The Nobel Prize in Chemistry 1999

The Royal Swedish Academy of Sciences has awarded the 1999 Nobel Prize in Chemistry to Professor Ahmed H. Zewail for his studies of transition states of chemical reactions by femtosecond spectroscopy.

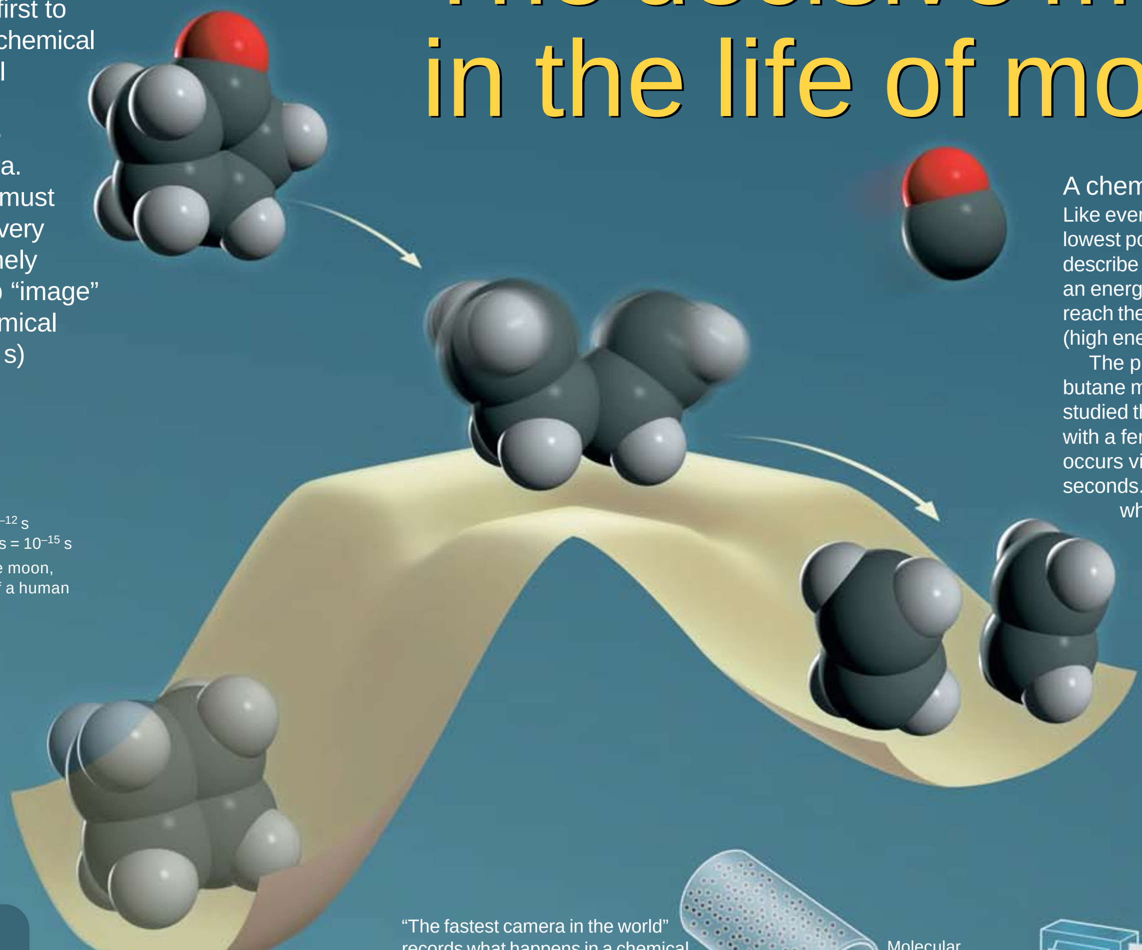
The decisive moments in the life of molecules

Ahmed Zewail receives the 1999 Nobel Prize in Chemistry for being the first to reveal the decisive moments of a chemical reaction – the moments when chemical bonds are broken and formed.

Zewail's technique uses what can be thought of as the world's fastest camera. The "shutter speed" of such a camera must be extremely high since molecules are very small (about 10^{-9} m) and move extremely rapidly (1 000 m/s). To obtain a sharp "image" of the molecules in the course of a chemical reaction requires a femtosecond (10^{-15} s) shutter speed.

1 ms	1 millisecond = 0.001 s = 10^{-3} s
1 µs	1 microsecond = 0.000 001s = 10^{-6} s
1 ns	1 nanosecond = 0.000 000 001 s = 10^{-9} s
1 ps	1 picosecond = 0.000 000 000 001 s = 10^{-12} s
1 fs	1 femtosecond = 0.000 000 000 000 001 s = 10^{-15} s

In one second light travels from the earth to the moon, while in one femtosecond it travels a fraction of a human hair's-breadth.

