

## FEMTOCHEMISTRY

ATOMIC-SCALE DYNAMICS OF THE CHEMICAL BOND  
USING ULTRAFAST LASERS

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by

AHMED H. ZEWAİL

California Institute of Technology, Pasadena, USA.

Over many millennia, humankind has thought to explore phenomena on an ever shorter time scale. In this race against time, femtosecond resolution ( $1\text{ fs} = 10^{-15}\text{ second}$ ) is the ultimate achievement for studies of the fundamental *dynamics of the chemical bond*. Observation of the very act that brings about chemistry – the making and breaking of bonds on their actual time and length scales – is the wellspring of the field of *Femtochemistry*, which is the study of molecular motions in the hitherto unobserved ephemeral *transition states* of physical, chemical and biological changes. For molecular dynamics, achieving this atomic-scale resolution using *ultrafast lasers* as strobes is a triumph, just as x-ray and electron diffraction, and, more recently, STM and NMR, provided that resolution for static molecular structures. On the femtosecond 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. This anthology gives an overview of the development of the field from a personal perspective, encompassing our research at Caltech and focusing on the evolution of techniques, concepts, and new discoveries.

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## I. PROLOGUE

In the history of human civilization, the measurement of time and recording the order and duration of events in the natural world are among the earliest endeavors that might be classified as science. The development of calendars, which permitted the tracking of yearly flooding of the Nile valley in ancient Egypt and of the seasons for planting and harvesting in Mesopotamia, can be traced to the dawn of written language. Ever since, time has been an important concept [1] and is now recognized as one of the two fundamental dimensions in science. The concept of time encapsulates an awareness of its duration and of the passage from *past* to *present* to *future* and surely must have existed from the very beginning with humans searching for the meaning of birth, life and death and, in some cultures, rebirth or recurrence.

My ancestors contributed to the beginning of the science of time, developing what Neugebauer [1] has described as *“the only intelligent calendar which ever existed in human history”*. The “Nile Calendar” was an essential part of life as it defined the state of yearly flooding with three seasons, the *Inundation* or *Flooding*, *Planting*, and *Harvesting*, each four months long. A civil year lasting 365 days was ascertained by about 3000 BC or before, based on the average time between arrivals of the flood at Heliopolis, just north of Cairo; nilometers were used in more recent times, and some are still in existence today. By the time of the First Dynasty of United Egypt under Menes in ca. 3100 BC, the scientists of the land introduced the concept of the “Astronomical Calendar” by observing the event of the helical rising of the brilliant star Sothis (or

Sirius). Inscribed on the Ivory Tablet, dating from the First Dynasty and now at the University Museum in Philadelphia, were the words, "Sothis Bringer of the Year and of the Inundation" [1, **Winlock**]. On the Palermo Stone, the *annals* of the kings and their *time-line* of each year's chief events were documented from pre-dynastic times to the middle of the Fifth Dynasty [1, **Breasted**]. Thus, as early as 3100 BC, they recognized a definite natural phenomenon for accurate timing of the coming flood and recounted the observed reappearance of the star as the New Year Day – real-time observation of daily and yearly events with the zero-of-time being well defined!<sup>1</sup>

In about 1500 BC, another major contribution to this science was made, the development of *Sun-Clocks*, or *Sundials*, using moving shadows [Fig. 1]. Now in Berlin, the sun-clock bearing the name of Thutmose III (or Thothmes after the Egyptian God Thoth of wisdom and enlightenment), who ruled at Thebes from 1447–1501 BC, shows the graduation of hours for daytime measurements. This clock with uneven periods for hours was man-made and transportable. For night time, the water-clock was invented, and the device provided even periods for timing. With these developments, the resolution of time into periods of *year*, *month*, *day* and *hour* became known and has now been used for more than three millennia. The durations of minutes and seconds followed, using the Hellenistic sexagesimal system, and this division, according to Neugebauer, "is the result of a Hellenistic modification of an Egyptian practice combined with Babylonian numerical procedures." About 1300 AD, the mechanical clock [1, **Whitrow**] was advanced in Europe, ushering in a revolution in precision and miniaturization; Galileo began studies of pendulum motions and their clocking, using his heartbeats (seconds), in 1582 AD. Our present time standard is the cesium atomic clock<sup>2</sup>, which provides precision of about  $1:10^{13}$ , i.e., the clock loses or gains one second every 1.6 million years. For this work, Norman Ramsey shared the 1989 Nobel Prize in Physics.

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

<sup>1</sup> Recognizing the incommensurability of the lunar month and the solar year, they abandoned the lunar month altogether and used a 30-day month. Thus the year is made of 12 months, 30 days each, with 5 feast days at the end of the year. The "Civil Calendar" was therefore 365 days per year and differs from the astronomical calendar of Sothis by approximately a  $1/4$  day every year. The two calendars must coincide at intervals of  $365 \times 4 = 1460$  years, and historians, based on recorded dates of the reappearance of Sothis in dynastic periods, give the four dates for the coincidence of both calendars: 139 AD, 1317 BC, 2773 BC, and 4233 BC ( $+139 - 3 \times 1460 = 4241$  BC). Even though the Egyptians discovered the astronomical calendar,  $365 - 1/4$  days, they decided, presumably for "bookkeeping", to use the civil calendar of 365 without leap years. They also divided the day into two periods of 12 hours each for day and night time. The remarkable calendar of years, months, days, and hours was adapted throughout history and formed the basis for the 365.25-day Julian (46 BC, Alexandria school) and 365.2422-day Gregorian (from 1582 AD, Pope Gregory XIII) calendars. In the words of the notable Egyptologist J. H. Breasted [1], "It has thus been in use uninterruptedly over six thousand years." Many historians regard the date around 4241 BC as the beginning of *history* itself as it defines the period of written records; anything earlier is *prehistory*.

<sup>2</sup> Since 1967 one second has been *defined* as the time during which the cesium atom makes exactly 9,192,631,770 oscillations.



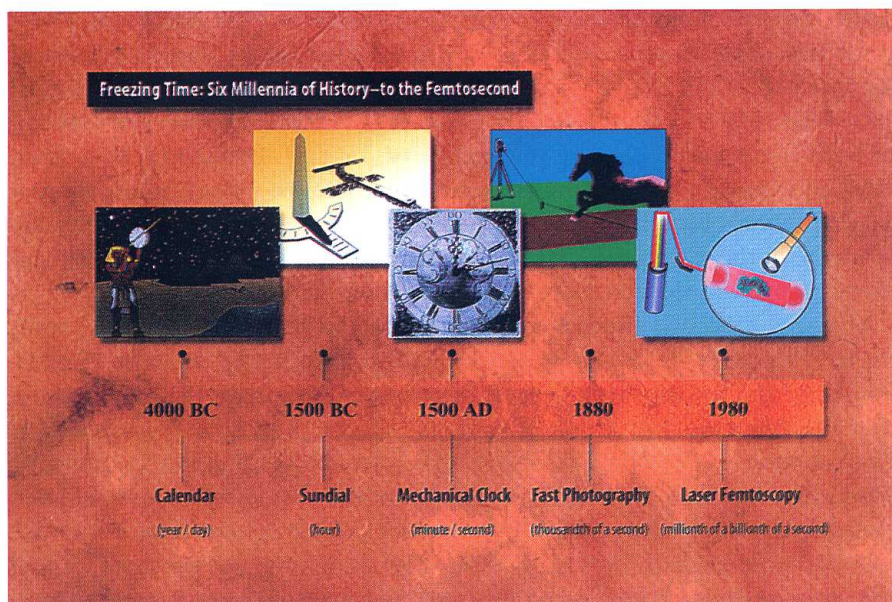


Figure 1. Timeline of some events in the history of measurements of time, from yearly calendars to the femtosecond regime (see text).

ear's ability to recognize a tone. Anything more fleeting than the blink of an eye ( $\sim 0.1$  second) or the response of the ear ( $\sim 0.1$  millisecond) was simply beyond the realm of inquiry. In the nineteenth century, the technology was to change drastically, resolving time intervals into the sub-second 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-1900's) 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 [2]. By the 1980's, this resolution became ten orders of magnitude better [see **Section II2**], reaching the femtosecond scale<sup>3</sup>, 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 [3], as khem became khemia, then alchemy, and eventually chemistry [3,4] – see the Stockholm Papyrus in **Fig. 2**. 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

<sup>3</sup> The prefix milli comes from Latin (and French), micro and nano from Greek, and pico from Spanish. Femto is Scandinavian, the root of the word for “fifteen”; nuclear physicists call femtometer, the unit for the dimensions of atomic nuclei, fermi. Atto is also Scandinavian.



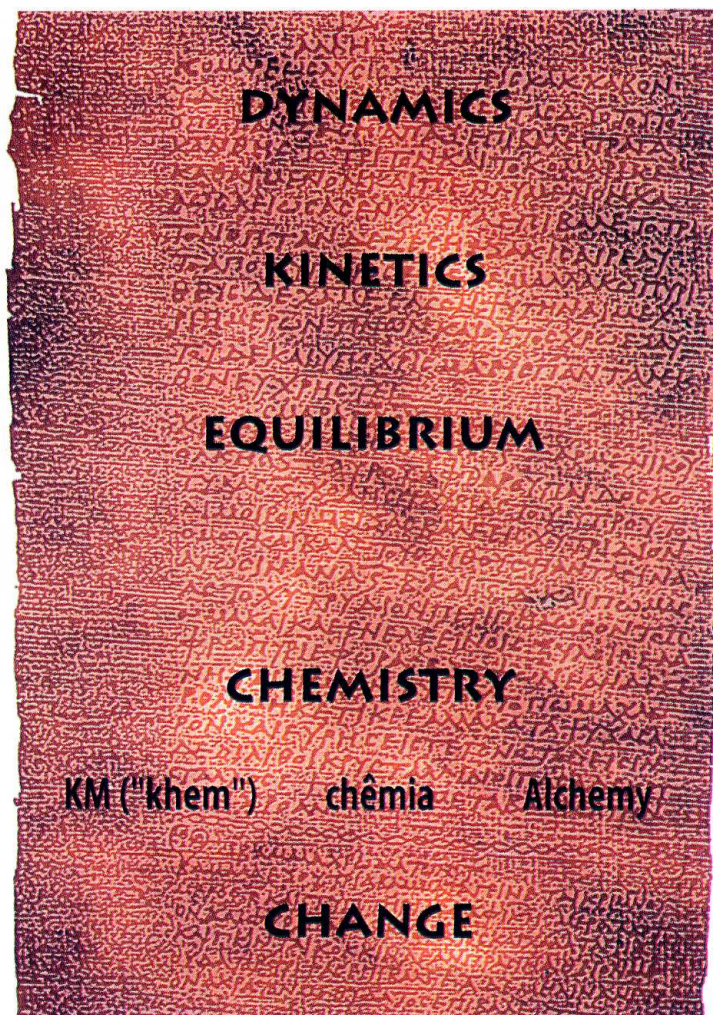


Figure 2. A page of the Stockholm papyrus (300 AD) describing the recipe for “making” (actually imitating) emerald. Note that *change* has been at the heart of chemistry from its millennia-old definition KM, to Chêmia and Alchemy, and to Chemistry. [Ref. B26, and references therein] Equilibrium, kinetics and dynamics are the foundation for the description of chemical changes.

is  $\sim 1$  km/second and, hence, to record atomic-scale dynamics over a distance of an ångström, the average time required is  $\sim 100$  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 fs 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 detai-



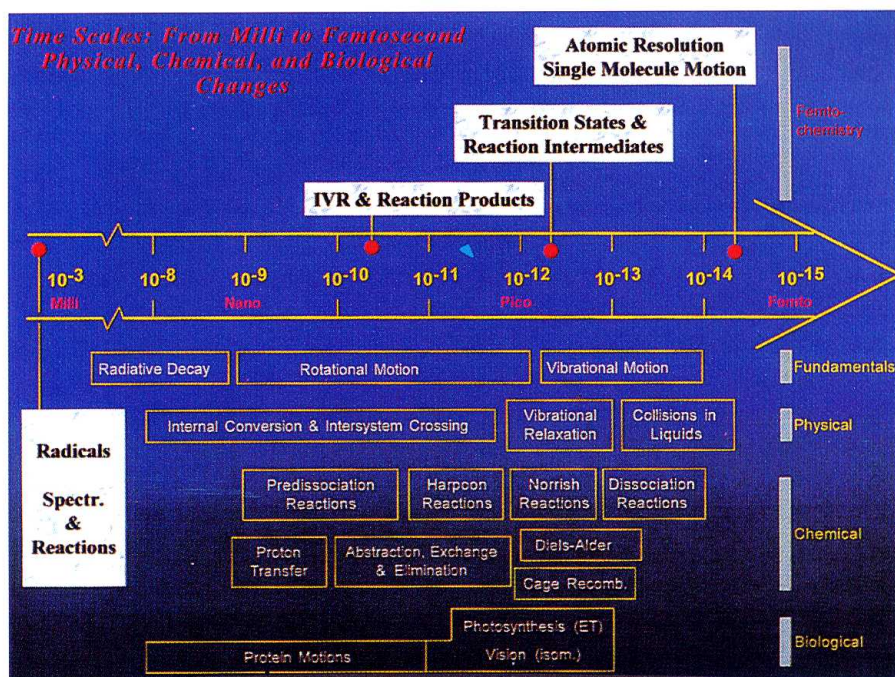


Figure 3. Time scales. The relevance to physical, chemical, and biological changes. The fundamental limit of the vibrational motion defines the regime for femtochemistry. Examples are given for each change and scale. [Ref. B4, B10]

led 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 [4].”

In femtochemistry, studies of physical, chemical or biological changes are at the fundamental time scale of molecular vibrations: the actual nuclear motions [Fig. 3]. In this sense, femtosience represents the end of the race against time, or, as the report of Ref. [5] puts it, “... reaching the end of the road”. For this same reason, Martens stated, “all chemistry is femtochemistry [5]”. 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, on this time scale, the time-dependent description of a *coherent*, single-molecule trajectory represents the classical nuclear “motion picture” of the reaction as its wave packet proceeds from the initial state, through transition states, and on to final products – the language of the actual dynamics! The fs time scale is unique for the creation of such coherent matter waves on the atomic scale of length, a basic problem rooted in the development of quantum mechanics and the duality of matter. Figure (4) highlights some steps made in the description of the duality of light-matter and time scales, and the Appendix discusses the importance of coherence for localization.

## Matter Waves Particle-type Control & Dynamics

### de Broglie (1924)

Einstein's light wave/particle

$$E = h \nu \quad E = c p$$

$$\therefore \lambda = h/p$$

Similarly, matter particle/wave

### Schrödinger (1926)

The Wave Equation – Stationary waves

$$H\Psi = E\Psi$$

### Schrödinger (1926)

Micro- to Macro-mechanics

Quantum to Newton Mechanics

$\Psi$  to wave group

### Femtochemistry & Quantum Limit (h):

#### Particle-type

$$\lambda_{\text{de Broglie}} (\text{initial localization}) = h/p$$

uncertainty in time measurement

$$\Delta x \Delta p \geq h/(2\pi) \quad \Delta t \Delta E \geq h/(2\pi)$$

for force free

$$\Delta x = p/m \Delta t \equiv v \Delta t$$

$$\Delta t \sim 10 \text{ fs} \quad \Delta x \sim 0.1 \text{ \AA}$$

$$\Delta t \sim 10 \text{ ps} \quad \Delta x \sim 100 \text{ \AA}$$

Figure 4. Matter waves and particle-type limit of dynamics. The atomic-scale de Broglie wavelength in the coherent preparation of a quantum system and in the uncertainty of probe measurements are both reached on the fs time scale. See also the Appendix and its Figure.

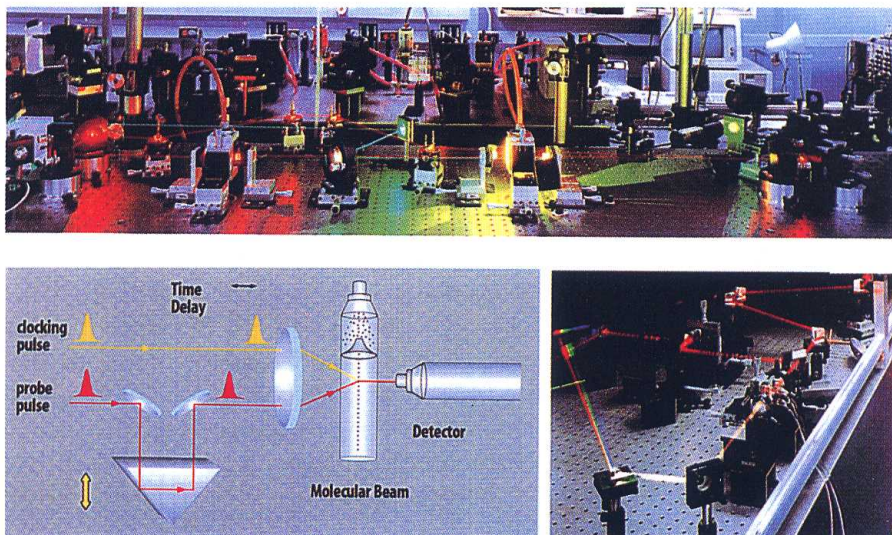
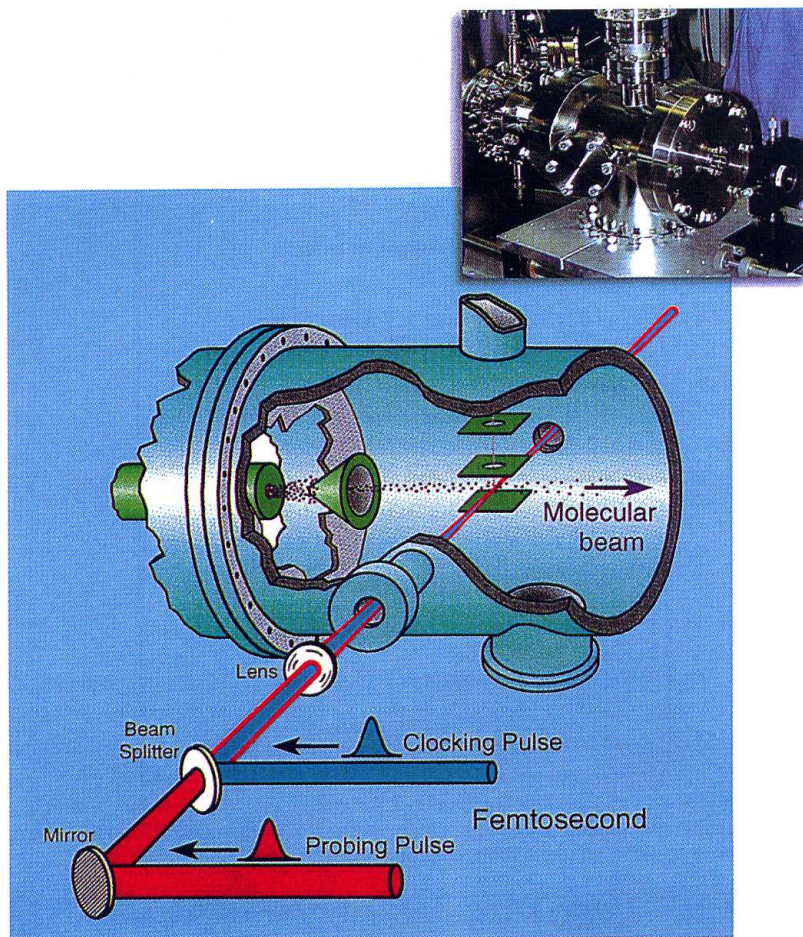


Figure 5. A femtochemistry apparatus typical of early Femtolands. (A, above) The laser system. (top) the first CPM oscillator used in Femtoland I; (bottom) the continuum generation to the right and the experimental layout for clocking to the left. (B, next page) The molecular beam apparatus of Femtoland III, together with a view of the beam/laser arrangement. [Ref. B1, B16, B28, 49]





This powerful concept of *coherence* lies at the core of femtochemistry and was a key advance in observing the dynamics at atomic resolution. 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 [Fig. 5A, B] proved to be essential for the initial development. Laser-induced fluorescence was the first probe used, but later we invoked mass spectrometry and non-linear optical techniques. Now numerous methods of probing are known [Fig. 6] and used in laboratories around the world; Coulomb explosion is the most recent powerful probe developed by Will Castleman [5] for arresting reactive intermediates, as mentioned in Section III.

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.

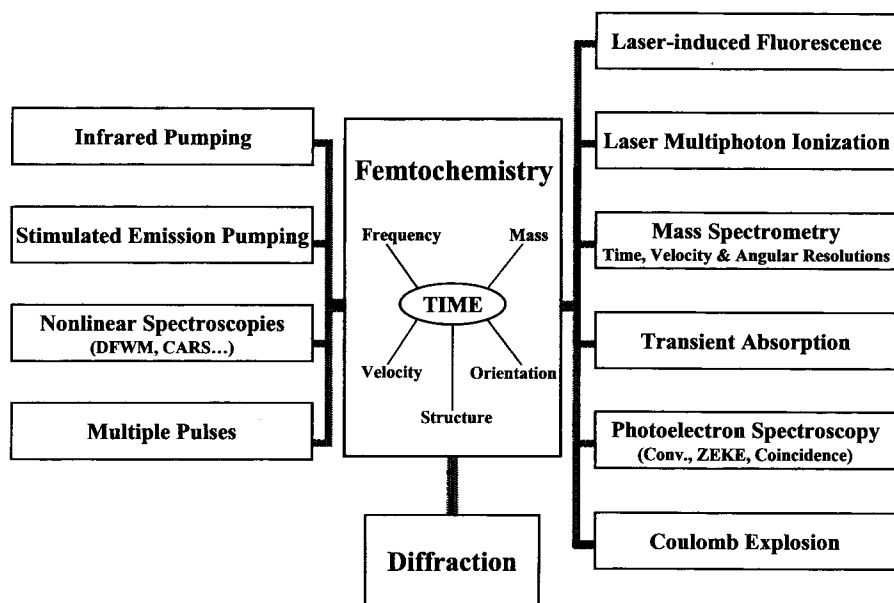


Figure 6. Techniques for probing in femtochemistry. Both excited and ground states have been probed by these methods. The correlations of time with frequency, mass, velocity and orientation were essential in the studies of complex systems. Diffraction represents the new effort for probing structures (see text and Fig. 29).

Studies have also been made in all 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 femtosience such as femtobiology [Fig. 7].

Twenty-four centuries ago, the Greek philosopher Democritus and his teacher Leucippus gave birth to a new way of thinking about matter's invisible and elementary entity, the atom. Richard Feynman once asked, if you had only one sentence to describe the most important scientific knowledge we possess, what would that sentence be? He said, "*everything is made of atoms.*" Democritus' atomism, which was rejected by Aristotle, was born on a purely philosophical basis, surely without anticipating some of the twentieth century's most triumphant scientific discoveries. Atoms can now be seen, observed in motion, and manipulated [6]. These discoveries have brought the microscopic world and its language into a new age, and they cover domains of length, time and number. The *length* (spatial) resolution, down to the scale of atomic distance (ångström), and the *time* resolution, down to the scale of atomic motion (femtosecond), have been achieved. The trapping and spectroscopy of a single ion (electron) and the trapping and cooling of neutral atoms have also been achieved. All of these achievements have been recognized by the awarding of the Nobel Prize to STM (1986), to single-electron and -ion trapping and spectroscopy (1989), to laser trapping and cooling (1997), and to laser femtochemistry (1999).



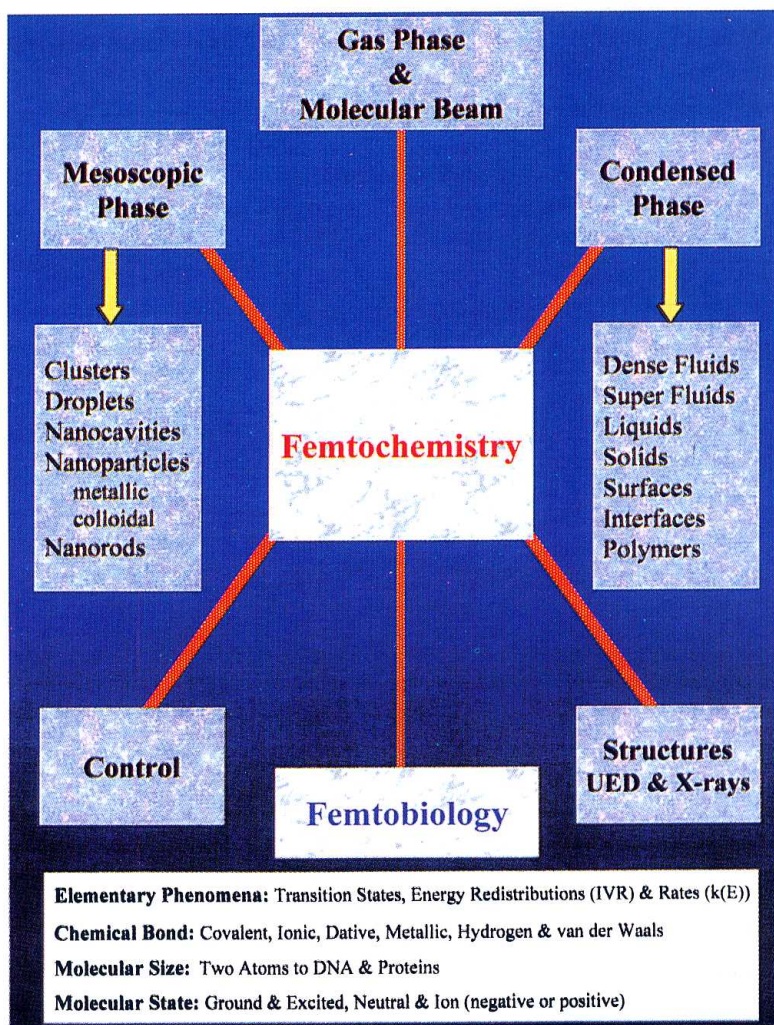


Figure 7. Femtochemistry and the scope of applications.

