

The Nobel Prize in Chemistry 1999

Extended Version of the Press Release

The Royal Swedish Academy of Sciences has awarded
the 1999 Nobel Prize in Chemistry to

Professor **Ahmed H. Zewail**, California Institute of Technology, Pasadena, USA.

The Academy's motivation: "... for his studies of transition states of chemical reactions by femtosecond spectroscopy. "

Abstract:

This year's Nobel Laureate, Professor **Ahmed Zewail**, is rewarded for his pioneering investigations of chemical reactions on the time-scale they really occur. This is the same timescale on which the atoms in the molecules vibrate, namely femtoseconds (1 fs = 10^{-15} seconds). Only recently have developments in laser technology enabled us to study such rapid processes, using ultra-short laser flashes. Professor Zewail's contributions have brought about a revolution in chemistry, with consequences for many other fields of science, since this type of investigation allows us to understand and predict important processes.

Development of "Femtochemistry" rewarded

When molecules undergo chemical reactions, their atoms move so fast that we cannot see it. But imagine that we could film the process with a high-speed camera and play it back in "slow motion". Chemists' curiosity has prompted increasingly advanced methods for studying even the smallest details of chemical reactions. The work rewarded with this year's Nobel Prize in Chemistry has demonstrated how it is possible to follow atoms and molecules in "slow motion" during a chemical reaction in which chemical bonds are broken and new ones created.

Professor Zewail is using a technique that may be described as the world's fastest camera. This uses laser flashes of such short duration that we are down to the time scale on which the reactions actually happen—femtoseconds. One femtosecond (fs) is 10^{-15} seconds, that is, 0,000000000000001seconds, which is to a second as a second is to 32 million years! This area of physical chemistry has been named *femtochemistry*.

Femtochemistry has enabled us to understand the underlying mechanisms why some chemical reactions occur but not others, and why reaction rates and yields are dependent on temperature. Inspired by Zewail's pioneering experiments some 10 years ago, scientists the world over are studying processes with femtosecond spectroscopy in gases, fluids and solids, on surfaces, in polymers and in biological systems. Applications range from how catalysts function and how molecular electronic devices should be designed, to the most delicate mechanisms of life processes and how the medicines of the future should be designed and produced.

How fast are chemical reactions?

Chemical reactions can, as we all know, proceed with very varying velocities—compare a rusting nail or a burning candle to exploding dynamite. However, common to most reactions is that their velocity increases as temperature rises, i.e. when molecular motion becomes more violent.

For this reason researchers already long ago assumed that a molecule first needs to be “activated”, kicked over a barrier so to speak, if it is to react. Expressed differently, when two molecules collide nothing normally happens, they just bounce apart. But if the temperature is high enough the collision may be so violent that they react with each other and new molecules form. Once a molecule has been given a sufficiently strong ‘temperature kick’ it reacts incredibly rapidly, whereupon chemical bonds break and new ones form.

The barrier is determined by the forces that hold the atoms together in the molecule (the chemical bonds), roughly like the gravitational barrier that a moon rocket from Earth must surmount before it is captured by the Moon's force-field. But until very recently little was known about the molecule's path up over the barrier and what the molecule really looks like when it is at the top, its '*transition state*'. The scientists understood this could be key information to understand a lot, from how life has arisen and evolved to how new drugs should be designed or how industrial processes should be made harmless to the environment.

Hundred years of research

Swedish physical chemist Svante Arrhenius (Nobel laureate in Chemistry 1903), inspired by Jacobus van't Hoff (the first Nobel Chemistry laureate, 1901), presented in 1889 the first clear description of how the rates of chemical reactions vary as function of temperature. His well known formula for the rate constant's temperature dependence:

$$k = A e^{-Ea/kT}$$

has been applied for more than a century by chemists and physicists. In this equation k in the exponent is Boltzmann's constant, T the temperature (in Kelvin) and E_a the so-called '*activation energy*', i.e. the height of the barrier up to a hypothetical state as Arrhenius called it, the '*activated complex*'. Obviously the ratio between E_a and kT in the exponent is crucial (kT is a measure of the energy of temperature motions according to Boltzmann, the founder of statistical mechanics) and we see how a high temperature could compensate a high barrier.