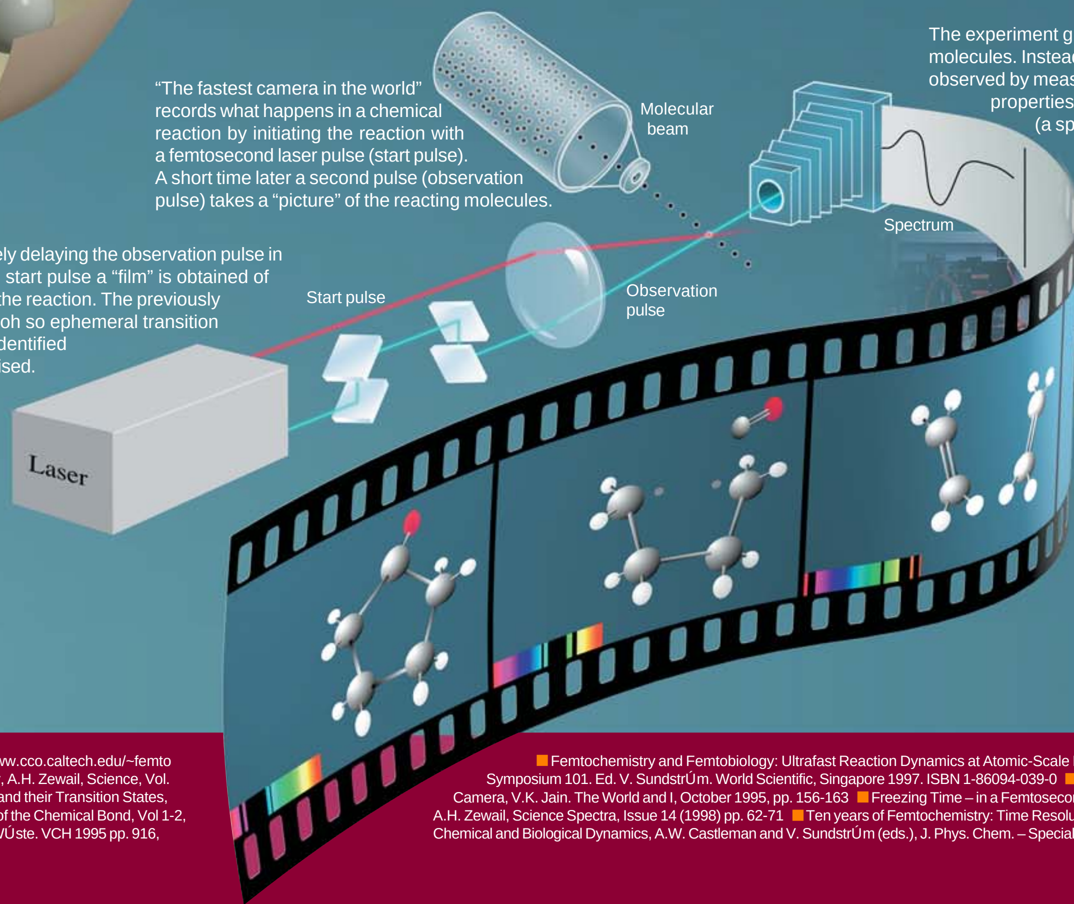


A chemical reaction – up hill and down dale

Like everything in nature, molecules strive to reach the lowest possible energy state. This makes it practical to describe reactions using energy surfaces. A molecule on an energy surface tries, like a child in a water-slide, to reach the lowest point. You need enough speed (high energy) to get up over the crests.

The picture to the left shows the ring opening of a cyclobutane molecule to form two ethylene molecules. Zewail studied this reaction by exciting cyclopentanone molecules with a femtosecond pulse. He could show that this reaction occurs via a transition state living a few hundred femtoseconds. This experiment settled an old argument over whether the reaction takes place in one step with simultaneous breaking of both bonds or in two steps, one bond breaking before the other.

We need to know the properties of the transition state if we are to understand, predict and perhaps modify the course of a reaction. For almost a hundred years the transition state remained a hypothetical species that few chemists believed could ever be observed. But this is precisely what Zewail has succeeded in doing.



"The fastest camera in the world" records what happens in a chemical reaction by initiating the reaction with a femtosecond laser pulse (start pulse). A short time later a second pulse (observation pulse) takes a "picture" of the reacting molecules.

The experiment gives no direct image of the molecules. Instead, the reacting molecules are observed by measuring certain characteristic properties, e.g. an optical property (a spectrum is obtained) or by recording the molecular masses (mass spectrometry).

By successively delaying the observation pulse in relation to the start pulse a "film" is obtained of the course of the reaction. The previously predicted but oh so ephemeral transition state can be identified and characterised.

