Lecture-7

CSO202: Atoms, Photons & Molecules

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The Nobel Prize in Chemistry 1999

Ahmed Zewail

"for his studies of the transition states of chemical reactions using femtosecond spectroscopy"

Femtochemistry

Chemistry on the 10^{-15} Sec time scale!

$A + B\text{-}C \rightarrow A\text{-}B + C$

Complete evolution of chemical event

Chemical reaction kinetics: Task of making a motion picture of a reaction.

Difficulties of a movie-maker: Too many transient actors on the stage!!!!!

Making new bonds and breaking old ones: subpicosecond time scale.

Femtosecond laser pulses : sub-angstrom motion could be watched!!!!!!

Time scale of reactions

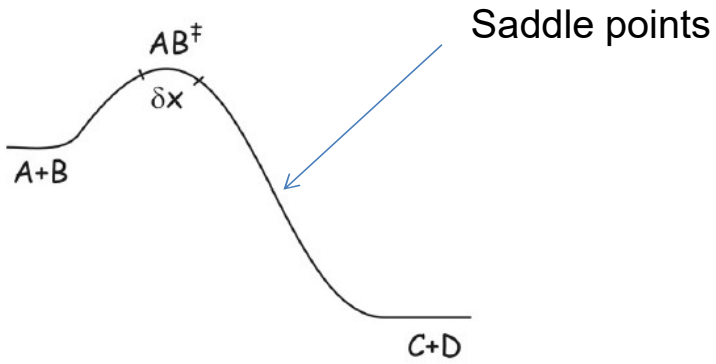
$$ABC^* \rightarrow [A \cdots BC]^{\ddagger *} \rightarrow A + BC \text{ (unimolecular)}$$

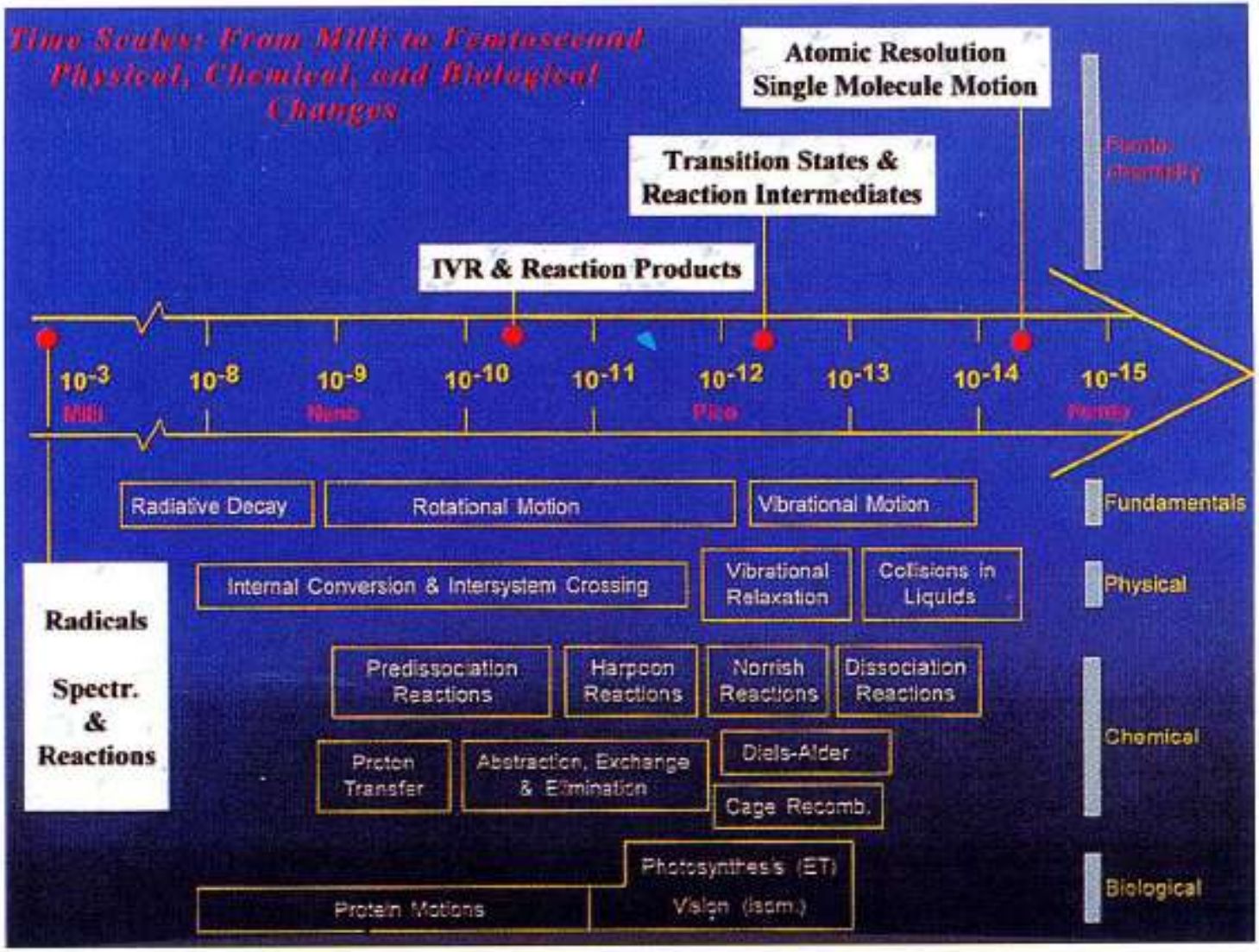
$$A + BC \rightarrow [ABC]^{\ddagger} \rightarrow AB + C \text{ (bimolecular)}$$