## II. DYNAMICS AND ARROW OF TIME

### (1) Origins – From Kinetics to Dynamics

#### *The Arrhenius Seminal Contribution*

At the turn of the 20th century, the study of reactivity was dominated by the question<sup>4</sup>: *How do reactions proceed and what are their kinetic rates?* Svante Arrhenius [7] gave the seminal description of the change in rates of chemical

<sup>4</sup> The main focus of prior studies was on the thermodynamics and equilibrium characteristics. Interestingly, chemical equilibrium was already established a century before (1798) by Claude Berthollet, during a visit to the Natron Lakes in Napoleonic times, through his studies of the reaction  $\text{Na}_2\text{CO}_3 + \text{CaCl}_2 \leftrightarrow 2\text{NaCl} + \text{CaCO}_3$  [S. W. Weller, *Bull. Hist. Chem.* **24**, 61 (1999)].

reactions with temperature and formulated in 1889 the familiar expression for the rate constant,

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

which, as Arrhenius acknowledged, had its roots in van't Hoff's (1884) equations [7]. For any two reactants, the rate constant ( $k$ ) depends on temperature ( $T$ ) according to an energy of activation ( $E_a$ ), which is different from the thermodynamic net energy change between reactants and products, and the dependence is exponential in form. ( $R$  is the universal gas constant). If we think of the reaction as a finite probability of reactant A colliding with B, then the rate is simply the collision frequency times the fraction of successful collisions with an energy equal to or more than  $E_a$ . Besides the value of equation (1) through the well-known plots of " $\ln k$  vs.  $1/T$ " to obtain the energy of activation  $E_a$ , Arrhenius introduced a "hypothetical body", now known as the "activated complex", a central concept in the theory of reaction rates: the reaction, because of collisions or other means, proceeds only if the energy is sufficient to exceed a barrier whose energy is defined by the nature of the complex. Since then, various experimental data for different temperatures  $T$  were treated with equation (1), yielding  $E_a$  and the pre-exponential factor  $A$ .

A few years after Arrhenius' contribution, Bodenstein (1894) [7] published a landmark paper on the hydrogen/iodine system, which has played an important role in the development of gas-phase chemical kinetics, with the aim of understanding *elementary* reaction mechanisms. In the twenties, Lindemann (1922), Hinshelwood (1926), Tolman (1920), and others [7&8] developed, for unimolecular gas-phase reactions, elementary mechanisms with different steps describing activation, energy redistribution, and chemical rates. By 1928, the Rice-Ramsperger-Kassel (RRK) theory was formulated, and Marcus, starting in 1952, blended RRK and transition state theory in a direction which brought into focus the nature of the initial and transition-state vibrations in what is now known as the RRKM theory [8].

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 [9].

#### *The London, Eyring and Polanyi Contributions*

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 [10], a breakthrough in thinking not only about the stable structure of the chemical bond, but also about how two atoms can interact at different separations. One year later (1928), for Sommerfeld's Festschrift (60th birthday), London [10] 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 [10], 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, expressed in atomic units of time!* But no one could have dreamed in the 1930's 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 a picosecond (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) [11], in 1935, Eyring, and independently Evans and Polanyi, formulated *transition-state theory*, which gave an explicit expression for Arrhenius' pre-exponential factor [11]:

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

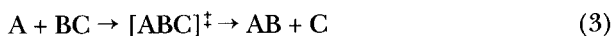
where  $k$  is Boltzmann's constant,  $h$  is Planck's constant and  $Q$  is the partition function. The key idea here is to assume the *equilibration* of the population between reactants and the transition state:  $A + B \leftrightarrow [TS]^\ddagger \rightarrow \text{products}$ . Thus, the rate constant can be related to the equilibrium constant for formation of the transition state,  $K^\ddagger$ , and hence  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ; physically,  $\Delta G^\ddagger$  ( $\Delta H^\ddagger - T\Delta S^\ddagger$ ) in the exponent gives the barrier energy (through  $\Delta H^\ddagger$ ) along the reaction coordinate, and the pre-exponential entropic term which reflects the change in vibrational modes perpendicular to the reaction coordinate. By comparing (2) with Arrhenius' equation (1),  $A$  can be identified;  $E_a$ , the activation energy, and  $E_0$ , the barrier energy, with zero-point energy corrections, are related [8, Laidler]. Kramers' (1940) classic work [11] modified the pre-exponential factor to include friction from the surrounding medium, with transition state theory giving an upper limit, and Casey Hynes, in the 1980's, provided a dynamical theory of friction with emphasis on time scales in the transition-state region and for solvent interaction [11]. In the 1950's, Marcus [11] obtained a transition-state type expression for reactions of electron transfer in solutions with the Gibbs free energy of activation expressing the dependence on solvent reorganization energies. This work was awarded the 1992 Nobel Prize.

According to transition state theory, the fastest reaction is given by  $kT/h$ , which is basically the "frequency" for the passage through the transition state

[Equation 2]. At room temperature this value is  $6 \times 10^{12} \text{ second}^{-1}$ , corresponding to  $\sim 170 \text{ fs}$ ; the time scale of molecular vibrations is typically  $10\text{--}100 \text{ fs}$ . This estimate is consistent with knowledge of the speeds of nuclei and the distance change involved in the reaction. In 1936 the first classical trajectory from Hirschfelder-Eyring-Topley molecular dynamics simulations of the  $\text{H}+\text{H}_2$  reaction showed the fs steps needed to follow the reaction profile, albeit on the wrong PES. Later, Karplus, Bunker and others showed a range for the time scales, ps to fs, depending on the reaction and using more realistic PES's [see 9 and 26].

#### *Transition State and Definition*

In general, for an elementary reaction of the type,



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

The above definition of the transition state follows the general description given by John Polanyi and the author [12], 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,  $\ddagger$ , displayed at the crest of the energy barrier to a reaction. As stated in Ref. 12, even if one restricts one's interest to the over-all 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, 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. This is specially important as we address the energy landscape of the reaction, as discussed in Section IV.

The cardinal choice of the transition state at the saddle point, of course, has its origin in chemical kinetics – calculation of rates – but it should be remembered that this is a mathematical 'single-point' with the division made to define the speed of a reaction [8]. Even in thermal reactions, there is enough of an energy distribution to ensure many types of trajectories. Furthermore, transition state theory is not a quantum theory, but a classical one, because of the assertion of a *deterministic* point. Quantum uncertainty demands some delocalization [8, Hase] and, as mentioned above, the theory invokes the equilibration of reactants and transition state populations, using statistical thermodynamics. In fact, the term transition state is used ambiguously to refer

both to the quasi-equilibrium *state* of the reaction and to the molecular *structure* of the saddle point. As discussed in Ref. 13 [Williams, Doering, Baldwin], the molecular species at the saddle point perhaps could be referred to as the *transition structure*; the *activated complex* is even more descriptive.

The location at the saddle point provides the highest energy that must be reached, defining the exponential probability factor; the dynamics (forces and time scales) are governed by the nature of the TS region. Provided that the energy landscape of the reaction is controlled by a narrow region, the structure of the transition state becomes important in structure-reactivity correlations; rates *vs.* Gibbs energy between the TS and the ground state. (It is also useful in designing TS analogs as enzyme inhibitors and TS complements as catalysts [13]). The position of the TS and its energy relative to that of reactants and products along the reaction path becomes relevant. In the mid 1930's, the Bell-Evans-Polanyi principle gave a predictive correlation between changes in barrier heights and the enthalpies of reactions, especially for a series of related reactions; the TS for an exoergic or an endoergic reaction is very different. In 1955, this led to Hammond's postulate which characterizes a reactant-like TS (so called "early" TS) for exoergic reactions, product-like TS (so called "late" TS) for endoergic reactions, and "central" TS for energy neutral reactions [8, Shaik]. John Polanyi, the son of Michael, formulated some concepts regarding energy disposal in relation to the position of the TS on the PES [14], using molecular dynamics simulations and experimental studies of chemiluminescence.

It should be recognized that selectivities, efficiencies, and stereochemistries are quantified only when the dynamics on the global energy landscape are understood. For example, the picture for simple reactions of a few (strong) bonds being made and broken is changed when the energy surface is nearly flat or there is a significant entropic contribution. Many transition states will exist in the region as in the case of protein folding [13, Fersht]. Finally, in the *transition state*, chemical bonds are in the process of being made and broken. In contrast, for *intermediates*, whose bonds are fully formed, they are in potential wells, typically "troughs" in the TS region. However, the time scale is crucial. In many cases, the residence time in intermediates approaches the fs regime characteristic of TS structures and the distinction becomes fuzzy. Moreover, for a real multidimensional PES, the non-reactive nuclear motions can entropically lock the system even though there is no well in the energy landscape. And the presence of shallow wells in the energy landscape does not guarantee that trajectories will visit such wells.

### *Transition State and Spectroscopy*

Various techniques have been advanced to probe transition states more directly, especially for elementary reactions. Polanyi's analogy [14] of transition-state spectroscopy, from "spectral wing emission", to (Lorentz) collisional line broadening studies, made earlier by A. Gallagher and others [see 12], 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 can be detected.) Emission, ab-

sorption, scattering and electron photodetachment are some of the novel methods presented for such time-integrated spectroscopies, and 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 [15] puts it, *short-time dynamics from long-time experiments*. (The renaissance of wave packet dynamics in spectroscopy, pioneered by Rick Heller, will be highlighted in **Section III4 and III6**). With these spectroscopies in a CW mode, a distribution of spectral frequencies provides the clue to the desired information regarding the distribution of the TS over successive configurations and potential energies. Recently, this subject has been reviewed by Polanyi and the author and details of these contributions are given therein [12], and also in [26].

## (2) Arrow of Time

In over a century of development, time resolution in chemistry and biology has witnessed major strides, which are highlighted in **Fig. 8** [16]. As mentioned before, the Arrhenius equation (1889) for the speed of a chemical reaction gave information about the time scale of rates, and 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 measurement, the hydrolysis of a solution of sucrose to glucose and fructose [8, Laidler]. In 1901, the first Nobel Prize for chemistry was awarded to van't Hoff for, among other contributions, the theoretical expressions (chemical dynamics) which 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 sub-second 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 non-radiative processes were a real advance in view of the fact that they were probing the "invisible", in contrast with radiative glows which were 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 [17]. For this contribution, Eigen and Norrish & 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 pro-

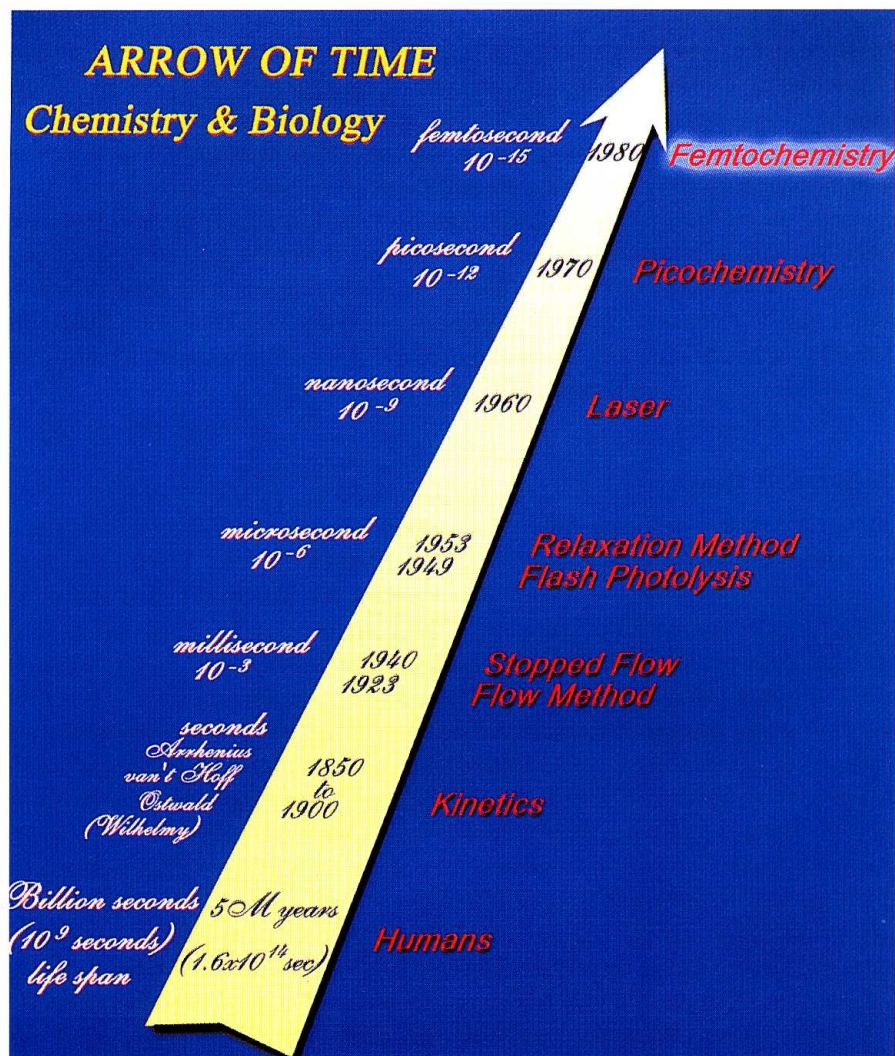


Figure 8. Arrow of Time in chemistry and biology, some steps over a century of development (see text). [Ref. B1]

duced 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 ten nanoseconds. In an ingenious experiment, Abraham and Lemoine (1899) [18] in France demonstrated that the Kerr response of carbon disulfide was faster than ten nanoseconds; it has now been measured to be about two picoseconds (with femtosecond response) [18]. They used an electrical pulse which 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<sub>2</sub> cell and analyzer). The rotation of the analyzer indicated the presence of birefringence in the cell for short optical delays; this birefringence disappeared for pathlengths greater than several meters, reflecting the total optical/electrical response time of 2.5 ns. In this landmark "pump-probe" experiment, they demonstrated in 1899 the importance of synchronization. The setting of time delays was achieved by varying the light path. Bloembergen [18] has recently given a historical perspective of short-pulse generation and Shapiro has reviewed the early developments, including mechanical, streak, spark, stroboscope, and other high-speed photography methods [see Refs. 2 & 18]. As pointed out in these references [18], flash photolysis utilized the above approach 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). Sub-picosecond pulses from dye lasers (Schäfer & Sorokin, 1966) were obtained in 1974 by Chuck Shank and Eric Ippen at Bell Labs, and in 1987 a six fs pulse was achieved [19]. In 1991, with the discovery of femtosecond pulse generation from solidstate Ti-sapphire lasers by Sibbett and colleagues [19], dye lasers were rapidly replaced and femtosecond pulse generation became a standard laboratory tool; the state-of-the-art [19], once 8 fs, is currently about 4 fs and made it into the Guinness Book of World Records (Douwe Wiersma's group [19]). The tunability is mastered using continuum generation [19, Alfano & Shapiro] and optical parametric amplification.

In the late sixties and in the seventies, ps resolution made it possible to study *non-radiative* processes, a major detour from the studies of conventional *radiative* processes to infer the non-radiative ones. As a beginning student, I recall the exciting reports of the photophysical rates of internal conversion and biological studies by Peter Rentzepis [20]; the first ps study of chemical reactions (and orientational relaxations) in solutions by Ken Eisensthal [21]; the direct measurement of the rates of intersystem crossing by Robin Hochstrasser [22]; and the novel approach for measurement of ps vibrational relaxations (in the ground state of molecules) in liquids by Wolfgang Kaiser and colleagues [23]. The groups of Shank and Ippen [19] have made impor-

tant contributions to the development of dye lasers and their applications in the ps and into the fs regime. Other studies of chemical and biological non-radiative processes followed on the ps time scale, the scale coined by G. N. Lewis as the “jiffy” – the time needed for a photon to travel 1 cm, or 33 picoseconds [24].

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 ps 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 [14, 25] were acknowledged by the 1986 Nobel Prize. From state and angular distributions of products, information about the dynamics of the collision was deduced and compared with theoretical calculations of the PES and with molecular dynamics simulations; the goal was to find self-consistency and to deduce an estimate of the lifetime of the collision complex. 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 important area are highlighted in the article by Dick Zare and Dick Bernstein [25] and in the book by Raphy Levine and Bernstein [9]. An overview of femtochemistry (as of 1988) in connection with these other areas is given in a feature article [26] by Zewail and Bernstein.

### III. FEMTOCHEMISTRY: DEVELOPMENT OF THE FIELD

The development of the field is highlighted in this section, from the early years of studying coherence to the birth of femtochemistry and the explosion of research, or, as the report of Ref. 5 puts it, “... *the revolution in chemistry and adjacent sciences.*” 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 [B14] names their contributions in the early stages of development. Here, references are given to the work and explicitly in the Figure Captions.

#### (1) The Early Years of Coherence

When I arrived in the US 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 I had the idea of exploring *coherence* as a new concept in dynamics, intra- and inter-molecular. This proved to be vital and fruitful.



*New Techniques for Molecules*

The Caltech offer included start-up funds of \$50,000 for capital equipment (\$15K for shop services), an empty laboratory of two rooms and an office next to it. A few months before moving to Caltech in May of 1976, I made the decision not to begin with the type of picosecond research I was doing at Berkeley as a postdoctoral fellow. Instead, 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. Prior to the final move, I came down from Berkeley for several visits in order to purchase the equipment and to outline the laboratories' needs for electricity, water, gases and so on; my feeling was that of a man left out in a desert with the challenge to make it fertile. We spent a significant fraction of the \$50K on setting up the apparatus for optical detection of magnetic resonance (ODMR) to study disordered solids. My experience at Penn with Professor Robin Hochstrasser and at Berkeley with Professor Charles Harris was to culminate in these experiments. The key questions I had in mind were: What is the nature of energy migration when a crystal is systematically disordered? Is it coherent, incoherent or partially coherent? Is there a relationship between optical and spin coherence?

While the ODMR apparatus was being built, I was thinking intensely about new laser techniques to probe the coherence of optical transitions (so-called optical coherence). I had the intuitive feeling that this area was rich and at the time had in mind several issues which were outlined in my research proposal to Caltech. Laser experiments were designed with objectives focused on the same issues outlined in the proposal. First, in the work I published with Charles Harris, and alone at Berkeley, the coherence probed had been that of spin (triplet excitons) and I felt that we should directly probe the optical coherence, i.e., the coherence between the excited electronic state and the ground state, not that between two spin states of the same excited state [Fig. 9]. Second, I did not believe that *the time scale* of spin coherence was the same as that of optical coherence. Later, I wrote a paper on the subject which was published in the *Journal of Chemical Physics* (1979) with the title: *Are the homogeneous linewidths of spin resonance and optical transitions related?*

I was convinced that essentially all molecular optical transitions in solids are inhomogeneous, that is, they do not reflect the true dynamics of a homogeneous ensemble, but rather the overlapping effects of sub-ensembles. This was the key point outlined in my research proposal to Caltech. If the new set of laser experiments at Caltech proved successful, we should be able to find the answer to these important (to me) questions. However, the funds remaining were insufficient to realize our dream for the new experiments. Fortunately, Spectra Physics, started in 1961 and now a huge laser company, was proud of a new product and was interested in helping us demonstrate the usefulness of one of the first single-mode dye lasers they produced. At Caltech, we had the pump argon-ion laser, from Wilse Robinson's Laboratory, and added the dye laser we obtained from Spectra Physics with the idea that we would purchase it if the experiments were successful. David Evans of



## Coherent Transients – phase control

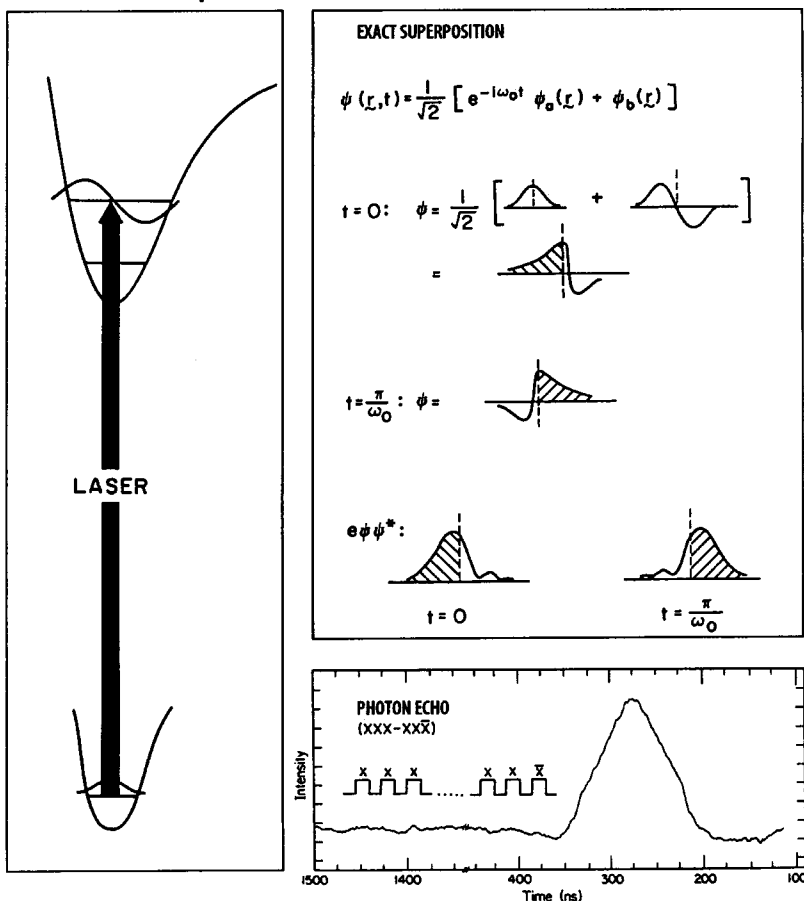


Figure 9. Molecular coherence and dephasing. Coherent transients from the superposition of states, and control of pulse phase (x or  $\bar{x}$ ) in multiple pulse experiments, the optical analog of NMR spectroscopy. The photon echo of iodine gas was observed on the spontaneous emission using the described pulse sequence. [Ref. B9, B13, B22, B23, 50]

Spectra Physics was instrumental in helping us achieve this goal. What was left were the low-temperature cryostat and electronics. We could not afford a real metal cryostat, so we custom-made a glass Dewar that could go down to 1.8 Kelvin. Most of the electronics were obtained on loan for several months. To generate laser pulses we used switching methods developed at JILA (Joint Institute for Laboratory Astrophysics) and IBM. The work at IBM by Dick Brewer's group triggered our interest in using electro-optic switching methods.

We succeeded in making the laser perform according to specifications and began the first experiments with phenazine crystals. This system, phenazine, has unique properties which I learned about in Robin Hochstrasser's laboratory. At Berkeley I published a paper outlining the nature of coherence in multidimensional systems and used phenazine as a prototype experimental

system. Our first laser transient at Caltech was beautiful. Unfortunately, the transient was from the electronics, not from the crystal, but we soon realized this! We decided to abandon this particular system for a while and to try an impurity crystal of pentacene in a host of terphenyl. We also decided to study gases, and some success came our way.

With the theoretical knowledge acquired in handling coherence effects, which requires expertise with density matrix formalism and its manipulation in geometrical frames, I had a novel idea: we should be able to detect *coherence* on the *incoherent* emission at optical frequencies. From many discussions with Alex Pines and Charles Harris at Berkeley, I knew the power of “adding” pulses in NMR and ESR. This idea was successful and indeed we were able to observe the photon echo on the spontaneous emission [Fig. 9] using three optical pulses. Only months after my arrival in May of 1976, we published our first scientific paper from Caltech. This success gave us confidence in the approach and in our understanding of the principles of coherence and its probing in molecular systems. We applied it to larger molecules with success but also encountered some disappointments. This work was followed by a variety of extensions to studies in gases and solids and also in a home-made (from glass) effusive molecular beam. The small group in our laboratory of optical coherence became productive and we had an exciting time. Our group and that of Douwe Wiersma in Holland were then the two most active in these areas of chemical research.

In the meantime, the work on disorder in solids began to yield interesting results and, surprisingly, we observed an unusual change in the degree of energy transfer with concentration, which we published as evidence of Anderson localization, a hot topic in the 1970's. This was followed by detailed studies of several systems and I wrote my first research proposal to the National Science Foundation (NSF). The research was funded! The then program director at NSF, Fred Stafford, was supportive of the effort and we have maintained our support from the Division of Materials Research to this day; the NSF's Chemistry Division continues to support our research. Knowledge of energy transfer was also helpful in another area. Terry Cole, a visiting scholar at Caltech, and I initiated work on the studies of Luminescent Solar Concentrators (LSC) using energy transfer between dyes as a key principle. This idea, too, was successful and funding for this research came in from SERI and from ARCO. The work on LSC resulted, ultimately, in a patent (with Sam Batchelder; issued in 1980) and in several publications. My research group was rapidly expanding.

After a year-and-a-half at Caltech, I was pleased to learn that my colleagues were considering my case for tenure. Tenure was granted a few months later, two years after my arrival at the Institute. I was both appreciative and pleased. We continued research in four areas: optical coherence phenomena and dephasing; disorder in solids; picosecond spectroscopy; and LSC. In my own department, some colleagues were not too excited about ‘this stuff of coherence and dephasing’ – thinking that it was *not relevant to chemistry*! Many chemists on the outside were also unsure what this was all about. In fact, a notab-

le chemist once said publicly at a conference I attended that coherence and dephasing had nothing to do with chemistry! On the physics side, I was invited to numerous conferences, including one in which the Nobel Laureate Willis Lamb asked me to have dinner to discuss our research. This was a special experience!

I was not convinced by these doubts and my faith helped us to continue along with the development. The concept of coherence turned out to be fundamental in femtochemistry, and it is now well accepted that coherence is a key process in the probing and controlling of molecular dynamics. With the success we had with observations and studies of coherence in different systems, I wrote an Account of Chemical Research article, published in 1980, with the title: *Optical Molecular Dephasing – Principles of and Probing by Coherent Laser Spectroscopy*. I felt that the nanosecond time scale we had mastered should be extended to the picosecond time scale, but did not wish to repeat the Berkeley experience with glass lasers. Fortunately, the design for the first sub-picosecond dye laser was reported in 1974 and we decided to build one to study the phenomena of coherence – but now on a shorter time scale.

#### *Optical Analogue of NMR: Controlling the Phase*

From the studies of optical transients, we learned that 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 capable of forming a *coherent* superposition of states. For two states of a transition (say  $\psi_a$  and  $\psi_b$ ), the coherent state can be written as

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

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 [see Fig. 9].

