

TIME AND MATTER – SCIENCE AT NEW LIMITS¹

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INTRODUCTION

Until 1800 AD, the ability to record the timing of individual steps in any process was essentially limited to time scales amenable to direct sensory perception – for example, the eye's ability to see the movement of a clock or the ear's ability to recognize a tone. Anything more fleeting than the blink of an eye (~0.1 second) or the response of the ear (~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. By the 1980's, this resolution became ten orders of magnitude better [see Section III], reaching the femtosecond scale, the scale for atoms and molecules in motion (see Fig. 1).

For matter, the actual atomic motions involved as molecules build and react had never been observed before in real time. Chemical bonds break, form, or geometrically change with awesome rapidity. Whether in isolation or in any other phase of matter, this ultrafast transformation is a dynamic process involving the mechanical motion of electrons and atomic nuclei. The speed of atomic motion is ~ 1 km/second and, hence, to record atomic-scale dynamics over a distance of an angström, the average time required

¹ Adapted from the Lecture published in *Les Prix Nobel* (1999).

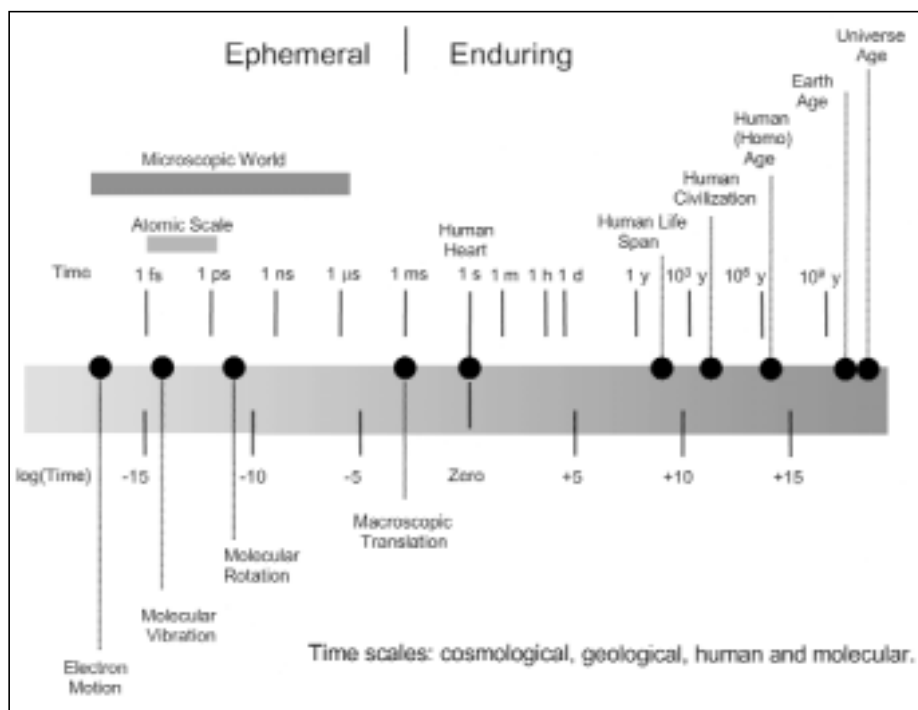


Figure 1. Time scales of cosmological, geological, human and molecular events; from the big bang to the femtosecond age.

is ~ 100 femtoseconds (fs). The very act of such atomic motions as reactions unfold and pass through their transition states is the focus of the field of femtochemistry. With femtosecond time resolution we can “freeze” structures far from equilibrium and prior to their vibrational and rotational motions, and study physical, chemical, and biological changes.

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

In order to study the motion, there exist three additional requirements. First, we need to *clock* the motion by defining its zero of time, also accurate to tens of femtoseconds. Second, the motion must be *synchronized* since millions of molecules are typically used in the recording of molecular motion. Third, molecular *coherence* (see below) must be induced to *localize* the nuclei. These requirements are satisfied by using a femtosecond pump (initiating) laser pulse, in what is referred to as a pump-probe configuration. For femtosecond studies, where femtosecond control of relative timing is needed, the laser pump and probe pulses are produced in synchrony, then the probe pulse is diverted through an adjustable optical path length. 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 micron 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 (femtosecond stroboscopy).

Applications are numerous. For example, studies in femtochemistry have spanned the different types of chemical bonds – covalent, ionic, dative and metallic, and the weaker ones, hydrogen and van der Waals bonds. In femtobiology, studies have continued to address the nature of dynamics in complex molecular systems, such as proteins and DNA. Studies have been made in the different phases of matter: gases and molecular beams; mesoscopic phases of clusters, nanostructures, particles and droplets; condensed phases of dense fluids, liquids, solids, surfaces and interfaces. New opportunities are also emerging with current interest in controlling molecular dynamics and in advancing diffraction methods for structural studies.

II. COHERENCE, DUALITY, AND THE UNCERTAINTY PRINCIPLE

The femtosecond time scale is unique for the creation of coherent molecular wave packets on the atomic scale of length, a basic problem rooted in the development of quantum mechanics and the duality of matter (Fig. 2). Molecular wave functions are spatially diffuse and exhibit no motion. Superposition of a number of separate wave functions of appropriately chosen phases can produce the spatially localized and moving coherent wave packet (Fig. 3). The packet has a well-defined (group) velocity and position which now makes it analogous to a moving classical marble, but at atomic resolution, and *without* violation of the uncertain-

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
 Ψ 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 2. Light and matter – some historical milestones, with focus on duality and uncertainty.