Terminal velocities of separation of fragments A and BC ~ 0.01 Angstrom fs^{-1}

~10^4 – 10^5 cm/s

Time required to break the bond ~ few 100 fs !!!!



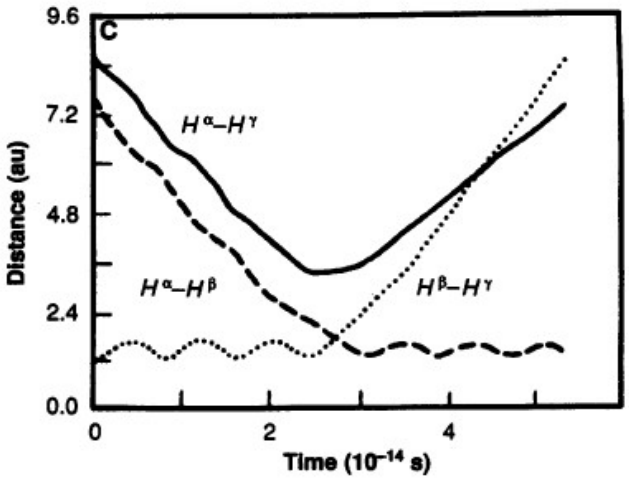

Time Scales: From Milli to Femtosecond Physical, Chemical, and Biological Changes
Atomic Resolution Single Molecule Motion
Transition States & Reaction Intermediates
IVR & Reaction Products
10-3
Milli
10-8
10-9
Nano
10-10
10-11
10-12
Pico
10-13
10-14
10-15
Femto
Radiative Decay
Rotational Motion
Vibrational Motion
Fundamentals
Internal Conversion & Intersystem Crossing
Vibrational Relaxation
Collisions in Liquids
Physical
Radicals
Spectr. & Reactions
Predissociation Reactions
Harpoon Reactions
Norrish Reactions
Dissociation Reactions
Chemical
Proton Transfer
Abstraction, Exchange & Elimination
Diels-Alder
Cage Recomb.
Photosynthesis (ET)
Protein Motions
Vision (isom.)
Biological