With pulse sequences, we could directly 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,  $\rho_{ab}$ . The term  $\langle a(t) a^*(t) \rangle$  is the population of state  $\psi_a$  and represents the diagonal density-matrix element,  $\rho_{aa}$ ;  $\langle a(t) a^*(t) \rangle$  decays with optical  $T_1$ . We were thus able to demonstrate the power of the optical analogue of NMR pulse techniques in learning about coherence and the origin of optical dephasing in molecular systems of interest to chemical dynamics. This advance changed the thinking of many with the recognition that it was impossible to deduce  $T_1$  and  $T_2$  from measurements of the line width of inhomogeneous transitions.

One feature of this work which 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 which 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 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.

By this time, our group's efforts were narrowing on two major areas. (Dick Bernstein, who was on the Visiting Committee for our Division, hinted that I was doing too much in too many areas!) The work on disorder and LSC was gradually brought to completion. Picosecond spectroscopy of rotational diffusion and energy transfer in liquids were similarly handled. I felt that the latter area of research was too crowded with too many scientists, a characteristic I do not enjoy when venturing into a new area. I must add that I was not too thrilled by the exponential (or near exponential) decays we were measuring and by the lack of molecular information. Our effort began to emphasize two directions: (i) the studies of coherence and dynamics of isolated molecules in supersonic beams and (ii) the development of the optical analogue of NMR spectroscopy. The low-temperature facility was put to use to study the dephasing and polarization of highly vibrationally-excited molecules in the ground state. Coherence in chemical dynamics was occupying my thinking, and I made a detour in the applications that turned out to be significant.

## **(2) The Marriage with Molecular Beams**

The Bell Labs design for the dye laser (passively mode-locked, CW, and cavity dumped) was too restrictive for our use and, even though we published several papers on studies in the condensed phase with 0.6 ps resolution, we decided to change to a new system. The synchronously pumped mode-locked (CW) dye laser allowed for tunability and also for photon-counting detection techniques. The power of single-photon-counting became apparent, and a new laser system, a synchronously pumped, cavity-dumped dye laser was constructed for studies of gas-phase molecular dynamics, but now with the benefit of all the expertise we had gained from building the first system used for studies in the condensed phase and for probing the torsional rigidity of DNA.

Stimulated by the work on coherence, and now with the availability of picosecond pulses, I 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 which 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, and I was familiar with its relationship to the description of radiationless transitions through the work of Joshua Jortner, Wilse Robinson and others. There was much theoretical activity about dephasing, but I felt that they were standard extensions and they did not allow for surprises. We decided on a new direction for the studies of coherence in a supersonic molecular beam.

Rick Smalley came to Caltech in May of 1980 and gave a talk entitled "Vibrational Relaxation in Jet-Cooled Polyatomics". He spoke about his exciting work on the naphthalene spectra. From the line width in the excitation spectra, he inferred the "relaxation time". At the time, the work by Don Levy, Lennard Wharton, and Smalley on CW (or nanosecond) laser excitation of molecules in supersonic jets was providing new ways to examine the spectroscopy of molecules and van der Waals complexes. Listening to Rick and being biased by the idea of coherence, I became convinced that the way to monitor the homogeneous dynamics was not through the apparent width but by using coherent laser techniques. This was further kindled by the need for direct measurement of energy redistribution rates; we were encouraged by Charlie Parmenter, after he had reported on a chemical timing method using collisions as a "clock" to infer the rate of energy redistribution. The first "real" supersonic molecular beam was huge. We did not know much about this kind of technology. However, in a relatively short time, it was designed and built from scratch, thanks to the effort of one graduate student who must have consumed kilos of coffee! The molecular beam and picosecond system were interfaced with the nontrivial addition of a spectrometer to resolve fluorescence in *frequency* and *time*. This was crucial to much of the work to come.

#### *The Anthracene Discovery: A Paradigm Shift*

Our goal in the beginning was to directly measure the rate of IVR (Intramolecular Vibrational-energy Redistribution), 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 these large systems was contrary to the popular wisdom and unexpected. The population during IVR was oscillating coherently back and forth [Fig. 10] 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, now *isolated* in a molecular beam, with many degrees of freedom. I knew this would receive attention and skepticism. We had to be thorough in our experimental tests of the observation and three of us went to the laboratory to see how robust the observation was. We published a Communication in the *Journal of Chemical Physics* (1981). Earlier there had been attempts by another group to observe such a "quantum coherence effect" in large molecules, but the observation turned out to be due to an artifact. Some scientists in the field were skeptical of our new observation and the 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.

We followed the initial publication with several others and the effect became even more pronounced with shorter time resolution. Physicists appreciated the new results. We published a *Physics Review Letter* on the nature of non-chaotic motion in isolated systems, and Nico Bloembergen and I wrote a review (1984) on the relevance to laser-selective chemistry [B21]. We and

other groups subsequently showed the prevalence of this phenomenon in large molecules. As is often the case in science, after the facts and in retrospect, the phenomenon was clear and was soon accepted; to some it even became obvious! 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 show the presence of “quantum coherence effect” in isolated complex chemical systems and only among selected vibrational states. In other words, out of the expected *chaotic motion* in the vibrational and rotational phase space we could see *ordered and coherent motion* despite the presence of numerous vibrational degrees of freedom (from  $S_0$  and  $S_1$  states). This point was theoretically appreciated by only a few scientists. In fact, at one point Stuart Rice and I drafted a paper on the subject, thinking of clarifying the point. At the time, researchers in high-resolution spectroscopy were observing complex spectra and attributing this complexity to chaotic vibrational motion in the molecule. Stuart and I argued that spectral complexity does not mean chaos, and the anthracene experiment was a clear demonstration in real time.

*Second*, the observation demonstrated that coherence had not previously been detected in complex systems, not because of its absence but due to the inability to devise a proper probe. Detection of total absorption or total emission (at all wavelengths) from molecules gives a non-selective window on the dynamics and in this way coherence cannot be detected. This was a key point for the success of the anthracene experiment for which both *time* and *wavelength* were resolved and correlated. For all subsequent work on wave packet dynamics, nuclear motion in chemical reactions, and femtochemistry, this concept of “window probing” was essential. The concept was further elucidated by resolving the phase character. By probing at two different wavelengths, we found that the quantum oscillations exhibit identical periods, but were phase shifted by exactly  $180^\circ$  (i.e., they are out-of-phase) [Fig. 10]. The two wavelengths resolved were those corresponding to emission of the initial vibrational state and to that of the vibrational state to which the population goes by IVR. Thus, if “total detection” was invoked, the in-phase and out-of-phase oscillations will add up to cancel each other and coherence would have remained undiscovered.

*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 “*non-concerted*” i.e., going in a sequential redistribution of vibrational energy. We could also obtain the time scale and the effect of molecular rotations on coherence of the vibrational motion.

*Fourth*, the observation illustrated the importance of the “preparation of non-stationary states” in molecules. This issue was of fundamental importance in radiationless transition theories involving multiple electronic states, and experiments by Jan Kommandeur and by Doug McDonald have shown this interstate coupling. The question of interest to us was: what nuclear states do we

## IVR - Coherent and Dissipative Regimes

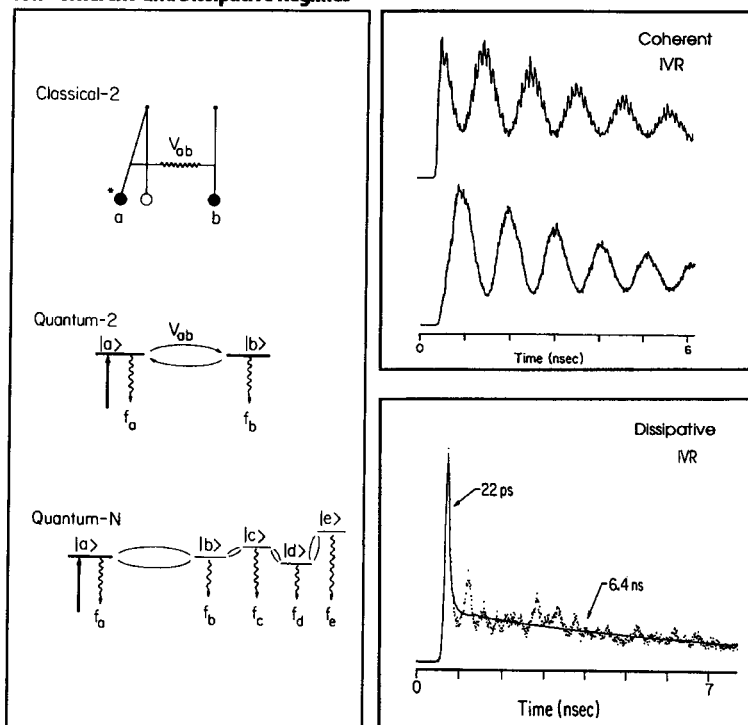


Figure 10. Dynamics of IVR, intramolecular vibrational-energy redistribution. The coherent, restricted and the dissipative regimes. Note the exact in-phase and out-of-phase oscillatory behavior between the vibrational states of the system (anthracene in a molecular beam). The theory for classical and quantum pictures (to the left) has been discussed in detail in the literature. [Ref. 51]; See also ref B20, B21.

prepare in the isolated molecule on a single surface? The anthracene experiment taught us that a coherent source spanning the stationary states can prepare a non-stationary state which evolves with time. Moreover, we can prepare molecules in-phase at time zero to observe the subsequent coherent dynamics. This concept indicates that the description, in terms of Schrödinger's molecular stationary states, is not cardinal and that the time-dependent picture is real and directly relevant to dynamics. Most textbooks describe dynamics in terms of stationary states and it took some time for this concept of a time-dependent description to be appreciated. I recently found a theoretical article by Roy Gordon published in the 1960's touching on similar issues. In femtochemistry, the concept of time-domain dynamics is what describes elementary motions.

*Fifth*, by directly probing coherence and its extent in isolated, complex molecular systems we advanced some concepts regarding the nature of IVR and its regions. We divided the regions of IVR into three basic ones: *no IVR*, *restricted IVR*, and *dissipative IVR*. We also established that the IVR picture of one vibrational state coupled to a continuum of vibrational levels is not adequate. Instead it is a multi-tier coupling among vibrational states.

This work and its implications were published in two series of papers and reviewed in two book chapters.

### *The Successful 036 Laboratory*

The laboratory known as 036 was in the sub-basement of Noyes. 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) reaction rates of a variety of systems. One of our first studies of reactions on the ps time scale, isomerization of stilbene, was stimulated by discussion with Robin Hochstrasser about his work on stilbene vapor at room temperature. He felt that if we could resolve the low-frequency modes in the molecular beam, we would derive a great deal of information on the torsional potential. We resolved these torsional modes. Furthermore, we decided to study the rates as a function of energy and in the process found the barrier for twisting around the double bond and observed coherent IVR in reactions, the first such observation. Even now, stilbene remains a member of our molecular family and continued studies have been pursued by us and others, also on the fs time scale.

The following list highlights some of the work [Fig. 11] done in this initial period from 1981 to 1983: (1) IVR in anthracene and stilbene; (2) *trans-cis* isomerization of stilbene; (3) quantum beats and radiationless transitions in pyrazine; (4) intramolecular hydrogen bonding in methyl salicylate; (5) intramolecular electron transfer in donor-bridge-acceptor systems; (6) IVR and dissociation of intermolecular hydrogen-bonded complexes; and (7) isomerization of diphenylbutadiene and styrene.

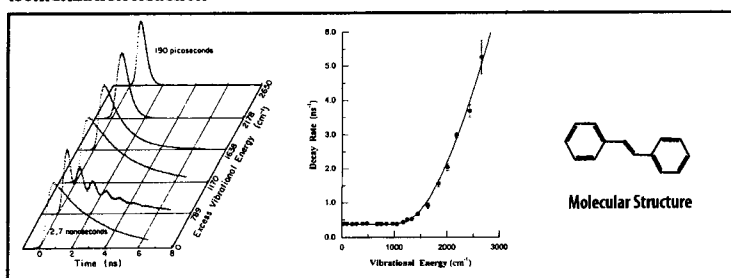
Over the years, in the same laboratory (036 Noyes), members of our group have made new extensions covering the following topics: isomerization in isolated molecules vs. in bulk solutions; nonchaotic multilevel vibrational energy flow; mode-specific IVR in large molecules; IVR dynamics in alkyl-anthracenes; isotope effects on isomerization of stilbene; charge transfer and exciton dynamics in isolated bianthracene; isotope effects on the intramolecular dephasing and molecular states of pyrazine; IVR dynamics in alkylanilines (the "ring + tail" system); mode-specific (non-RRKM) dynamics of stilbene-rare gas vdW complexes; solvation effects on intramolecular charge transfer; IVR dynamics in *p*-difluorobenzene and *p*-fluorotoluene (real time vs. chemical timing); IVR dynamics in deuterated anthracenes; dynamics of interstate coupling in chromyl chloride; dynamics of IVR and vibrational predissociation in anthracene-Ar<sub>n</sub> (*n* = 1,2,3); structural effects on the dynamics of IVR and isomerization in stilbenes; and dynamics of IVR and vibrational predissociation in *n*-hexane solvated *trans*-stilbene. The research resulted in a series of publications.

### *Changing A Dogma: Development of RCS*

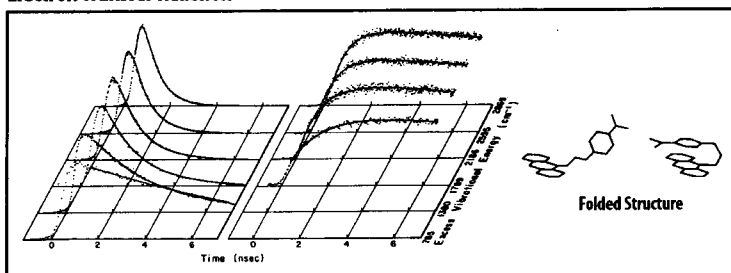
The success with the anthracene experiment made us ask a similar question, but now regarding the coherent *rotational motion* of isolated, complex molecules. There were theories around which discarded its possibility because of



## Isomerization Reaction



## Electron Transfer Reaction



## Microscopic Solvation

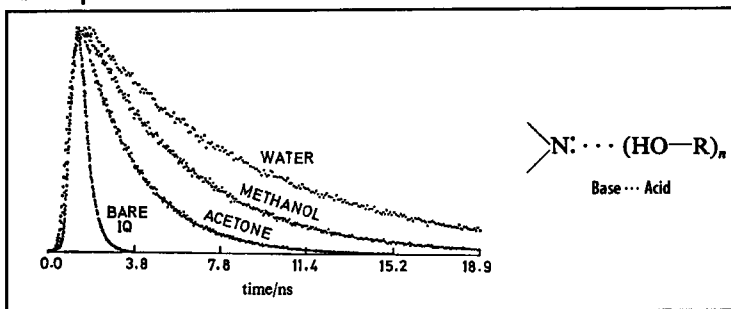


Figure 11. Some examples of studies in the 036 Laboratory. The isomerization of stilbene, intramolecular electron transfer, and solvation in clusters are examples of the studies made in the early 1980's (see text); IQ = isoquinoline. [Ref. B3, 52].

the general belief that Coriolis interactions, anharmonicity and other interactions would destroy the coherence. We worked out the theoretical implications 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 which 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 deduced. Coherence in rotational motion was clearly

evident and could be probed in a manner similar to what we had done with vibrational coherence. The approach was again met with some skepticism regarding its generality as a molecular structure technique. However, it is now accepted by many as a powerful Doppler-free technique; more than 120 structures have been studied this way. The method [Fig. 12] is termed “*Rotational Coherence Spectroscopy (RCS)*” and is successfully used in many laboratories. Some book chapters and review articles have been published on the subject [see **Bibliography**].

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.

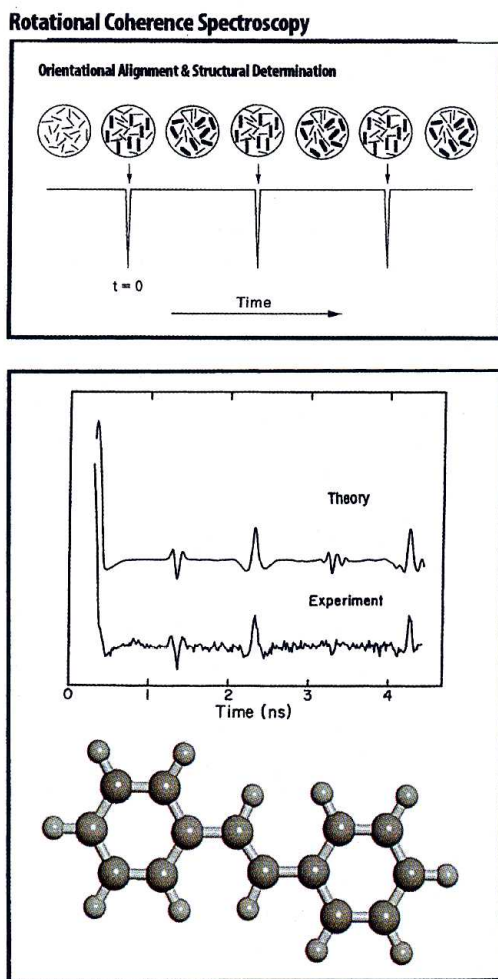


Figure 12. Rotational Coherence Spectroscopy (RCS), the concept and first experimental observation made in a beam of trans-stilbene. [Ref. B7, B13, 53]

### (3) The Transition to the Sub-Picosecond Regime

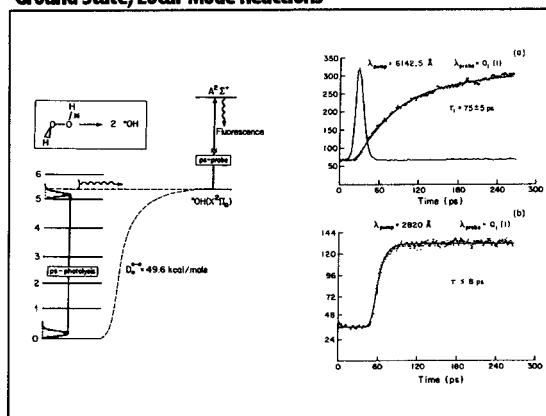
By the early 1980's, our laser time resolution for studying molecules in supersonic jets was 15 picoseconds and detection was made using a microchannel plate ( $\sim 40$  ps). With this resolution, we had already studied reactions such as the isomerization (twisting) of stilbene, charge-transfer, and intra- and intermolecular proton and hydrogen atom transfer. How could we improve the time resolution and study, in a general way, the elementary steps of reactions? The only approach I knew of was to use two pulses, one to "pump" and the other to "probe". Unlike liquid-state studies, where the approach was proven successful, in this case, the density of a molecular beam is very low. Furthermore, it was not clear how to establish the zero of time *in situ* in the molecular beam and how to avoid temporal broadening due to propagation effects.

#### *A New Beam Machine: Pump-Probe Mass Spectrometry*

I thought we should build a second generation beam apparatus to house a time-of-flight mass spectrometer. From the physics literature, it was clear that single-atom detection could be observed using ionization techniques with lasers, and such detection had already been successful with nanosecond lasers. Unlike many nanosecond studies, we should propagate the two picosecond (and later femtosecond) pulses in the *same* direction, otherwise we would lose the ultrashort time resolution! The same beam machine was equipped with optics for laser-induced fluorescence detection. We began a new direction of research in a separate laboratory of our group. The new beam was built and integrated with two independently tunable dye lasers. This proved to be a precursor to the femtochemistry work as this taught us to master pump-probe picosecond and sub-picosecond experiments on chemical reactions. In this same laboratory, we studied with a resolution of a few ps: (1) dissociation reactions; (2) ground-state, overtone-initiated reactions; (3) van der Waals reactions and others [Fig. 13]. We wrote a series of papers on *state-to-state microcanonical rates*,  $k(E)$ , and addressed 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 vibration [Fig. 13]. The coupling between theory and experiment stimulated my interest in

## Ground State, Local-Mode Reactions



## Reaction Rates of NCNO as a Function of Energy

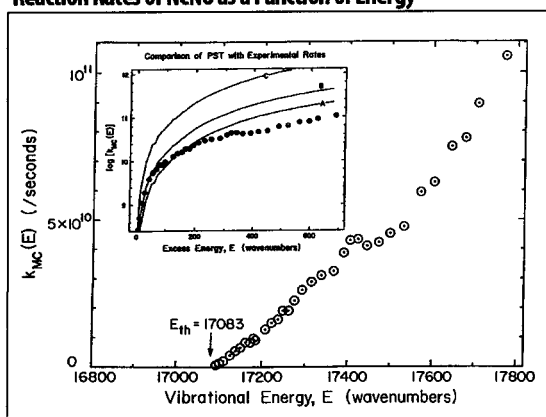


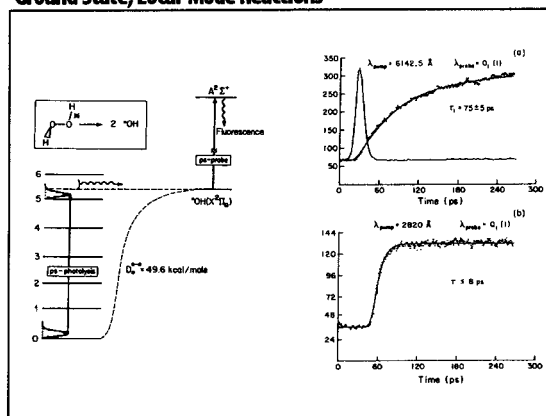
Figure 13. Microcanonical Rates of Reactions: (top) Ground-state reaction of  $\text{H}_2\text{O}_2$  initiated by local-mode excitation; (bottom) the dissociation of  $\text{NCNO}$  as a function of energy, showing the breakdown of conventional phase-space theory at energies above threshold. [Ref. B1, 54]

the nature of transition states which generally live for less than a picosecond. The thirst for even shorter time resolution became real!

### The First ICN Experiment: Sub-picosecond Resolution

In the early 1980's, the technology of pulse compression became available and we ordered, from Spectra Physics, a pulse compressor – a fiber optic arrangement to reduce the laser pulse width to sub-picosecond. The company indicated that it would take them several months to build one, and that the only one available was at Purdue University in the laboratory of Professor Duane Smith, one of the first two graduate students I had at Caltech. I mentioned to Duane my excitement about the experiment, which was intended to *directly* monitor the elementary bond breakage in a molecule, and asked if it was possible to borrow his compressor. The triatomic molecule ICN was chosen because the CN radical could be conveniently monitored by laser-in-

## Ground State, Local-Mode Reactions



## Reaction Rates of NCNO as a Function of Energy

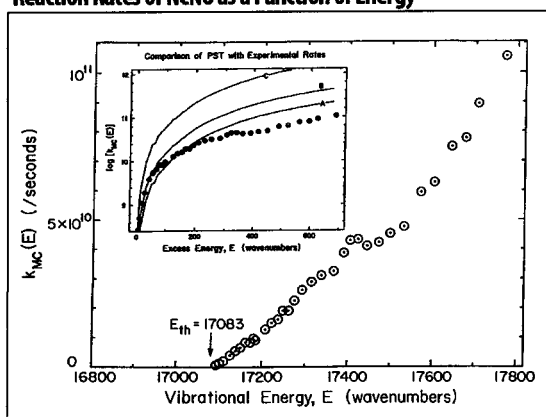


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duced fluorescence; we had been encouraged by the positive experience we had had with CN from NCNO and with earlier ps results on ICN. Also, ICN had been central to studies of dissociation reactions and to photofragment spectroscopy. Previous work, without time resolution, had provided a measurement of the so-called anisotropy parameter  $\beta$  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. Duane shipped the compressor and joined us for two weeks. We observed the first ICN *sub-picosecond* transient, thus establishing the new methodology. In the same year, we wrote a paper which 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  $\sim 10\text{\AA}$  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 fs resolution is the ideal one and that our next step in research should be in this direction.

Several factors influenced the fast entry into femtochemistry. The development in 1981 by Richard Fork, Ben Greene and Chuck Shank of the colliding pulse mode-locked (CPM) ring dye laser took the pulse duration into the 90-fs regime. By 1985, when we were involved in the ICN experiment, 27-fs pulses were generated with the help of intracavity pulse compression. Soon after, in 1987, 6-fs pulses were obtained by amplification and extracavity compression [19]. With such short pulses and with the help of the earlier development of continuum generation by Bob Alfano and Stanley Shapiro [19], continuously tunable fs pulses became available and only (!) required expertise in ultrafast lasers and nonlinear optics.

The interaction with several colleagues was a stimulating force in the initial effort. With Rudy Marcus and Vince McKoy, my colleagues at Caltech, I discussed many experiments and theories, especially on our way to lunch at the Athenaeum, Caltech's faculty club. John Polanyi came to Caltech in 1982 as a Fairchild Scholar. John saw the importance of (CW) transition-state spectroscopy, and his paper in a book I edited (proceedings of the conference in Alexandria) was on this subject, for the reactions  $\text{H} + \text{H}_2$  and  $\text{NaI}$  dissociation (wing emission). For some reason, we did not discuss fs transition-state spectroscopy at this time, but instead we (with John providing all the notes in writing) were interested in intense-laser-field stimulated emission in the  $\text{NaI}$  system and in the field "dressing" of the potentials. I do not know why I did not think of this system as the first one for femtosecond transition-state spectroscopy. This may have been due to the earlier experience we had with the ICN picosecond experiments. Later, the potentials John sent from Toronto were helpful in my thinking of the  $\text{NaI}$  experiment.

At nearby UCLA, the arrival of Dick Bernstein to the area was a real bles-

sing. He was extremely excited about the developments and the possibilities for real-time studies of molecular reaction dynamics. It was at his house in Santa Monica that the word *femtochemistry* was coined, helped by a discussion in the company of his wife Norma and brother Ken. Dick also came to Caltech as a Fairchild Scholar in 1986, and in 1988 we wrote a feature article together (published in *Chemical & Engineering News* [26]). We had great fun writing this article and we learned an enormous amount about molecular reaction dynamics. We also had a genuine collaboration on bimolecular reactions and published a paper in 1987. Dick came to Caltech again in 1990, but sadly died before ending his sabbatical; a number of experiments, particularly the new direction of surface femtochemistry, were designed as part of our plan. Finally, the collaboration I had with Rich Bersohn, while he was at Caltech as a Fairchild Scholar, was enlightening. We discussed the classical picture of fs spectroscopy of dissociating molecules, and Rich and I wrote a theoretical paper on this subject.