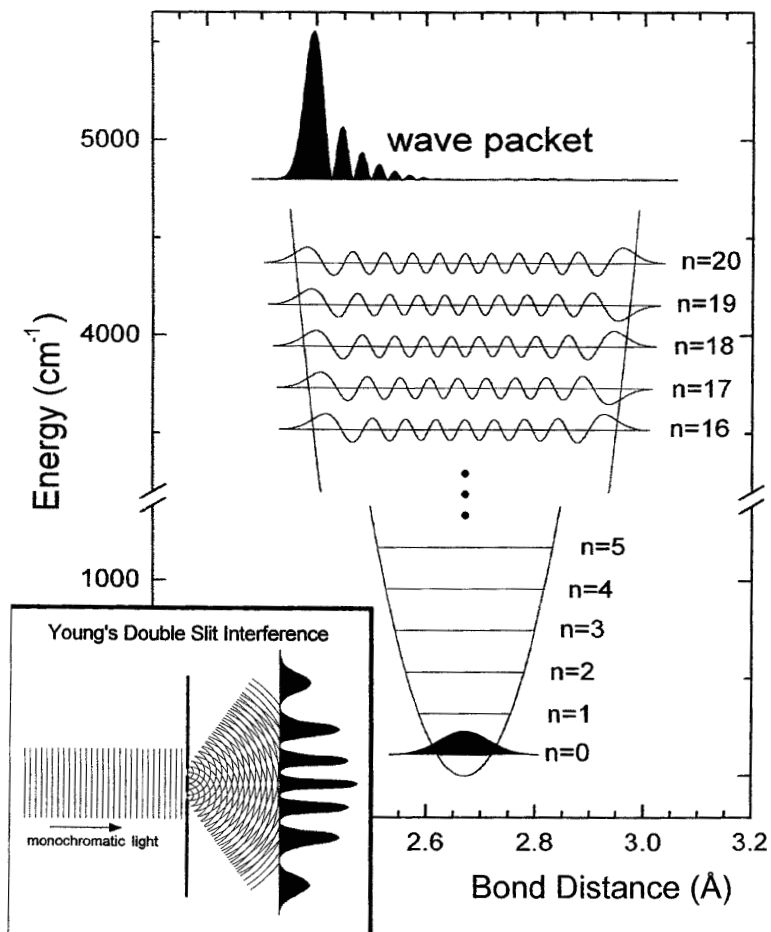


Figure 3. Coherent, localized wave packet (de Broglie length $\sim 0.04 \text{ \AA}$) of a diatomic molecule (iodine); 20 fs pulse. The contrast with the diffuse wave function limit (quantum number n) is shown. The inset displays a schematic of Thomas Young's experiment (1801) with the interference which is useful for analogy with light.

ty principle; this point regarding violation of quantum uncertainty was of major concern to many scientists and has been detailed elsewhere. As long as the wave packet (typical width $\sim 0.05 \text{ \AA}$) is sufficiently localized on the scale of all accessible space ($\sim 0.5 \text{ \AA}$ or more), as in the figure, a description in terms of the classical concepts of particle position and

momentum is entirely appropriate. In this way, localization in time and in space are simultaneously achievable for reactive and nonreactive systems, as discussed below.

The observation of motion in real systems requires not only the formation of localized wave packets in each molecule, but also a small spread in position among wave packets formed in the typically millions of molecules on which the measurement is performed. The key to achieving this condition is generally provided by the well-defined *initial*, equilibrium configuration of the studied molecules before excitation and by the “*instantaneous*” femtosecond launching of the packet. The spatial confinement (in this case $\sim 0.05 \text{ \AA}$) 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 in a bond-distance range much smaller than that executed by the motion. The femtosecond launching ensures that this narrow range of bond distance is maintained during the entire process of preparation, as shown below. Unless molecular and ensemble coherences are destroyed by intra- and/or inter-molecular perturbations, the motion is that of a *single-molecule trajectory* (Fig. 4).

This powerful concept of *coherence* was a key advance in observing the dynamics with atomic-scale 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 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 and used in laboratories around the world.

III. ARROW OF TIME: A CENTURY OF DEVELOPMENT

Time resolution in chemistry and biology has witnessed major strides, which are highlighted in (Fig. 5). 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. 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