The formula was given a more sophisticated interpretation in the 1930-ies when Henry Eyring and Michael Polanyi independently formulated '*transition-state theory*' based on dynamics in microscopic systems (single molecules) and presented an explicit expression for Arrhenius' pre-exponential factor A . One assumption made by the theory was that the transition state is passed extremely rapidly, on the time scale of molecular vibrations. That it would ever be possible to perform experiments in such short times was something no one dreamt of.

But this was exactly what Ahmed Zewail set out to do. He had realised, from an experiment in the 1970-ies on anthracene molecules at low temperature, that molecules could be brought to vibrate in pace. '*Coherent preparation*' of a sample system is thus a key point in all his experiments. We shall return to this concept.

A new research field is born

At the end of the 1980s Zewail performed a series of experiments that were to lead to the birth of a new research field called femtochemistry. This could be described as using a high-speed camera (the world's fastest!) to image molecules during the actual course of chemical reactions and trying to capture snap-shots of them just in the transition state. The camera was based on new laser technology, with light flashes of some tens of femtoseconds.

The time it takes for the atoms in a molecule to perform one vibration is typically 10-100 fs. That chemical reactions should take place on the same time scale as when the atoms oscillate may be compared to two trapeze artists "*reacting*" with each other on the same time scale as that on which their trapezes swing back and forth.

Inspired by Zewail's experiments and exploiting his principles, scientists the world over study femtosecond-resolved processes in gases, liquids, solid materials, on surfaces, in polymers and in biological systems. The applications range from studies of elementary reactions, i.e. the smallest steps in a chain of reactions, to molecular dynamics (how the molecules and atoms in them move). We can now address problems such as the mechanisms for breaking and forming

chemical bonds, and the transferring of protons, electrons and energy within or between molecules. Femtosecond Spectroscopy has created a revolution because it makes it possible, for the first time, to “see” in real time, and thus to understand and predict, what is really happening in chemical reactions. That includes in principle almost anything: from the processes in the candle flame and the exploding dynamite to the most delicate details of the life processes.

Towards increasingly shorter times

What would a TV broadcast of a soccer game be without slow-motion photography that afterwards shows the fastest and smallest movements of the players’ legs and arms and the ball when a goal is scored? Similarly, the chemists’ curiosity on what really happens during a chemical reaction has, over the years, led to increasingly more sophisticated methods to improve time resolution.

Light was early used to detect chemical processes: different substances have different colours and using an instrument called a spectrophotometer and a watch one could follow the transformation (*kinetics*) of different substances into each other. A major advance was achieved in 1923 by two Englishmen, Hartridge and Roughton, who let two solutions arriving through separate tubes meet and be mixed, then letting the mixture flow swiftly through an outlet tube of glass. By looking into this tube at different distances from the point of mixing, they could follow the reaction down to times as short as thousands of a second. Today a billion (10^{12}) times better time resolution can be achieved by instead letting molecules of molecular beams in vacuum collide and use ultrashort laser flashes to look at the emerging beam of product molecules.

But first, let us stop at another milestone. It was another two Englishmen, Ronald Norrish and George Porter, Nobel Laureates in Chemistry 1967, who improved time resolution by using a flash lamp so they could study molecules with millisecond to microsecond lifetimes. They shared the prize with a German scientist, Manfred Eigen, who reached a similar time resolution by exposing his chemical solution to a pressure or electrical shock or a heat shock. Further some million times better resolution was later achieved in studies of collisions between molecules in vacuum, work for which the Americans Dudley Herschbach, Yuan Lee and John Polanyi were awarded the Nobel Prize in Chemistry in 1986.

What did the chemists see as time resolution was successively improved? The first success was the discovery of substances formed along the way from the original reactant substances to the final products, substances termed *intermediates*. In the beginning these intermediates were generally still comparatively stable. Each improvement of the time resolution led to new links in a reaction chain in

terms of increasingly more unstable, i.e. short-lived, intermediates, being fitted into the puzzle of understanding how the reaction mechanism worked.