#### (4) The Femtosecond Dream

##### *A Piece of Good Fortune*

To achieve the fs 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 establishment of fs lasers and molecular beam technologies required a “quantum jump” in support. Shaul Mukamel invited me to a workshop in Rochester (October 1985) on intramolecular vibrational redistribution and quantum chaos. I spoke about “IVR and chemical reactivity”, and there in the audience were two program directors from the Air Force Office of Scientific Research: Larry Davis and Larry Burggraf. They requested a preliminary proposal immediately, and I sent one in October, followed by a complete proposal in January of 1986.

The proposal was funded and approved in August of 1986, to start in November of the same year. Larry Davis saw to it that we could order the equipment needed as soon as possible and made the necessary arrangements to do so; AFOSR continues to support our program. We did not have laboratory space to house the new equipment, but Caltech responded. Fred Anson, our Division Chairman at the time, arranged for the space (which once housed the X-ray machines of Linus Pauling) and Murph Goldberger, our President, provided funds for the renovation without delay – Murph appreciated the physics and Fred saw the importance of the new research to chemistry. By Thanksgiving (1986), we entered the new laboratory, and the CPM laser was operational at the “femtosecond party” on December 11, 1986. We focused again on the ICN reaction, but this time on the fs time scale in FEM-TOLAND I.

##### *The Classic Femtosecond ICN Discovery*

The goal of the ICN experiment was to resolve in time the transition-state configurations *en route* to dissociation:

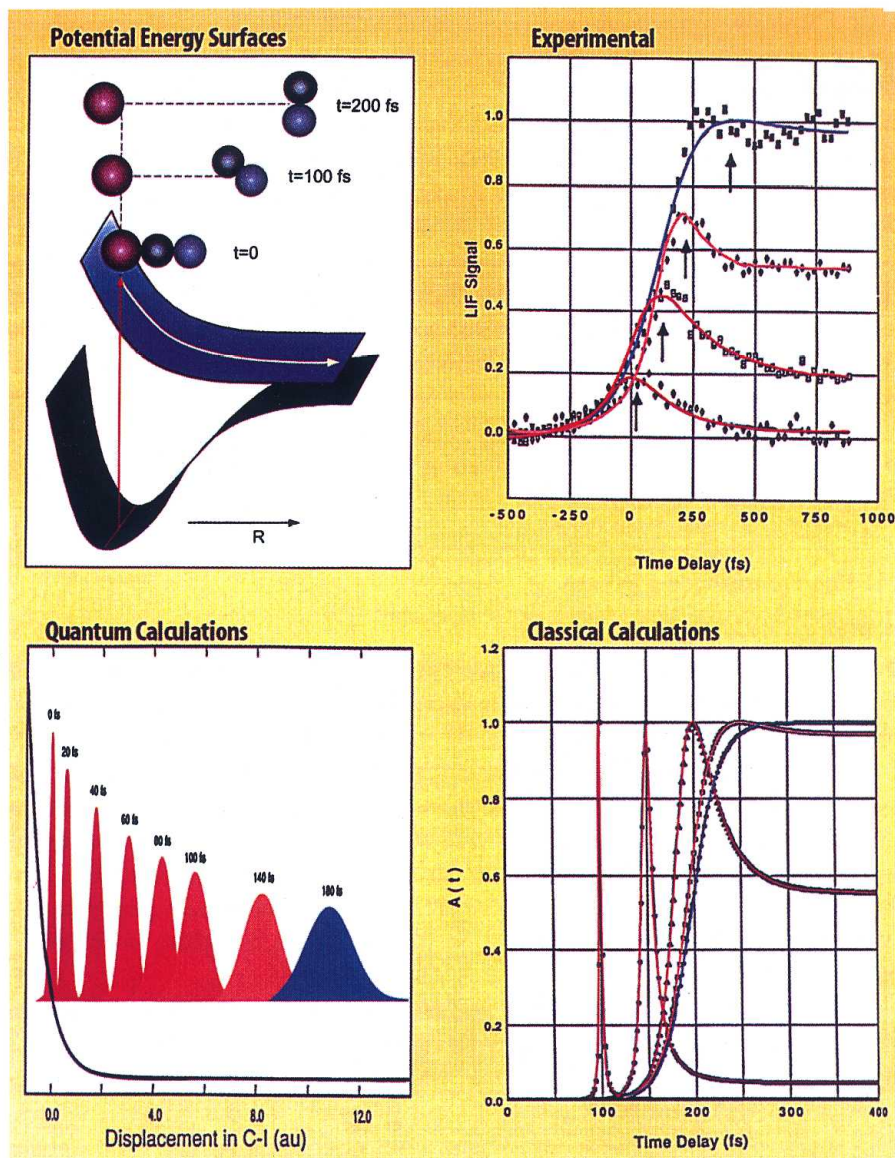


Figure 14. Femtochemistry of the ICN reaction, the first to be studied. The experimental results show the probing of the reaction in the transition state region (rise and decay) and the final CN fragment (rise and leveling) with precise clocking of the process; the total time is 200 fs. The I fragment was also detected to elucidate the translational energy change with time. Classical and quantum calculations are shown (see text). [Ref. B1, B4, B6, B14, B16, B18, B19, B28, 55]



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  $\text{I} \cdots \text{CN}^{\ddagger}$  [Fig. 14]. The first  $\text{I} \cdots \text{CN}^{\ddagger}$  transient surprised us, but after long and late hours of discussions and control experiments it became clear that, indeed, the transition



configurations or the final products could be separately monitored in real time. 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, as discussed in the prologue. The basic observations made [Fig. 14] in the ICN experiment could be related to the fs nuclear dynamics; the delayed appearance of the CN (on-resonance) and the build-up and decay of transition configurations (off-resonance) was understood using simple classical mechanics and even a helpful kinetic picture of  $A \rightarrow B \rightarrow C$ , 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:

$$\tau = \int_{R_0}^R \frac{dR'}{v(R')} \quad \tau^\ddagger = \frac{\Delta V(R^\ddagger)}{v(R^\ddagger)|F(R^\ddagger)|} \quad (6)$$

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 ( $\tau$ ) 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 fs resolution. This experiment on the dynamics of bond breaking and another one on the dynamics of bond making ( $H + CO_2 \rightarrow OH + CO$ ) events were generally well received by colleagues in the scientific community worldwide. They even had impact on the public press with significant write-ups in popular newspapers and magazines such as *New York Times*, *Los Angeles Times*, *Discover*, ... etc. Isaac Asimov, H. C. von Baeyer, Gary Taubes, Philip Ball, and other notable science writers gave an exposition of this published work. Many books and textbooks referred and continue to refer to this 1987 discovery.

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

$$\Psi(R,t) = \sum_i c_i \cdot \psi_i(R) \cdot \exp(-iE_i t / \hbar) \quad (7)$$

which evolves in time, similar to the two-level problem [Equation 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 [Equation 7] give rise to the interferences (quantum coherence) 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 fs 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 1920's [Fig. 4] 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<sup>5</sup>; Sections III4 and III6 highlight the 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 for 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 [Fig 14]. The model described the experimental trends quite well, just as did the quantum picture. 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  $\delta$ -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.

#### *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

<sup>5</sup> Schrödinger wrote a theoretical paper [*Naturwissenschaften* 14, 664 (1926)], pointing out the transition from micro- to macro-mechanics using the superposition of eigenstates. There was a correspondence between Schrödinger and Lorentz on this problem and the difficulty of making wave groups or wave packets.

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 ionic) along the reaction coordinate, I thought we would have fun with these systems. Moreover, their unique historical position in crossed molecular beam experiments ("The Alkali Age") made them good candidates for the "femto age". The reaction of NaI, unlike ICN, involves two electronic coordinates and one nuclear coordinate, the separation between Na and I. 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 [Fig. 15] and made us feel very confident about the ability of FTS to probe transition states and final fragments. The results also illustrated the importance of coherent wave packets in quasi-bound systems. The NaI experiment was a watershed event leading to an entirely new *paradigm* in the field of femtochemistry and establishing some new concepts for the dynamics of the chemical bond.

*First*, we could show experimentally that the wave packet was highly localized in space,  $\sim 0.1\text{\AA}$ , 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 – the world of 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 fs 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, and compellingly demonstrated that conversion from the energy space to the time domain is not needed.

*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 1930's, Linus Pauling's description of this bond was static at equilibrium; only now can the dynamics be described 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

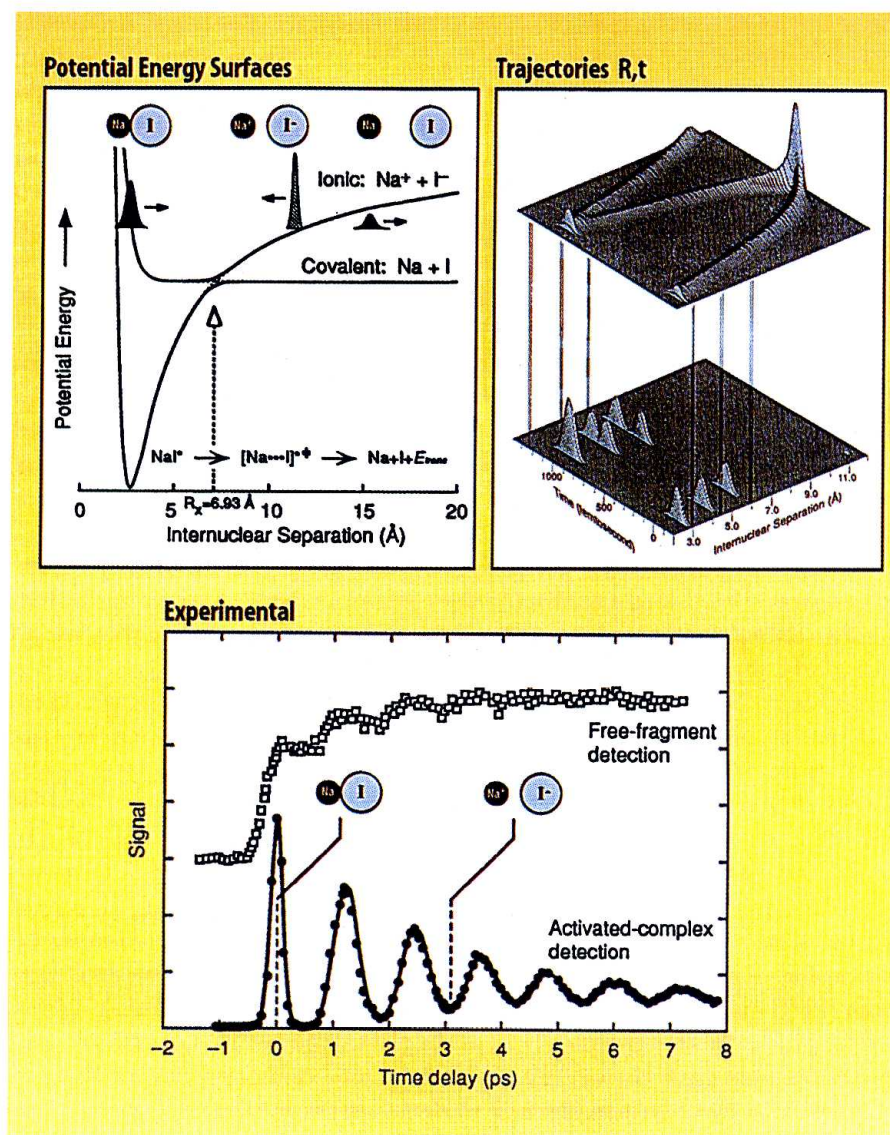


Figure 15. Femtochemistry of the NaI reaction, the paradigm case. The experimental results show the resonance motion between the covalent and ionic structures of the bond, and the time scales for the reaction and for the spreading of the wave packet. Two transients are shown for the activated complexes 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 (top). [Ref. B1, B4, B12, B14, B17, B19, B28, 56]

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*, London); (2) direct observation of recurrences (echo-type), reflecting rephasing at long times ( $t = 20\text{--}40 \text{ ps}$ ), and their relationship to quantum interference effects due to the resonance behavior of the motion on the co-

valent and ionic potentials (this work was published in Chemical Physics Letters); (3) studies of the effect of the velocity of the nuclei on the crossing-to-products probability, providing the interaction matrix element for the coupling between the covalent and ionic potentials, and the classical and quantum treatment of the dynamics (these studies were published in the Journal of Physical Chemistry and 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 the 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.

#### *The Saddle-Point Transition State*

Our next goal was to examine reactions governed by multidimensional (nuclear) potentials, starting with “barrier reactions” which 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. The IHgI system was the so-called “gift experiment” I suggested to a new postdoctoral fellow in our group, who joined us in 1988 from Ken Eisenhal’s group. Stunning observations were made – the product HgI was *coherently* formed from the transition state [Fig. 16]. Also, the transition state, which absorbs a probe fs pulse in the red, as opposed to the HgI product which absorbs in the UV, was found to live for 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 coherence of rotational motion (real-time alignment) and learned about the geometry of the (initially prepared) transition-state, activated complex IHgI\*<sup>‡</sup>.

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 [Fig. 16] in our group addressing, in depth, the actual meaning of classical TS structure (see Section IV). Features of this reaction were similarly 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*, coherent nuclear motion can be observed on *multi-dimensional surfaces* involving multiple-bond breakage (or formation). *Second*,

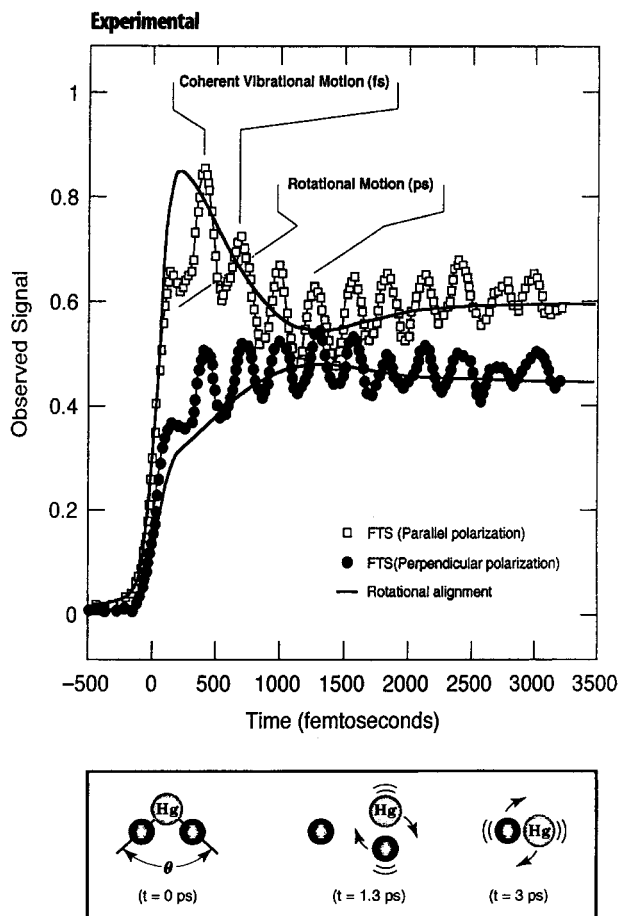
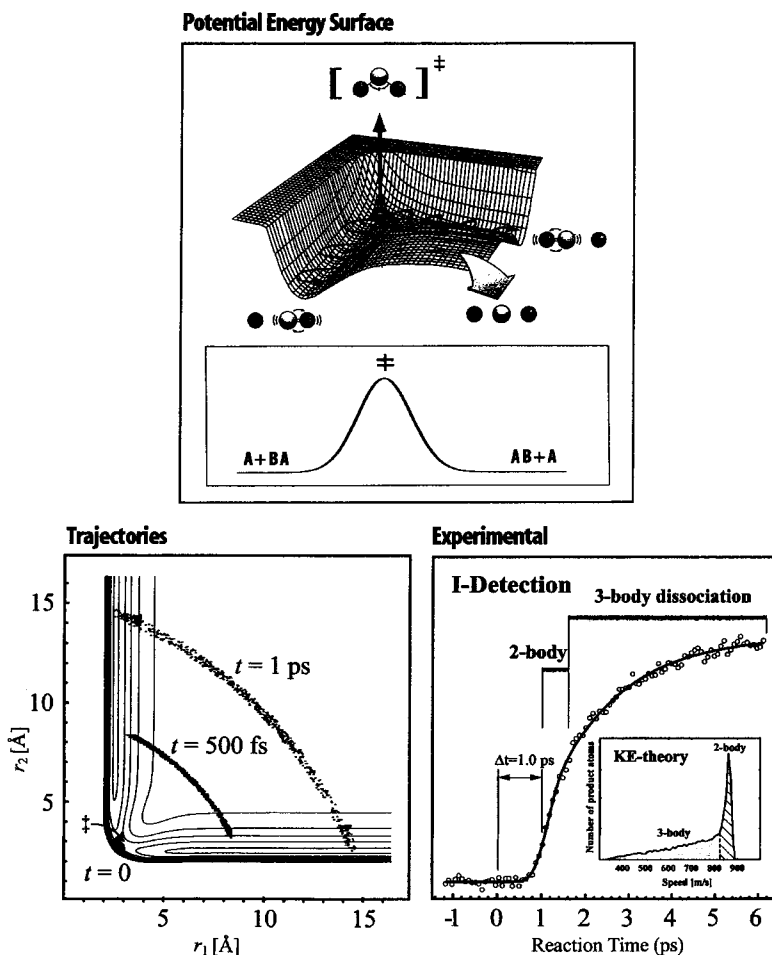


Figure 16. Femtochemistry of the IHgI reaction, the saddle-point transition state (barrier reactions). The experimental results show both the coherent vibrational and rotational motions of the reaction (A, above). The transition state  $\text{IHgI}^{\ddagger}$  and final fragment HgI were probed. We also probed the I fragment and the change of translational energy with time. The classical trajectory calculations are shown in (B, next page), 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 done (not shown). This ABA system is a prototype for saddle-point transition states. [Ref. B1, B4, B6, B10, 57]

coherence survives the entire reaction journey, even in multi-dimensional systems, and yields selective *coherence-in-products*. *Third*, for the first time, a *saddle-point TS* can be seen evolving in real time. *Fourth*, the *TS* can be aligned (oriented) at zero time and seen evolving into rotations of the diatom (AB) and the translation of the A and AB fragments – the vibrational (scalar) and rotational (vectorial) motions were easily separated using polarized fs pulses.

#### *The Uncertainty Principle Paradox*

At the time when I was giving lectures on the above examples of elementary reactions, some were raising a question about the “energy resolution” of the fs experiments: *How can a broad-energy pulse probe a sharp resonance?* In the con-



ventional teaching on spectroscopy of “eigenstates”, one thinks of stationary states and their populations (diagonal elements of the density matrix [Equation 4]), but now we must think of coherent states. 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 [Fig. 17]. Serendipity was at work. We were initiating studies of the FTS of  $\text{CdI}_2$  (from the family of  $\text{HgI}_2$ ) and instead observed the wave packet motion of  $\text{I}_2$ , made from the samples of  $\text{CdI}_2$  without our knowledge! It turned out that when we heated  $\text{CdI}_2$ , we made  $\text{I}_2$ , which gave us striking oscillatory transients. 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  $\text{I}_2$ ; the time scales were separated (fs vs. ps) and the vibrational (scalar) and rotational (vectorial) motion 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

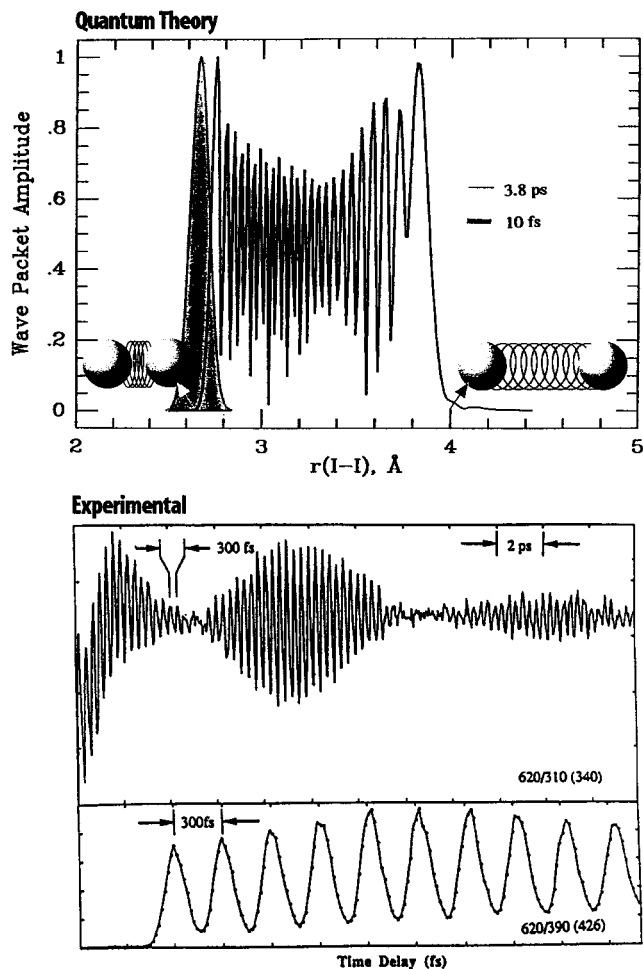


Figure 17. Femtosecond, real time observation of the vibrational (and rotational) motion of iodine. The experiments show the anharmonic nature of the bound motion. Quantum theory indicates the limit for creating a localized wave packet on the fs time scale. The localized wave packet describes the classical spring motion. [Ref. B1, B6, B17, B18, B25, 58]

study of the ICl system. It became evident that: (1) *the uncertainty in energy for short pulses works in our favor*, and the shorter the pulses, the better the 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* (London) and detailed later in the *Journal of Chemical Physics*. Because the initial experiments were made on a diatomic molecule, the significance of this piece of work was originally missed, until later when many complex systems showed surprisingly similar behavior. The real message of this I<sub>2</sub> 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.



*Bimolecular, Bond Making & Breaking: Bernstein's Passion*

Bimolecular reactions were ready for a femtosecond treatment, to observe the “simultaneous” processes of bonds being broken and formed. With Dick Bernstein (1987), we had studied the  $\text{IH}/\text{CO}_2$  system. The problem was that, for bimolecular reactions, the transient 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 HI and  $\text{CO}_2$  in a single molecular beam. But now, with the two reagents 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 given 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 termed this the “birth of OH from  $\text{H} + \text{CO}_2$ ”. Wittig’s group improved the time resolution and studied the energy dependence of the rates. **Fig. 18** gives a summary for this system.

The  $\text{H} + \text{CO}_2$  *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*  $\text{HOCO}^\ddagger$  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  $\tau$  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 redistribution with the nuclei essentially “frozen” in configuration. Obtaining  $\tau$  directly is critical for the nature of the *transition state/intermediate*. This is particularly true when  $\tau$  is much longer than the vibrational and rotational periods, and all other methods will fail in deducing  $\tau$ . *Third*, it provided a direct *test of theory* at the *ab initio* level. High quality *ab initio* calculations of the PES and dynamics have been made available by David Clary, George Schatz, John Zhang and many others. Theory compares favorably with experiments showing that resonances must be considered – the vibrations of HOCO bottleneck the trajectories. The reaction  $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$  is one of the key reactions in both combustion and atmospheric chemistry, and represents the most studied 4-atom reaction, both theoretically and experimentally [see Ref. 27].

We constructed FEMTOLAND II, and I thought it would be interesting to examine “halogen bimolecular reactions”. Precursors, of which the  $\text{H-Br}/\text{I-I}$  system is a prototype, were chosen to study bimolecular halogen atom + halogen molecule reactions. Upon breaking the HBr bond, the hydrogen goes many ångströms away from the field of the reaction (in femtoseconds) and we are left with the  $\text{Br} + \text{I}_2$  collision. This halogen reaction had a history in crossed molecular beam experiments and comparison with real-time experimental results would be interesting. The  $\text{Br} + \text{I}_2$  reaction was examined and found to occur through a sticky ( $\sim 50$  picoseconds) collision complex. It is a stable intermediate of  $\text{BrII}$ , and there is no other way we know of to deter-

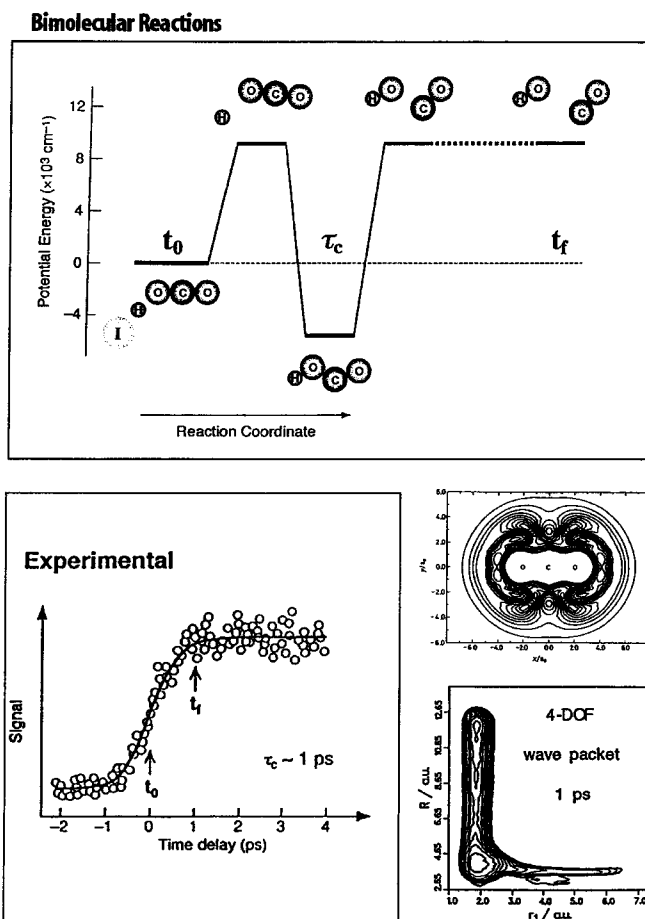


Figure 18. Femtochemistry of the bimolecular  $\text{H}+\text{CO}_2$  reaction. The precursor in this molecular beam experiment is  $\text{HI}/\text{CO}_2$  in a van der Waals complex. The initial experiments utilized ps pulses, but later sub-ps pulses were used (see text). Theoretical *ab initio* calculations of the PES and the dynamics (classical, semiclassical and quantum wave packet) have all been reported; the PES and wave packet calculations are from the work of D. Clary, G. Schatz and J. Zhang. [27] The transit species  $\text{HOCO}^\ddagger$  lives for  $\sim 1$  ps. Similar studies were made of reactive  $\text{Br}+\text{I}_2$  and of the inelastic collision between  $\text{I}$  and  $\text{CH}_3\text{I}$ . [Ref. B1, B5, B10, B16, B19, 59]

mine its lifetime and dynamics. We examined classical trajectories of motion and compared them with the experimental results. In more recent work, the McDonald 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. The analogy between full-collision ( $\text{Br} + \text{I}_2$ ) and half-collision ( $h\nu + \text{I}_2$ ) dynamics was based on the change in bonding, and we used frontier orbitals to describe such an analogy. 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  $\text{CH}_4 + \text{O} \rightarrow \text{CH}_3 + \text{OH}$ , using  $\text{CH}_4 \cdot \text{O}_3$  as a precursor.