Theoretical femtochemistry

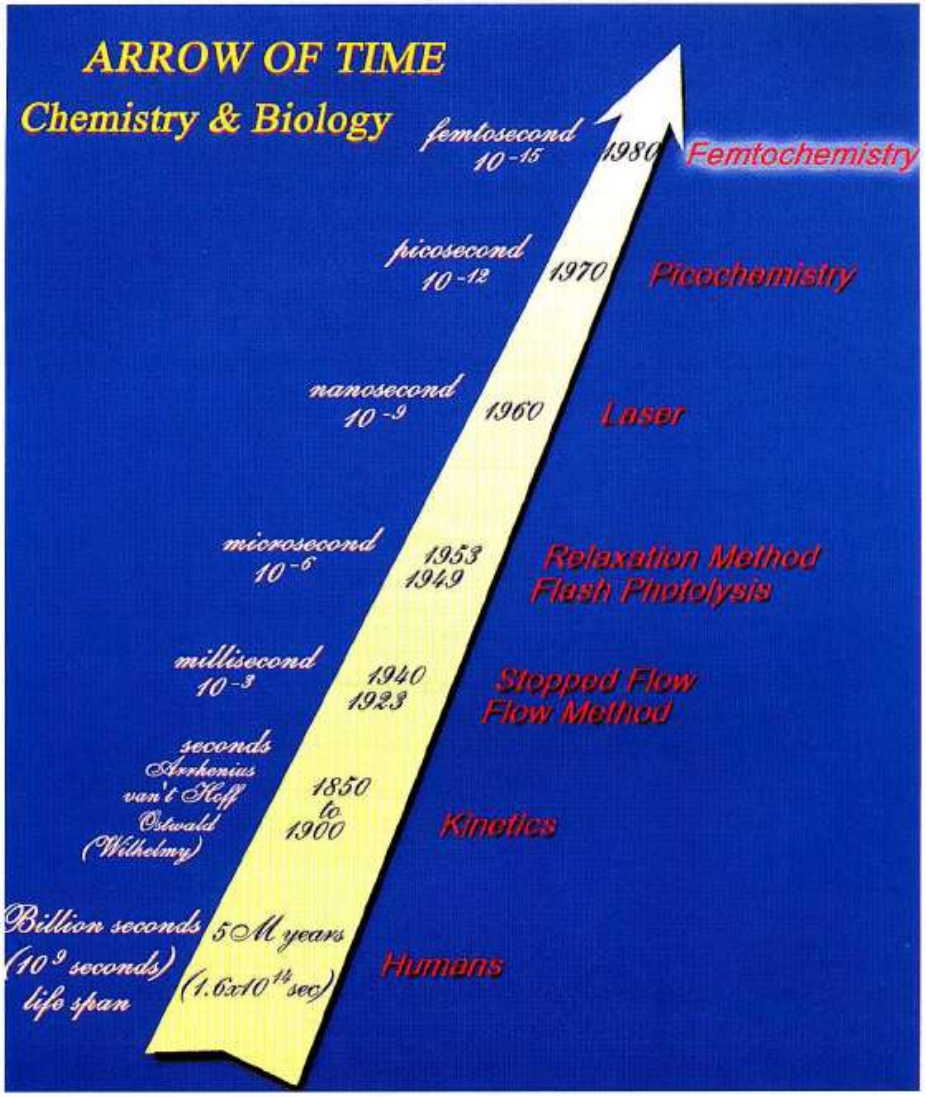
1930: Evans, Polanyi & Eyring $\rightarrow$ **concept of Transition state**

1936: Hirschfelder, Eyring, and Topley

$$H^{\alpha} + H^{\beta} - H^{\gamma} \rightarrow H^{\alpha} - H^{\beta} + H^{\gamma}$$



Flash photolysis with only ms (10^{-3} s) resolution in 1949 !!!


ARROW OF TIME
Chemistry & Biology
femtosecond
10 -15
1980
Femtochemistry
picosecond
10 -12
1970
Picochemistry
nanosecond
10 -9
1960
Laser
microsecond
10 -6
1953
1949
Relaxation Method
Flash Photolysis
millisecond
10 -3
1940
1923
Stopped Flow
Flow Method
seconds
Arrhenius
van't Hoff
Ostwald
(Wilhelmy)
1850
to
1900
Kinetics
Billion seconds
(10 9 seconds)
life span
5 M years
(1.6x10 14 sec)
Humans

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**

for showing that it is possible with rapid laser technique to see how atoms in a molecule move during a chemical reaction.

The Academy's citation:
For his studies of the transition states of chemical reactions using femtosecond spectroscopy.

