

NOVE FIZIČKOHEMIJSKE METODE

FEMTOHEMIJA

MILENA PETKOVIĆ

# Time Scales: From Milli to Femtosecond Physical, Chemical, and Biological Changes

## Atomic Resolution Single Molecule Motion

### Transition States & Reaction Intermediates

### IVR & Reaction Products



Radiative Decay

Rotational Motion

Vibrational Motion

Internal Conversion & Intersystem Crossing

Vibrational Relaxation

Collisions in Liquids

Radicals

Spectr.  
&  
Reactions

Predisociation Reactions

Harpoon Reactions

Norrish Reactions

Dissociation Reactions

Proton Transfer

Abstraction, Exchange & Elimination

Diels-Alder

Cage Recomb.

Protein Motions

Photosynthesis (ET)

Vision (isom.)

Femto-chemistry

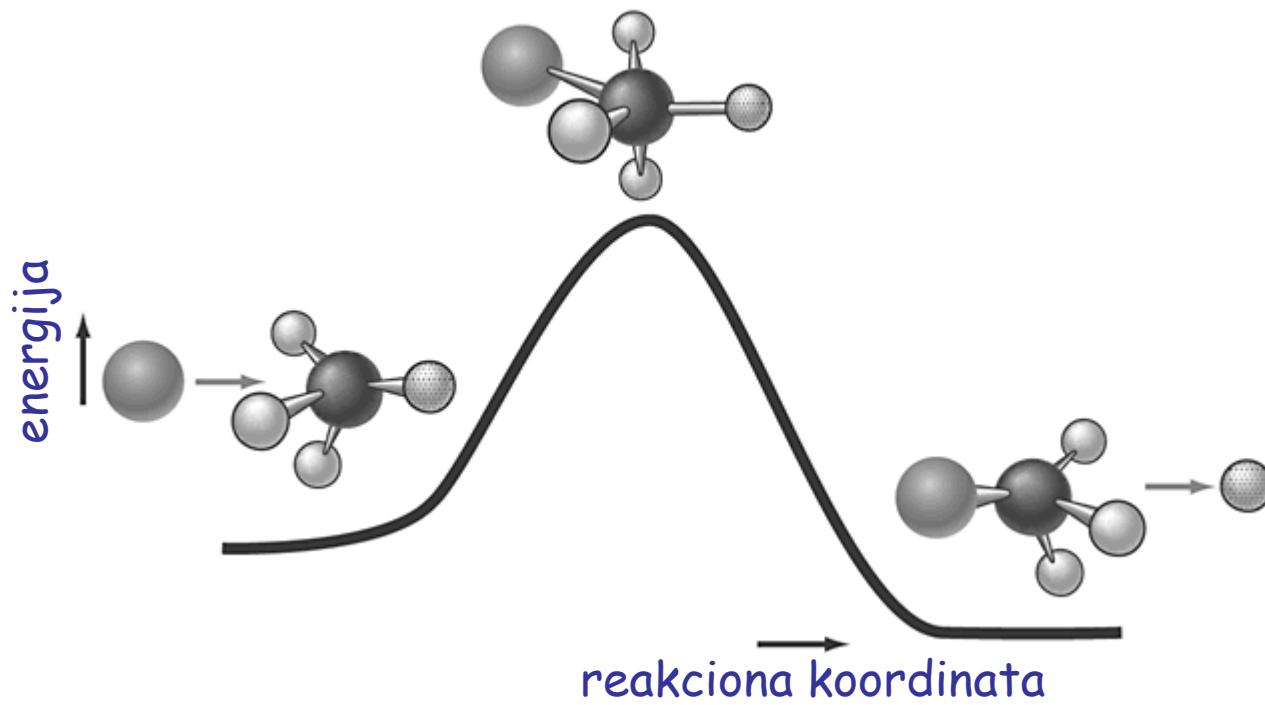
Fundamentals

Physical

Chemical

Biological

# PRAĆENJE TOKA HEMIJSKE REAKCIJE



# "Rođenje" ultrabrzih tehnologija

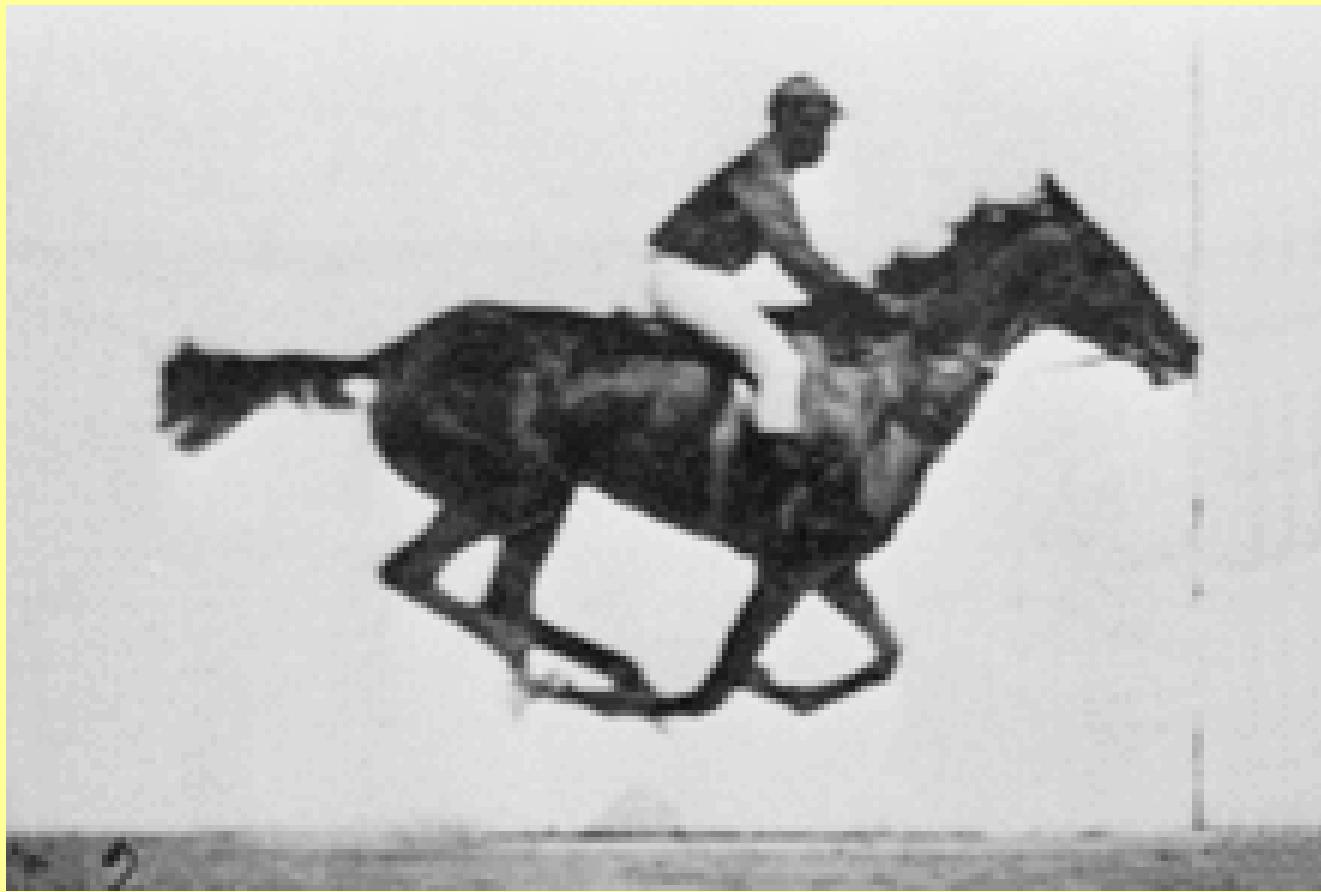


Konj u pokretu (The horse in motion)

Fotograf: Edvard Majbridž (Eadweard Muybridge)

Palo Alto, Kalifornija 1872 → 1878.