The contribution for which Ahmed Zewail is to receive the Nobel Prize means that we have reached the end of the road: the times of the smallest reaction steps—no chemical reactions occur faster than this. We then no longer speak about reaction *kinetics* but of reaction *dynamics*. With femtosecond spectroscopy we can, for the first time, observe in ‘slow motion’ what really happens as the reaction barrier is crossed and hence also understand the mechanistic background to Arrhenius’ formula for temperature dependence and to the formulae for which van’t Hoff was awarded his Nobel Prize.

Femtochemistry in practice

To achieve a “molecular movie” of a chemical reaction, Zewail mixes the reactants in the form of molecular beams in a vacuum chamber. In a simple case, a so-called unimolecular reaction step, it suffices with a molecular beam of one kind of substance. He then causes an ultrafast laser, which produces pulses lasting a few tens fs each, to inject two pulses onto the molecules: first a powerful *pump pulse* which excites the molecule to a higher energy state and in this way starts the reaction. The pump pulse is followed by a second (weaker) pulse, the *probe pulse* at a wavelength chosen to detect, e.g., the original molecule or an altered form of it. This pulse is timed to arrive at precise intervals after the reaction has been started, to reveal how long it takes for various molecular species to appear or vanish. The new shapes the molecule may take when it has been excited – perhaps going through one or more transition states—have spectra that may serve as fingerprints. The time interval between pulses can be varied simply by delaying the probe pulse by letting it travel a detour via some mirrors. Not a long detour since light travels fast: the distance 0.03 mm in 100 fs!

To better understand what happens, the fingerprints and the time elapsing are then compared with theoretical simulations based on quantum chemical calculations (Nobel Prize in Chemistry 1998) for spectra and energies of the molecules in their various states.

The first experiments

In his first series of experiments Zewail studied the unimolecular disintegration of iodine cyanide into iodine atom and cyano radical: $\text{ICN} \rightarrow \text{I} + \text{CN}$. In 1987 his research team, in an article in the Journal of Chemical physics with the somewhat sensational title “Real-time femtosecond probing of “transition states” in chemical reactions”, reported that they have managed to observe a transition state

corresponding to the I-C bond on its way to breaking—the whole reaction being over in 200 fs.

In another important experiment (published in 1988) Zewail and his group studied the dissociation of sodium iodide (NaI): $\text{Na}^+ \text{I}^- \rightarrow \text{Na} + \text{I}$. The pump pulse excites the ion pair $\text{Na}^+ \text{I}^-$ which has an equilibrium distance of 2.8 Å between the nuclei (Fig. 1a) to an excited form $[\text{Na-I}]^*$ which at this short bond distance assumes a covalent bonding character. However, its properties change when the molecule vibrates: when the Na and I atoms are at their outer turning points, 10–15 Å apart the electron, ie structure is ionic, $[\text{Na}^+ \dots \text{I}]^*$, as one electron has moved from Na to I. When the atoms move back together the bonding becomes covalent again: $[\text{Na-I}]^*$, and so forth.

A critical point during the vibration is when the distance is 6.9 Å. As seen in Figure 1a, this is where the excited state (upper curve) and ground state (lower curve) are very close to each other. At this point there is a great probability that the excited $[\text{Na-I}]^*$ will either fall back to its initial state $[\text{Na-I}]$ or decay into sodium and iodine atoms.