The picture shows part of Zewail's "camera". It is a complex array of lasers, mirrors, lenses, prisms, molecular beams, detection equipment and more.

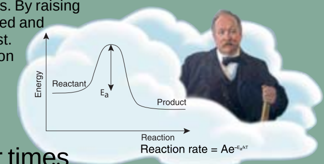
Zewail – King of Femtoland

Ahmed H. Zewail was born near Alexandria in Egypt. He has now been working for many years at Caltech, Pasadena, USA, where he directs a large Laser Femtochemistry laboratory, called Femtoland. He is also Director of the Laboratory for Molecular Sciences (LMS).

In 1878 the photographer Muybridge was able to capture movement with the fastest camera of the time. His series of pictures once settled a $ 25 000 bet. The wager was about whether a galloping horse at any time has all four hooves off the ground.

The Arrhenius Legacy

The Swedish chemist Svante Arrhenius (Nobel Prize 1903) was interested in how the rate of a chemical reaction varies with temperature. He concluded that there must exist an intermediate in the transformation from reactants to products. Later, this intermediate came to be known as the transition state. Imagine this state as the highest point on an energy surface, the crest of a hill over which the reacting molecules must pass to form products. By raising the temperature, more energy is added and more molecules can get over the crest. Arrhenius related the rate of a reaction to the height of the energy barrier (E_a) and to the temperature (T).



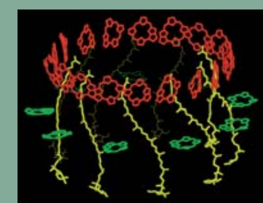
Towards ever-shorter times

1889	Arrhenius predicts the existence of transition states in chemical reactions.
1920s	Mixing experiments give information on the millisecond time-scale.
1949	Flash photolysis is introduced and makes it possible to study chemical reactions without the reactants needing to be mixed. The method is based on the fact that light can initiate chemical reactions (photochemistry). The microsecond time-scale is reached.
1960	The laser is invented and rapidly makes the nano- and picosecond time-scales available. Milli- to picosecond time-scales give valuable information on chemical reactions, but direct molecular motion is still impossible to observe.
1987	Zewail's first femtochemistry experiments.
1999	Guinness Book of Records gives duration of shortest reported light pulse as 4.5 femtoseconds.

Towards the future with femtochemistry

Some research applications of femtochemistry:

Biology
The processes of photosynthesis in which light energy is converted to chemical energy are being studied in detail with femtochemistry methods. Knowledge gained can be used for developing processes and materials for artificial photosynthesis.



Photosynthetic pigment molecules for collection of the sun's light energy.

Materials science
Future electronics will be based on light-driven processes since this allows faster components of greater capacities. Femtochemistry methods are already being used to study materials for tomorrow's electronics.

Chemistry
Being able to control chemical reactions is the chemist's dream! Knowledge from femtochemistry experiments affords opportunities for doing this and can lead to chemicals with unique new properties.

Medicine
Femtochemistry methods can be used for studying photochemical reactions used in medicine, e.g. for photodynamic cancer therapy.

Further reading:

■ Information on the 1999 Nobel Prize in Chemistry (press release): www.kva.se ■ The Femtoland web page: www.cco.caltech.edu/~femto ■ The Birth of Molecules, A.H. Zewail, Scientific American, Vol. 262, Dec. 1990, pp. 40-46 ■ Laser Femtochemistry, A.H. Zewail, Science, Vol. 242 (1988), pp. 1645-1653 ■ Femtochemistry: Recent progress in studies of Dynamics and Control of Reactions and their Transition States, A.H. Zewail, J. Phys. Chem. (Centennial Issue), Vol. 100 (1996) 12701-12 ■ Femtochemistry: Ultrafast Dynamics of the Chemical Bond, Vol 1-2, A.H. Zewail. World Scientific 1994 pp.915, ISBN 9810219407 ■ Femtosecond Chemistry, Vol 1-2, Eds. J. Manz, L. WÚste. VCH 1995 pp. 916, ISBN 3-527-29062-1

■ Femtochemistry and Femtobiology: Ultrafast Reaction Dynamics at Atomic-Scale Resolution, Nobel Symposium 101. Ed. V. SundstrÚm. World Scientific, Singapore 1997. ISBN 1-86094-039-0 ■ The World's Fastest Camera, V.K. Jain. The World and I, October 1995, pp. 156-163 ■ Freezing Time – in a Femtosecond, J.S. Baskin and A.H. Zewail, Science Spectra, Issue 14 (1998) pp. 62-71 ■ Ten years of Femtochemistry: Time Resolution of Physical, Chemical and Biological Dynamics, A.W. Castleman and V. SundstrÚm (eds.), J. Phys. Chem. – Special Issue (1998), pp. 4021.

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