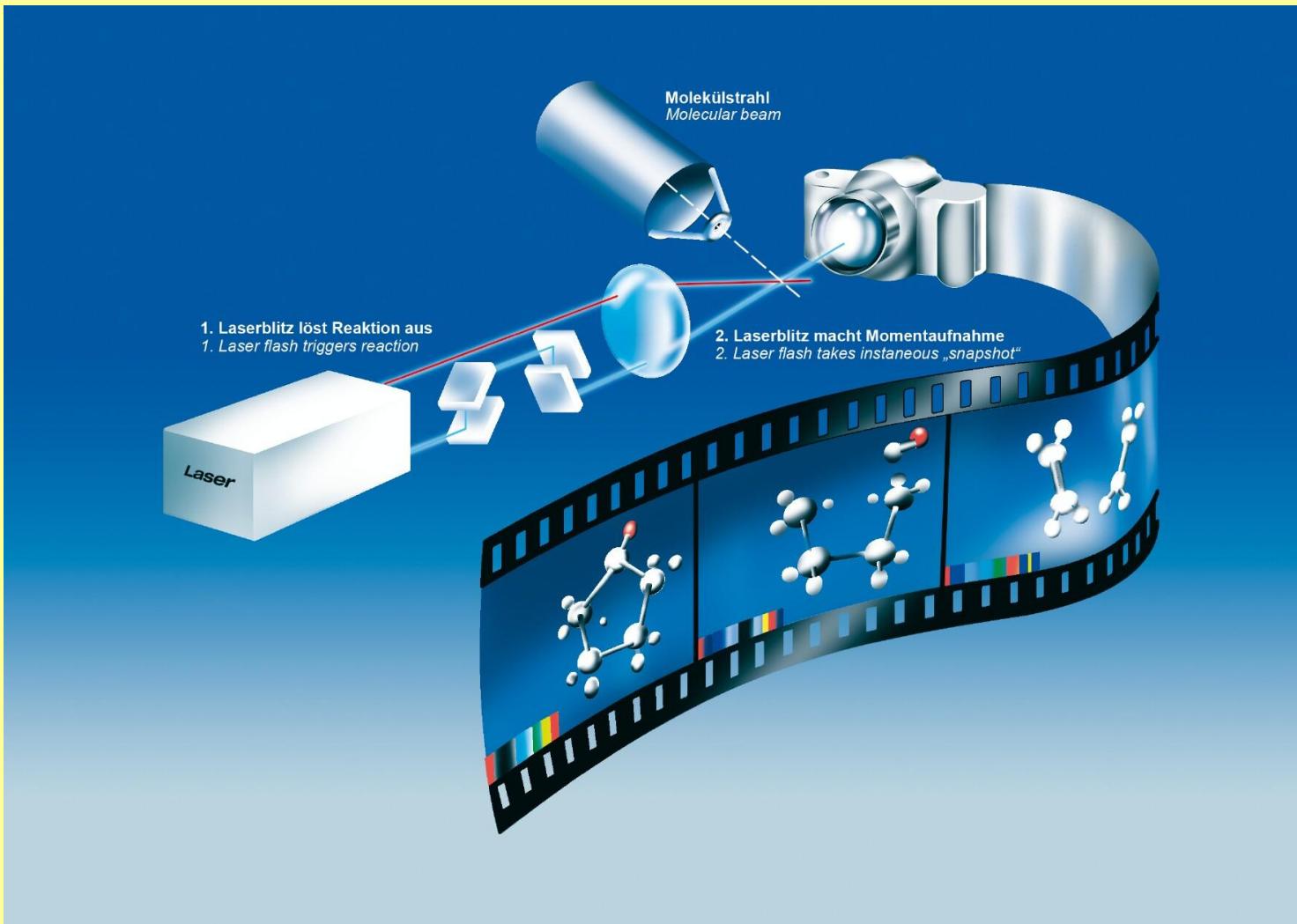
# "Rođenje" ultrabrzih tehnologija

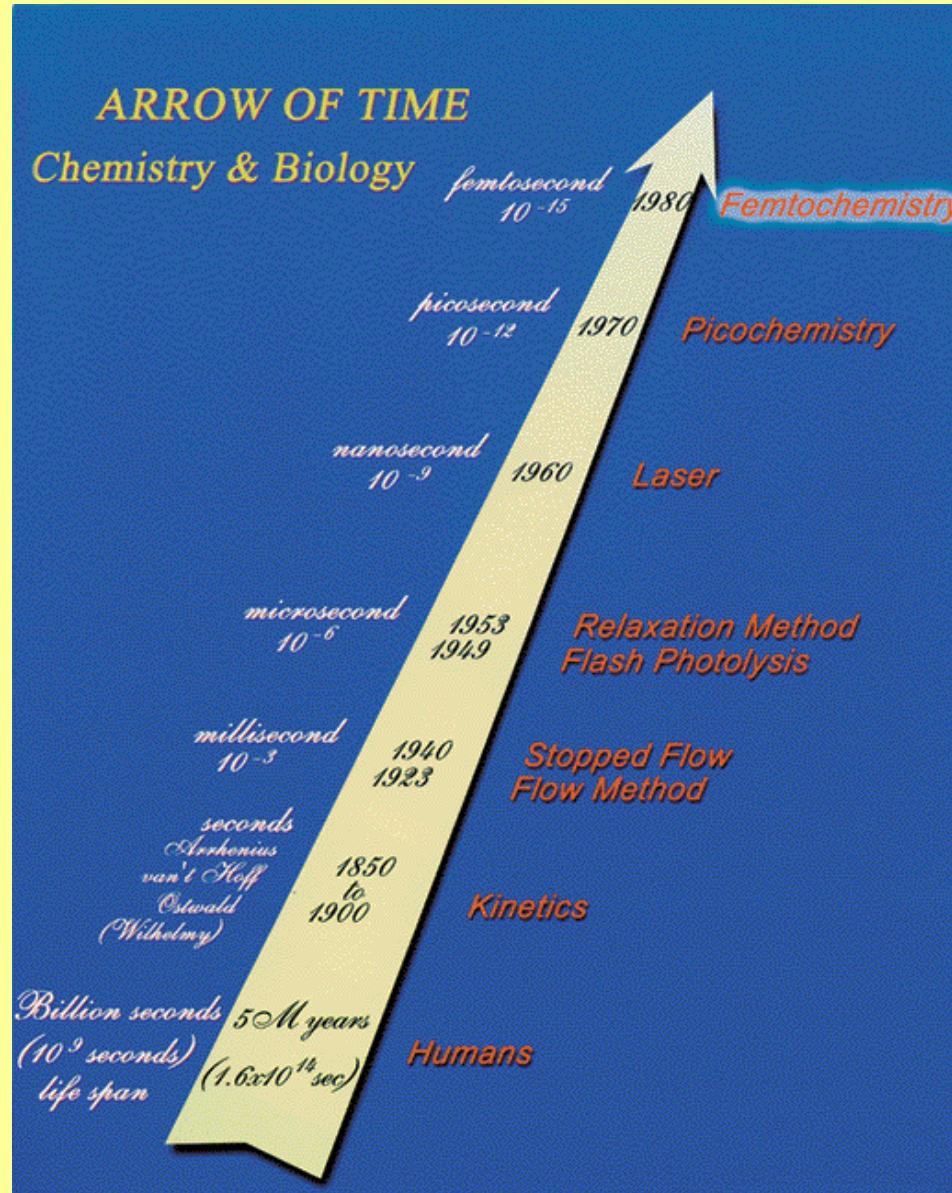


Seli Gardner u galopu - animirano 2006.  
na osnovu Majbridžovih fotografija

# Cilj:

“film” koji prikazuje položaj jezgara  
u toku hemijske reakcije



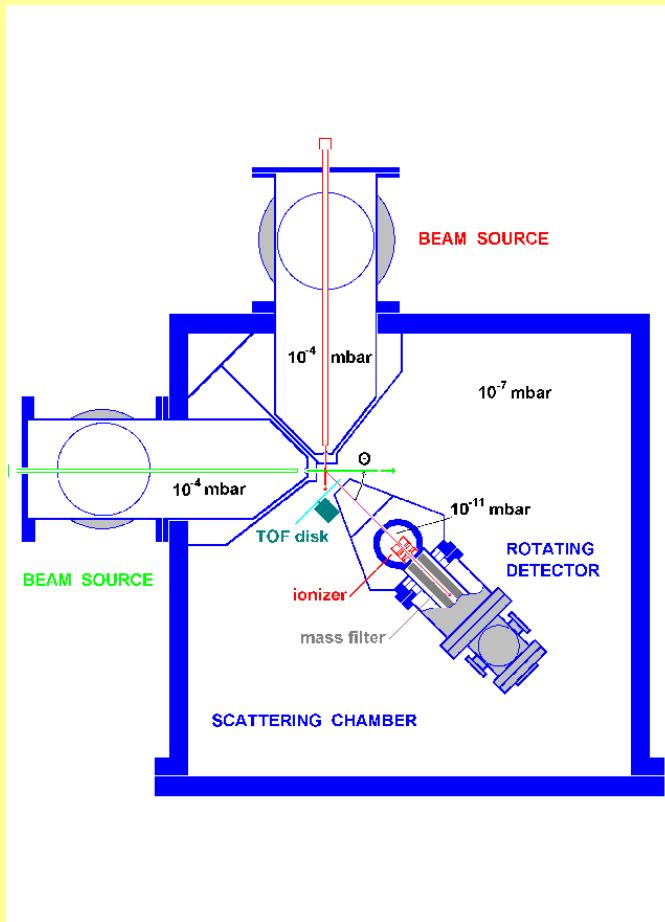


Ahmed Zewail - Nobel lecture

# TEHNOLOGIJA MOLEKULSKIH SNOPOVA

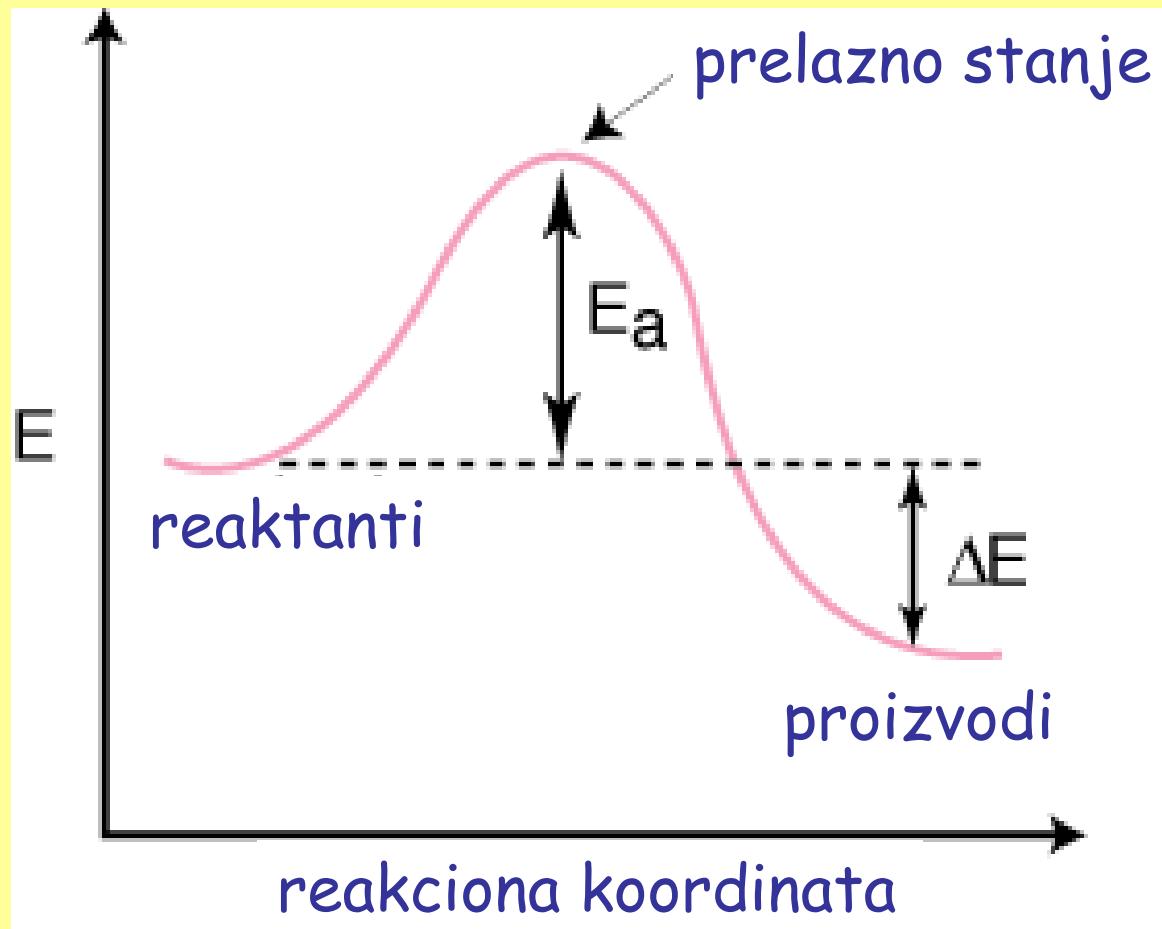
1986 - Nobelova nagrada za hemiju

Dudley Robert Herschbach, Yan T. Lee & John C. Polanyi



Hamlet!

# PRELAZNO STANJE



vreme života  $\approx 10 - 100$  fs



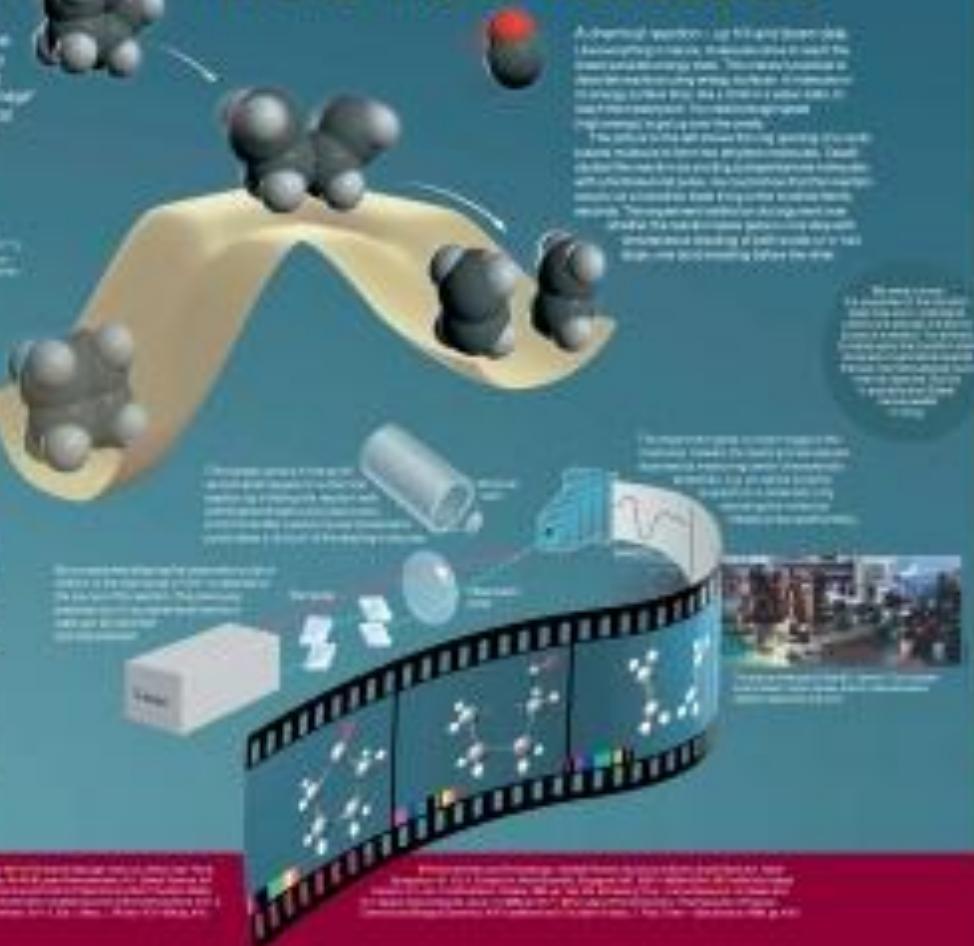
# The Nobel Prize in Chemistry 1999

The Royal Swedish Academy of Sciences has awarded the 1999 Nobel Prize in Chemistry to Professor Ahmed H. Zewail for his studies of femtosecond dynamics in chemistry by means of supersonic expansion.