*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. I proposed the idea in 1991 in a Faraday Discussion paper [B17], 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, both on 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, with a group of graduate students and post-doctoral fellows participating. In a Nature paper in 1997, we reported our state-of-the-art experimental development of the methodology. We also developed a “difference-method” which allows us to record the structure of radicals, carbenes and intermediates, and with higher sensitivity, as discussed below in **Section III6**.

*Clusters, Dense Fluids & 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 to 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. I find complex reactions 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.

*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, [Equation 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 [29] was an important contribution, as it pointed out the linkage between “spin” and “optical” coherence experiments: even in the absence of a magnetic field, used in the former, one can use a rotating frame picture to describe such optical 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 [B9] 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 1970's, well developed theoretically and heavily imbedded in theories of radiationless transitions formulated to explain the origin of non-radiative decays. Wilse Robinson, Joshua Jortner, Stuart Rice and many 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 preparing a doorway state which "dephases" and "relaxes" depending on electronic coupling matrix element, Franck-Condon factors and the density of states [30].

For IVR [Section III 2], 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 non-stationary *vibrational* packet, with the role of rotations and vibrational couplings explicitly expressed. The probability of being in the initial state  $\psi_0$  is:

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

where the sum is over a product of coefficients  $\alpha$ , and displays the interference of states  $i$  and  $j$ , together with their damping rate  $\Gamma$ . This treatment was useful because: (1) it gives a direct view of IVR, from the initial non-stationary 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. On the other hand, selectivity provides rich information on the nature and extent of IVR, the level structure and the phase changes; and (3) it shows that  $P(t)$  is a measure of vibrational chaos, defining what we called restricted or nonchaotic IVR – coherence among vibrational states of a *single* electronic potential. Similarly, we considered the theory for rotational coherence using polarization-analyzed probes. This was treated in a series of papers with focus on the phenomenon of pure rotational coherence and its utility for molecular structural determination, and the rotational dephasing time.

At the time of the first femtochemistry experiment, I was thinking of the coherent state – wave packet – as an extension of the above picture. However, the span of states is now sufficient to create a localized, in R-space, atomic-scale wave packet [Equation 7]; see also Section III.6. We needed a classical picture to connect with Newtonian mechanics, a simplified picture of the motion. The first of such models was published after we considered the theoretical treatment of absorption of fragments *during* reactions. We obtained the following expression:

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

where  $C$  is a constant and  $W = V(t) - V(t^\ddagger)$  is the potential (or more general-

ly, the difference of the two potentials probed);  $\delta$  is a half-width of the pulse (and damping). For exponential repulsion,  $V = E \operatorname{sech}^2(vt/2L)$  with  $L$  defining the length scale and  $v$  being the speed at the total energy  $E$ . Accordingly, the time for bond breakage can be related to FTS observables [Section III4]:

$$\tau_{\text{BB}} = (L/v) \ln(4E/\delta) \quad (9b)$$

This expression defines bond breakage time when the potential drops to a value of  $\delta$ . The model is basic and describes the reaction trajectory  $R(t)$  or  $\tau(R)$ . It provides a simple connection between observations and the dissociation time, transition-state lifetime, and the forces of the potential [see Equation 6 and Fig. 14]. While Dick Bernstein was at Caltech, we extended the model to obtain the potential using an inversion approach. We published two papers on the subject. Peter Sorokin and colleagues at IBM have addressed different limits of the classical regime in connection with their original studies of fs transient absorption of dissociation [B50].

Next, we considered the treatment of the effect of alignment and orientation on femtochemical reaction dynamics. I considered the time evolution of alignment and coherence for a single rotational angular momentum and then averaged the different trajectories to define the coherence time;  $\tau_c$  (in ps) becomes simple and equal to  $2.2[B < E_R >]^{-1/2}$ , where  $B$  is the rotational constant and  $< E_R >$  is the average thermal rotational energy ( $\text{cm}^{-1}$ ) produced in the reaction fragment(s). We applied this to reactions and I wrote a paper on the subject, published in 1989 [B18]. This was followed, in collaboration with Spencer Baskin, by a paper describing the 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 [31] reformulated the time-dependent picture for applications in spectroscopy, and Jim Kinsey and Dan Imre [31] 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 [31] and, subsequently, by many others. In Section III6, we discuss the contributions made in the 1980's 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. There is a parallelism between the experimental diversity of applications in different areas and the impressive theoretical applications to many experiments and systems. This is summarized in the (1996 Nobel Symposium) book edited by Villy Sundström on Femtochemistry and Femtobiology [28]. 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 [30]) Jortner provides a unifying over-

view of molecular dynamics in femtochemistry and femtobiology, and Mukamel gives an exposition of a general approach using the density matrix formalism. In the same volume, Clary presents the state-of-the-art in quantum theory of chemical reaction dynamics while Marcus and Casey Hynes review transition state theories for rates and dynamics.

Theory and experiment are now hand-in-hand, and many laboratories are doing both. For elementary chemical reactions, the above classical/quantum picture captured the essence of the observation and in many cases the comparison between theory and experiment was tested critically. For complex systems, our theoretical effort has taken on a different 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 [32].

### *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 the book chapter I wrote for the volumes edited by Manz and Wöste [B6] and in the two volumes of our collected works [16].

At Caltech, over the years, we have constructed different types of lasers depending on the particular development and the resolution needed, picosecond to femtosecond [see Fig. 19]; one apparatus is shown in Fig. 5. Since 1976, and in evolutionary order, these are:

- (1) Passive mode-locked, and cavity-dumped, dye laser (pumped by a CW argon ion laser); Ippen and Shank cavity design. Pulse characteristics: 615–625 nm, 2.4 ps (and 0.7 ps), 2 nJ, 100 kHz repetition rate.
- (2) Synchronously pumped, mode-locked dye laser system (pumped by an actively mode-locked argon ion laser). Pulse characteristics: 550–600 nm, 3.1 ps, 1.8 nJ, 82 MHz repetition rate.
- (3) Mode-locked argon ion laser. Pulse characteristics: 514.5 nm, 150 ps, 12 nJ, 82 MHz repetition rate.
- (4) Synchronously pumped, cavity-dumped dye laser (pumped by a mode-

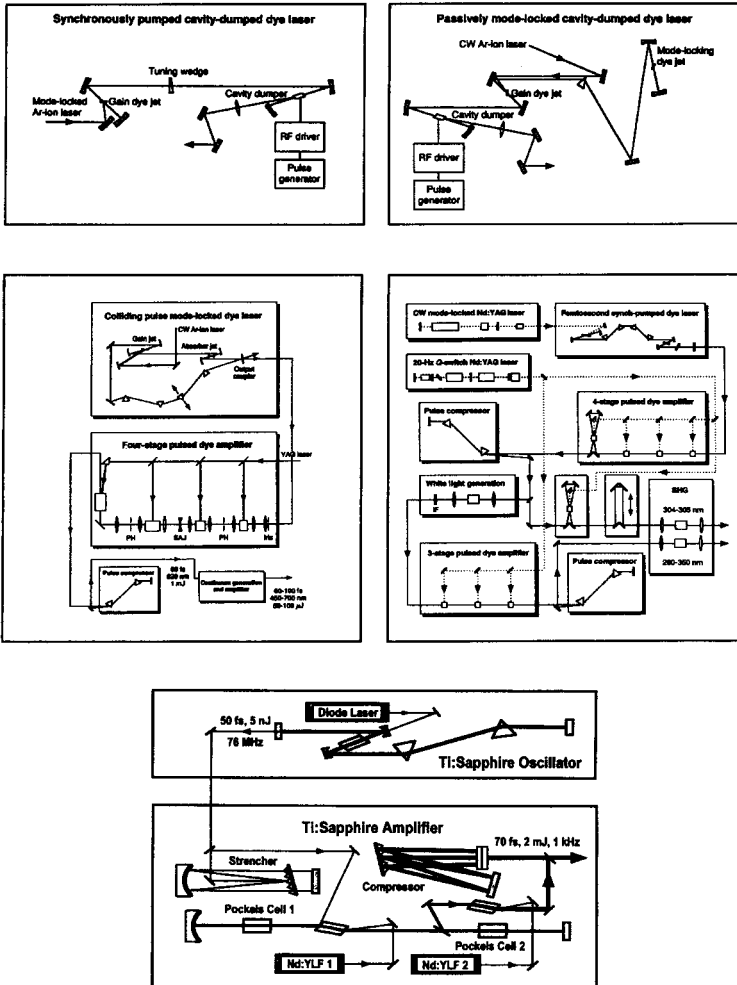
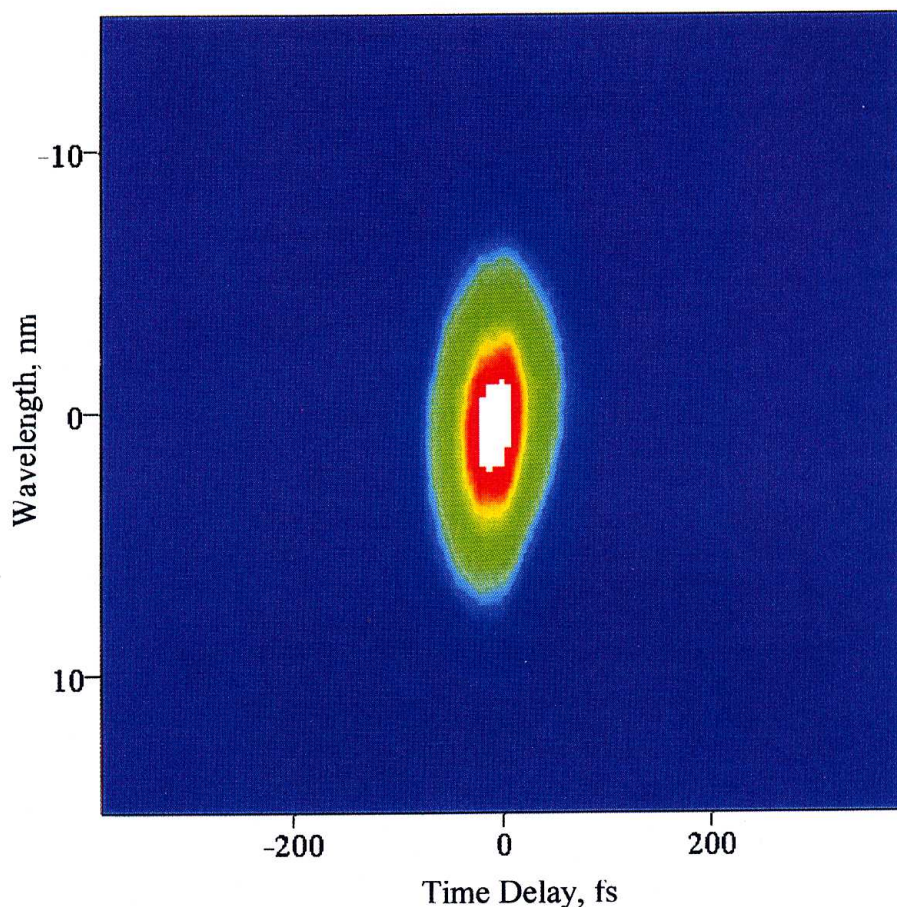


Figure 19. Examples of (A, above) the laser systems utilized in different laboratories (for more details see text and Ref. B6) (B, next page) the two-dimensional (time & wavelength) correlated pattern of a fs pulse (M. Chachisvilis, unpublished work from this laboratory).

locked argon ion laser). Pulse characteristics: 550–750 nm, 15 ps, 20 nJ, 4 MHz repetition rate.

- (5) Mode-locked (CW) Nd:YAG laser which synchronously pumps two dye lasers, with two amplifiers pumped by a 20 Hz Q-switched Nd:YAG laser. Pulse characteristics: 550–750 nm, 3–5 ps, ~ 1 mJ, 20 Hz repetition rate.
- (6) Dye lasers as described in (5) with an extra-cavity pulse compressor (using a fiber-grating optics arrangement) to obtain ~ 0.4 ps pulses.
- (7) Colliding-pulse mode-locked (CPM) ring dye laser (pumped by a CW argon ion laser), and amplified in a four-stage dye amplifier pumped by a YAG laser. A compression at the output of the amplifier was also used. Pulse characteristics: 615–625 nm, 70 fs, ~ 0.5 mJ, 20 Hz repetition rate.
- (8) Synchronously pumped, cavity-dumped dye lasers (two), pumped by a



Q-switched, mode-locked Nd:YAG laser. Pulse characteristics: 550–750 nm, 50 ps, 10  $\mu$ J,  $\leq$  1000 Hz repetition rate.

- (9) 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. Pulse characteristics: 500–700 nm, 150 fs, 1 mJ, 20 Hz repetition rate.
- (10) CPM laser-amplifier system similar to (7), used for ultrashort electron pulse generation. Pulse characteristics: 615–625 nm, 60 fs, 1 mJ, 30 Hz repetition rate.
- (11) Ti:sapphire laser system, Sibbett-type, argon-ion pumped; Ti:sapphire amplifier pumped by Nd:YAG laser. Pulse characteristics: 750–850 nm, 50 fs, 0.7 mJ, 1 kHz repetition rate; one OPA system.
- (12) Ti:sapphire laser system; oscillator, diode pumped and amplifier (Ti:sapphire) Nd:YLF (2) pumped – all solid state (no gas lasers). Pulse characteristics: 750 nm to 850 nm, 50 to 100 fs, 2 mJ, 1 kHz repetition rate. With two Optical Parametric Amplifiers (OPA), the tunability 1.1  $\mu$  to 2.6  $\mu$ , with nonlinear conversions, 200 nm to 2.6  $\mu$ .



- (13) Ti:sapphire laser system, same as (12), 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 auto-correlation 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 non-linear 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 2-D image [Fig. 19]. 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 for selectivity and sensitivity, 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 electron transfer in isolated bimolecular reactions and in clusters. For absorption-type measurements, we introduced non-linear 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 detection methods are: energy-resolved and ZEKE photoelectron spectroscopy, Coulomb explosion, ion-electron coincidence ionization techniques, absorption and photodetachment spectroscopy. The range of wavelength is from the IR to the far UV. Absorption, emission, reflection, ionization, and diffraction have all been involved [Fig. 6].

### (5) Femtocopia – 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 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. Fig. 20 gives a summary of the different areas studied at Caltech with chronological flow from the south to the north!

#### *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

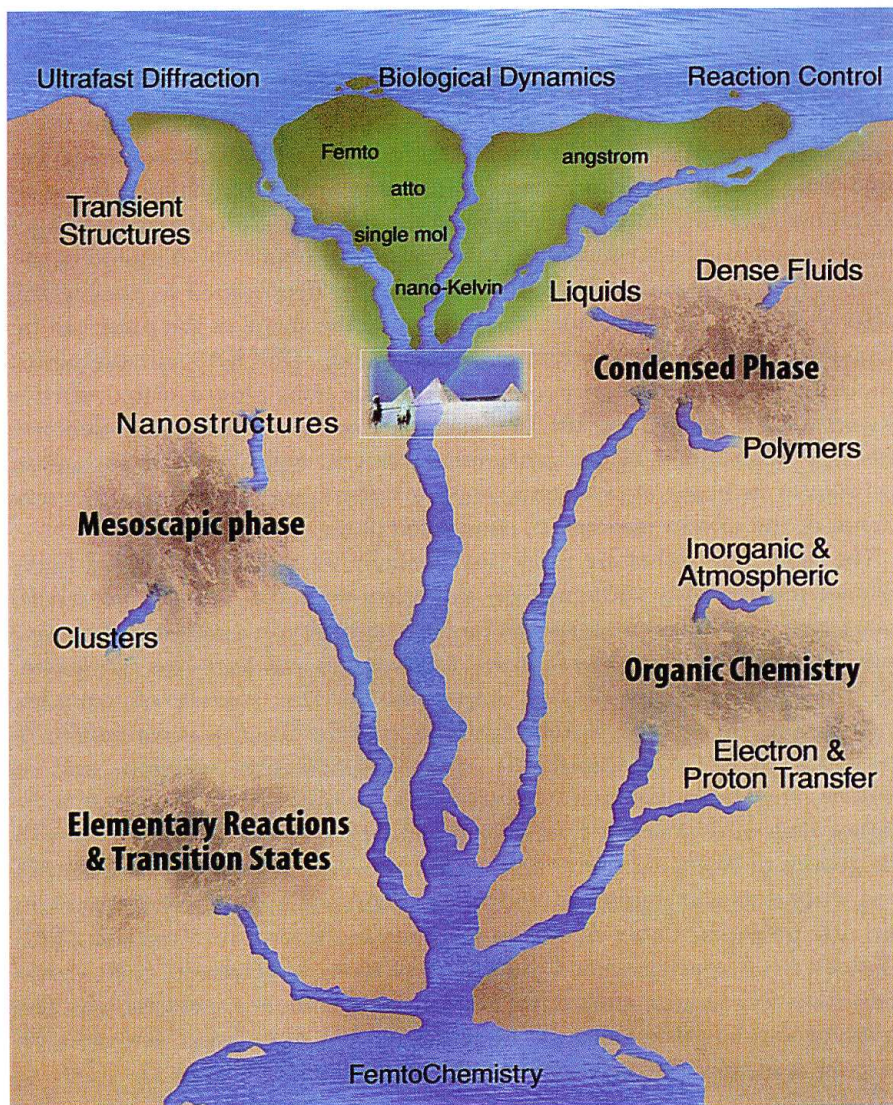


Figure 20. Femtochemistry branches, from the early days of studying elementary reactions and transition states ("southern part") to current activities ("northern part"). The flow has produced the different branches studied at Caltech.

- (ii) Dynamics of the (saddle) Transition State
- (iii) Dynamics of (bimolecular) Bond Breakage – Bond Formation

#### *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 [Fig. 21]. The technique of femtosecond – resolved kinetic-energy-time-of-flight (KETOF) provided a new dimension to the experiment – correlations of *time*, *speed*, and *orientation*

## Fs-Resolved Mass Spectrometry

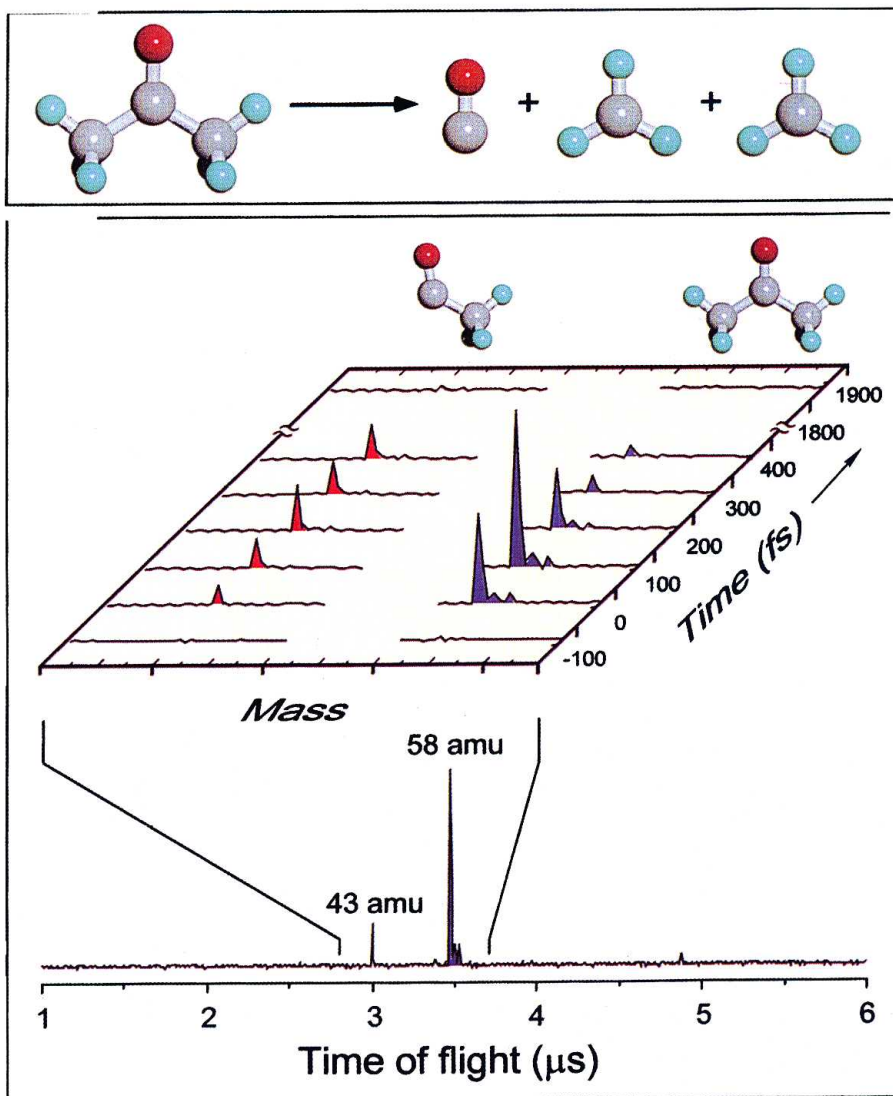


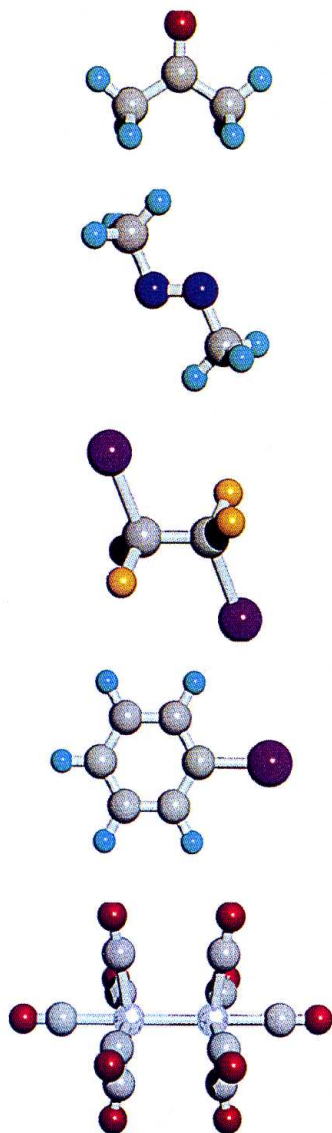
Figure 21. Femtosecond mass spectrometry, a 2D correlation important in the studies of reactive intermediates. The example given here is for the reaction of acetone (Norrish-type I) and its non-concerted behavior. [Ref. B10, 60]

which give *scalar* and *vectorial* dynamics. The examples of reactions include [Figs. 21–26]:

- (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



## Bond Breakage



## Bond Breakage/Bond Format

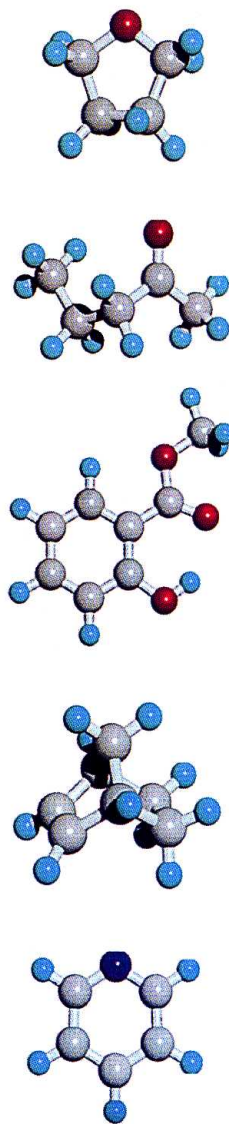


Figure 22. Molecular structures of different reactions studied, typical of the systems discussed in text for organic and organometallic femtochemistry: Acetone, Ref. 60; Azomethane, Ref. 61; Diiodoethane, Ref. 62; Iodobenzene, Ref. 63;  $\text{Mn}_2(\text{CO})_{10}$ , Ref. 64; Cyclic ethers, Ref. 65; Aliphatic ketones for Norrish-II reactions, Ref. 66; Methyl salicylate, Ref. 67; One of the structures studied for addition and elimination reactions, Ref. 68; Pyridine for valence isomerization, Ref. 69.