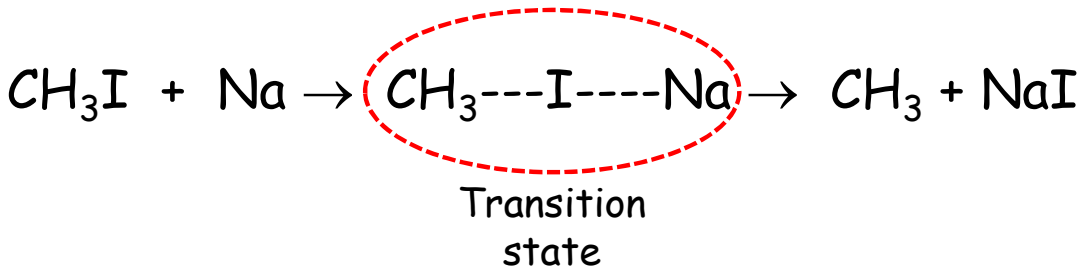
When I arrived in the US as a graduate student in 1969, nine years after the invention of the first laser, I had no idea of what lasers were about. When appointed to the Caltech faculty as an assistant professor in 1976, I was not thinking or dreaming of femtosecond time resolution. But I had the idea of exploring *coherence* as a new concept in dynamics, intra- and inter-molecular. This proved to be vital and fruitful.

------- Ahmed Zewail

FTS

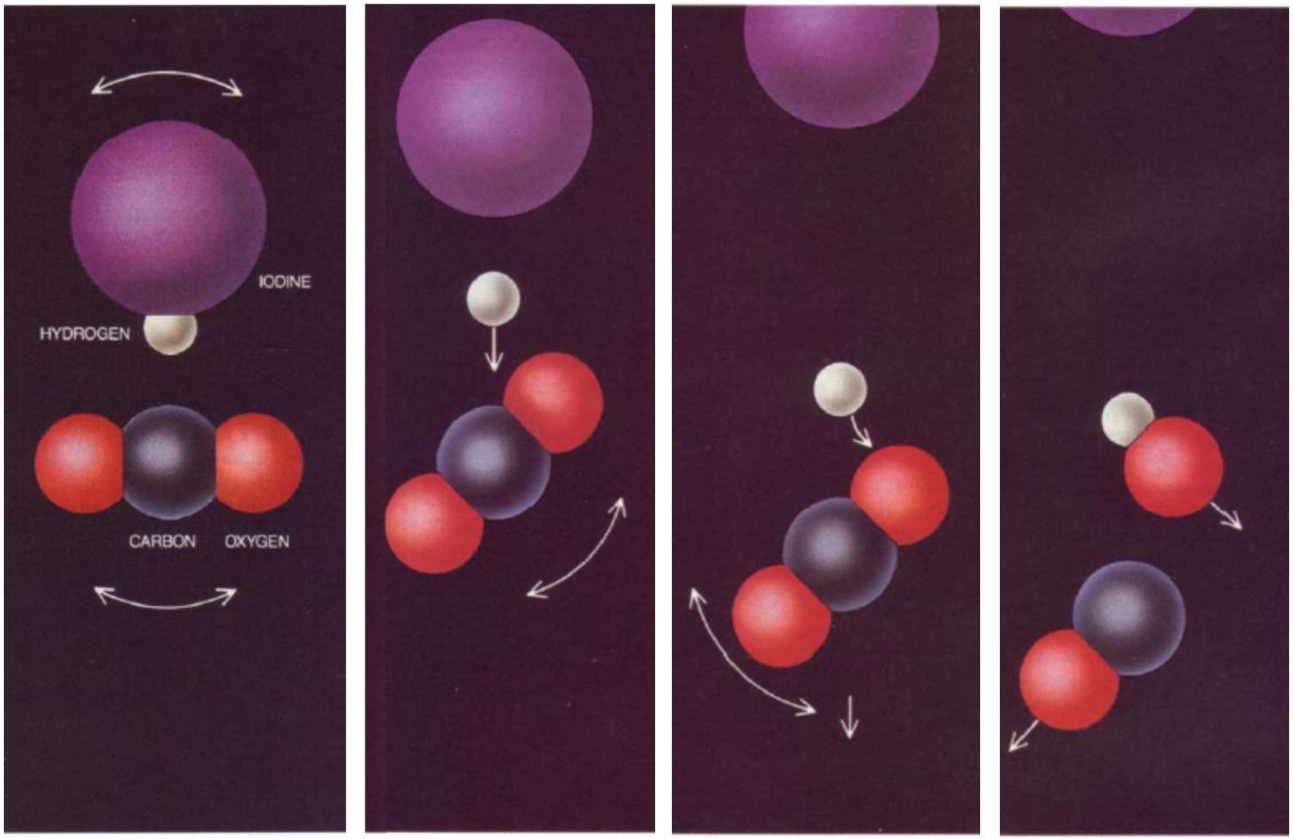
Femtosecond Transition State Spectroscopy