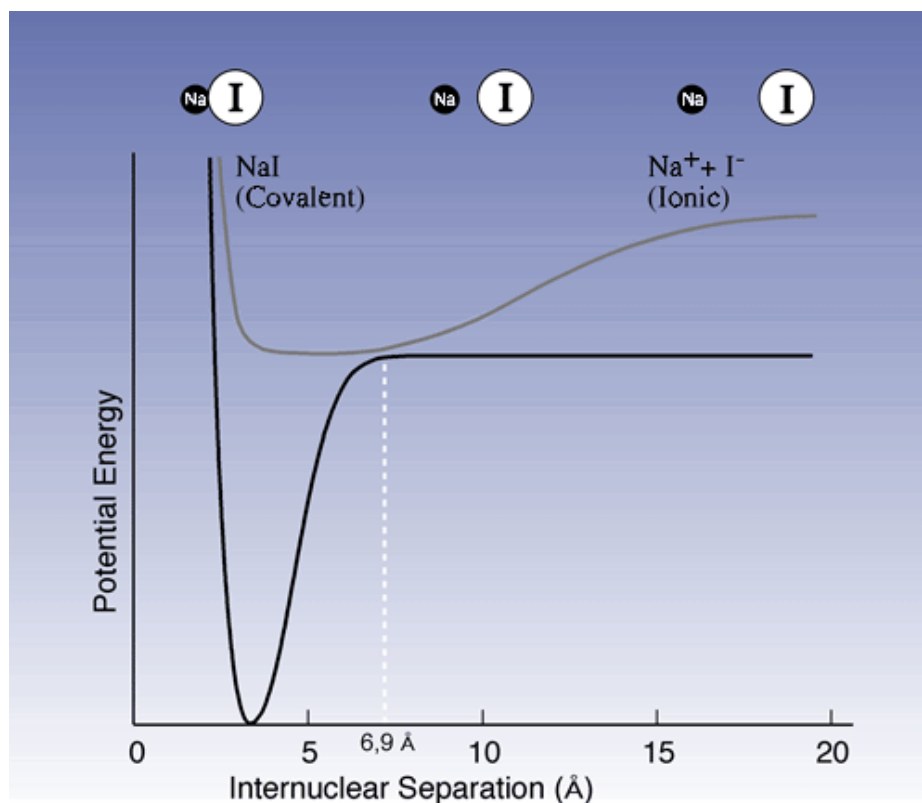


Fig. 1a) Potential energy curves showing the energies of ground state (bottom curve with deep minimum) and excited state (top curve) for NaI as function of the distance between the nuclei.

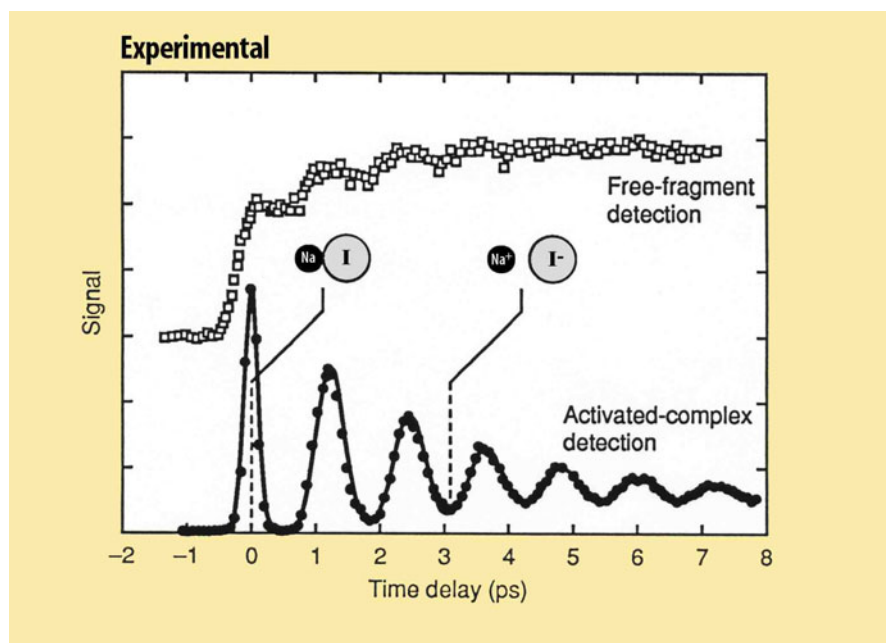


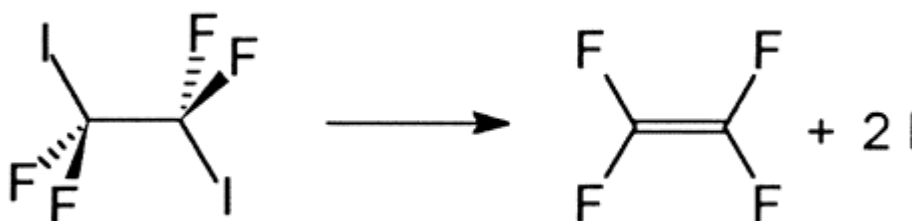
Fig. 1b) Experimental observations of coherent vibrations (so-called wavepacket motion) in femtosecond-excited NaI, on one hand manifested in terms of amount of activated complex $[\text{Na-I}]^*$ at covalent (short) distance, on the other as bursts of free Na atoms. At the experimental conditions the reaction probability is about 0.1, i.e. about one tenth of the vibrations lead to reactants.