A  
1999 Zewail receives the 1999 Nobel Prize in Chemistry for being the first to study the molecular motions in a chemical reaction – the moments when chemical bonds are broken and formed.  
Decades ago people used to be taught that all reactions took place slowly. The "old adage" of such a reaction had to be extremely high since molecules move very slowly ( $\sim 10^{-2}$  m/s). But about 10 years ago it was discovered rapidly ( $\sim 10^8$  s) that molecules undergoes "femtosecond" ( $\sim 10^{-15}$  s) processes. Many of these processes in the course of a chemical reaction requires a femtosecond. In this picture we see:



## The decisive moments in the life of molecules



### The birthplace of today



### Decisive steps forward



### Toward the future with femtochemistry

Femtosecond dynamics in chemistry has already opened up many new fields of research. One example is the study of biological processes at the molecular level. Another is the development of new materials with unique properties. Femtosecond dynamics is also being used to study the fundamental principles of quantum mechanics. These include the nature of the electron, the behavior of atoms in a magnetic field, and the properties of subatomic particles. The applications of femtosecond dynamics are vast and varied, from the study of the early universe to the development of new medical treatments.



KUNGLIGA VETENSKAPSAKADEMINS  
FORSKNINGSSÄFÄR OCH FÖRENING

Medlemsförbundet för svenska vetenskapsakademier  
och föreningar

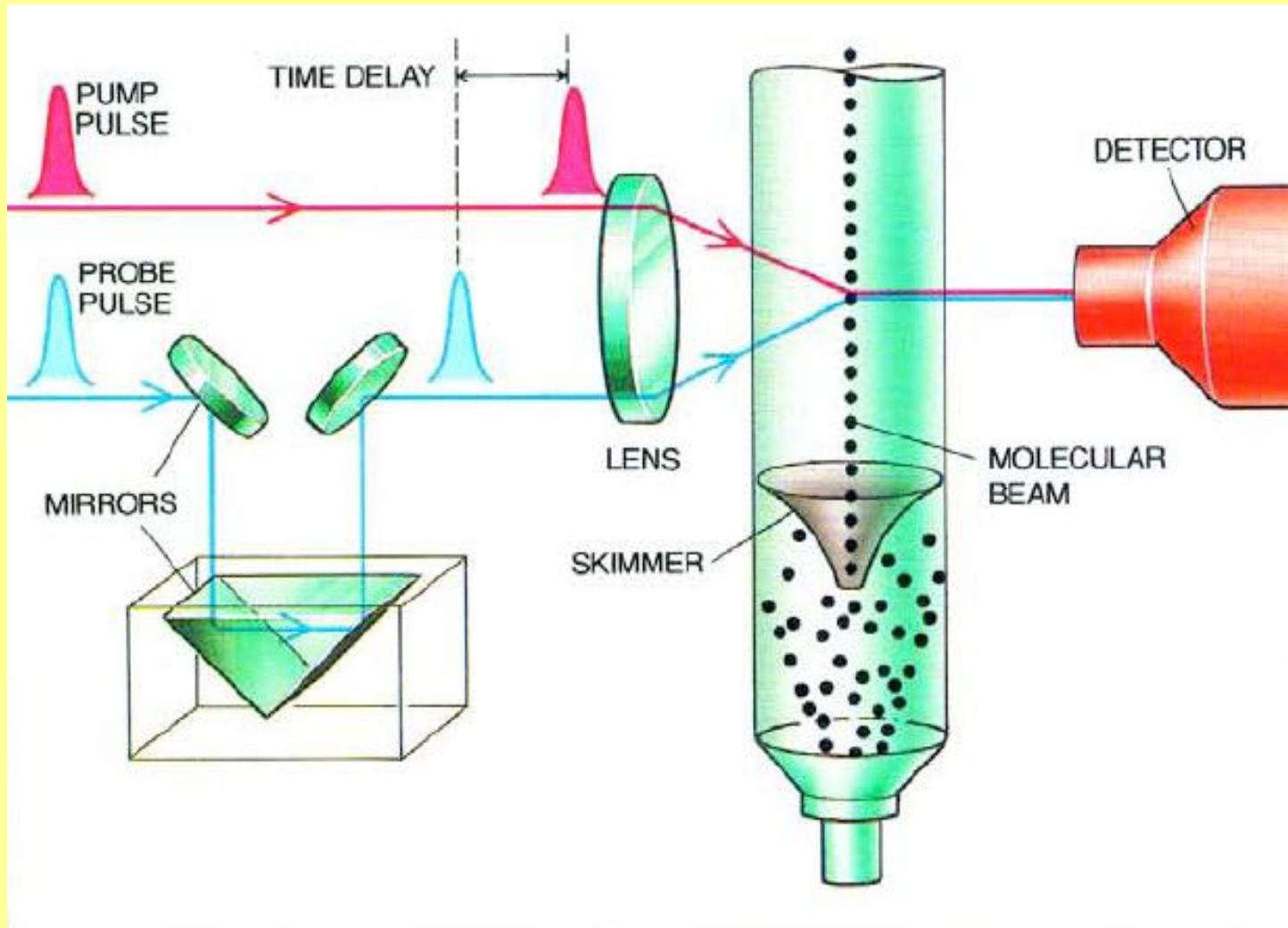
Medlemsförbundet för svenska vetenskapsakademier  
och föreningar

Medlemsförbundet för svenska vetenskapsakademier  
och föreningar

"In less than a trillionth of a second, atoms can collide, interact and give birth to molecules. With lasers and molecular beams, it is now possible to witness the motions of molecules as one substance changes to another."

Ahmed Zewail

# FEMTOSEKUNDNI LASERI



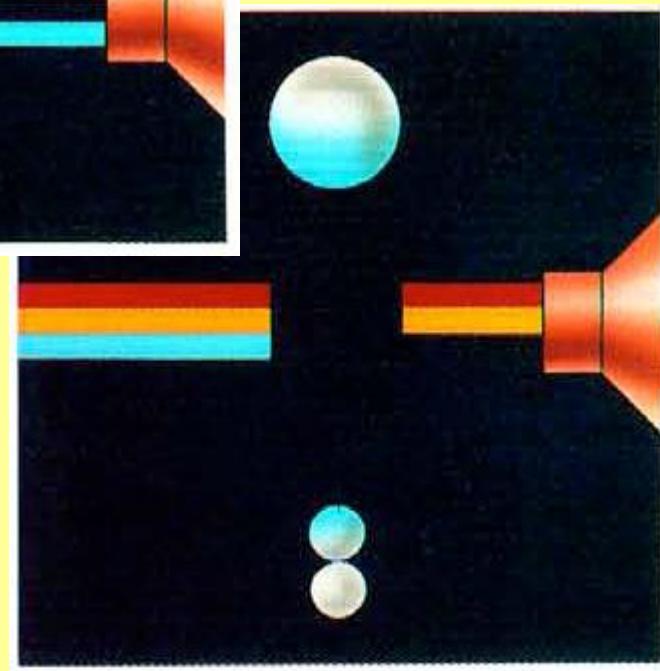
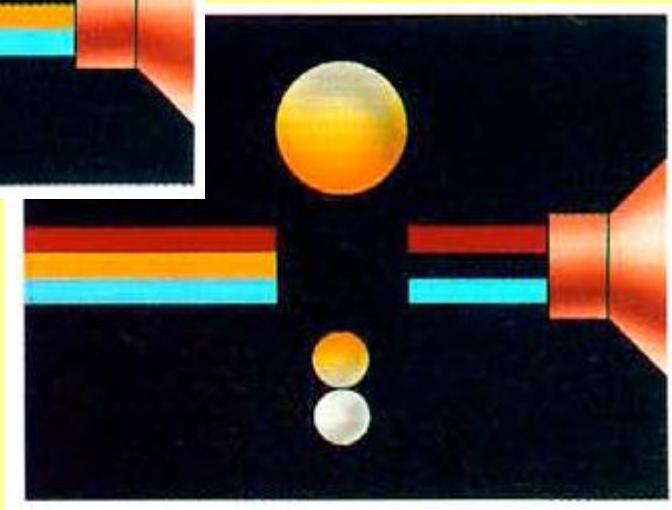
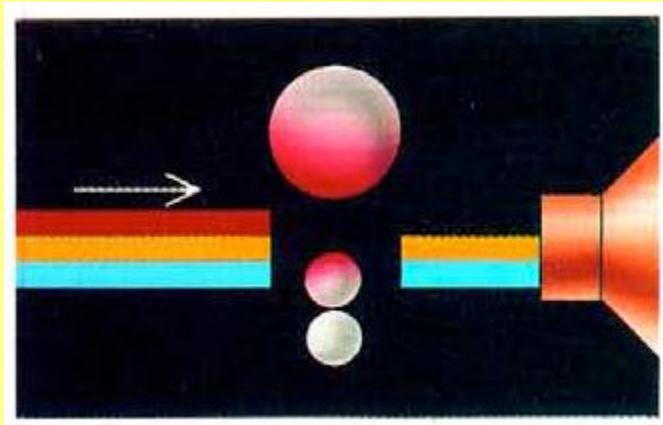
# KAŠNJENJE PROBA PULSA

$$c = 3 \cdot 10^8 \text{ m/s}$$

$$\Delta l = 1 \mu\text{m} \rightarrow \Delta t = (1 \cdot 10^{-6} \text{ m}) / (3 \cdot 10^8 \text{ m/s}) = 3,33 \cdot 10^{-15} \text{ s} \\ = 3,33 \text{ fs}$$

$$\Delta l = 100 \mu\text{m} \rightarrow \Delta t = (1 \cdot 10^{-4} \text{ m}) / (3 \cdot 10^8 \text{ m/s}) = 3,33 \cdot 10^{-13} \text{ s} \\ = 333 \text{ fs}$$

# Promena u spektru - "otisak prstiju" atoma u pokretu



## **Elementarni fenomeni:**

- prelazna stanja
- preraspodela energije
- brzine hemijskih reakcija

## **Hemijske veze:**

- kovalentne
- jonske
- dativne
- metalne
- vodonične veze
- vandervalsovski kompleksi

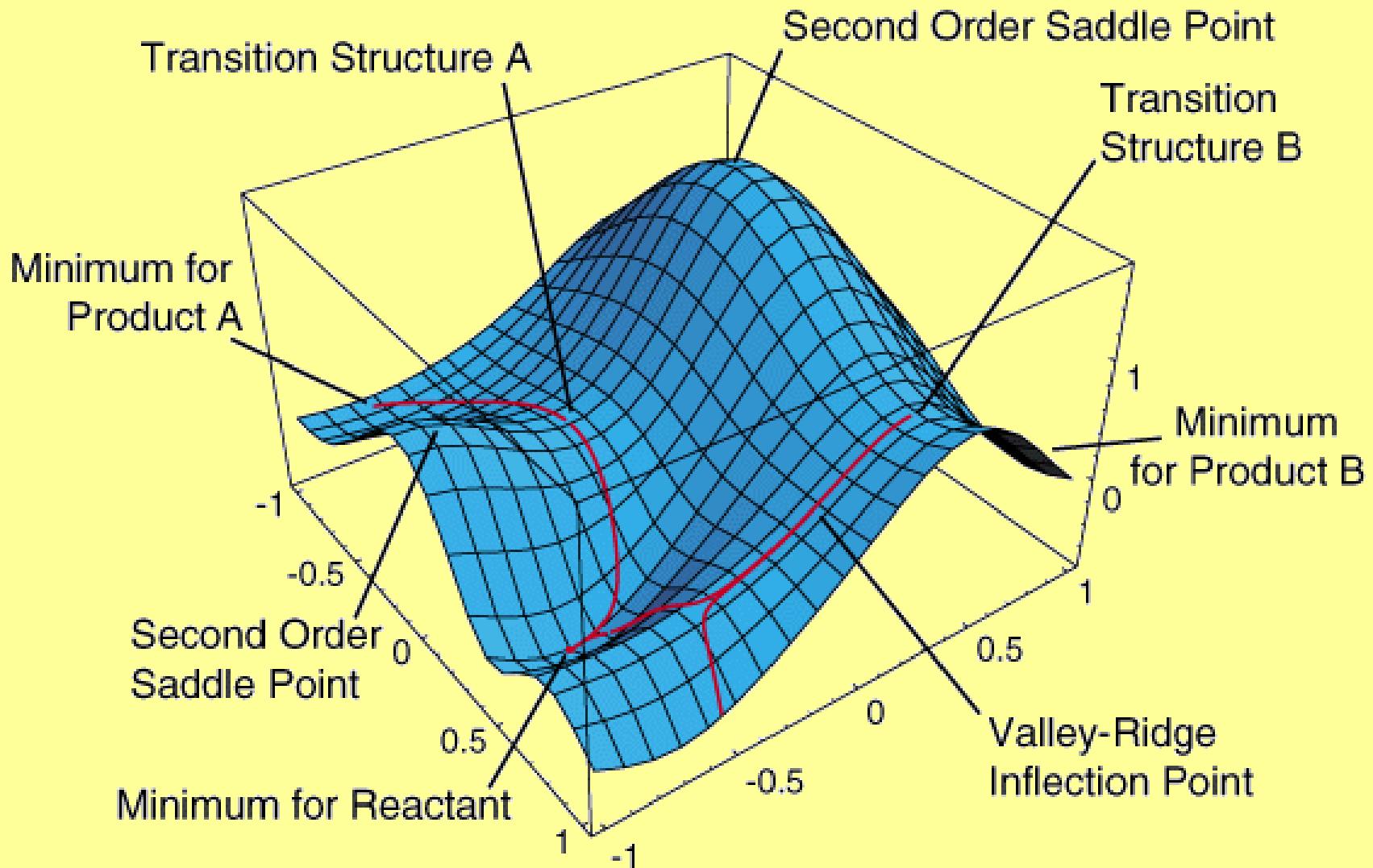
## **Stanja molekula:**

- osnovno i pobuđena stanja
- neutralne čestice i joni

## **Dimenzije molekula:**

- dvoatomski molekuli
- ...
- DNK i proteini

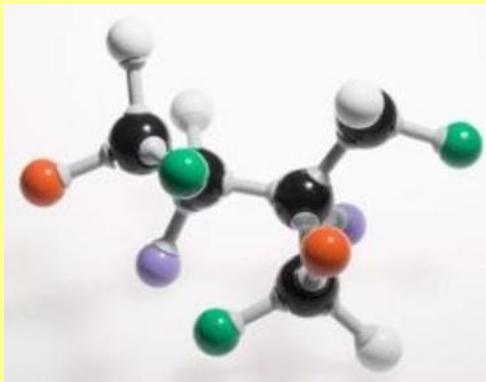
# TEORIJSKI PRISTUP



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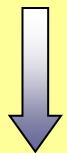
vremenski zavisna Šredingerova jednačina