Concept of Coherence

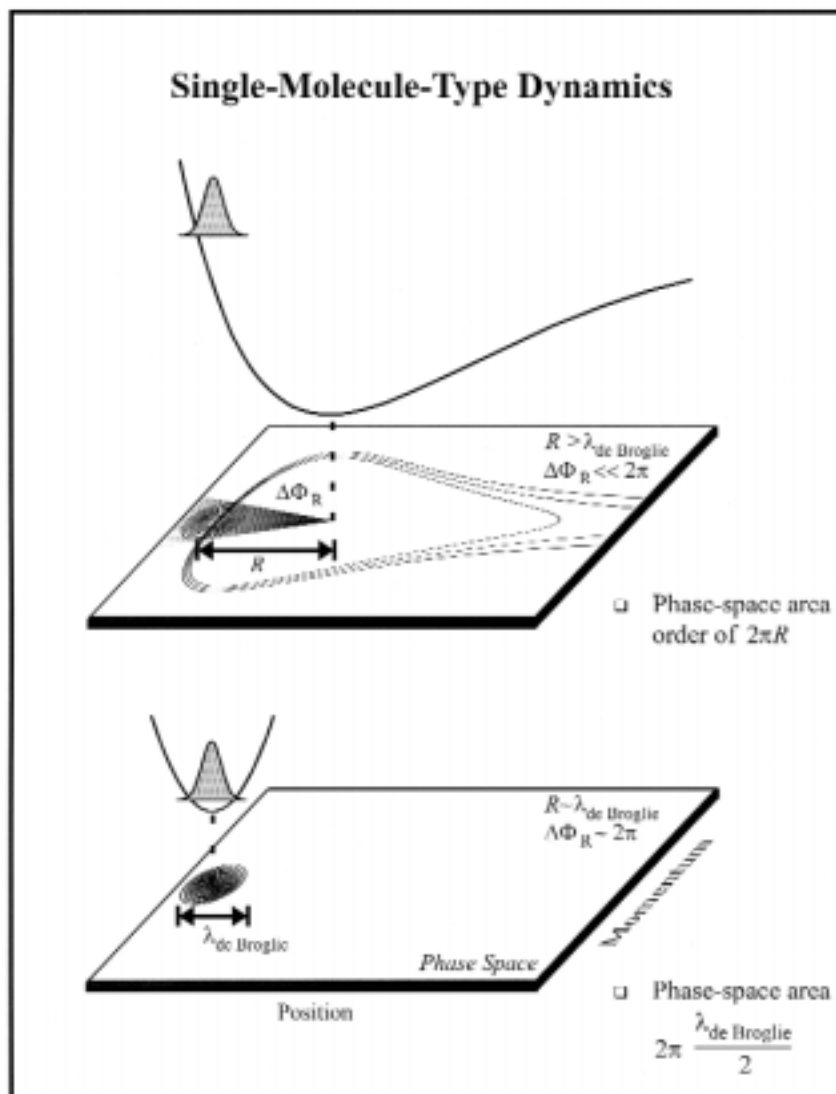


Figure 4. Concept of coherence, fundamental to the dynamics with atomic-scale resolution and in the control of reactivity. For details, see references by the author in the section, Further Reading.

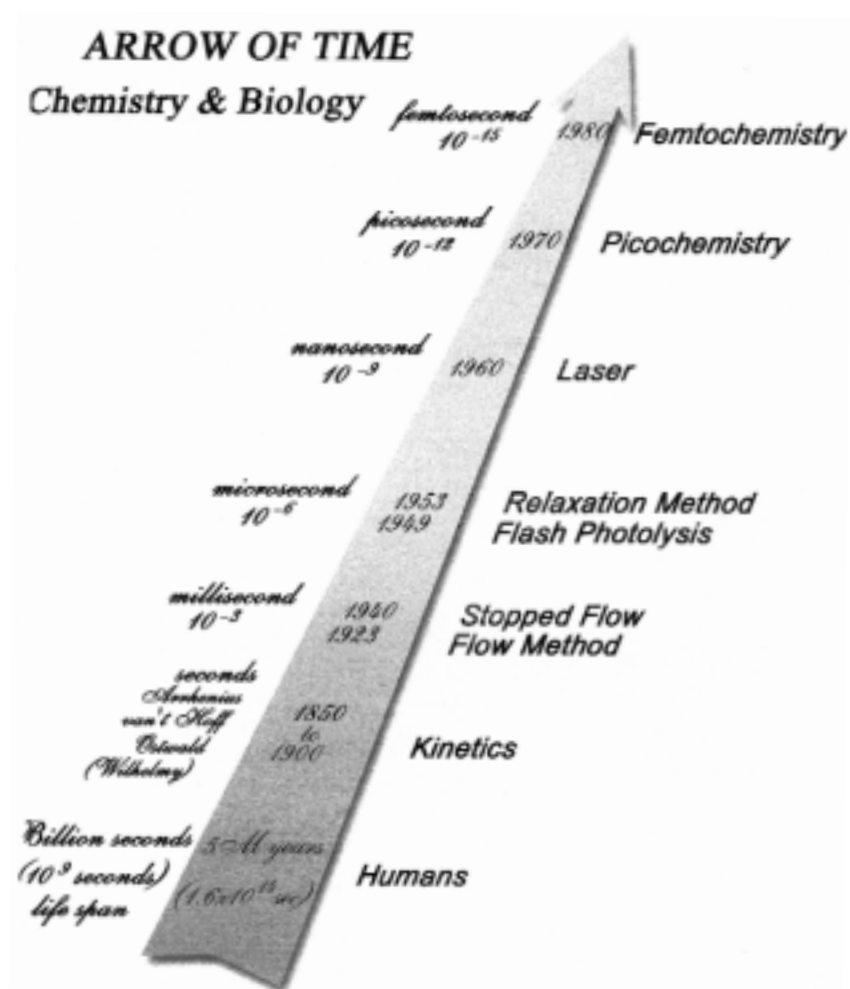


Figure 5. Arrow of Time in chemistry and biology – some of the steps in over a century of development (see text).

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.

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) 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 fs response). 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, CS₂ 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. They demonstrated in 1899 the importance of synchronization in a pump-probe configuration. The setting of time delays was achieved by varying the light path.

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. For this contribution, Eigen and Norrish and Porter shared the 1967 Nobel Prize. Flash photolysis utilized the above pump-probe approach, but one of the flashes was made very intense 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 (see below). 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 and Sorokin, 1966) were obtained in 1974 by Chuck Shank and Eric Ippen at Bell Labs, and in 1987 a six fs pulse was achieved. In 1991, with the generation of fs pulses from solid-state Ti-sapphire lasers by Sibbett and col-

leagues, dye lasers were rapidly replaced and fs pulse generation became a standard laboratory tool; the state-of-the-art, once 8 fs, is currently ~ 4 fs and made it into the Guinness Book of World Records (Douwe Wiersma's group). The tunability is mastered using continuum generation (Alfano & Shapiro) and optical parametric amplification.