Consider a chemical transformation



In any chemical reaction the motions of the electrons and nuclei of atoms determine how the molecules interact, and those interactions in turn create the forces that govern the reaction's dynamics.

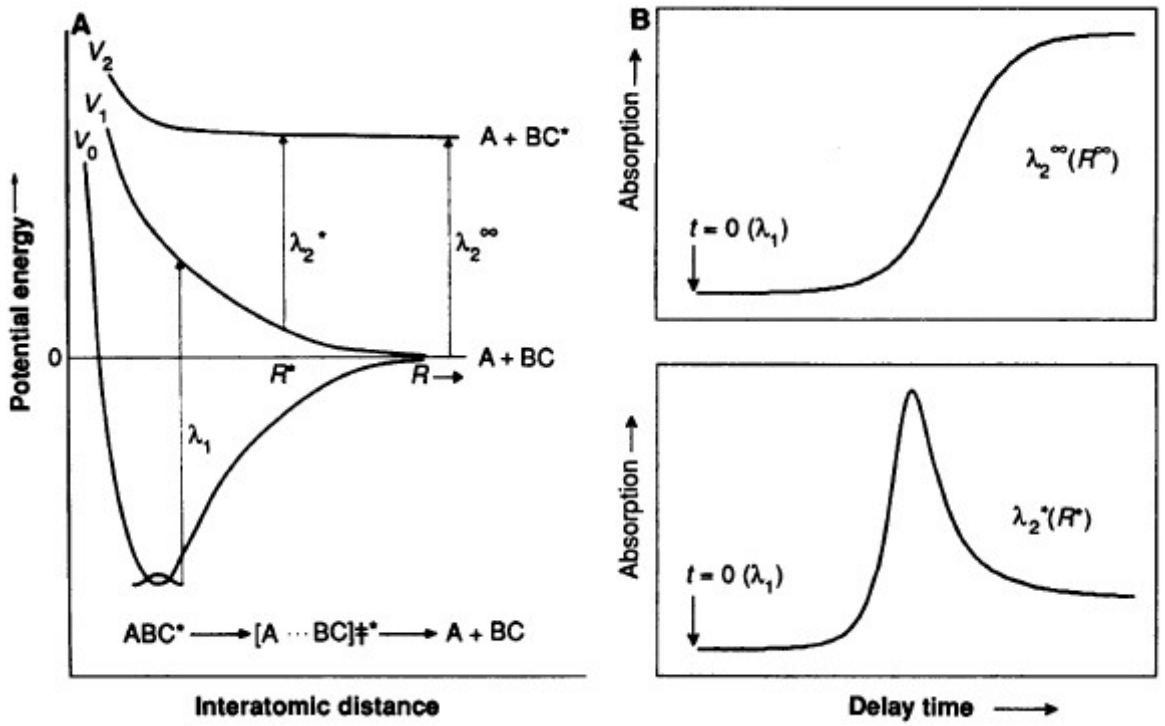
If one can determine how molecular motions change during the critical transition phase, we can understand how new chemical bonds form and old ones disappear.



$CO_2 + HI = CO + .OH + .I$

Molecular structures for a reaction in progress involving two molecules (bimolecular).