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = \hat{H}(t)\Psi(t)$$



$$\Psi(t)$$

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = \hat{H}(t)\Psi(t)$$



## PERTURBACIONI RAČUN

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$

$$\hat{H}_0 \psi_k = E_k \psi_k$$

$$\psi_k(t) = \psi_k e^{-\frac{i}{\hbar} E_k t}$$

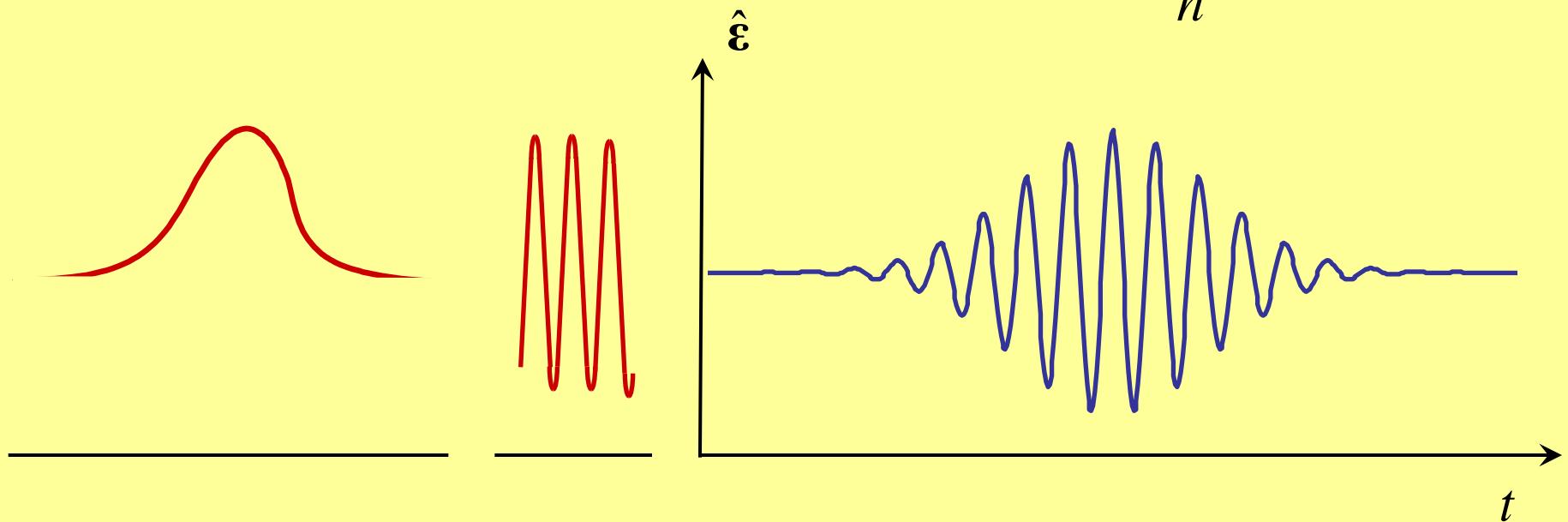
perturbacija  
(laserski puls)

$$\Psi(t) = \sum_k c_k \psi_k(t) = \sum_k c_k \psi_k e^{-\frac{i}{\hbar} E_k t}$$

# ULTRAKRATKI LASERSKI PULS

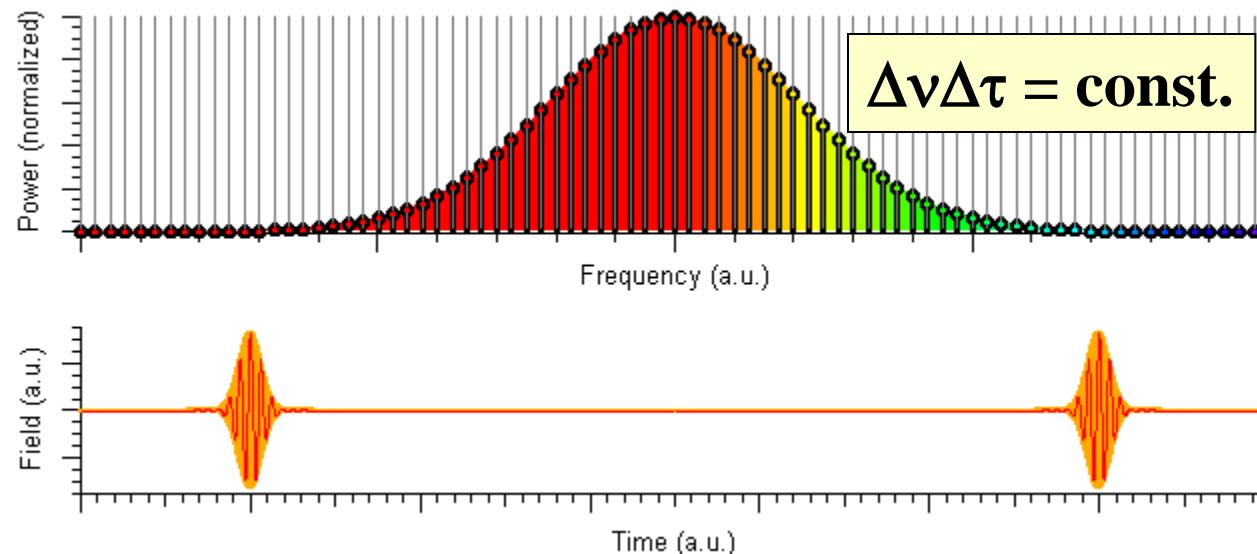
$$\hat{\mathbf{e}}(t) = \hat{\mathbf{e}}_0 e^{-\frac{t^2}{\alpha T^2}} \cos(\omega t)$$

$$\omega \approx \frac{E_m - E_0}{\hbar} = \omega_{m0}$$



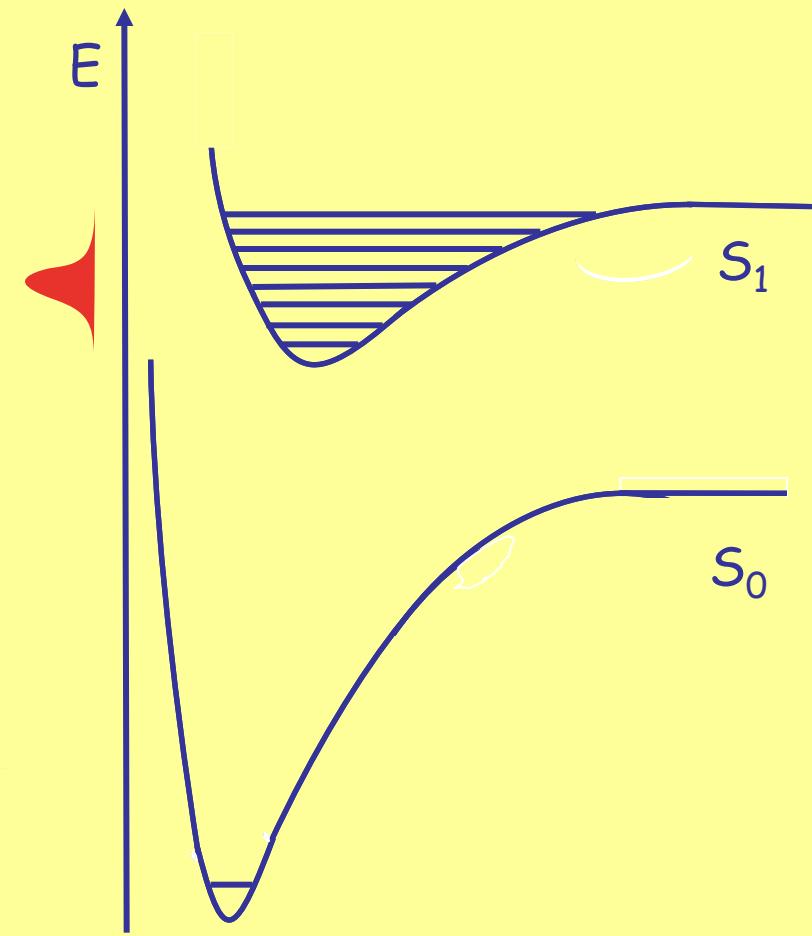
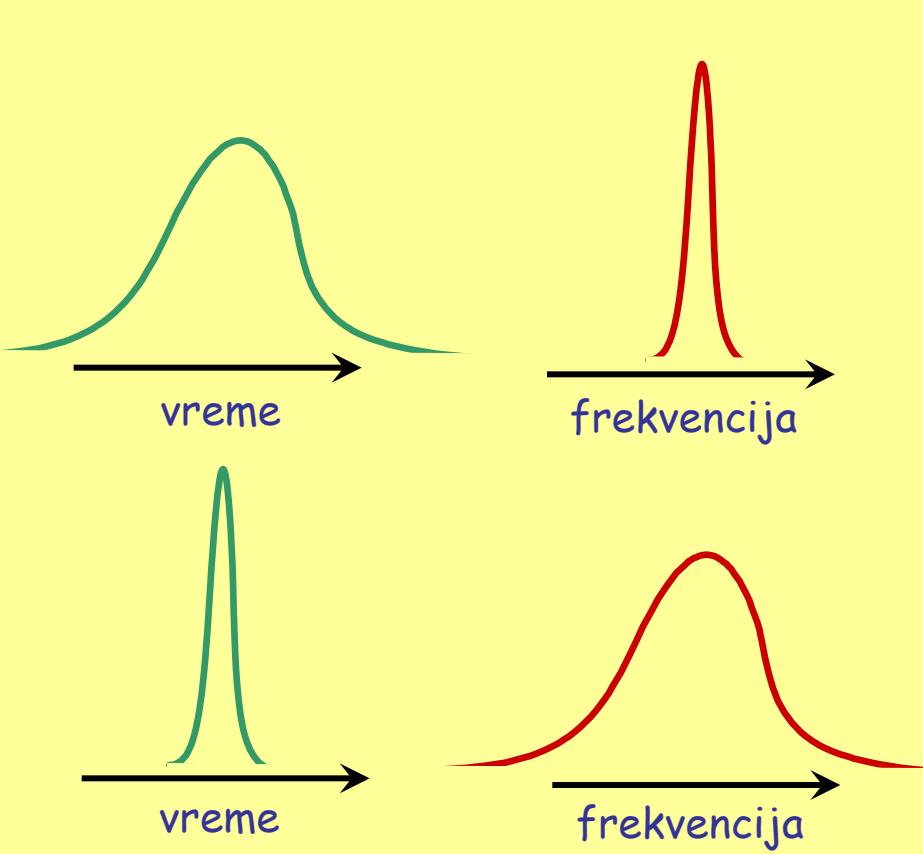
$$\hat{V}(t) = -\hat{\mathbf{\mu}} \cdot \hat{\mathbf{e}}(t)$$