In the late sixties and in the seventies, picosecond 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; the first ps study of chemical reactions (and orientational relaxations) in solutions by Ken Eisensthal; the direct measurement of the rates of intersystem crossing by Robin Hochstrasser; and the novel approach for measurement of ps vibrational relaxations (in the ground state of molecules) in liquids by Wolfgang Kaiser and colleagues. The groups of Shank and Ippen have made important contributions to the development of dye lasers and their applications in the ps and into the fs regime. Other studies of chemical and biological nonradiative 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.

IV. THE BIRTH OF THE FIELD

Stimulated by earlier work done at Caltech in the 1970's and early 80's on coherence and intramolecular vibrational-energy redistribution (IVR), we designed in 1985 an experiment to monitor the process of bond breakage ($\text{ICN}^* \rightarrow \text{I} + \text{CN}$). The experimental resolution at the time was ~ 400 fs and we could only probe the formation of the CN fragment. We wrote a paper, ending with the following words: *"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 (~ 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."* This realization led, in two years time, to the study of the same reaction but with ~ 40 fs time resolution, resolving, for the first time, the elementary process of a chemical bond and observing its transition states.

One year later in 1988, we reported on the NaI discovery which represents a paradigm shift for the field. There were two issues that needed to be established on firmer bases: the issue of the uncertainty principle and the influence of more complex potentials on the ability of the technique 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: 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 femtochemistry experiments on NaI and NaBr, and the results were thrilling and made us feel very confident about the ability to probe transition states and final fragments. The experiments established the foundation for the following reasons:

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 – 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 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 strength, the branching of trajectories, etc. In the 1930's, Linus Pauling's description of this bond was *static* at equilibrium; now we can describe the *dynamics* in real time by preparing structures far from equilibrium. Numerous theoretical and experimental papers have been published by colleagues and the system enjoys a central role in femtodynamics.

The success in the studies of elementary (NaI and ICN) reactions triggered a myriad of other studies in simple and complex systems and in different phases of matter. These studies of physical, chemical, and biological changes are reviewed elsewhere (see Further Readings Section). Fig. 6 gives a summary of the scope of applications in femtochemistry, and Fig. 7 lists four general concepts which emerged from these studies. Fig. 8 highlights

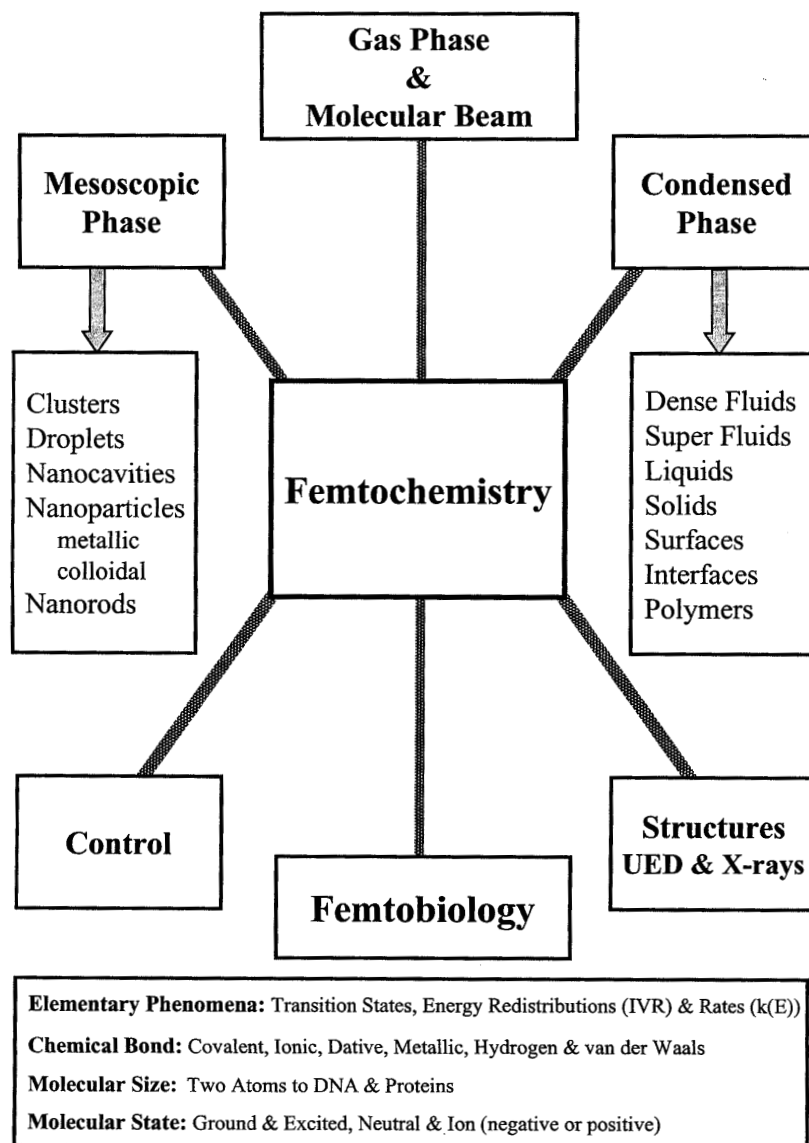


Figure 6. Areas of study in femtochemistry (and femtobiology) and the scope of applications in different phases.