Femtosecond pump-probe spectroscopy

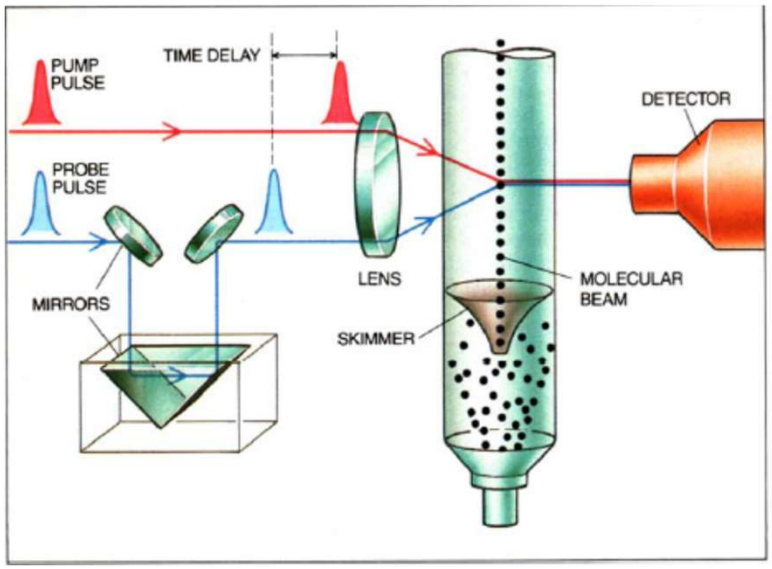


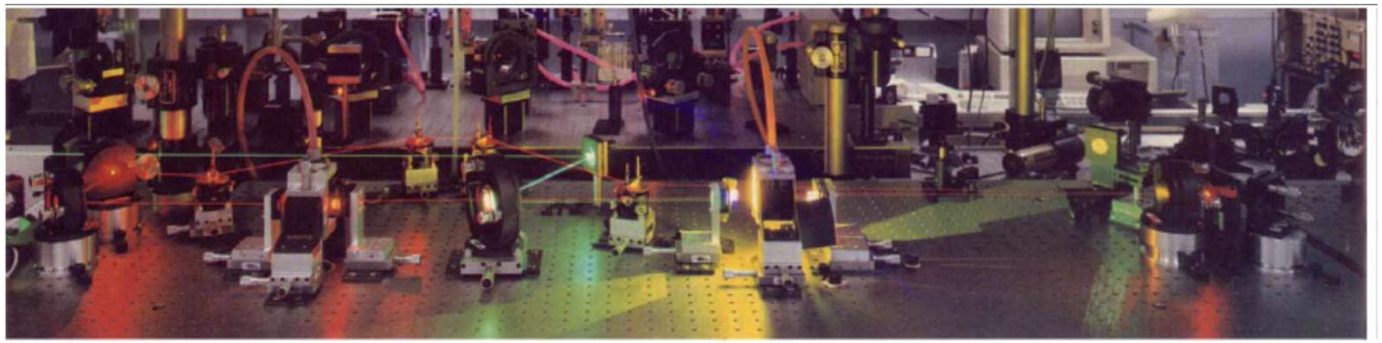
Question

How can one study transition state(s) in real time?