# OSNOVNI PRINCIPI ULTRABRZIH LASERA



# HAJZENBERGOVA RELACIJA NEODREĐENOSTI

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$



# TRADICIONALNA I ULTRABRZA SPEKTROSKOPIJA

tradicionalna spektroskopija

$$T \rightarrow \infty$$

$$\varepsilon(t) = \varepsilon_0 \cos(\omega t)$$

monohromatsko zračenje

ultrabrzta spektroskopija

$$T \rightarrow 0$$

$$\varepsilon(t) = \varepsilon_0 e^{-\frac{t^2}{\alpha T^2}} \cos(\omega t)$$

širok opseg frekvencija

# ULTRABRZA SPEKTROSKOPIJA (1)

osnovno elektronsko stanje

$$i\hbar \frac{\partial \varphi_k(x,t)}{\partial t} = \hat{H}_0 \varphi_k(x,t)$$

$$\varphi_k(x,t) = \varphi_k(x,0) e^{-\frac{i}{\hbar} E_k t}$$

$$\hat{H}_0 \varphi_k(x,0) = E_k \varphi_k(x,0)$$

$$\Psi(x,0) \equiv |\Psi(0)\rangle = |\varphi_0(0)\rangle = \sum_n c_n(0) |\phi_n(0)\rangle$$

pobuđeno elektronsko stanje

$$i\hbar \frac{\partial \phi_n(x,t)}{\partial t} = \hat{H}_0 \phi_n(x,t)$$

$$\phi_n(x,t) = \phi_n(x,0) e^{-\frac{i}{\hbar} E_n t}$$

$$\hat{H}_0 \phi_n(x,0) = E_n \phi_n(x,0)$$

# ULTRABRZA SPEKTROSKOPIJA (2)

$$|\Psi(0)\rangle = |\varphi_0(0)\rangle = \sum_n c_n(0) |\phi_n(0)\rangle$$

$$c_m(0) = \langle \phi_m(0) | \varphi_0(0) \rangle$$

$$|\Psi(0)\rangle = \sum_n \langle \phi_n(0) | \varphi_0(0) \rangle |\phi_n(0)\rangle$$

$$|\Psi(t)\rangle = \sum_n \langle \phi_n(0) | \varphi_0(0) \rangle |\phi_n(t)\rangle = \sum_n \langle \phi_n(0) | \varphi_0(0) \rangle |\phi_n(0)\rangle e^{-\frac{i}{\hbar} E_n t}$$

# ULTRABRZA SPEKTROSKOPIJA (3)

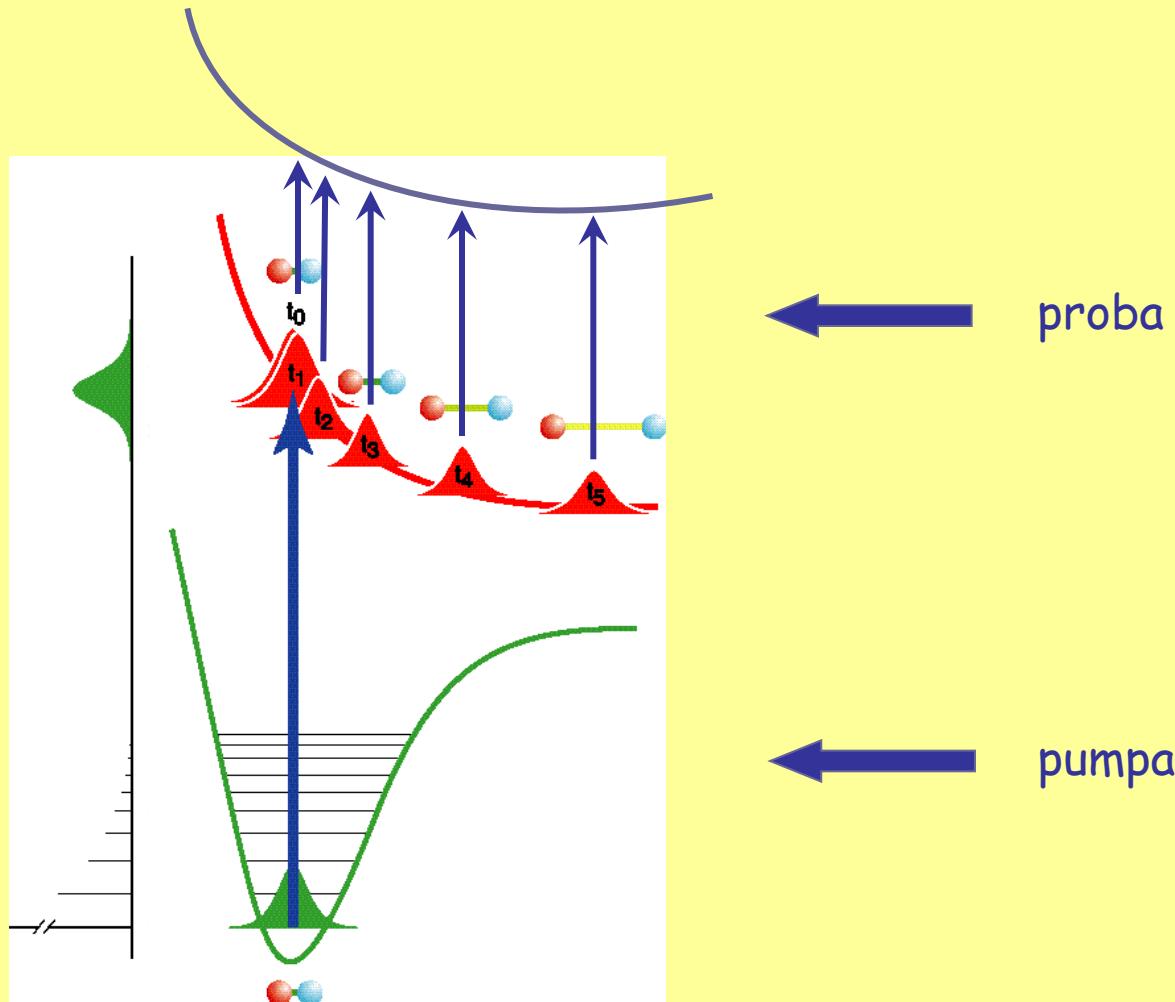
$$|\Psi(t)\rangle = \sum_n \langle \phi_n(0) | \varphi_0(0) \rangle |\phi_n(0)\rangle e^{-\frac{i}{\hbar} E_n t}$$

$$\langle x \rangle = \langle \Psi(t) | x | \Psi(t) \rangle$$

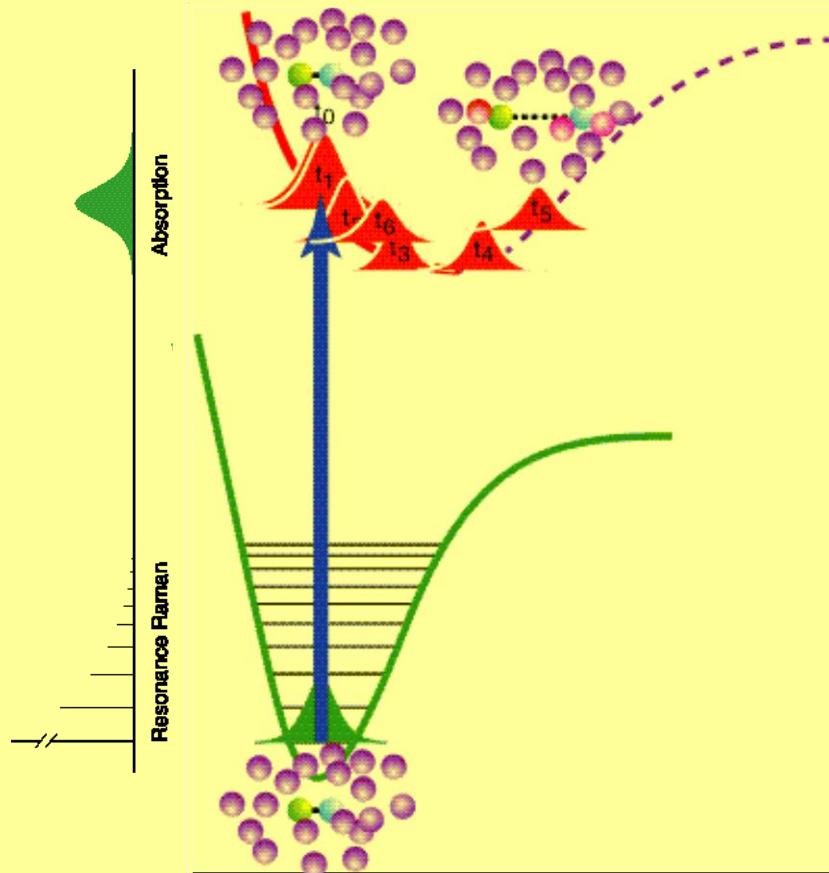
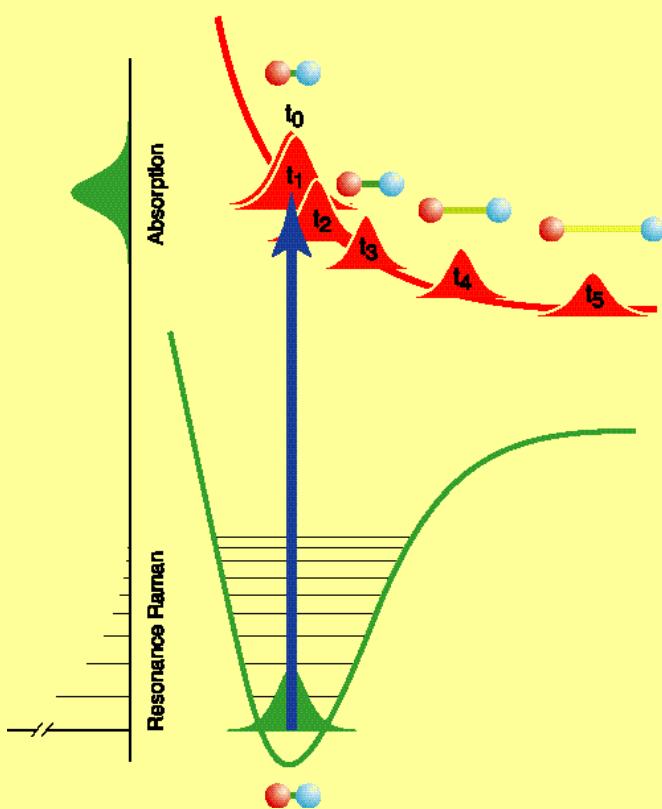
$$\langle x \rangle = \sum_m \sum_n \langle \varphi_0(0) | \phi_m(0) \rangle \langle \phi_n(0) | \varphi_0(0) \rangle \langle \phi_m(0) | x | \phi_n(0) \rangle e^{-\frac{i}{\hbar} (E_n - E_m) t}$$

DINAMIKA!