What Zewail and his coworkers found was that they could follow the activated complex as it moved back and forth between covalent and ionic structures (Figure 1b) and, moreover, that bursts of free sodium atoms were produced in pace with these oscillations. The explanation was that the pump pulse had created a sample of excited molecules all starting at the point 2.8 \AA and thereafter vibrating in synchrony. Then they will all pass the magic point 6.9 \AA at the same time, explaining why they reacted almost at the same time and thus the oscillatory production of sodium atoms in the experiment.

This is the crucial point of Zewail's femtochemistry: to use a femtosecond pulse to, so to say, blow the whistle to start all the molecules at the same time and at the same point of their vibration cycles. A consequence of the synchronisation of the molecules ("coherent preparation" of the system), is that although the measurement by the later probe pulse will include a huge number of molecules, typically millions, their behaviour will not have blurred out but, thanks to the coherence, be like that of a classical vibrator, like a vibrating spring. In turn this enables observation of the movements of the nuclei during the vibration and thus a characterisation of the transition state with high spatial resolution (about 0.1 \AA in NaI).

Zewail also studied bimolecular reactions, such as the reaction between hydrogen atoms and carbon dioxide: $\text{H} + \text{CO}_2 \rightarrow \text{CO} + \text{OH}$ which occurs in the atmosphere and during combustion, and which he showed proceeding via a long-lived (1000 fs) intermediate molecule HOCO.

A question that has occupied many chemists is why certain chemical bonds are more reactive than others and what happens if there are two equivalent bonds in a molecule: will they break simultaneously or one at a time? In other words is it a one-step or a two-step process? To answer such questions, Zewail and coworkers studied the dissociation of tetrafluorodiiodoethane ($\text{C}_2\text{I}_2\text{F}_4$) into tetrafluoroethylene (C_2F_4) and iodine atoms (I).



They discovered that the two C–I bonds, which appear equivalent in the original molecule, break consecutively (the first bond cleavage takes 200 fs and the second one takes 100 times as long).

Never is research so important as when the results are unexpected. Zewail studied a seemingly simple reaction between benzene (a ring of six carbon atoms, C_6H_6) and iodine (I_2), a molecule consisting of two iodine atoms. When the two molecules come close together they form a complex. The laser flash makes an electron from benzene jump over to the iodine molecule, which then becomes negatively charged while benzene becomes positively charged. The negative and positive charges attract each other. The bond between the two iodine atoms is stretched as the one closest to benzene is attracted toward benzene, the other then goes off and flies away. All happens within 750 fs. Zewail found however that this is not the only way in which iodine atoms can be produced. Sometimes the electron fails and falls back onto benzene. But this is beyond the point of no return as far as the iodine is concerned: like a rubber band stretched to its limit and then breaks, the bond between them snaps and the two iodine atoms are both flying off.

Correspondingly, in a recent study of the complex between diethyl sulphide and iodine, Zewail shows that after charge separation induced by a fs pulse, a back electron transfer occurs in less than 150 fs, followed by the rupture

of the I–I bond with the release of the first I-atom in 510 fs. The second I-atom is trapped for 800 fs and then departs. From the observed times, the angular distributions and the speeds of the emitted I-atoms, the detailed reaction pathway and the structures of the complexes may be deduced.

These experiments illustrate important aspects of electron transfer and both reveal more complex reaction mechanisms than earlier anticipated.

Explosion of research

A much studied model reaction in organic chemistry is ring opening of cyclobutane to yield two ethylene molecules or the reverse, addition of two ethylenes to form cyclobutane. This reaction has been dealt with theoretically by two previous Nobel Laureates in chemistry, Woodward (Prize 1965) and Hoffmann (Prize 1981) and is considered a classic case of so-called concerted reactions. The reaction should thus proceed through one transition state as shown in Figure 2 to the left.