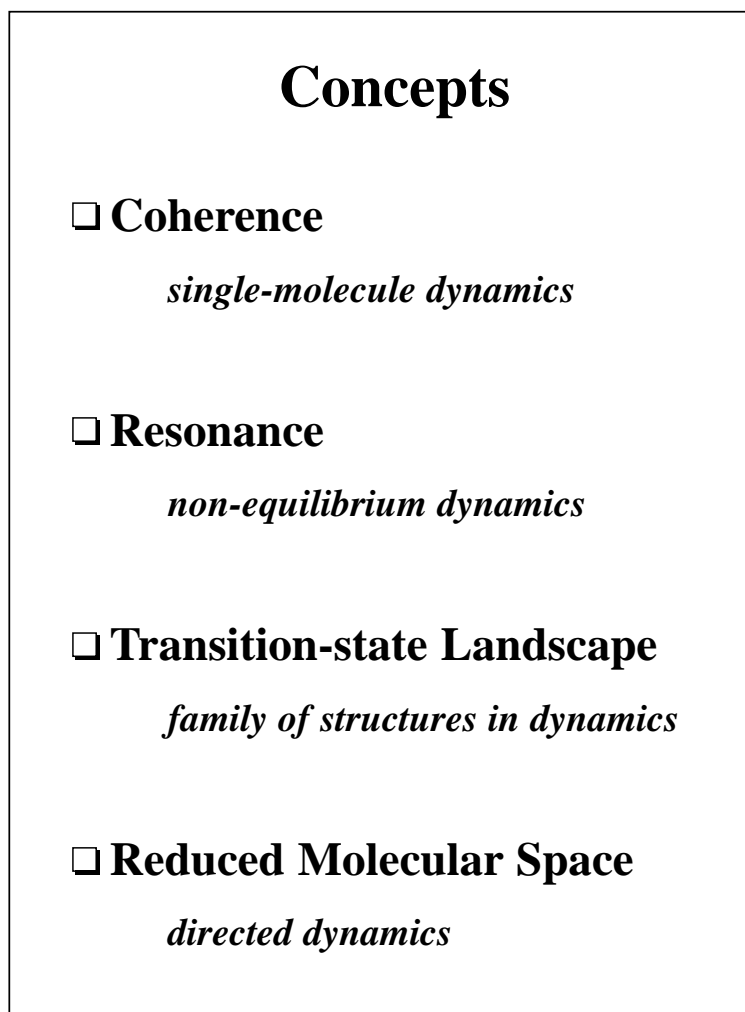


Figure 7. Concepts central to dynamics with femtosecond resolution. For details, see references by the author in the section, Further Reading.

Femtoscience & Femtotechnology

Some General Applications

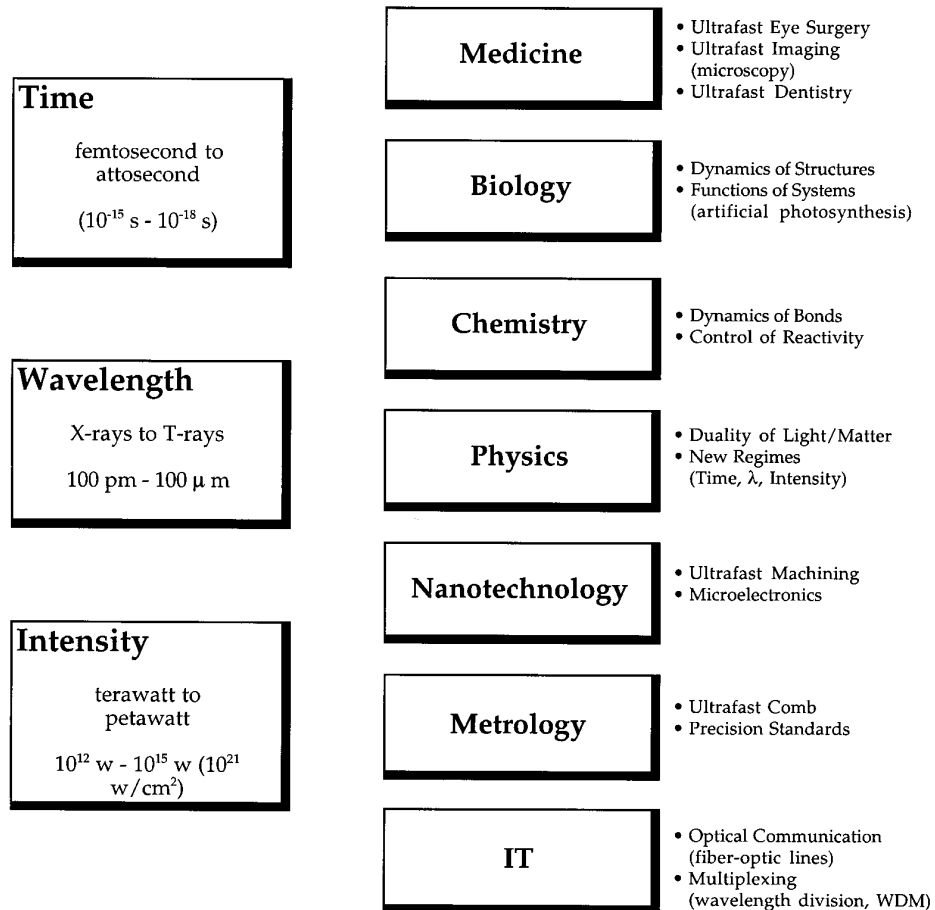


Figure 8. Some other areas of advances, from physics to medicine to technology. For reviews, see Further Reading section.

some general applications of femtoscience and femtotechnology, which are the results of advances made in new limits of time resolution, wavelength extension, and intensity or brightness (see Further Reading).

V. OPPORTUNITIES FOR THE FUTURE

Three areas of study are discussed here:

(A) Transient Structures from Ultrafast Electron Diffraction

Electron diffraction of molecules in their ground state has been a powerful tool over the past 50 years, and both electron and x-ray methods are now being advanced in several laboratories for the studies of structural changes. We have reported the latest advance in UED, 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. The direct observation of transient structural changes in the course of a reaction was published recently in PNAS and in Science.