- (vii)  $\beta$ -Cleavage Reactions
- (viii) Elimination Reactions
- (ix) Valence Structure Isomerization
- (x) Reactive Intermediates

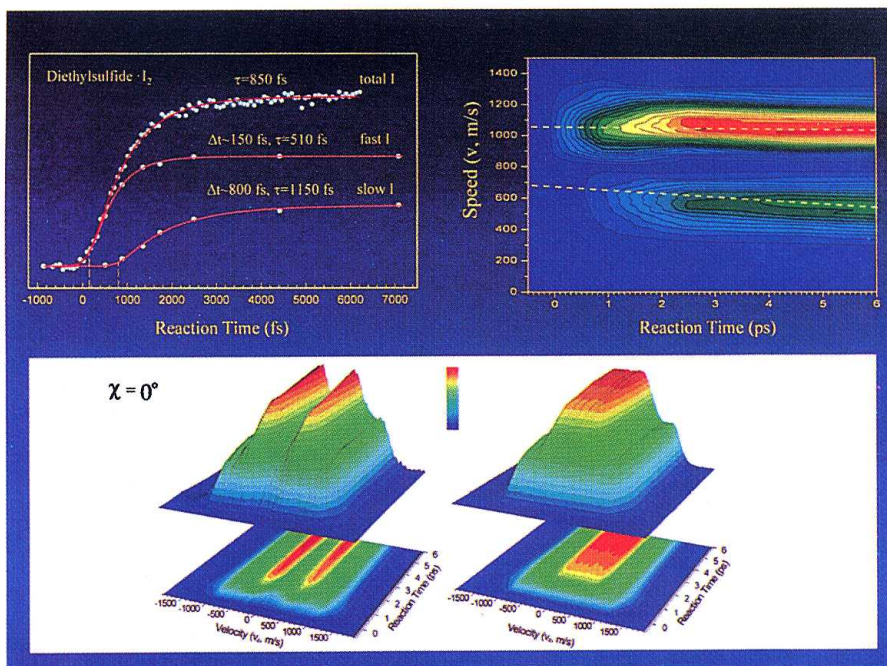
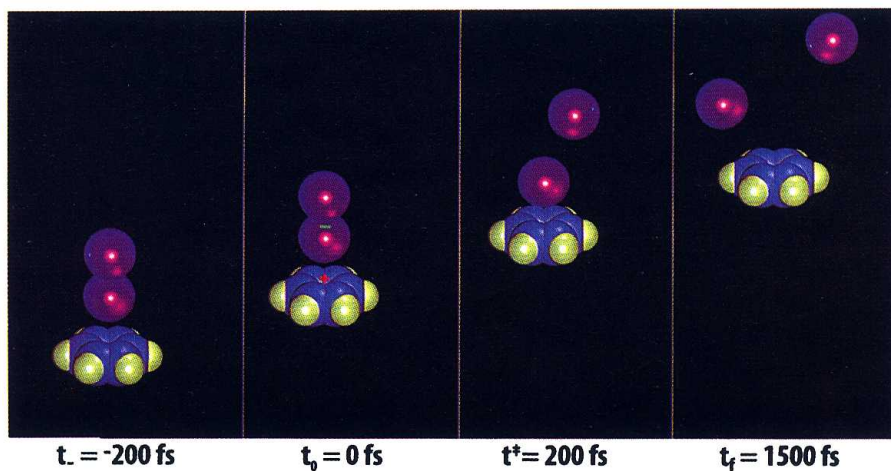


Figure 23. Femtochemistry of bimolecular electron-transfer reactions, the classic case of donors (e.g. benzene or diethylsulfide) and acceptors (e.g. iodine or iodomonochloride). (A, above) The experimental results clearly show the distinct velocity and time correlations, and thus the two-speed distributions and time scales of the reaction on the global PES. (B, below) Snapshots of the atomic motions according to experimental findings. [Ref. 70]

### *Electron & 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 [Figs. 11, 22, 23]. For proton transfer, three classes of reactions were of interest, those of bi-



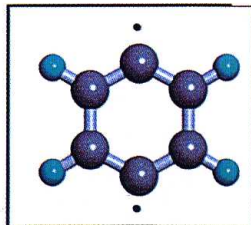
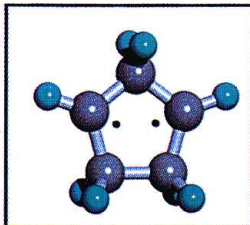
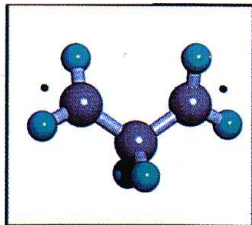
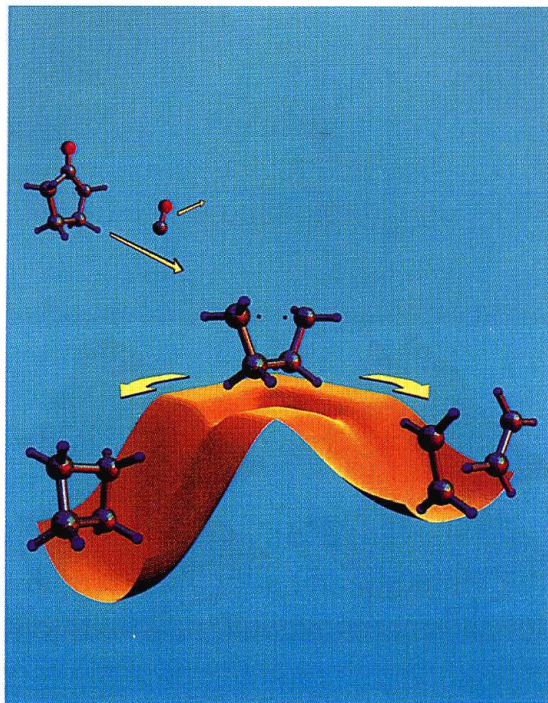
**Reactive Intermediates**

Figure 24. Reactive intermediates on the femtosecond time scale. Here, tetramethylene, trimethylene, bridged tetramethylene and benzyne are examples of species isolated on this time scale (see Fig. 22 for others). [Ref. 71]

molecular and intramolecular reactions, and those involving double proton transfer (base pair models):

- (i) Bimolecular Electron Transfer Reactions
- (ii) Intramolecular Electron Transfer and Folding Reactions
- (iii) Acid-Base Bimolecular Reactions
- (iv) Intramolecular Hydrogen-Atom Transfer
- (v) Tautomerization Reactions: DNA Mimics

### *Inorganic & Atmospheric Chemistry*

We extended the applications of femtochemistry to complex inorganic reactions of organometallics [Fig. 22]. Organometallic compounds have unique functions and properties which are determined by the dynamics of metal-me-



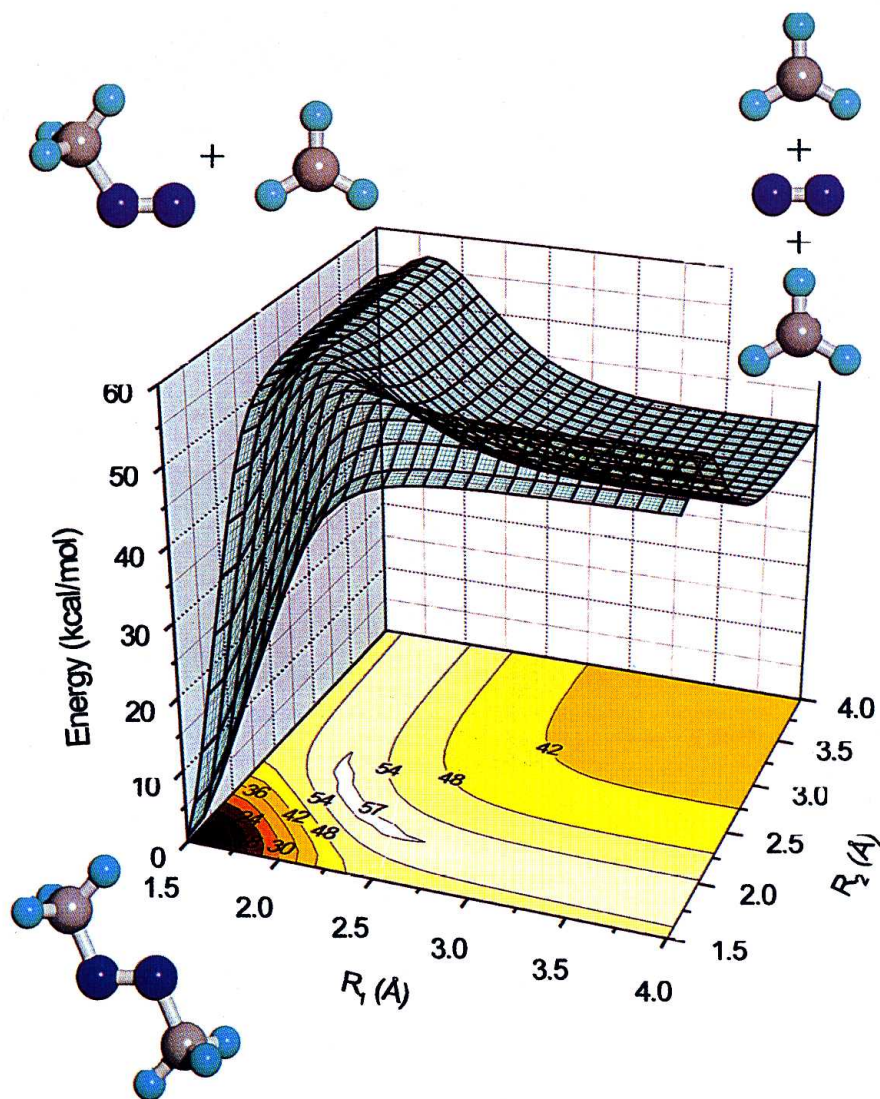


Figure 25. Reaction dynamics of azomethane, based on the experimental, femtosecond studies (Fig. 22, References). The *ab initio* PES was obtained from state-of-the-art calculations (Ref. 72) which show the two reaction coordinates (C-N) relevant to the dynamics. A third coordinate, which involves a twisting motion, was also studied. Note the concerted and non-concerted pathways.

tal (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  $\text{OClO}$ , a reaction of relevance to ozone depletion.

#### *The Mesoscopic Phase: Clusters & Nanostructures*

We have studied different types of reactions but under microscopic solvation conditions in clusters. These include [Fig. 27]:

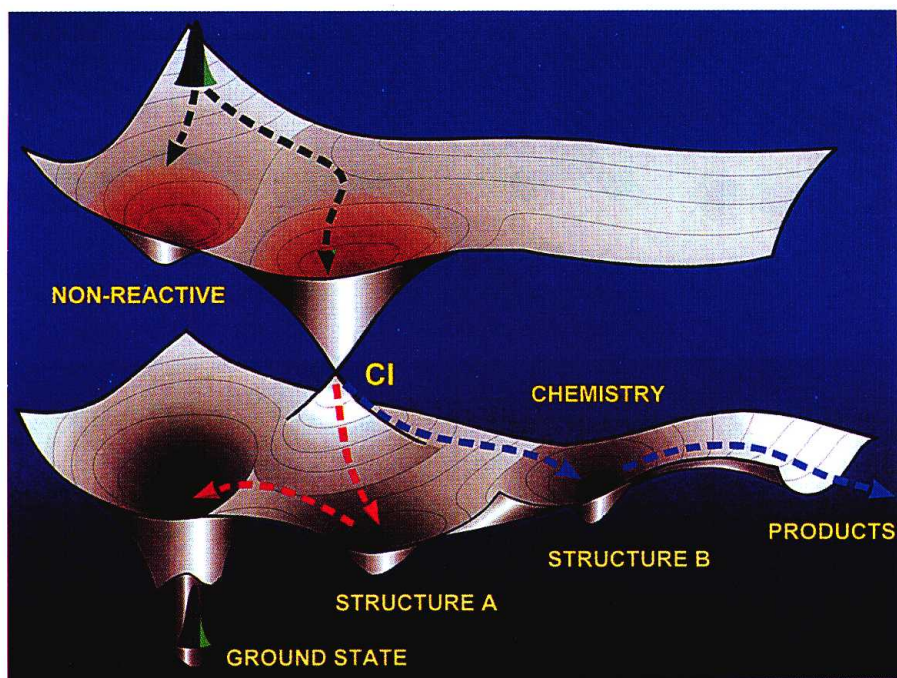


Figure 26. Generalized schematic showing reactive and non-reactive pathways (bifurcation) of wave packets. Both the photophysical and photochemical processes are shown with the conical intersection (CI) playing a crucial role. Examples are given in Ref. 73.

- (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

#### *The Condensed Phase: Dense Fluids, Liquids & 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: bond breakage and caging; valence structure isomerization; and double proton transfer. Similarly, we studied systems of nanocavities and polymers. Some highlights include [Fig. 28]:

- (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



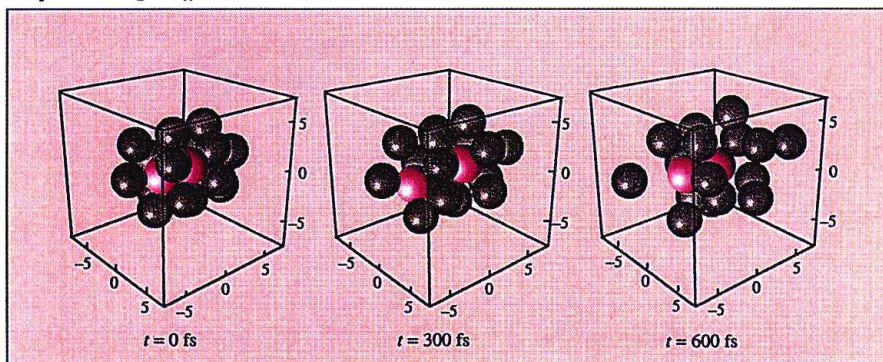
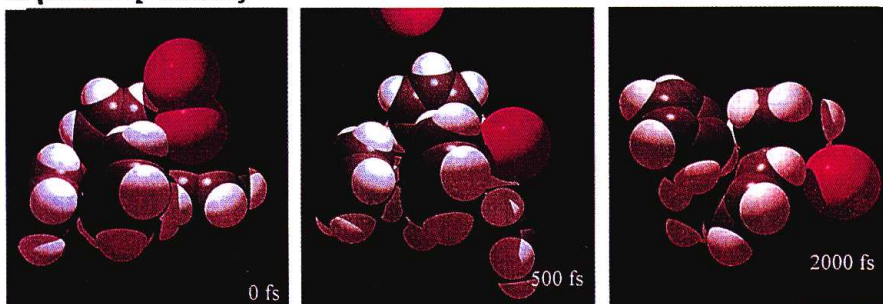
**Snapshots of  $I_2 \cdot Ar_{17}$** **Snapshots of  $I_2 \cdot \text{benzene}_5$** 

Figure 27. Femtosecond dynamics in the mesoscopic phase, reactions in solvent clusters. Several examples are given: (A, above) 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.) (B, next page) Shown is the study of acid-base reactions of naphthol with ammonia, changing the number of solvent molecules from 0 to 10. The isomerization of stilbene was similarly studied; the number of solvent hexane was varied from 0 to 6. [Ref. 74]

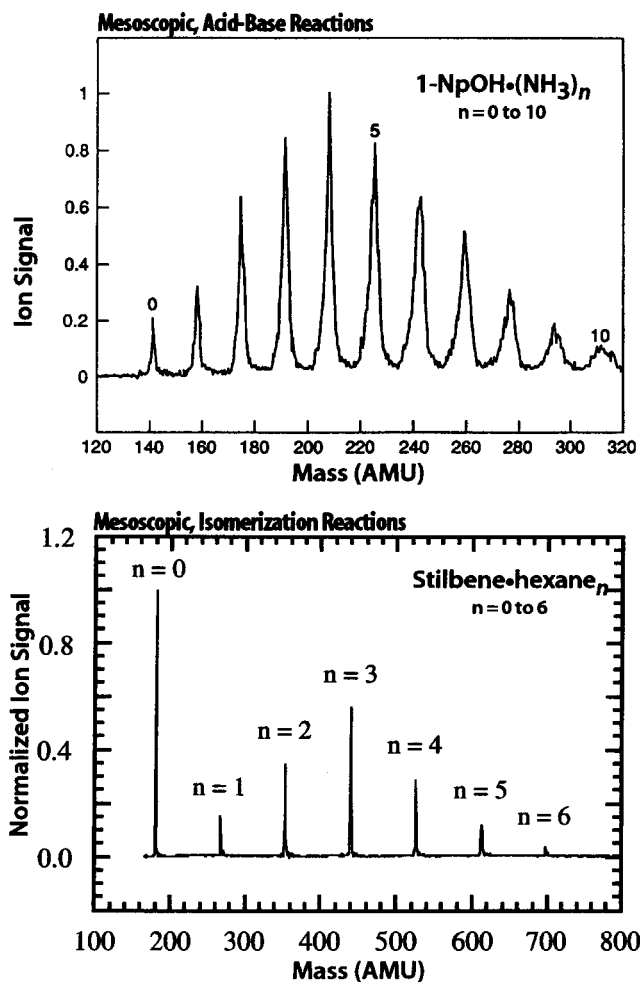
- (v) Dynamics of Energy Flow in Polymers
- (vi) Dynamics of Small & Large Molecules in Cyclodextrins

**(6) Opportunities for the future**

Three areas of study are discussed.

*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 in *Nature* (London) the latest advance in UED [Fig. 29], 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 ps and sub-ps time scale.

With UED, we have been able to study molecular structures and branching ratios of final products on the ps 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]. Specifically, we observed the transient intermediate in the elimination reaction of 1,2-diiodotetrafluoroethane (C<sub>2</sub>F<sub>4</sub>I<sub>2</sub>) to produce the corresponding ethylene derivative by the breakage of two carbon-iodine bonds [see Fig 29B and C]. The evolution of the ground-state intermediate (C<sub>2</sub>F<sub>4</sub>I radical) was directly 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 for the short-lived C<sub>2</sub>F<sub>4</sub>I radical favor the classical structure over the bridged structure. *Ab initio* calculations were made to compare theory with experiments.



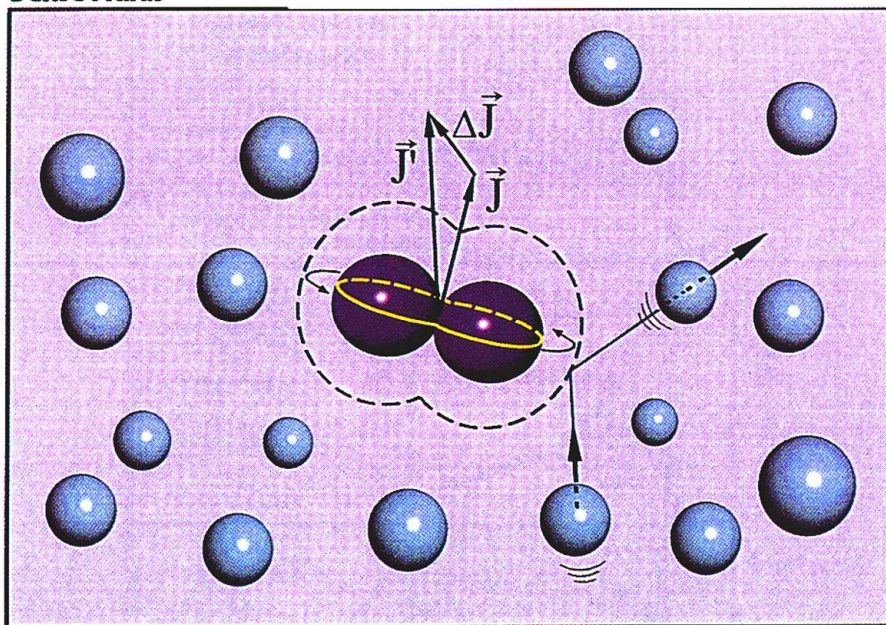
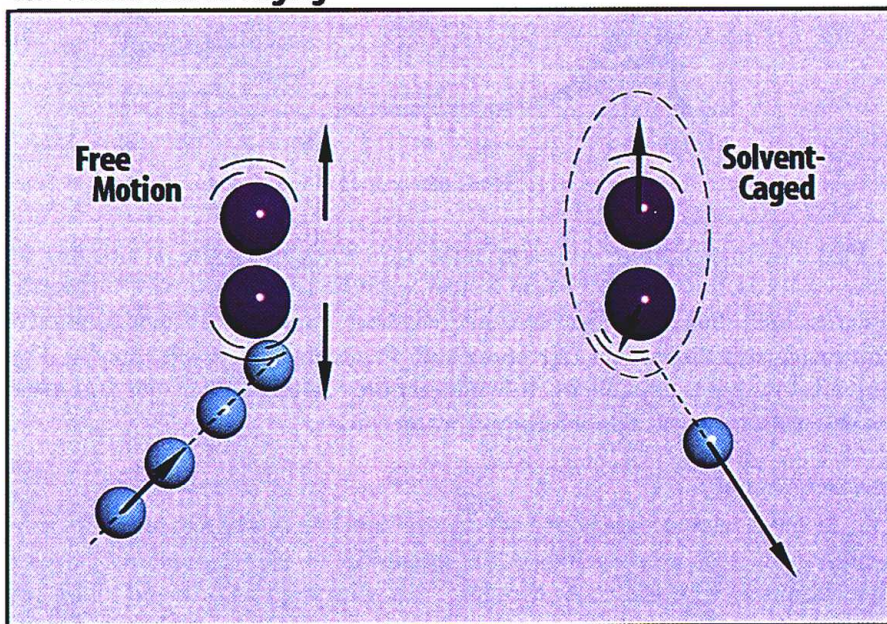
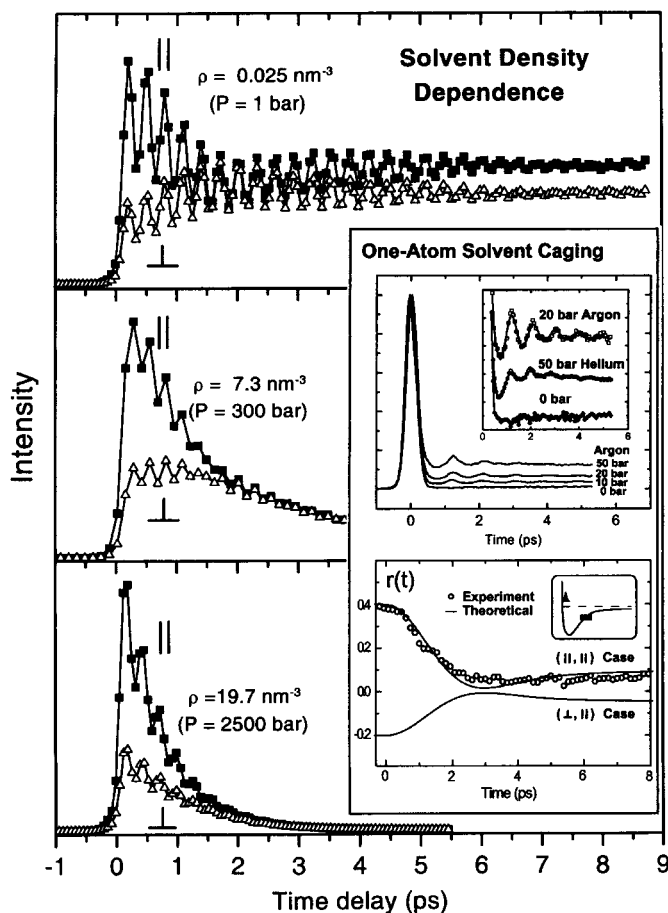
**Dense Fluids****One-Atom Solvent Caging**

Figure 28. Femtosecond dynamics in the condensed phase: (A, above) dense fluids; (B, next page) the coherent vibrational and rotational motions observed in dense fluids as a function of density and down to the one-atom collision with iodine; (C, page 173) nanocavities of cyclodextrins and polymers of polydiacetylenes; liquids (not shown, but references are given [75]). Studies in these media include the one-atom coherent caging, J-coherence friction model, coherent IVR in polymer chains, anomalous  $T_2$  behavior in dense fluids. [Ref. 75]

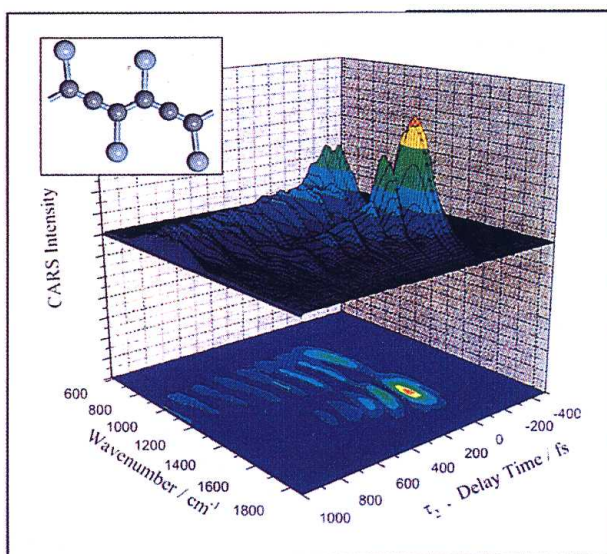
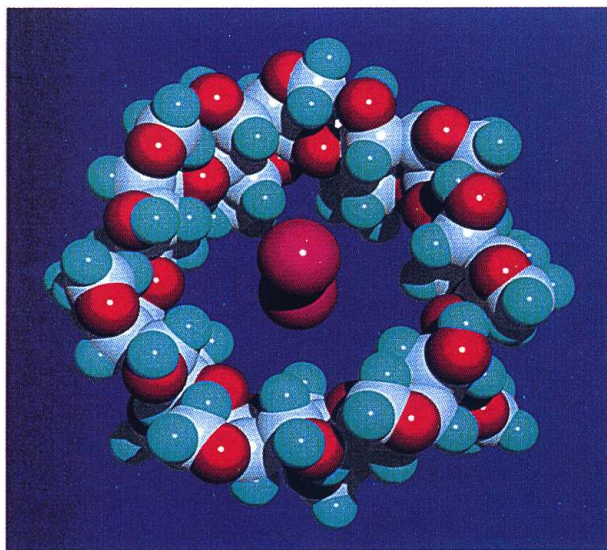


This leap in our ability to record structural changes on the ps and shorter time scales bodes well for many future applications to complex molecular systems, including biological systems. We have completed a new apparatus equipped with diffraction detection and also with mass spectrometry. This universal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

### Reaction Control

Our interest in this area goes back to the late 1970's when a number of research groups were reporting on the possibility of (vibrational) mode-selective chemistry with 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. This approach was popularized enthusiastically, but 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 selectivity was lost in the quasi-continuum vibrational mani-





fold of molecules, but 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” [33].

