in this article refer to original publications. I hope that by mentioning their work, they recognize the crucial role they have played in the journey of femtochemistry at Caltech, the "science village" I have enjoyed over the years. There have been a number of friends and colleagues who have supported the field and made the experience enjoyable and humanly worthwhile—to them I wish the very best. All are with us today, except one: Dick Bernstein. Major support of this research came from the National Science Foundation, the U.S. Air Force Office of Scientific Research, and the Office of Naval Research, and it is a pleasure to acknowledge all of these organizations for making it possible.

The International Roster of the Caltech Group, 1976−1999

1976 Rajiv Shah, Duane Smith, Daniel Dawson, Thomas Orlowski, Barry Schwartz, Roy Mead

1977 William Lambert, David Millar, Joseph Perry, Kevin Jones, Albert Nichols

1978 Dennis Diestler, Richard Powell, Yoshinori Hirata, Jean-Pierre Lemaistre, Samuel Batchelder

1979 Anne-Marie Merle, Wing Ki Liu, Raymond Robbins, Mark Burns, Peter Felker

1980 Max Glasbeek, Hector Rubalcava

1981 Jack Syage, Warren Warren, Brian Keelan

1982 Eugene Ryabov, John Shepanski, Bernard Sipp, Lutfur Khundkar, Norbert Scherer, Edward Sleva, Isaac Xavier

1983 Fida Al-Adel, David Semmes

1984 Fuad Doany, Joseph Knee, Spencer Baskin, Lawrence Peng

1985 George Bird, Peter Felker,* Marcos Dantus

1986 Mark Rosker, Todd Rose, Peijun Cong, Christopher Sipes

1987 Dino Tinti, Earl Potter, Paul Tripodi, Dean Willberg

1988 Robert Bowman, John Breen, Ahmed Heikal

1989 Martin Gruebele, Maurice Janssen, Amine Mokhtari, Gareth Roberts, Ian Sims

1990 Michael Gutmann, Luis Bañares, Jennifer Herek, Chuck Williamson, Soren Pedersen

1991 Marcos Dantus,* Scott Kim, Qianli Liu

1992 Thomas Baumert, Christoph Lienau, Juen-Kai Wang

1993 Hua Guo, Ralf Fröchtenicht, Arnulf Materny, Sang Kyu Kim, Sing Chong, Dongping Zhong

1994 Hans Frey, James Cheng, Chaozhi Wan, Hyotcherl Ihee

1995 Abderrazzak Douhal, Spencer Baskin,* Marcus Motzkus, Stefan Preuss, Brent Horn

1996 Jianming Cao, Julius Su

1997 Alfred Scala, Eric Diau, Mirianas Chachisvillis, Torsten Fiebig, Klaus Møller, Osama Abou-Zeid, Thorsten Bernhardt, Hogan Yu

1998 Udo Gomez, Vladimir Lobastov, Steven De Feyter, Matthias Manger, Ramesh Srinivasan, Hern Paik

1999 Joseph Casanova, Dongping Zhong*, Boyd Goodson, Souzhong Zou, Robert Clegg, Carsten Kötting

* Postdoctoral (after the Ph.D. from Caltech)

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