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 (Fig. 9) is capable of studying complex systems in the gas and other phases. It holds great promise with opportunities for the future.

(B) Biological Dynamics

There have been important contributions to femtobiology and these include: studies of the elementary steps of vision; photosynthesis; protein dynamics; and electron and proton transport in DNA. In proteins such as those of photosynthetic reaction centers and antennas, hemoglobins, cytochromes and rhodopsin, a femtosecond event, bond breaking, twisting or electron transfer occurs. There exist global and coherent nuclear motions, observed in these complex systems, and it is possible that the complexity is not as complicated as we think. 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.

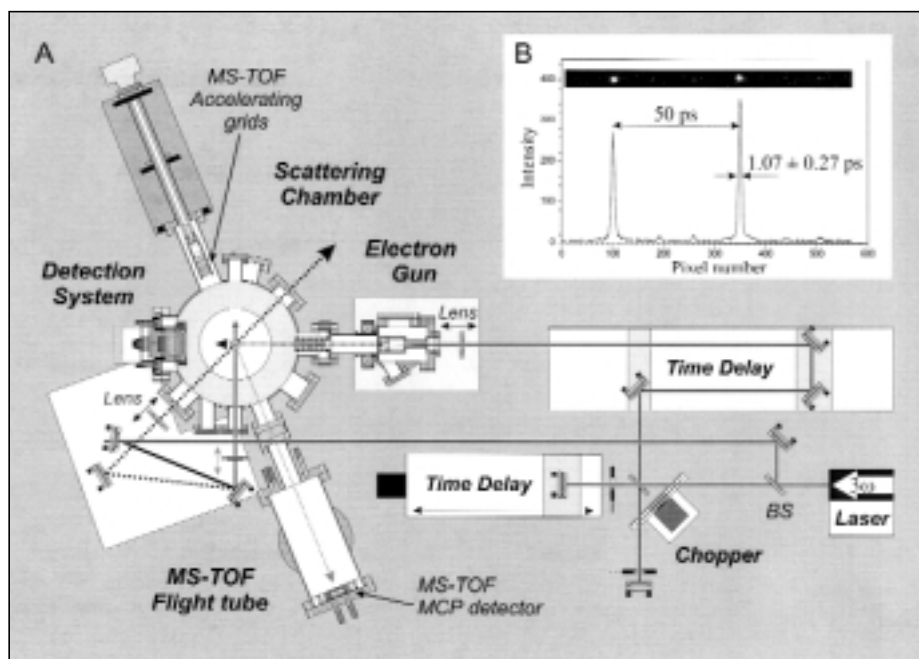


Figure 9. Ultrafast electron diffraction machine built at Caltech for the studies of molecular structures with spatial and temporal resolution on the atomic scale.

For DNA, we found that the local involvement of the base pairs controls the time scale of electron transfer. The degree of coherent transport critically depends on the time scale of molecular dynamics defining the so-called dynamical disorder. Static disorder, on the other hand, is governed by energetics. The measured rates 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 electron transfer, and oxygen reduction in models of metallo-enzymes. For the former, we have studied, with fs resolution, the protein Human Serum Albumin (HSA), probed with small (ligand) molecules. This protein is important for drug delivery. The ligand recognition is controlled by the time scale for entropic changes which involves the solvent. For model enzymes of O_2 transport, we examined novel picket-fence structures which bind oxygen to the central metal with $\sim 85\%$ efficiency at room temperature. In this system, we observed the release of O_2 in 1.9 ps and the

recombination was found to occur on a much longer time scale. These are fruitful areas for future research, especially in that they provide prototype systems for O₂ reduction in the transition state at room temperature. Studies in femtobiology are continuing in our laboratory and include the recognition in protein-DNA complexes (Fig. 10).

(C) 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. It turned out that its generalization could not be made without knowing and controlling the time scales of IVR in molecules. Moreover, state-selective chemistry is quite different from bond-selective chemistry. The second avenue was that of IR multiphoton chemistry. In this case, it was shown that the initial IR coherent pumping could be used for selective isotope separation. Such an approach has proven successful, even on the practical scale, and Vladelin Letokhov has called the process "incoherent control".

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 (Fig. 11). The title of the paper was: Laser Selective Chemistry – Is it Possible? The subtitle stated the message, "With sufficiently brief and intense radiation, properly tuned to specific resonances, we may be able to fulfill a chemist's dream, to break particular selected bonds in large molecules." Ultrashort pulses should be used to control the system in the desired configuration by proper choice of the *coherence time* (duration) and delay and the ability to *localize* the system in phase space.

Experimentally, we had already developed methods for the control of the phase of the field of optical pulses with the idea of using the *phase* ("pulse shaping") to control molecular processes – collisions, inhomogeneous broadenings and even photon locking which could inhibit relaxation; the time scale was ns and for the control of IVR, fs pulses were needed. Prior to this work, the optical pulse field,

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

was simply defined by the envelope A(t) and the frequency ω ; the phase $\phi(t)$