Answer

Need ultrafast probe and detection technique

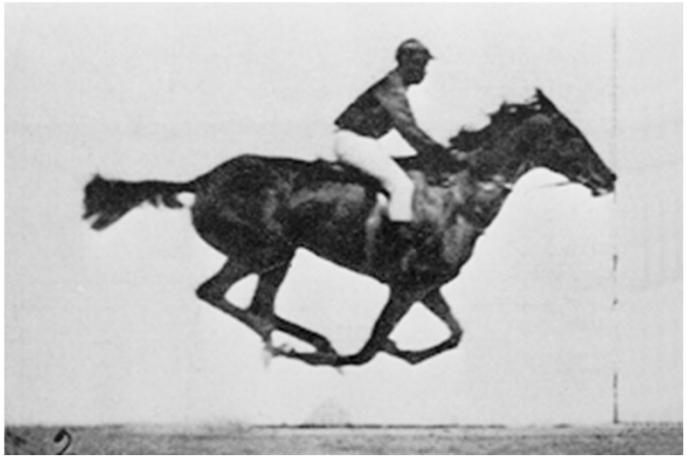




J. Chem. Phys., **1987**, *87(4)*, 2395

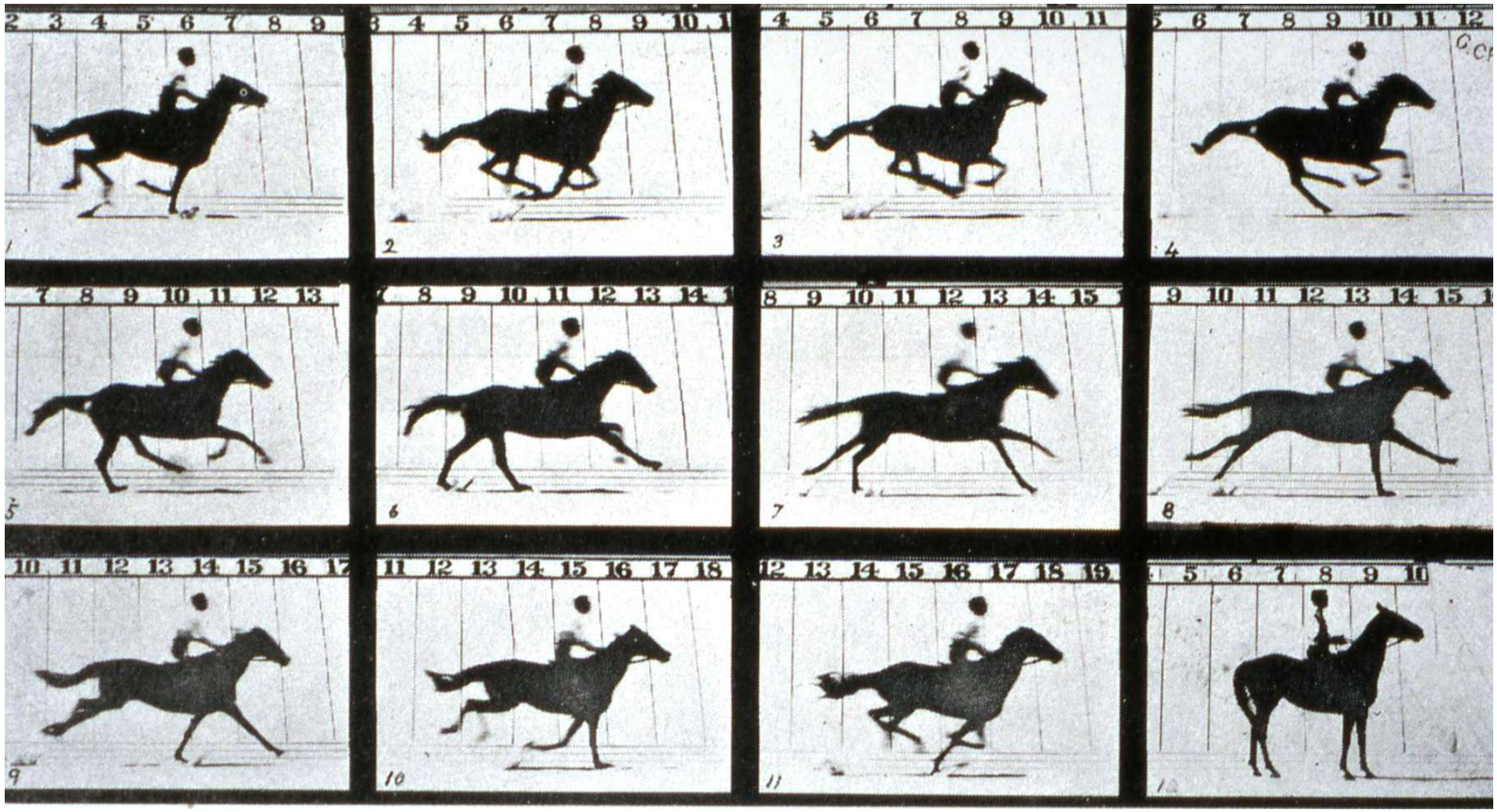
Trotting Horse

Movie →



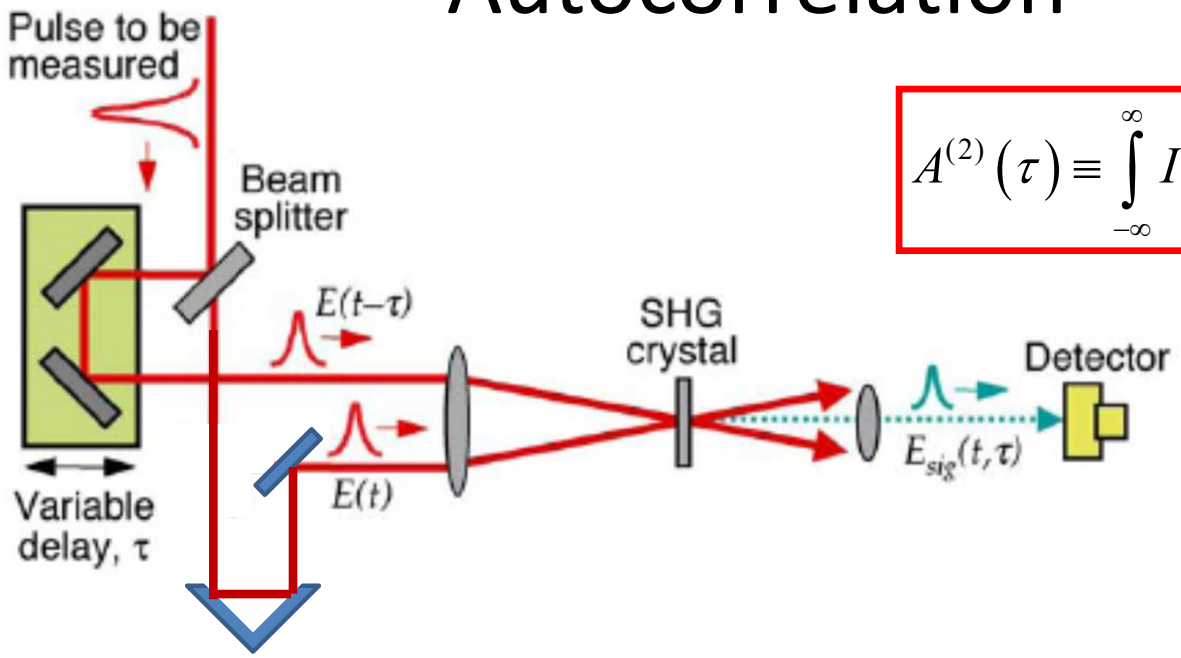
There was a debate over the question of whether all four hooves of a