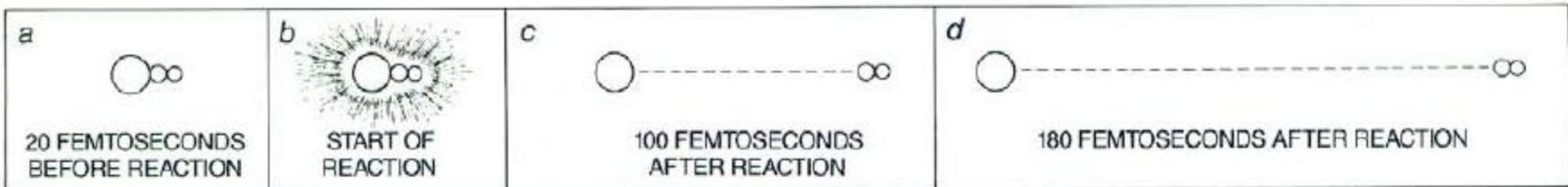
# PUMPA-PROBA METOD



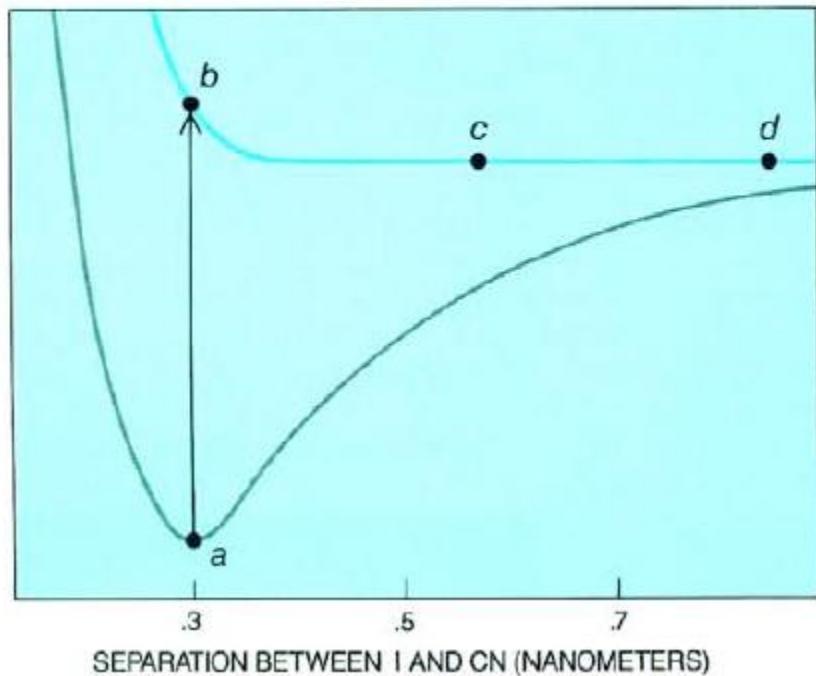
# FOTODISOCIJACIJA DVOATOMSKOG MOLEKULA



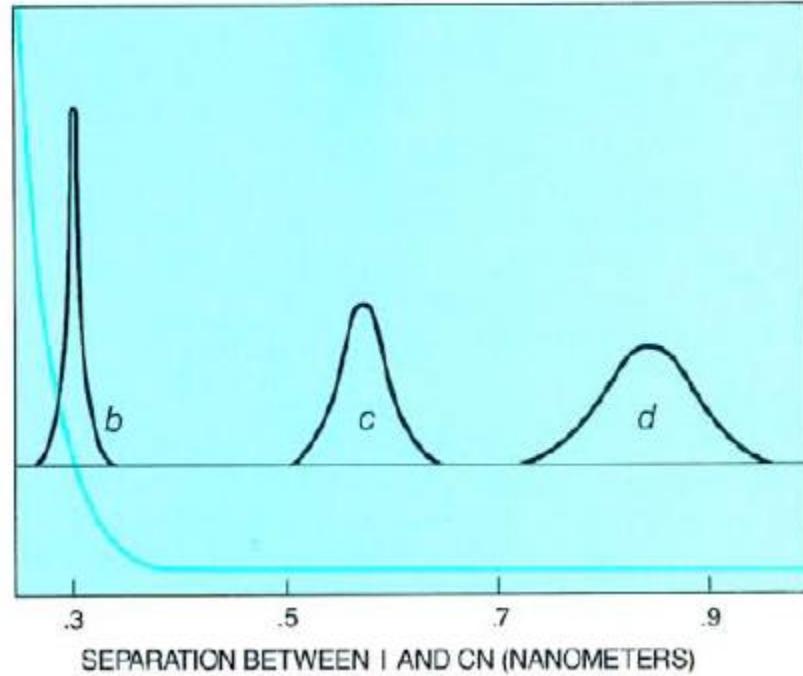
# ICN



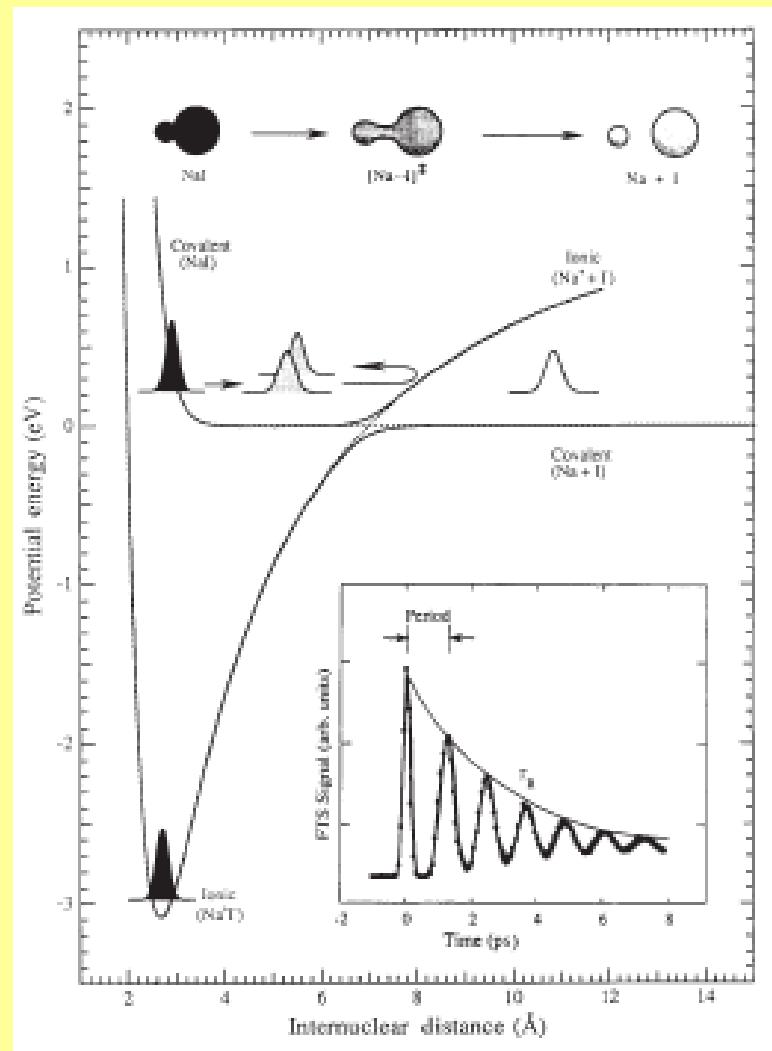
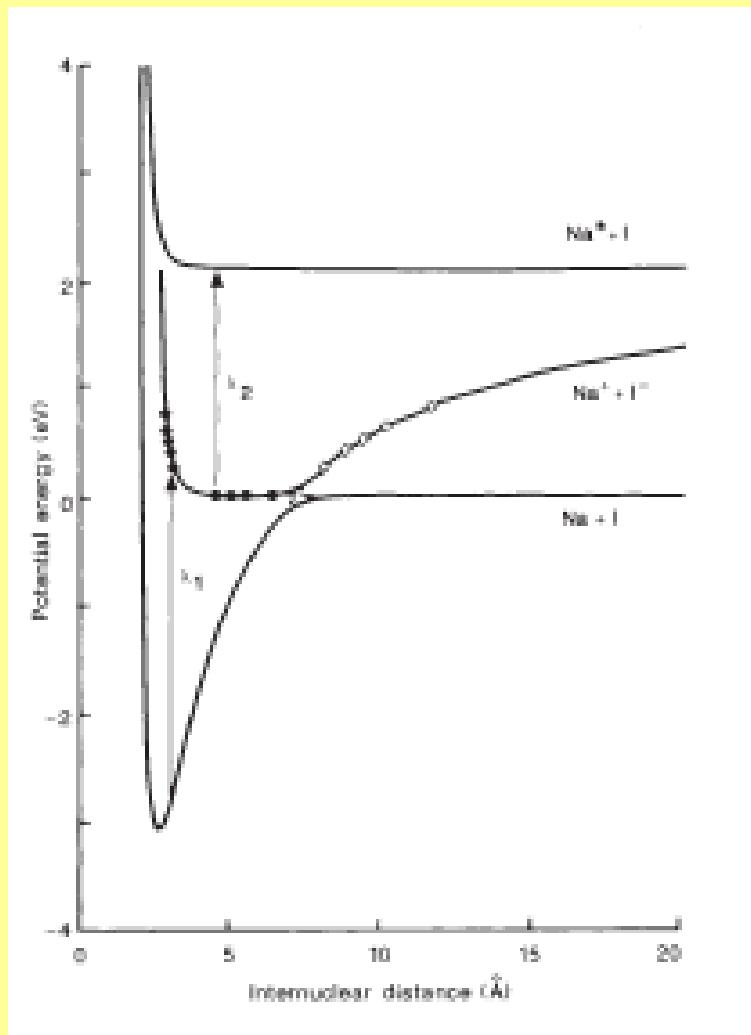
POTENTIAL ENERGY