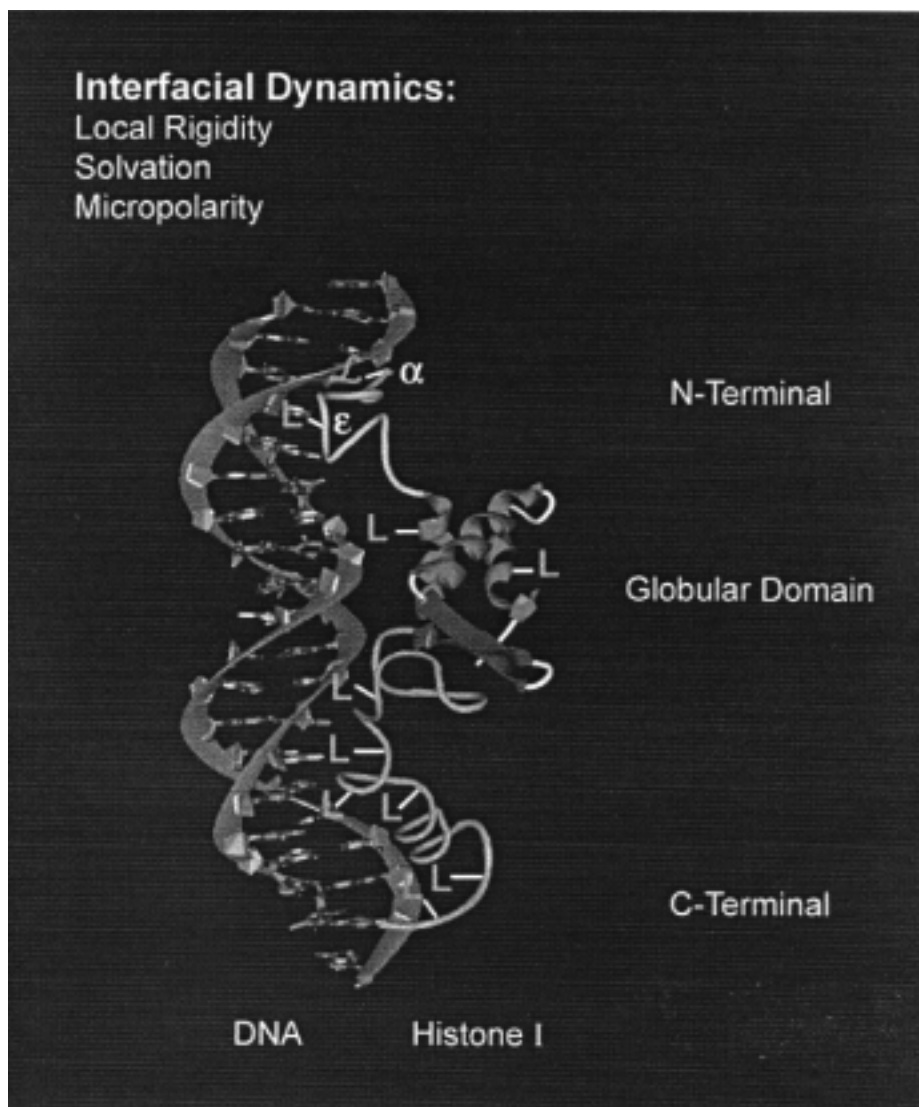
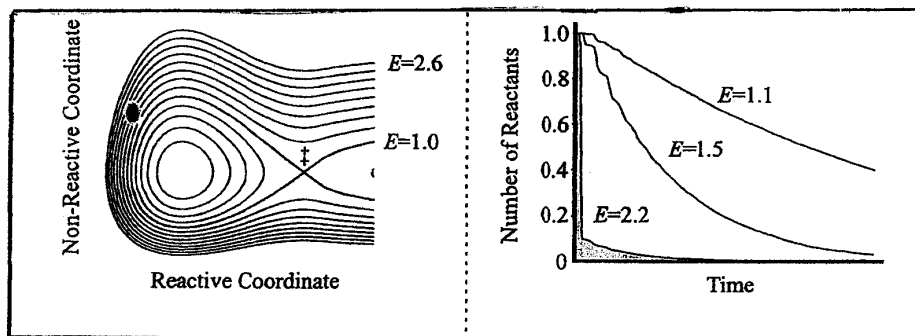


Figure 10. The protein (histone I)/DNA system studied in this laboratory, with the aim of elucidating the dynamics and the elements important in molecular recognition and chromatin condensation.



Møller and Zewail

Figure 11. Matter control with ultrashort laser pulses; suggestion made in the 1980 paper and the experimental demonstration and theoretical justification published nearly 20 years later.

was unknown. By controlling $\phi(t)$ we were able to make sequences of phase-coherent multiple pulses (optical analogue of NMR) and to tailor a composite “single” pulse with a prescribed $\phi(t)$. For example, 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. Similarly, by choosing pulse sequences such as $x-y-x(\bar{x})$ we experimentally locked the system and thus lengthened its relaxation time considerably.

On the fs time scale, we studied some elementary reactions, and recently, we turned our attention to complex molecular systems, but this time to implement the 1980 idea. In a series of molecules of increasing complexity, but retaining the same reaction coordinate, we studied selectivity control (IVR and entering near the transition state); the rate of reaction was two to three orders of magnitude larger than the expected *statistical* limit. This work was published in *Science* and promises to be significant for achieving non-statistical chemistry by localization at high energy, in time and space (see Figs. 4, 11). The concept suggests that control at high (chemical) energies is more realistic, in contrast with the conventional wisdom which asserts the need for low energies – time is of the essence! Further studies should explore other systems.

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. Applications of the Tannor-Rice-Kosloff scheme will continue in this area of control on the fs time scale. 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, similar 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 for a targeted second harmonic generation or a yield of chemical reaction as reported by Gustav Gerber's group in Würzburg.

Kent Wilson showed the importance of chirped pulses in focusing and reflecting wave packets and, in a more recent contribution, he, with Warren Warren, used the evolutionary feedback approach to optimize the fluorescence of a molecule in solution. It should be noted that all of the above schemes change the coherent composition of the initial packet and hence the evolution in different channels – but the evolution dictated by the natural forces of the atom remains unchanged! Intense fields may do so. We did not discuss here CW control schemes such as the one advanced by Paul Brumer and Moshe Shapiro.

VI. PERSPECTIVES

The key to the explosion of research can perhaps be traced to three pillars of the field.