However, alternatively it might proceed via the breaking of just one C–C bond and the formation of an intermediate, tetramethylene (a so-called *diradical* having two free unpaired electrons), which in turn has to pass a second transition state before yielding the final products (Figure 2, right hand side). Again we have the question: a (concerted) one-step mechanism or a two-step mechanism? And again the experimental answer is not that of the simplest model: Zewail and coworkers discover that tetramethylene is indeed a possible intermediate, with a lifetime of 700 fs.

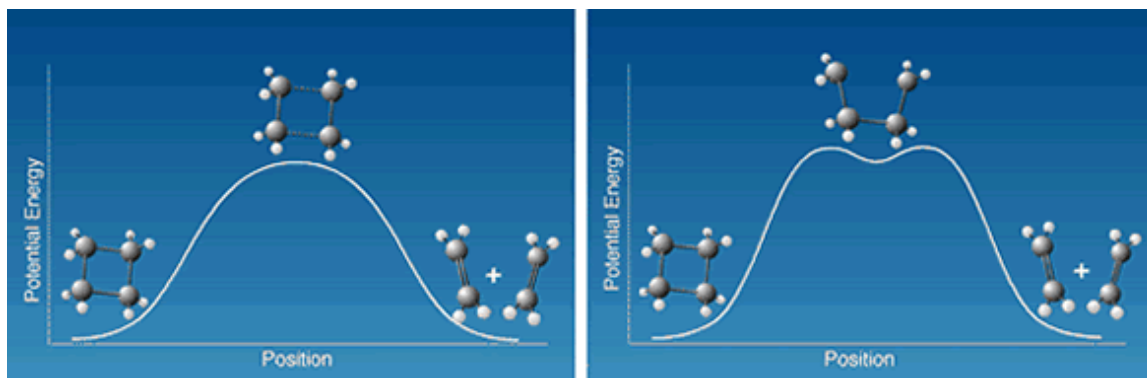
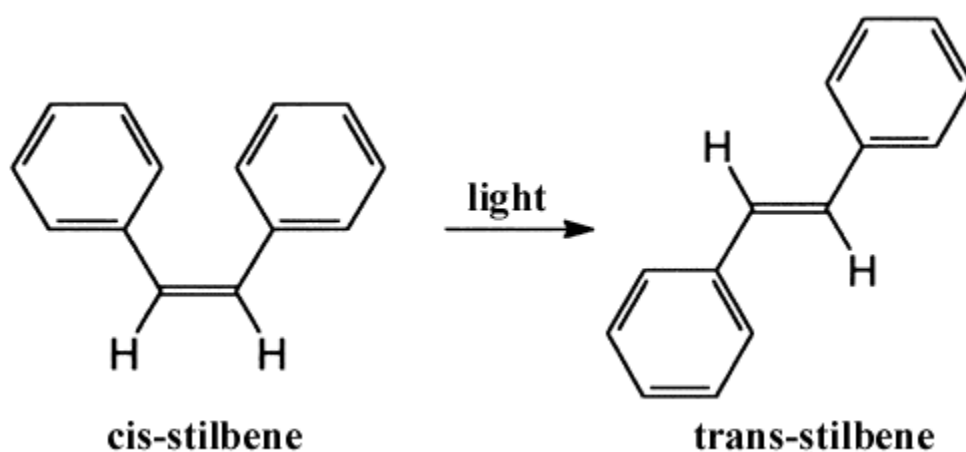


Figure 2.

How does cyclobutane dissociate into ethylene (or the reverse, how can cyclobutane form from two ethylene molecules) if thermally activated? The left-hand figure shows how the energy of cyclobutane varies if the two bonds are stretched and break simultaneously. The right-hand figure shows the case where one bond at a time breaks, so that the reaction goes via an intermediate (tetramethylene diradical).

Another type of reaction studied with femtosecond spectroscopy is the light-induced conversion of a molecule from one structure to another, photoisomerisation. The conversion of the *stilbene* molecule, which includes two benzene rings, between the *cis* and *trans* forms was observed by Zewail and his coworkers.