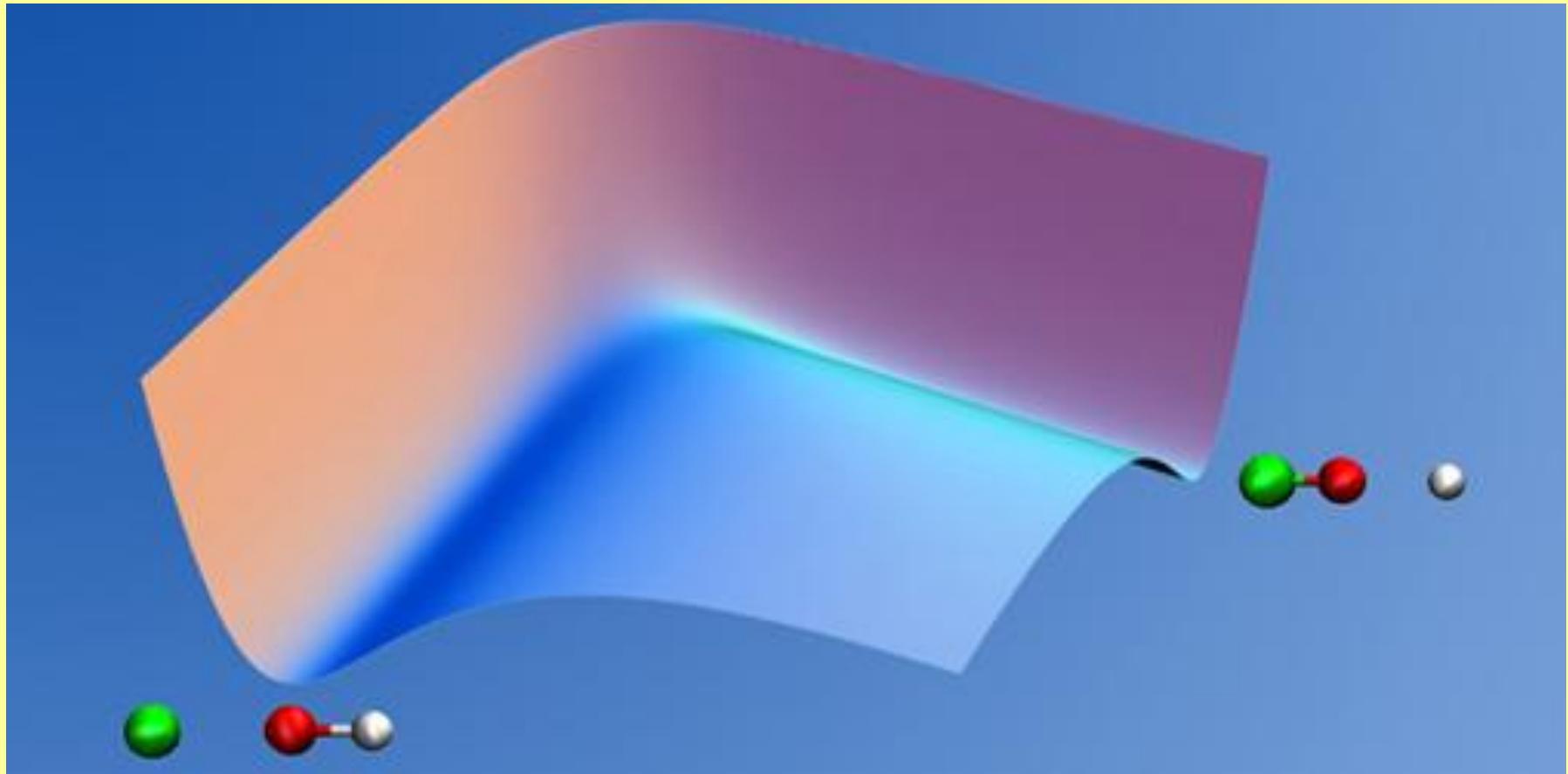
POTENTIAL ENERGY

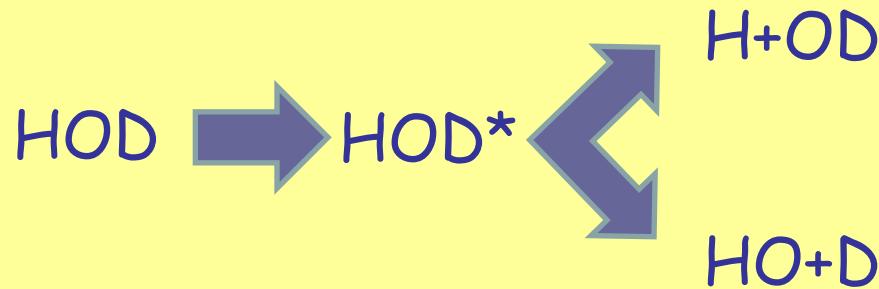


# NaI



# KONTROLA HEMIJSKE REAKCIJE



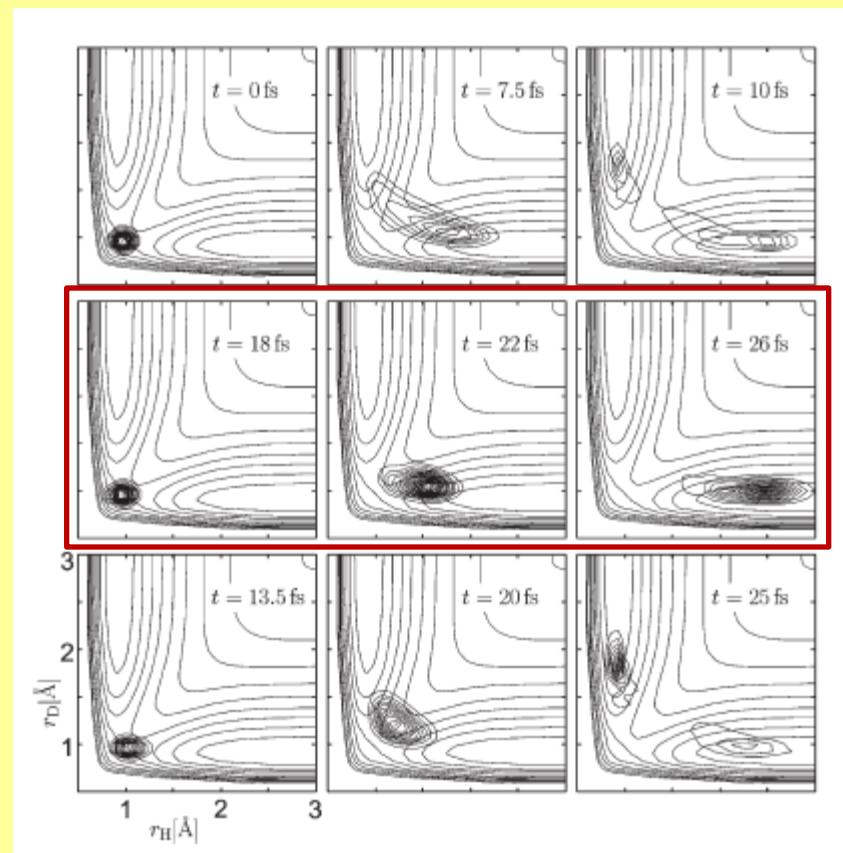
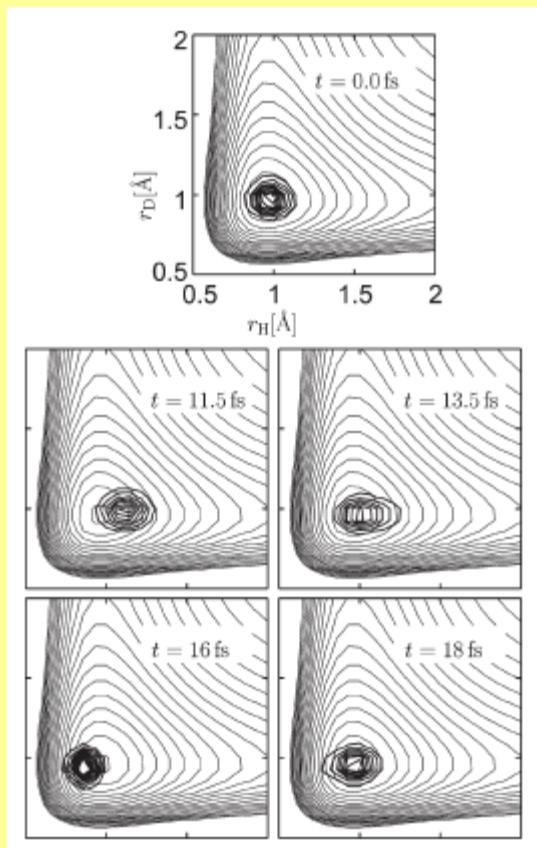
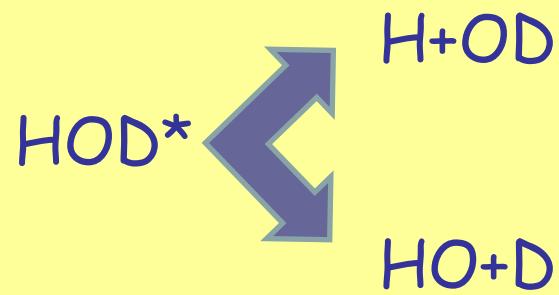


$$HOD(S_0, v=0) \xrightarrow{IR} HOD(S_0, v \neq 0)$$

$$\xrightarrow{UV} HOD(S_1) \rightleftarrows HO+D \quad H+OD$$

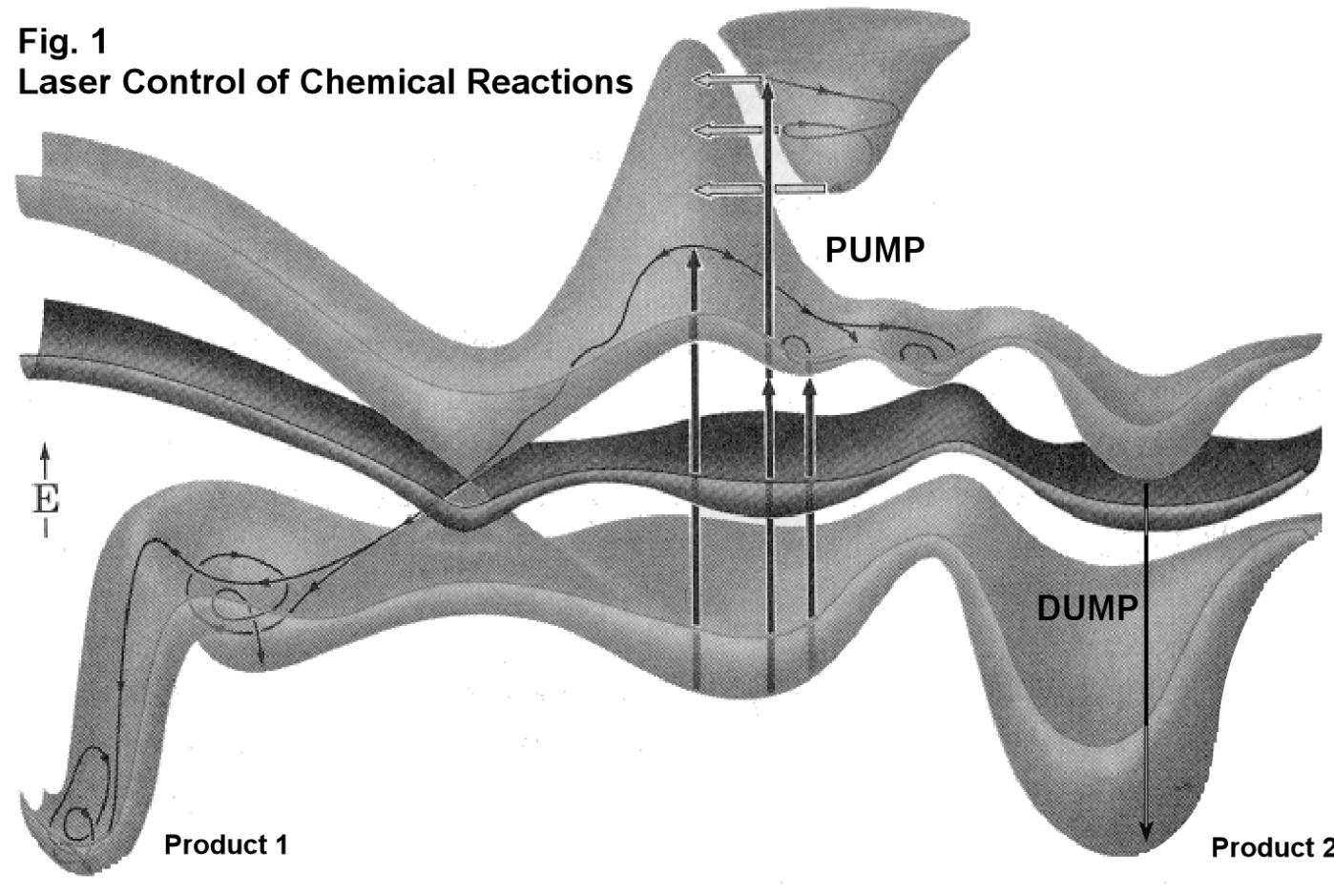
$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} |\Psi_g(t)\rangle \\ |\Psi_e(t)\rangle \end{pmatrix} = \begin{pmatrix} \hat{H}_{gg}(t) & \hat{H}_{ge}(t) \\ \hat{H}_{eg}(t) & \hat{H}_{ee}(t) \end{pmatrix} \begin{pmatrix} |\Psi_g(t)\rangle \\ |\Psi_e(t)\rangle \end{pmatrix}$$

$$\hat{H}_k(t) = \hat{H}^0 - \vec{\mu}_k \cdot \vec{\epsilon}(t) \quad k = gg, ee$$



# KONTROLA HEMIJSKE REAKCIJE

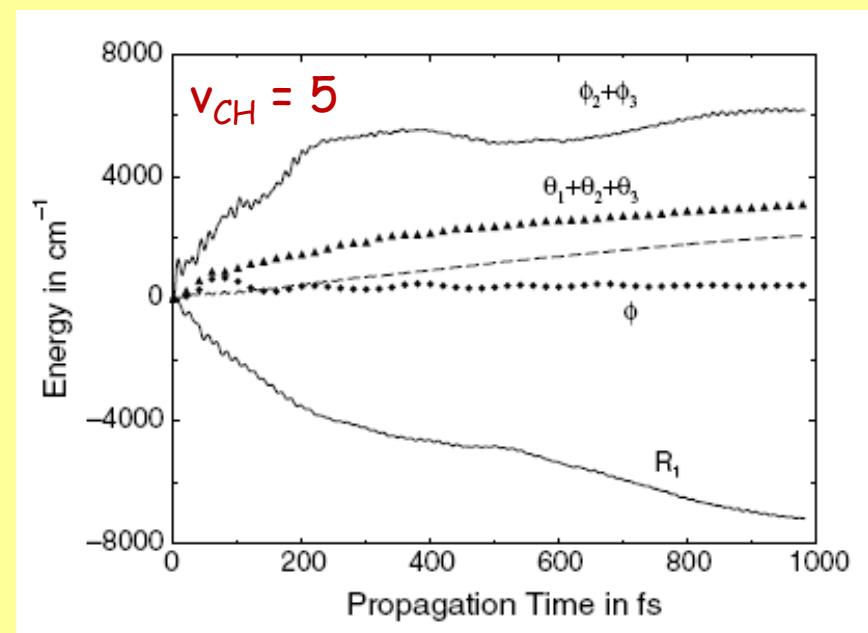
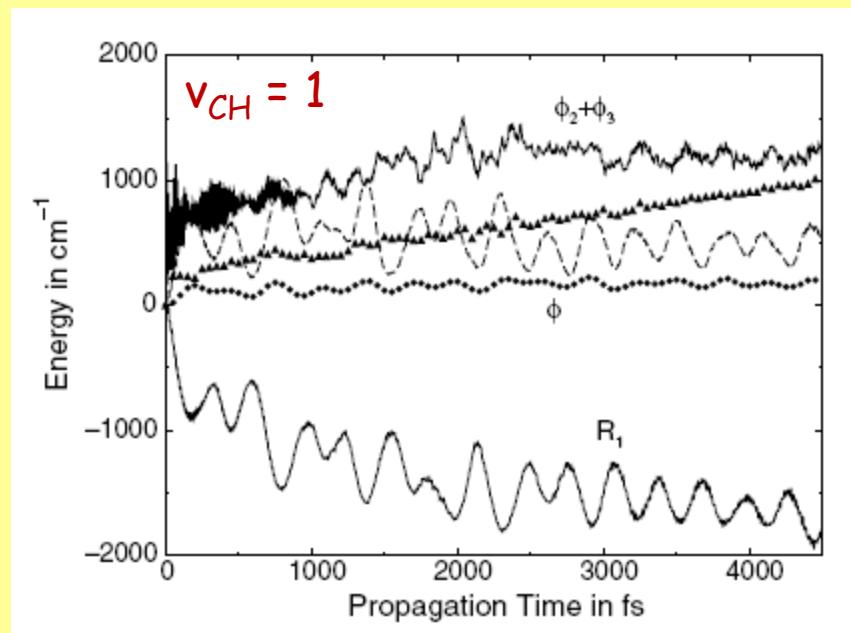
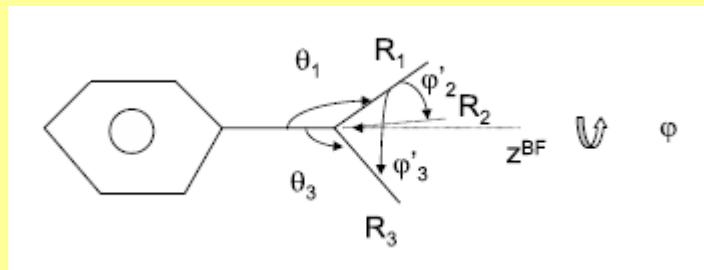
Fig. 1  
Laser Control of Chemical Reactions