(A) 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 1950's (milli)microsecond time scale to present femtosecond resolution, opened the door to studies of new phenomena and to new discoveries; (ii) the cornerstone of reactivity, the transition state of structures in motion, could be clocked as a molecular species TS^\ddagger , providing a real foundation to the theoretical hypothesis for ephemeral species $[TS]^\ddagger$, and leading the way to numerous new studies. Extensions will be made to study transition state dynamics in complex systems, but the previous virtual status of the transition state has now given

way to experimental reality; (iii) inferences deduced from “rotational periods” as clocks in molecular reactions can now be replaced by the actual clocking of the nuclear (vibrational) motion. In the 1960’s, there was some thought that the relevant time scale for chemistry and biology was the microsecond (or longer) 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 detailed above and summarized below.

(B) Atomic-Scale Resolution

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

(C) Generality of the Approach

Three points are relevant: (i) In retrospect, the femtosecond time scale was just right for observing the “earliest dynamics” at the actual vibrational time scale of the chemical bond; (ii) the time resolution offers unique opportunities when compared with other methods. Processes often appear complex because we look at them on an extended time scale, during which many steps in the process are integrated; (iii) the methodology is versatile and general, as evidenced by the scope of applications in different phases and of different systems. It is worth noting that both *excited* and *ground state* reactions can be studied. It has been known for some time that the use of multiple pulses can populate the ground state of the system and, therefore, the population and coherence of the system can be monitored. The

use of CARS, DFWM, SRS, π -pulses or 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; and the other utilizes CARS for the study of polymers in their ground state, as we did recently. Ground-state dynamics have also been studied by novel fs photodetachment of negative ions, and the subfield of fs dynamics of ions is now active in a number of laboratories.

VII. 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 tenth anniversary of femtochemistry, Will Castleman and Villy Sundström put this advance in a historical perspective. The recent Nobel report addresses with details the field and its position in over a century of developments (see Further Readings). Fig. 6 summarizes areas of study and the scope of applications in different phases and Fig. 8 highlights some advances in other areas, including medicine, nanotechnology, and metrology (see Further Reading). Developments will continue and new directions of research will be pursued. Surely, studies of transition states and their structures in chemistry and biology will remain active for exploration in new directions, from simple systems to complex enzymes and proteins, and from probing to controlling of matter.

Since the current femtosecond lasers (4.5 fs) are now providing the limit of time resolution for phenomena involving nuclear motion, one may ask: Is there another domain in which the race against time can continue to be pushed? Sub-fs or attosecond resolution may one day allow for the direct observation of the coherent motion of electrons. I made this point in a 1991 Faraday Discussion review and, since then, not much has been reported except for some progress in the generation of sub-fs pulses. In the coming decades, this may change and we may view electron rearrangement, say, in the benzene molecule, in real time, recalling, as in the femtosecond domain, "the uncertainty problem" is not a problem provided coherence of electron states is created.

Additionally, there will be studies involving the combination of the "three scales", namely time, length and number. We should see extensions

to studies of the femtosecond dynamics of *single molecules* and of *molecules on surfaces* (e.g. using STM). Combined time/length resolution will provide unique opportunities for making the important transition from molecular structures to dynamics and to functions. We may also see that all of femtochemistry can be done at micro-to-nano Kelvin temperatures, utilizing lasers and other cooling techniques.

It seems that on the femtosecond to attosecond time scale we are reaching the “inverse” of the big bang time, with the human heartbeat “enjoying” the geometric average of the two limits (Fig. 1). 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. Perhaps we are approaching a universal limit of time and matter!

FURTHER READING

Reports and Articles

- (1) J.-M. Hopkins and W. Sibbett, “Ultrashort-Pulse Lasers”, *Scientific American*, 283 (Sept. Issue), 73-79 (2000).
- (2) A.H. Zewail, “Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond using Ultrafast Lasers”, in *Les Prix Nobel*, Stockholm, Sweden, pp. 110-203 (1999); *Angewandte Chemie*, Intern. Ed., 39, 2586-2631 (2000); German Ed., 112, 2688-2738 (2000)
- (3) A.H. Zewail, “Laser Selective Chemistry – Is it Possible?”, *Phys. Today* 33, 2-8 (1980).
- (4) A.W. Castleman and V. Sundström (eds.), “Ten years of Femtochemistry: Time Resolution of Physical, Chemical and Biological Dynamics”, *J. Phys. Chem. – Special Issue* (1998), pp. 4021-4404
- (5) <http://www.nobel.se/announcement-99.html>
- (6) B.M. Garraway and K.-A. Suominen, “Wave Packet Dynamics: New Physics and Chemistry in Femto-time”, *Rep. Prog. Phys.* 58, 365-419 (1995).

Some Books

- (1) V. Sundström (ed.), *Femtochemistry & Femtobiology*, World Scientific, Singapore (1997) [Nobel Symposium].
- (2) P. Gaspard and I. Burghardt (eds.), *Chemical Reactions and Their Control on the Femtosecond Time Scale*, *Adv. Chem. Phys.* 101, Wiley, New York (1997) [Solvay Conference].

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- (3) A.H. Zewail, *World Scientific, Femtochemistry - Ultrafast Dynamics of the Chemical Bond*, Vols. I and II, New Jersey, Singapore (1994).
 - (4) E. Schreiber, *Femtosecond Real-Time Spectroscopy of Small Molecules & Clusters*, Springer, New York (1998).
 - (5) H.C. von Baeyer, *Taming the Atom*, Random House, New York (1992).
 - (6) P. Ball, *Designing the Molecular World*, Princeton Univ. Press, Princeton (1994).