The discovery [Section III2] of coherent and selective vibrational oscillations (in-phase and out-of-phase) in a large molecule such as anthracene made me think of 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) which triggered significant interest in the issue of chaotic *vs.* coherent “motion” of packets in isolated mo-

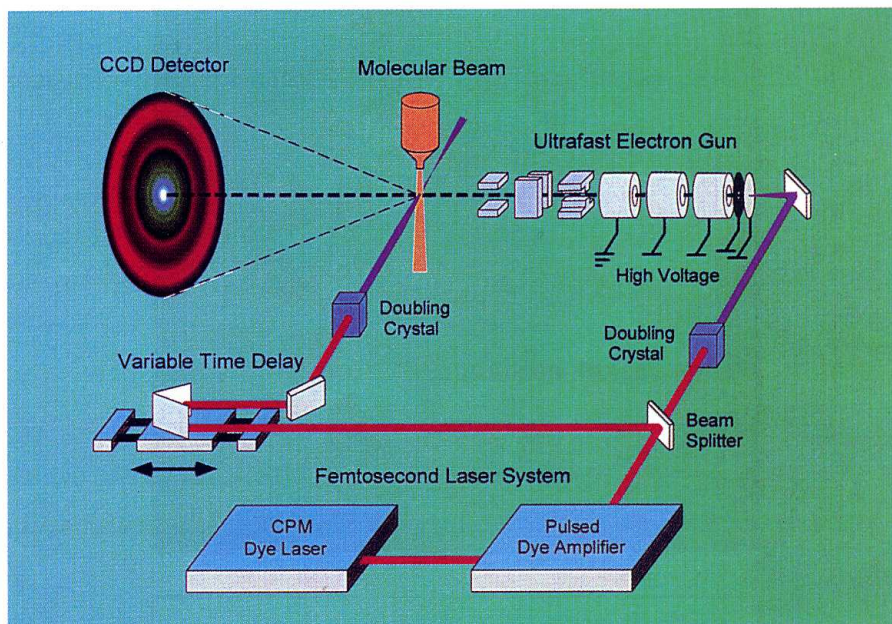
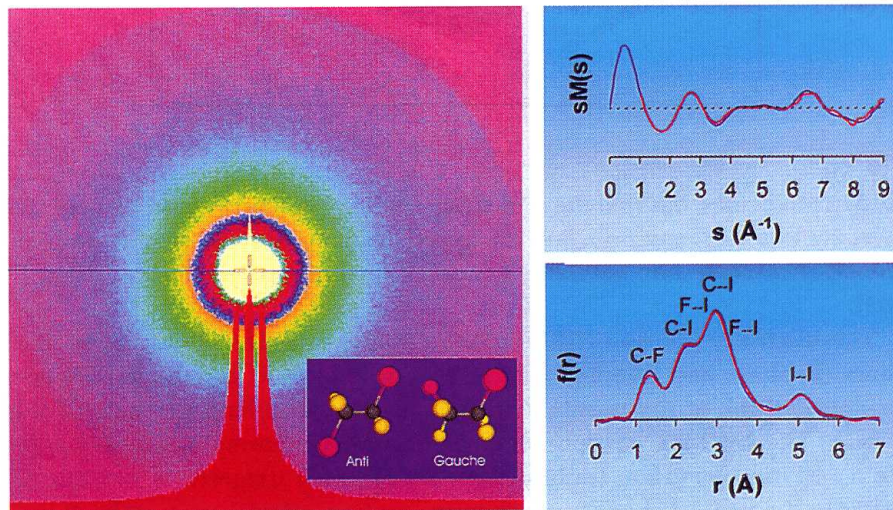


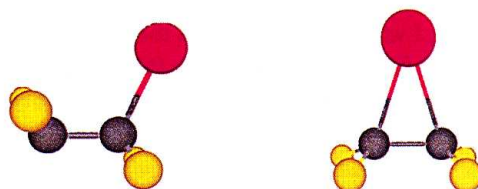
Figure 29. Ultrafast Electron Diffraction (UED). (A, above) The experimental arrangement; (B, below) A 2-D image (CCD) and the obtained molecular scattering  $sM(s)$  and radial distribution  $f(r)$  functions; (C, next page) The temporal change observed on a bond population, elucidates the structure of the reaction intermediate shown as two possibilities (see text). [Ref. B17, 76]

lecules. Some of us believed that, despite the complexity of the vibrational mode structure, coherence would be robust, provided it could be disentangled through proper preparation and probing. In fact, in a discussion with Richard Feynman (at Caltech) about the anthracene results, he informed me of a related problem noticed by Fermi, when both were at Los Alamos: A li-

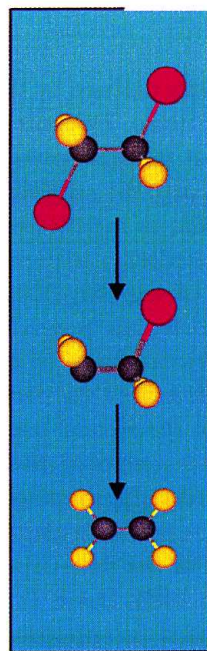
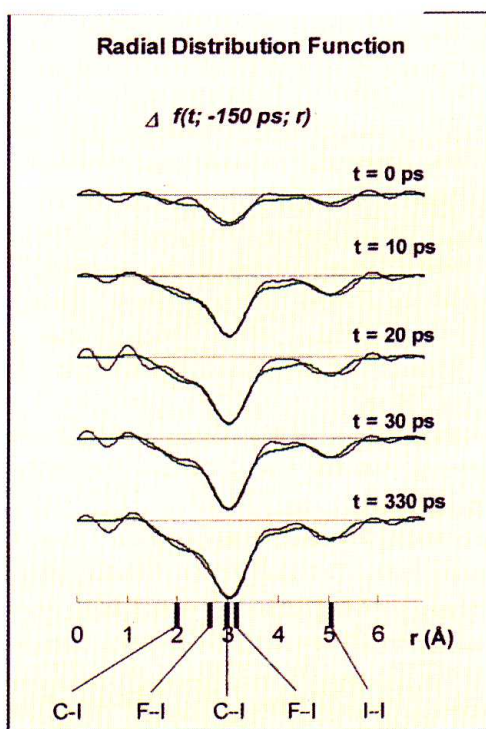




## Reaction Intermediates



## Ultrafast Electron Diffraction



near chain of springs (vibrations) showed recurrences when the energy was initially localized (on the computer) in one spring. They expected dissipation and not recurrences. Nico Bloembergen and I wrote a feature article (1984) emphasizing this point of coherent motion and its significance to mode-selective chemistry [B21]. Stuart Rice believed strongly in the concept of coherence and, as I mentioned before, 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 CW or long-time lasers) to control the outcome of a chemical reaction [B24]. 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."* In this article, I was concerned with the problem of IVR and so-called chaotic behavior. Stimulated by our work on IVR and coherence [Section III], I thought that ultrashort pulses should be used to control the system in the desired configuration by proper choice of the time duration and delay and by the preparation of the packet which is controlled by the coherence width. 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 [Section III]; the time scale was ns and for the control of IVR, fs pulses were needed. Prior to this work, the optical pulse field,

$$E(t) = E_0 A(t) \cos[\omega\tau + \phi(t)], \quad (10)$$

was simply defined by the envelope  $A(t)$  and the frequency  $\omega$ ; 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 in Section III; see Fig. 30. In fact with composite shaped-pulses, a sequence of phase segments and tilt angles (in the rotating frame) of, e.g.,  $60_x-300_x-60_x$ , we showed experimentally that the emission of a molecule can be made twice that as when a normal single pulse was used [Fig. 30]. 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 [34], Warren has discussed pulse shaping and its relevance to quantum control.

On the fs time scale, the theoretical work of Heller [Section III] 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 [35], 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 fs resolution, we began testing the idea of timing of pulses on small molecular systems [Fig. 30]. We first began with a single experiment on the control of the population in bound states (iodine). Then we reported results on the control of the yield in the reaction  $Xe + I_2 \rightarrow XeI + I$  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 fs pulses to control the branching of the NaI reaction; these, together with the experiment by Gustav Gerber's group on  $Na_2(Na_2^+ + e \text{ vs. } Na + Na^+ + e)$ ,

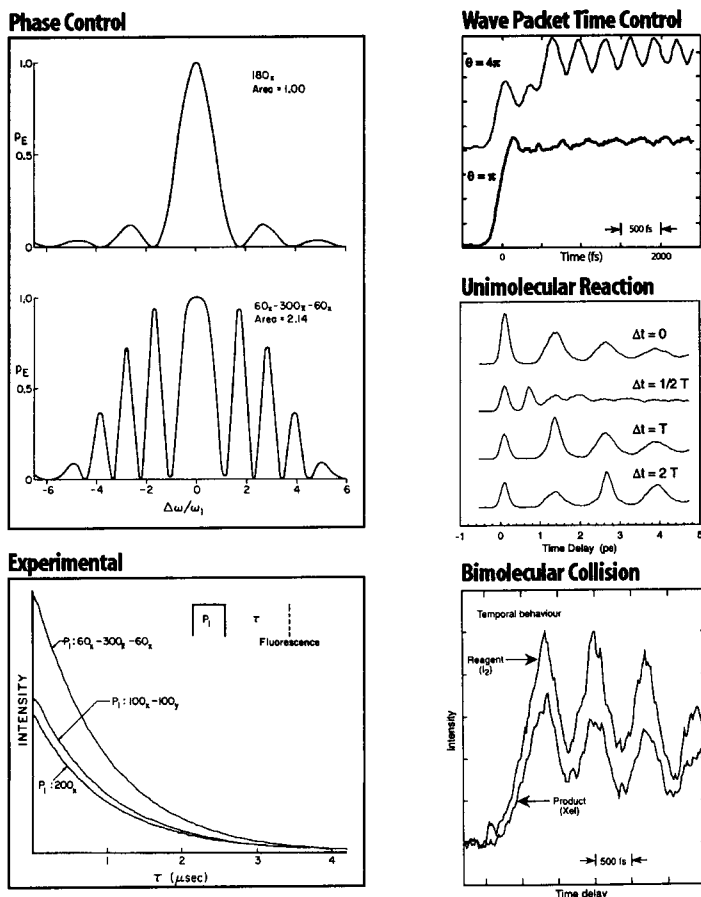
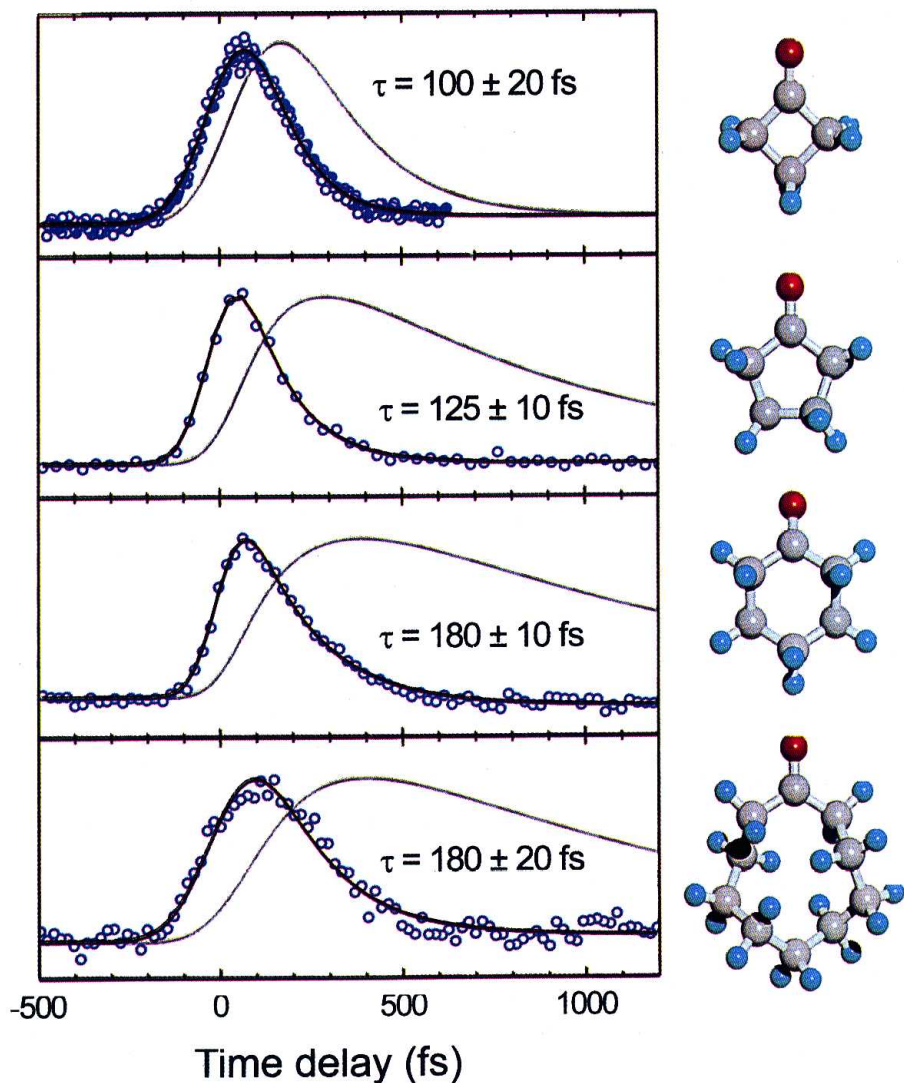


Figure 30. Control by the phase and/or the delay, or the duration of optical pulses. (A, above) (Left) The effect of a designed composite pulse on the fluorescence of a molecule (iodine), showing the large experimental enhancement for the labeled phase-controlled sequence. (Right) Control of the population ( $I_2$ ), of unimolecular reactions ( $\text{NaI}$ ), and of a bimolecular collision ( $\text{Xe} + \text{I}_2$ ), see text. (B, next page) Localized wave packet control of the preparation at high energy on the femtosecond time scale, which is shorter than that of IVR. The series has the same reaction coordinate (C-C bond) but the molecular size has increased in complexity. The behavior is far from being statistical. [Ref. B20, B24, 77]

are prototypes for the Tannor-Rice-Kosloff scheme. Phase-locked pulses were extended to the fs 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 fs pulses to implement the 1980 idea. In a series of molecules of increasing complexity, but retaining the same reaction coordinate, we illustrated selectivity by beating IVR (and entering near the transition state); the rate of reaction was two to three orders of magnitude larger than the expected *statistical* limit. This work was published in Science [Fig. 30] and promises to be significant for achieving non-statistical chemistry at high energies. The concept suggests that control at high energies (chemical energies) is more rea-



listic, in contrast with the conventional wisdom which asserts the need for low energies – time is of the essence! Another example of non-statistical femtochemistry comes from the work on surfaces [36]. Recently, the group in Berlin (Ertl and Wolf [36]) demonstrated, in an elegant experiment, the critical role of fs resolution in inducing oxidation (*vs.* desorption) of CO on Ru surfaces – the fs non-equilibrated electron distribution of the surface gives a selective chemistry different from that of equilibrated phonon distribution, or thermal heating.

In the future, there will be extensions and new directions in fs 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 fs 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, simi-

lar to a composite pulse of the type described above. The technique of liquid-crystal-display developed by Andy Weiner for fs 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 nicely for a targeted second harmonic generation or a yield of chemical reaction as reported by Gerber's group in Würzburg [37]. Kent Wilson [37] 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, reminiscent of the composite pulse experiment we described above. In pulse shaping, the field is optimized and forms a complex pattern which is used through many generations to reach the fitted, desired population.

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 [38]. Clearly these areas of control by ultrafast pulse timing ( $t$ ), phase ( $\phi$ ) (shape), spatial localization ( $R$ ) and intensity to alter the potential ( $V$ ) offer new opportunities for the future. Many theoretical efforts have already been advanced ahead of current experiments and Manz' group is providing new possibilities, including deracemization by controlled pulses – timed and shaped [see his review of 1500 references in **Ref. 28**, to all work]. We did not discuss here the CW control scheme advanced by Paul Brumer and Moshe Shapiro, nor can we give references to all work done in this area.

### *Biological Dynamics*

There have been important contributions to femtobiology and these include [**Refs. 28 & 39, and references therein**]: 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; for the chemistry and the efficiency to be unique, the system utilizes the organized structure around the “active center” with the necessary restraint on transition states and energy flow. Thus, in my view, the early fs events are critical to understanding the function of complex systems, as they reflect the important locality in biological dynamics.

Our efforts in this direction have so far focused on DNA twisting dynamics, electron transfer in DNA assemblies, DNA base-pair models, and on 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 last few years. With donors (D) and acceptors (A) covalently



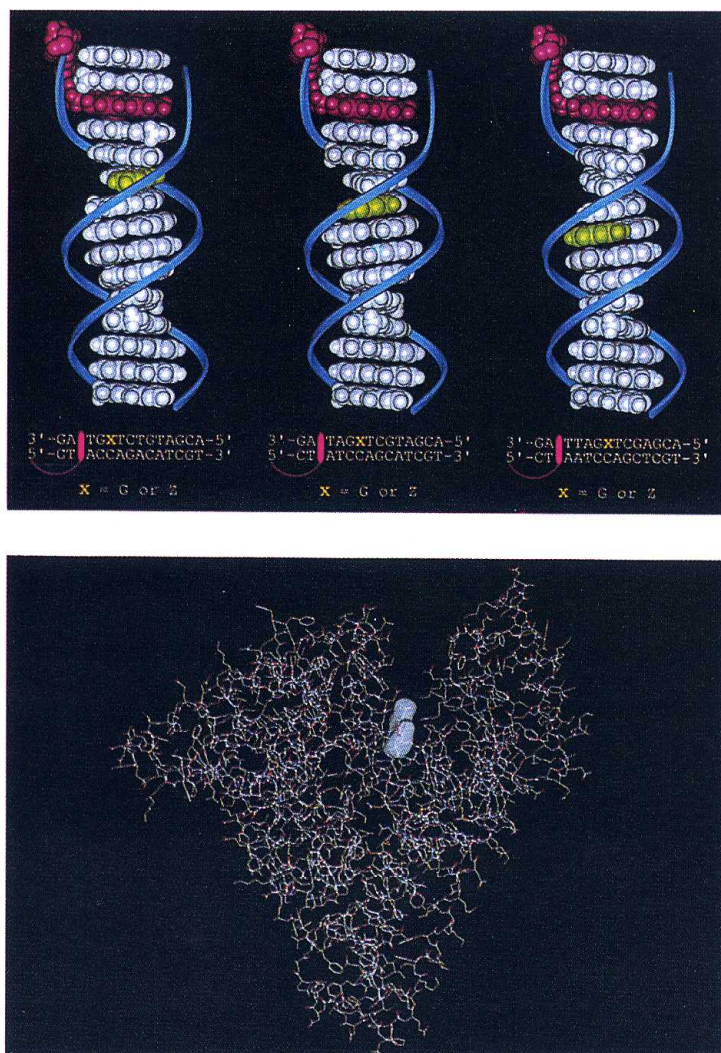
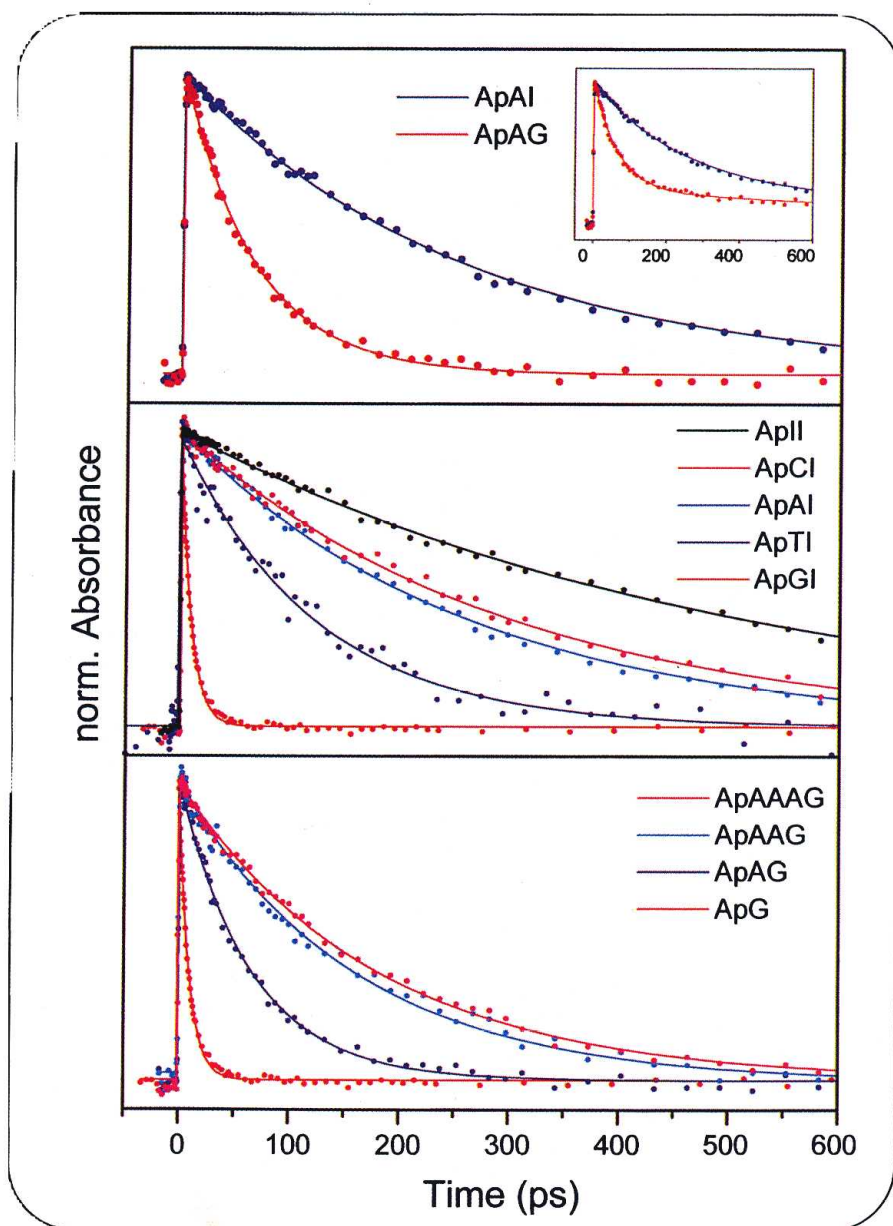


Figure 31. Femtosecond dynamics of biological systems, DNA assemblies and protein complexes. (A, above) The systems studied are the DNA with donors and acceptors at fixed distances (top) and protein HSA with the molecule HPMP shown in the interior. The focus of research is on electron transfer and molecular dynamics in the former and on probing solvation and ligand-recognition effects in the latter. (B, next page) Some illustrative femtosecond transients of DNA assemblies. Aminopurine was used for the initial excitation, and the effect of different bases G, C, A, T was studied at a fixed distance. The time scale of torsion dynamics was known from studies we and others made before. [Ref. 78, 79]

bonded to DNA, studies of ET on more well defined assemblies were made possible, and the effect of distance could be addressed. With fs 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,  $\beta$ . 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 [Fig. 31] and the distance range 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 [Fig. 31], and oxygen reduction in models of metallo-enzymes

[Fig. 32]. For the former, we have studied, with fs 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

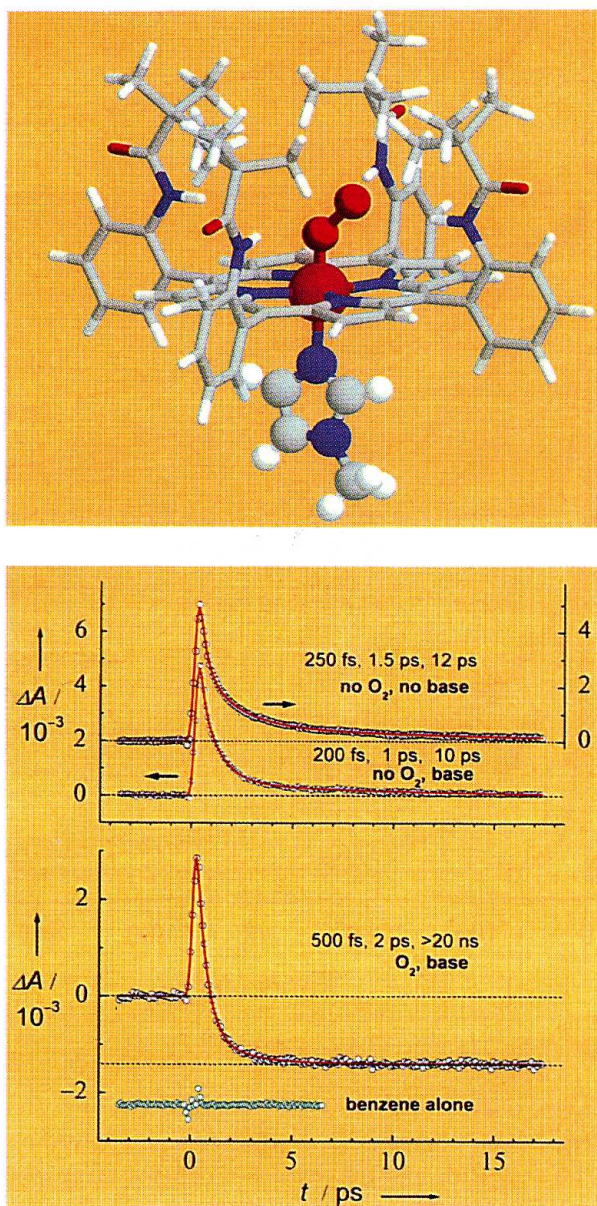


Figure 32. Femtosecond dynamics of model biological systems, hemoglobin and myoglobin, DNA base pairs, and photosynthetic assemblies. Shown here are the structure of Dioxygen-picket fence Cobalt Porphyrins and the fs transients which show the time scales involved and the release of  $\text{O}_2$  in 1.9 ps at room temperature. These studies on this and the other model systems (not shown) are part of the continued effort in this area. [Ref. 80]

model enzymes, we examined novel picket-fence structures which bind oxygen to the central metal with  $\sim 85\%$  efficiency at room temperature. In this system [Fig. 32], we observed the release of  $O_2$  in 1.9 ps and the recombination was found to occur on a much slower time scale. These are fruitful areas for future research, especially in that they provide prototype systems for  $O_2$  reduction with complex metallo-porphyrins in the transition state, similar to the smaller systems of benzenes/halogens (discussed in Fig. 23) but at room temperature. We published our first report recently in *Angewandte Chemie* in collaboration with Fred Anson's group at Caltech.