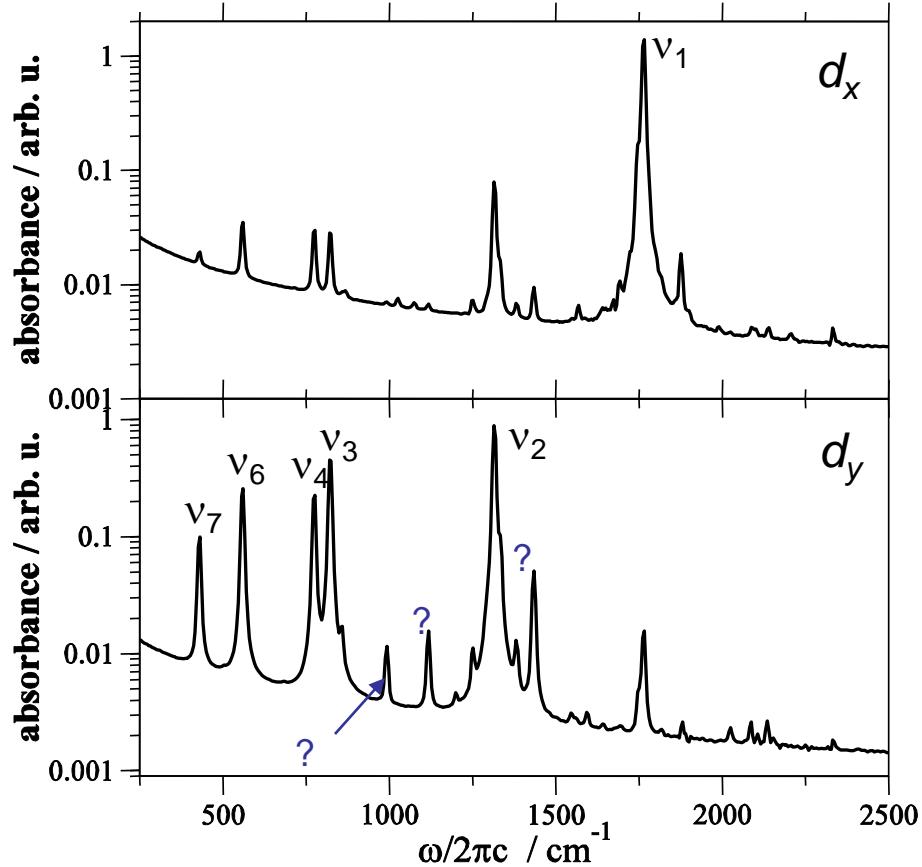
J. Michl and V. Nobačić-Koutecky, Electronic aspects of organic Photochemistry,  
John Wiley & Sons: New York, 1990

# INTRAMOLEKULSKA PRERASPODELA VIBRACIONE ENERGIJE

IVR - intramolecular vibrational energy redistribution



# IC SPEKTRI - ASIGNACIJA TRAKA



M. Petković, Chem. Phys. 331 (2007) 438

<sup>a</sup> Orphal et al. J. Phys. Chem. A 101 (1997) 1062

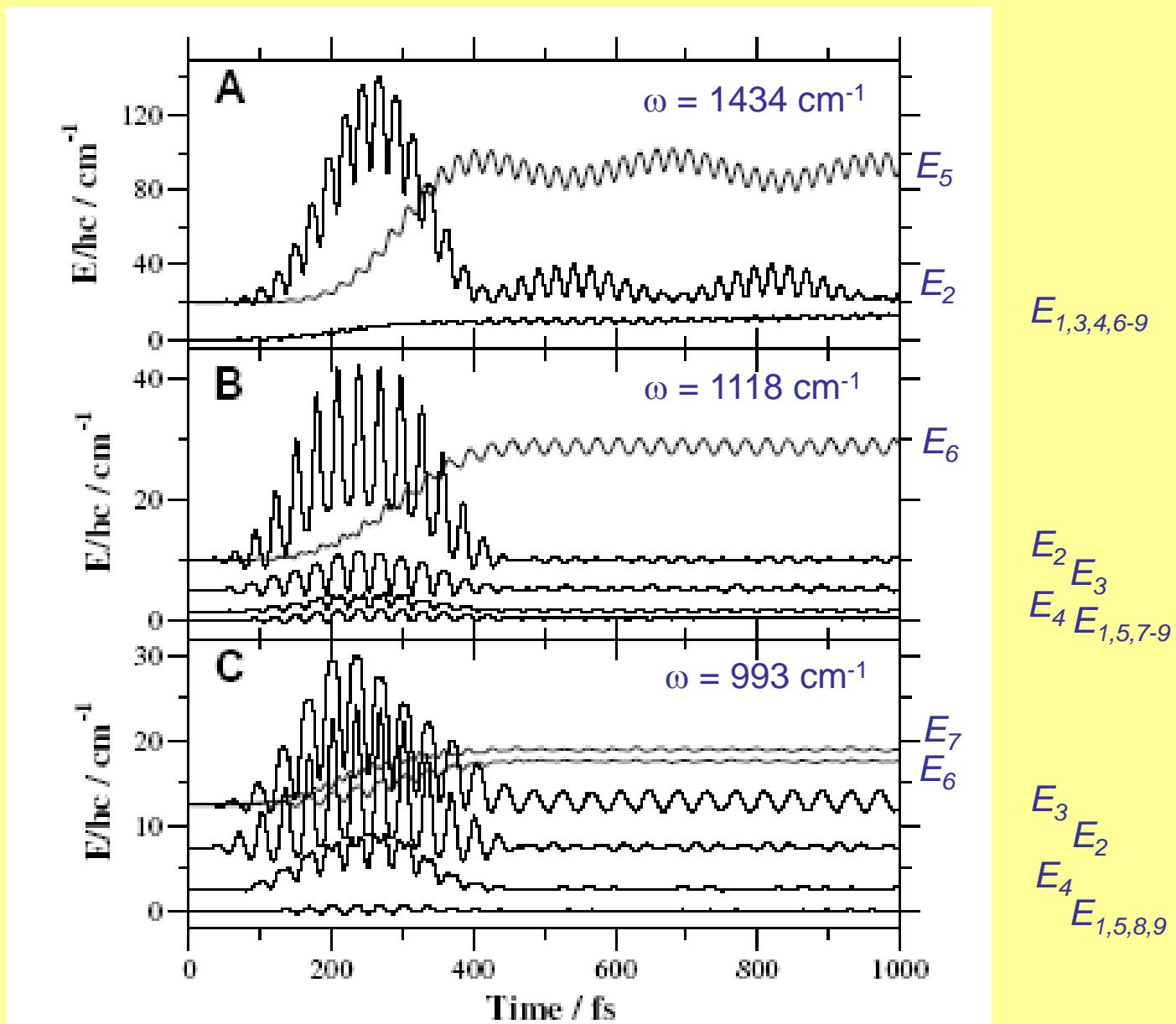
<sup>b</sup> Miller et al. Spec. Acta 23A (1967) 223

stepen slobode	frekvencija / $\text{cm}^{-1}$		
	harm.	anh.	eksp. <sup>a</sup>
$\nu_1$	1800	1766	1737
$\nu_2$	1342	1314	1293
$\nu_3$	828	820	809
$\nu_4$	786	777	780
$\nu_5$	731	719	711
$\nu_6$	561	561	563
$\nu_7$	436	431	434
$\nu_8$	250	254	273
$\nu_9$	135	158	122

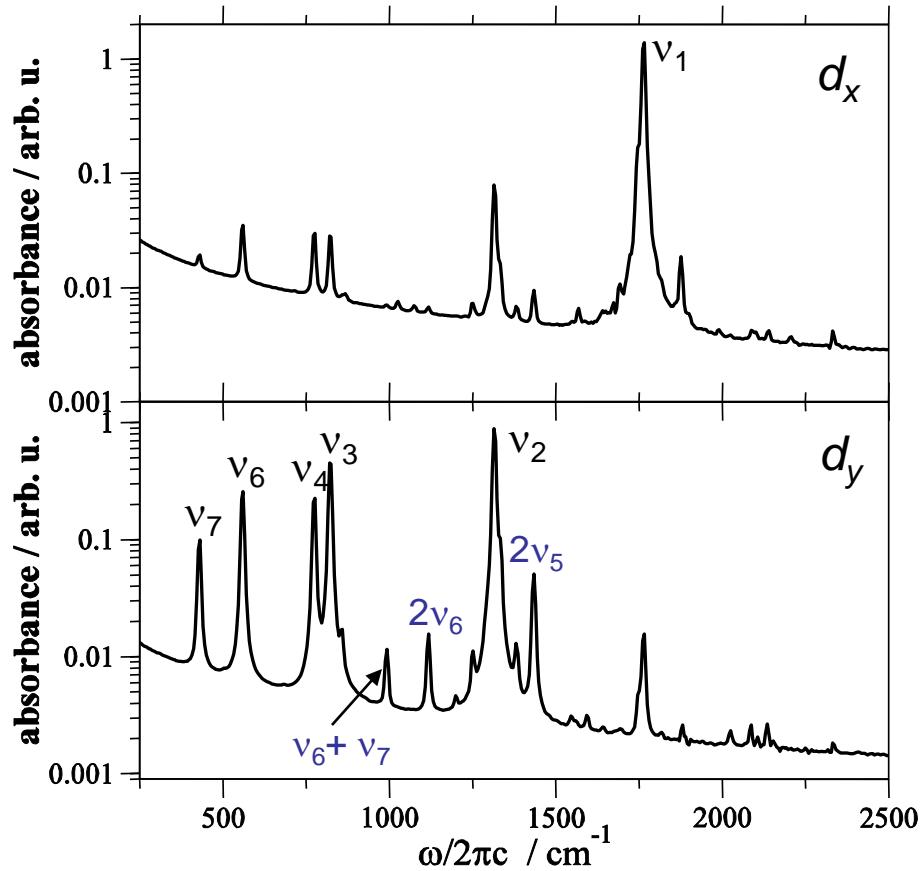
  

prelaz	frekvencija / $\text{cm}^{-1}$	
	izr.	eksp. <sup>b</sup>
?	1434	1424
?	1118	1119
?	993	988

# IC SPEKTRI - ASIGNACIJA TRAKA



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	izr.	eksp. <sup>b</sup>
$2v_5$	1434	1424
$2v_6$	1118	1119
$v_6 + v_7$	993	988

# REZIME

$\Delta E \cdot \Delta t \geq \hbar/2 \rightarrow$  Ultrakratki pulsevi stvaraju talasni paket koji predstavlja superpoziciju stacionarnih stanja.

Ultrakratki pulsevi omogućuju direktno praćenje molekulske dinamike:

- **kidanje i stvaranje molekulskih veza**
- preraspodelu vibracione energije
- kontrolu hemijske reakcije
- asignaciju traka (spektroskopija)
- ...

# PRIMENA

- elementarne reakcije i prelazna stanja
- organska hemija
- reakcije prenosa elektrona i/ili protona
- reakcije organometalnih jedinjenja
- atmosferska hemija
- klasteri i nanostrukture
- gusti fluidi, tečnosti i polimeri
- kontrola hemijskih reakcija
- dinamika bioloških sistema
- ...