They demonstrated that upon exciting the *cis* form (left) with a femtosecond pulse, the central double bond of this ethylene-like molecule is weakened, allowing a rotation of both benzene rings (Bz) through 90° into a twisted intermediate form in about 300 femtoseconds, to finally yield the 180° *trans* form (right). Such a coherent twisting motion upon photo-excitation has also been observed by other researchers for *retinal*, which is part of the pigment rhodopsin responsible for light detection in our eyes. The high rate of the reaction (200 fs), and the observation of a coherent vibration that continues to oscillate in the reaction product, could explain the high efficiency (70%) of the reaction, a prerequisite for light-sensitive vision.

Another biologically important example where femtochemistry has explained efficient energy conversion is in chlorophyll molecules, which capture light in photosynthesis. In the mentioned examples energy economy is a crucial point, more specifically how the energy is redistributed in an excited molecule. In a big molecule the energy can generally “leak out” through many vibrational channels. The indicated examples of high efficiency of photoisomerisation indicate that there is a mechanism to quickly localise the energy to some part in the molecule (to one specific double bond in stilbene and retinal).

Another interesting aspect of femtosecond studies is recently emerging experimental evidence for cases when an assumption behind earlier reaction theories, namely that the energy added to a molecule will redistribute itself to

equilibrium before anything else happens, is not justified for short times. The energy-equilibrium assumption lies behind the factor $e^{-E_a/kT}$ in Arrhenius' formula. Under such circumstances, temperature is not defined and a theory that considers the explicit energy distribution in the molecule must instead be used.

Femtosecond studies according to Zewail's concept are being performed intensely the world over, using not only molecular beams but studying also processes on surfaces and on clusters, e.g. to understand and improve catalysts, in liquids and solvents (to understand mechanisms of the dissolving of, and reactions between, chemical substances in solution) and in polymers (e.g. to develop new material for use in electronics). In addition, femtochemistry has been applied to the study of many important biological systems.

Knowledge of mechanisms of chemical reactions is also important for our ability to control the reactions. A desired chemical reaction is often accompanied by a series of unwanted, competing reactions that lead to a mixture of products and hence the need for separation and cleansing. If the reaction can be controlled by initiating reactivity in selected bonds, this could be avoided.

Femtochemistry has fundamentally changed our view of chemical reactions. From a phenomenon described in terms of rather vague metaphors such as 'activation' and 'transition state' we can now see the actual movements of individual atoms: we can speak of their motions in time just as we imagine them: they are no longer invisible.

The explosive development of femtochemistry research, which this year's Nobel Laureate initiated, is therefore not surprising. With the world's fastest camera available, only the imagination sets bounds for new problems to tackle.

*By Professor Bengt Nordén
Member of the Nobel Committee for Chemistry*

Further reading

M.A. El-Sayed, I. Tanaka and Y. Molin "*Ultrafast Processes in Chemistry and Photobiology*" Blackwell Science 1995 306 pp, ISBN 0-86542-893-X

S. Pedersen, J.L. Herek and A.H. Zewail "*The validity of the Diradical Hypothesis: Direct femtosecond studies of the transition-state structures.* Science Vol 266 (1994) 1359- 1364.

A. H. Zewail *The birth of molecules* Scientific American December 1990 p 40-46.

V.K. Jain "*The World's Fastest Camera*" *The World and I*, October 1995 p 156-163.

Nationalencyklopedin (Swedish), *Fysikalisk kemi* (B. Nordén)

Nobel Symposium: *Femtochemistry & Femtobiology: Ultrafast Reaction Dynamics at Atomic-Scale Resolution* (Editor: V. Sundström) World Scientific, Singapore 1996.

Ahmed H. Zewail was born in 1946 in Egypt where he grew up and studied at the University of Alexandria. After continued studies in the U.S.A. he graduated with a PhD in 1974 at the University of Pennsylvania. After two years at the University of California at Berkeley he was employed at Caltech where he has the Linus Pauling Chair of Chemical Physics. Zewail is Egyptian and American citizen.

The amount of the Nobel Prize Award is SEK 7, 900, 000.