trotting horse are simultaneously out of contact with the ground at any point in its stride.

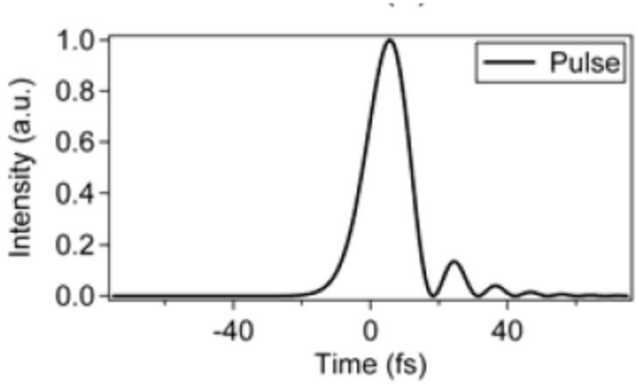
Eadweard Muybridge resolved this!

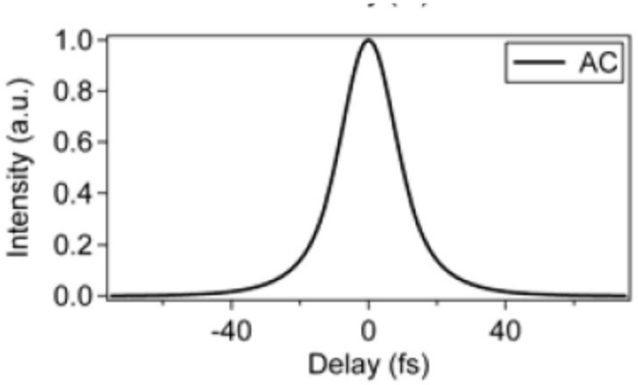


Autocorrelation

$$A^{(2)}(\tau) \equiv \int_{-\infty}^{\infty} I(t) I(t-\tau)\, dt$$







Autocorrelation