In the future, new extensions are anticipated. The nature and control of enzymatic reactions, the catalytic function of the transition state, and the design of artificial biological functions seem to be areas of great promise for dynamical studies. Also, it is envisaged that the recording of a large biological structure changing with time and with atomic resolution may be realized. Already some success in studies of small chemical systems utilizing ultrafast electron diffraction have been reported. X-ray diffraction is another direction. The ultimate goal is the recording of all coordinates in space and time. The impact on problems such as protein folding and molecular recognition is clear.

#### IV. IMPACT AND CONCEPTS – A RETROSPECTIVE

In retrospect, the key to the explosion of research cited in Ref. B60 can perhaps be traced to three pillars of femtochemistry:

##### Time Resolution – Reaching the Transition-State Limit

Three points are relevant: (i) The improvement of nearly ten orders of magnitude in time resolution, from the (milli)microsecond time scale (Eigen, Norrish & 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 [B60]; (iii) inferences deduced from “rotational periods” as clocks in uni- & 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 1960's, there was some thought [40] 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 fs nuclear motion, as discussed in Section III (Development of Femtochemistry) and in

what follows. The new vision is summarized in the following statement [40]: “*The study of chemical events that occur in the femtosecond time scale is the ultimate achievement in half a century of development and, although many future events will be run over the same course, chemists are near the end of the race against time.*” Manfred Eigen, who gave the 1967 Nobel Lecture with the title “Immeasurably Fast Reactions” – “Die ‘Unmessbar’ Schnellen Reaktionen” – told me, when I teased him about the title, that nobody in the 1950s anticipated the laser and the short pulses they can provide.

### 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). Because of coherence, we can speak of the motion classically and visualize it as the change actually occurs; (ii) the issue of *the uncertainty principle*. Many thought 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 before, localization is consistent with the two uncertainty relationships [Fig. 4] and coherence is the key. The energy uncertainty  $\Delta E$  should be compared with bond energies:  $\Delta E$  is 0.7 kcal/mol for a 60 fs pulse [see details in Ref. B17]. In the condensed phase, localization may become shorter lived, but the basic picture is still valid [41].

It took time for this concept of coherence to be appreciated, not only among some chemists, but also among notable physicists. In 1972, at a Welch Conference, picosecond time resolution was of concern because of the perceived fundamental limitation imposed on time and energy by Heisenberg’s uncertainty principle. After his lecture on lasers in chemistry, the physicist Edward Teller had a lively exchange with another physicist and friend, Eugene Wigner. Even for picosecond resolution the question was asked, *is there a natural, real limit to the time...?* In the Welch Prize Address (1997), I highlighted these exchanges [42]. Jacob Bigeleisen [24], although concerned about the uncertainty principle, asked why not venture into the “millijiffy” (femtosecond) range?

### 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 time scale of the chemical bond, defining the earliest time possible; (ii) the methodology is versatile and general, as evidenced by the scope of applications in different phases and of different systems. Moreover, it has stimulated new directions of research in both experiment and theory in areas such as quantum control and ultrafast diffraction; (iii) the time resolution offers unique opportunities when compared with other methods.

First, processes often appear complex because we look at them on an extended time scale, during which many steps in the process are integrated. On the fs time scale, these steps are resolved, and the process breaks down into a series of simpler events. Second, only this time resolution can give the dynamics of transition states/intermediates in real time since for reactions neither the spectra of reactants nor those of products are directly relevant. This point was amply demonstrated in complex reactions, such as those of transient, reactive intermediates of organics. Even for simple, reactive systems this is still true. For example, the spectral bandwidth of the reactant, dissociative ICN has no information about the actual dynamics of the nuclear separation between I and CN fragments or about the transient configurations, as it only reflects the steepness of the potential at the initial nuclear configuration. For unreactive molecules, there is a different complexity; the spectra are usually inhomogeneously broadened, especially in complex systems. Finally, with time resolution, we can observe the motion without resorting to a mathematical construct from eigenstates or other indirect methods.

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 [23]. The use of CARS, DFWM, SRS,  $\pi$ -pulses or the use of direct IR excitation are some of the approaches possible. Two recent examples demonstrate this point: one invokes the use of IR fs pulses to study reactions involving hydrogen (bond) motions in liquid water, work done in France and Germany [43]; and the other utilizes CARS for the study of polymers in their ground state which we published in collaboration with the groups of Kiefer and Materny [Fig. 28]. Ground-state dynamics have also been studied by novel fs photodetachment of negative ions, and the sub-field of fs dynamics of ions is now active in a number of laboratories [44].

### Some Concepts

New concepts and phenomena have emerged and include: Localization of wave packets; reaction path coherence, single-molecule trajectory; reaction landscapes *vs.* path; bifurcation; chemical *vs.* spectroscopic dynamics (time scales); concertedness; dynamical active space; non-statistical (non-ergodic) behavior; dynamical caging (by energy loss as opposed to barrier confinement); microscopic friction (energy *vs.* mechanical); and inhomogeneous dynamics of “soft matter” (e.g. biological) systems, with a whole range of time scales. These concepts have been discussed in the original publications, and below, only a few will be highlighted:

(1) *Resonance (Non-equilibrium 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 which is not a stationary-state picture. With coherent preparation of molecules it is possible to prepare a non-stationary (*non-equilibrium*) state of a given nuclear structure and for the system to evolve in time. In our studies this was shown for vibrational redistribution, for rotational orientation, and for wave packet nuclear motions. Such non-stationary evolution does not violate the uncertainty principle and is fundamental to chemical dynamics.

(2) *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 [45]. Second is the ability to “transform” the ensemble’s incoherent behavior to a coherent molecular trajectory. This is achieved because on the fs time scale the system can be promoted and localized in space with a localization length ( $\Delta R$ ) only limited by the uncertainty of the initial system, typically  $\sim 0.05$  Å; all molecules which do not interact span this range. The chemical length scale ( $R$ ) of interest is several ångströms and this is why the system behaves as a single-molecule trajectory [Fig. 33]. Because the initial state is promoted nearly intact on the fs 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  $\Delta R$  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 fs 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 out the non-statistical behavior through the preparation of a localized configuration [Fig. 33], as opposed to an incoherently-prepared configuration (by, for example, chemical activation) or a spatially-diffuse configuration (by long-time experiments). The concept is powerful and basic to many phenomena: atomic-scale motion; reaction path coherence (from TS to products); reaction landscape trajectories as opposed to a single reaction path; energetic *vs.* entropic structures near transition states and conical intersections; coherent caging by a solvent; bifurcation and others.

(3) *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 fs 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



## Concept of Coherence

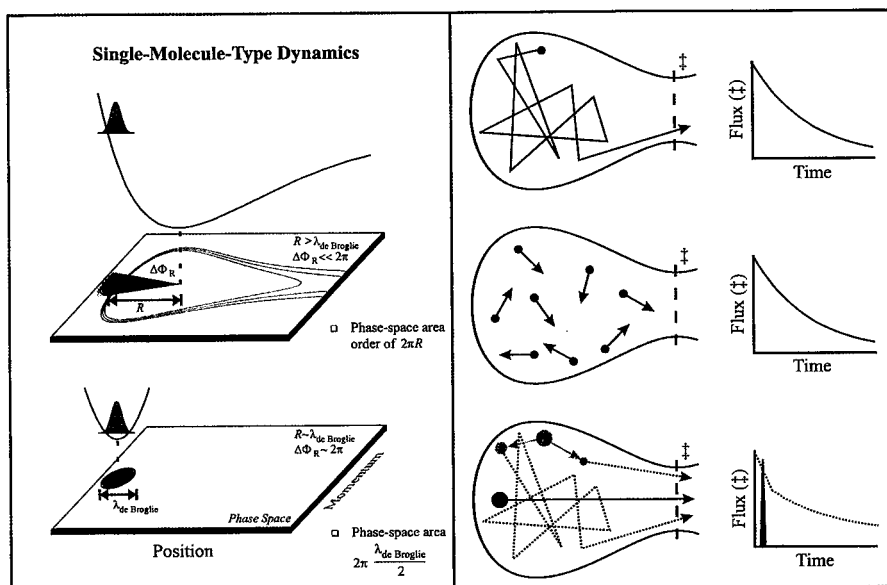


Figure 33. Concept of coherence, both in the dynamics at the atomic scale and in the control of non-statistical behavior. Shown is the phase space picture, describing the robustness of coherence (left); note the phase-space area of the initial state relative to that of the reaction. (Right) We present, 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.

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 discussed in **Section II** 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 [see **Sections II & III**].

(4) *Reduced Space (Directed Dynamics)*: Another important concept in dynamics is the reduction of nuclear space to the sub-space critical to reactivity and

nonradiative behavior in complex systems. Here, the fs 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 dynamical isotope effect in elementary reactions, bifurcation to chemical and photophysical channels by conical intersections, concertedness and stereochemistry in organic reactions, non-statistical 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  $\sigma^*$  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 essential 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 [46]. The report in Ref. 5 addresses with details the field and its position in over a century of developments. 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 [47], 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? Sub-fs 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 [B17] and, since then, not much has been reported except for some progress in the generation of sub-fs pulses [46, Corkum, Harris]. In the coming decades, this may change and we may view electron rearrangement, say, in the benzene molecule, in real time. Additionally,

there will be studies involving the combination of the “three scales” mentioned in the prologue, 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 [Fig. 34], 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 [48]. Perhaps we are approaching a universal limit of time!

Personally, I did not originally expect the rich blossoming in all of the directions outlined in this anthology; many more could, unfortunately, not be mentioned because of the limited space. What is clear to me is that my group and I have enjoyed the odyssey of discovery, seeing what was not previously possible, acquiring new knowledge and developing new concepts. Perhaps the best words to describe this feeling are those of the English archaeologist, Howard Carter, on November 25<sup>th</sup> 1922 when he got his first glimpse of the priceless contents of Tutankhamen’s Tomb – *At first, I could see nothing, ... then shapes gradually began to emerge....* Lord Carnarvon, who financed the excava-

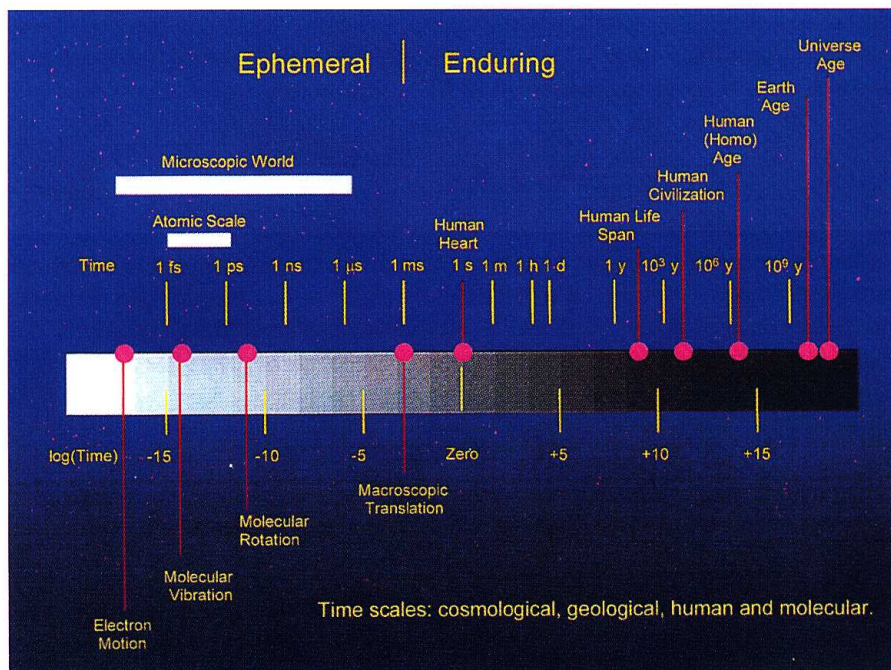


Figure 34. Time Scales of cosmological, geological, human and molecular events. Here, the time scale spans more than thirty orders of magnitude, from the big bang to the femto age. [Ref. B25]



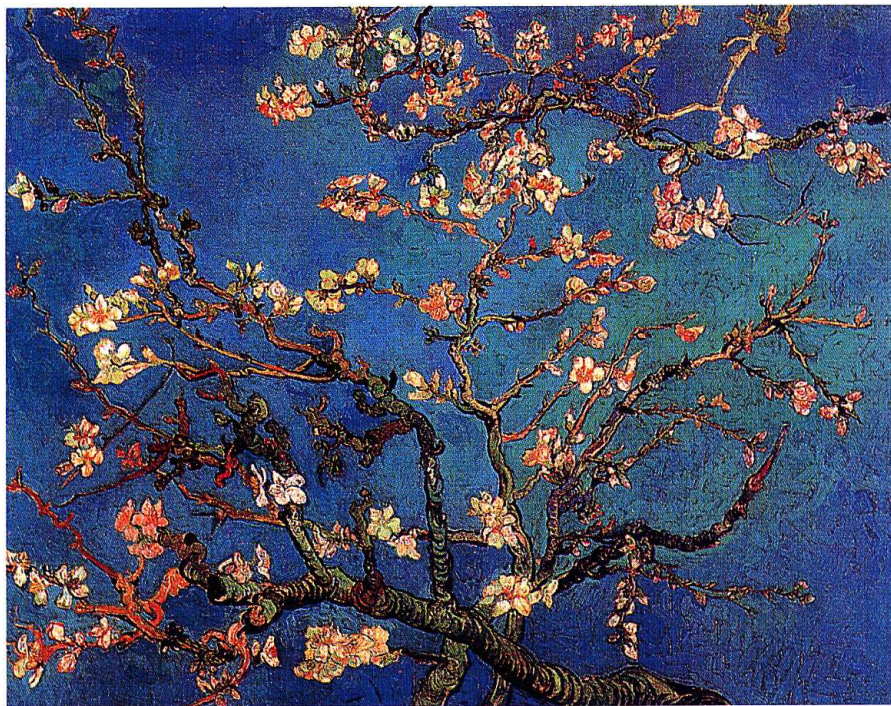


Figure 35. The Almond Blossom (st. Rémy, 1890) of Vincent van Gogh (1853–1890). With a good beginning, even if branching is unpredictable, the blossoms are rich and the big picture is beautiful. [L. A. County Museum of Art]

tion of this discovery, asked, when looking with Carter, *What do you see?* Carter replied, “*Beautiful Things*”, “*Beautiful Things*”. This is the thrill of discovery in science, too. It seeks to unveil the hidden simplicity and beauty of Nature’s truth. On a recent visit to the Los Angeles Art Museum with my wife, I stood in front of van Gogh’s masterpiece – Almond Blossom [Fig. 35] – and wondered about the beauty of the big picture and the unpredictability of its details. That, also, is in the nature of scientific discoveries.

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.*”

## APPENDIX

### A Primer for Femtoscopy, Coherence and Atoms in Motion

#### *Pump-Probe Femtoscopy*

In high-speed photography, a *continuous* motion is broken up into frames (“freezing”) using a brief exposure time. For example, in Muybridge’s experiment (Section I), the shutter speed (exposure time) was ~2 milliseconds

and the speed of the motion was  $\sim 10$  m/s, resulting in a well-defined resolution (speed  $\times$  exposure time) of 2 cm; the number of frames per second was about twenty since the cameras were 0.5 m apart. The huge contrast with molecular experiments is due to vast differences in speed ( $\sim 1$  km/s), resolution ( $\sim 10^{-8}$  cm) and the number (millions) of molecules involved. Given the molecular speed and resolution, the ultrashort *strobes* must provide exposure time on the order of 100 femtoseconds, and in one second  $10^{13}$  frames could be recorded! Ultrafast pulsed laser techniques have made direct exploration of this temporal realm a reality (**Sections II & III**). Spectroscopy, mass spectrometry and diffraction play the role of ultra-high-speed photography in the investigation of molecular processes.

A femtosecond laser 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 or photographing 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. This method of probing, although different from Muybridge's, is in principle equivalent to his use of the cameras (with shutters) as probes. 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.

With this methodology, the process to be studied is clocked from the instant that the substance under investigation absorbs radiation from the pump pulse. Passage of a probe pulse through the sample at some later point in time provides a snapshot of the status of the system at that time. 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 (**Fig. 5**). The finite speed of light translates the difference in path length into a difference in arrival time of the two pulses at the sample;  $1\mu$  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.

#### *Coherence and Atomic Motion*

In a classical description, the motions of nuclei would be particle-like, i.e., they would behave as “marbles on a potential”. At the scale of atomic masses and energies, however, the quantum mechanical wave/particle duality of matter comes into play, and the notions of position and velocity common to classical systems must be applied cautiously and in accord with the uncertainty principle, which places limits on the precision of simultaneous measure-



ments. In fact, the state of any material system is defined in quantum mechanics by a spatially varying "wave function" with many similarities to light waves. Since the wave nature of light is a much more familiar concept than that of matter, we will use light to introduce the idea of wave superposition and interference, which plays an important role in atomic motion.

When light from two or more sources overlaps in space, the instantaneous field amplitudes (not intensities) from each source must be added together to produce the resultant light field. A well-known example is Young's two-slit experiment, in which light from a single source passes through two parallel slits in a screen to produce, in the space beyond, two phase-coherent fields of equal wavelength and amplitude. At points for which the distances to the two slits differ by  $n + \frac{1}{2}$  wavelengths (for integer  $n$ ) the two waves add to zero at all time, and no light is detected. Elsewhere, the amplitudes do not cancel. Thus, a stationary pattern of light and dark interference (**Fig. A**, next page, **inset**) fringes is produced ("light + light  $\rightarrow$  darkness + more light!"). Knowledge of the wavelength of light and the spacing of fringes projected on a screen provide a measurement of the separation of the slits. In x-ray diffraction such interferences make it possible to obtain molecular structures with atomic resolution – the positions of the atoms replace the slits.

In studies of motion, we have exploited the concept of coherence among molecular wave functions to achieve atomic-scale resolution of dynamics – the change of molecular structures with time. Molecular wave functions are spatially diffuse and exhibit no motion. Superposition of a number of separate wave functions of appropriately chosen phases can produce a spatially localized and moving coherent superposition state, referred to as a wave packet (**Fig. A**, next page); constructive and destructive interference (as in the interference of light waves) is the origin of such spatial localization. The packet has a well-defined (group) velocity and position which now makes it analogous to a moving classical marble, but at atomic resolution. The femtosecond light induces the coherence and makes it possible to reach atomic-scale spatial and temporal resolution, without violation of the uncertainty principle.

In the figure, a snapshot is shown of the position probability (in red) of a wave packet, formed from wave functions  $n = 16$  to 20 with weighting according to the distribution curve at the left of the figure. This was calculated for the harmonic wave functions representing the vibrational states of a diatomic molecule, in this case iodine ( $n$  is the quantum number). As time advances, the wave packet moves back and forth across the potential well. As long as the wave packet (width  $\sim 0.04$  Å) is sufficiently localized on the scale of all accessible space ( $\sim 0.6$  Å between the walls of the potential), 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**). Note that the width of the packet prepared by a 20 femtosecond pulse is very close to the uncertainty in bond distance for the initial  $n = 0$  ground state. To prepare the packet at the inner turning point with the given phase composition, it must be launched vertically at the internuclear separation of  $\sim 2.4$  Å; if

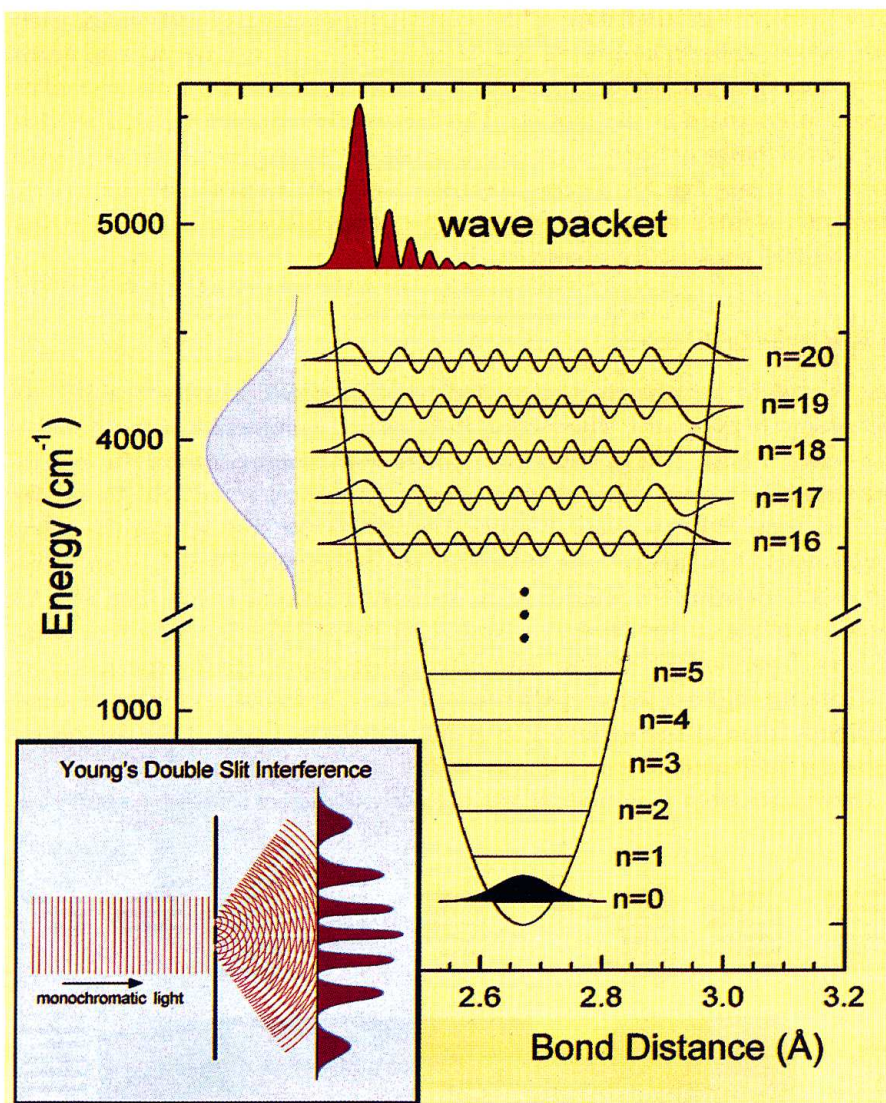


Figure A. The wave packet and wave function limits for molecular systems, in this case a diatomic molecule. The analogy with light interference is depicted – Thomas Young's experiment of 1801 [B25].

launched from the shown  $n = 0$  distance, the packet will have a different phase composition and will be localized initially in the center of the well.

The observation of motion in a real system 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” femto-second launching of the packet. The spatial confinement (in this case  $\sim 0.04$



Å) of the initial ground state of the system ensures that all molecules, each with its own coherence among the states which form its wave packet, begin their motion on the excited potential 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 (see Fig. 33). Unless the molecular and ensemble coherences are destroyed by intra- and/or inter-molecular perturbations, the motion is that of a classical *single-molecule trajectory*.

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The story told here involves many dedicated students, post-doctoral fellows and research associates. Their contributions are recognized in the publications cited. I hope that by mentioning their work, they recognize the crucial role they have played in the journey of femtochemistry at Caltech. To me the exciting time with my research group represents the highlight of the story. For 20 years I have always looked forward to coming to work with them every-day and to enjoying the science in the truly international family [Fig. 36]. All members of the current research group have helped with the figures presented here. I particularly wish to thank Dongping Zhong for the special effort and care throughout the preparation and Ramesh Srinivasan for his devoted help with some of the figures. The artistic quality of many of the figures reflects the dedicated efforts of Wayne Waller and his staff.

There have been a number of friends and colleagues who have supported

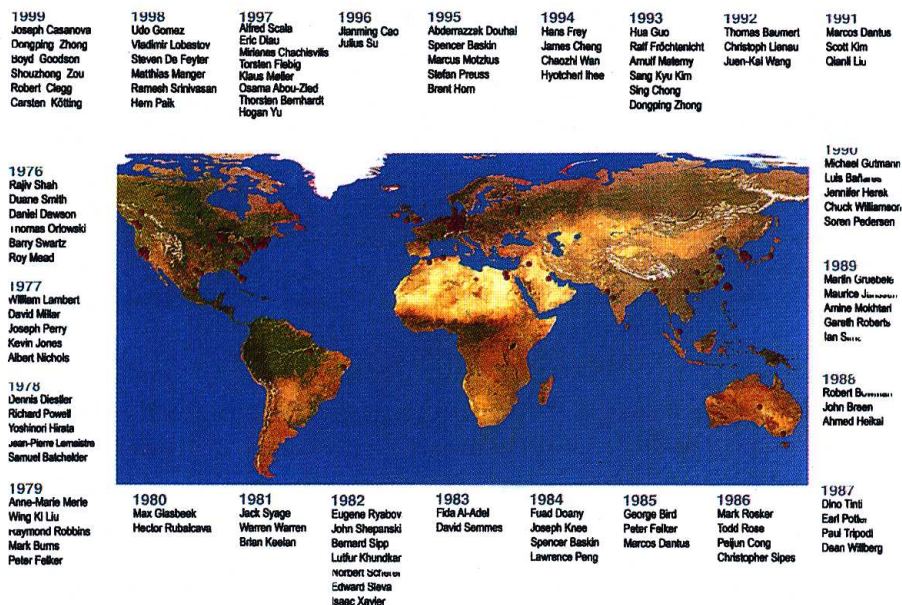


Figure 36. The International Roster of the Caltech group, from 1976–1999. The red circles are usually composite of many dots, reflecting the more than one hundred graduate students, post-doctoral fellows and visiting associates, who made up the research team over the years.

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. Caltech proved to be the ideal scientific institution for me, not only because of the strong science it radiates, but also because of its culture, the “science village”. I will never forget the impact of the “round table” at the Athenaeum. Vince McKoy, friend, colleague and neighbor at Caltech, has been the source of enjoyment and stimulation for over 20 years; Vince has taken an almost daily interest in our progress! Over the years I have enjoyed discussions with Spencer Baskin whose critical and wise judgment served as a sounding board for penetrating physics concepts.

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Over the past 20 years at Caltech my group and I have published some 300 scientific papers. The following list includes *some reviews, feature articles, and a few books*:

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