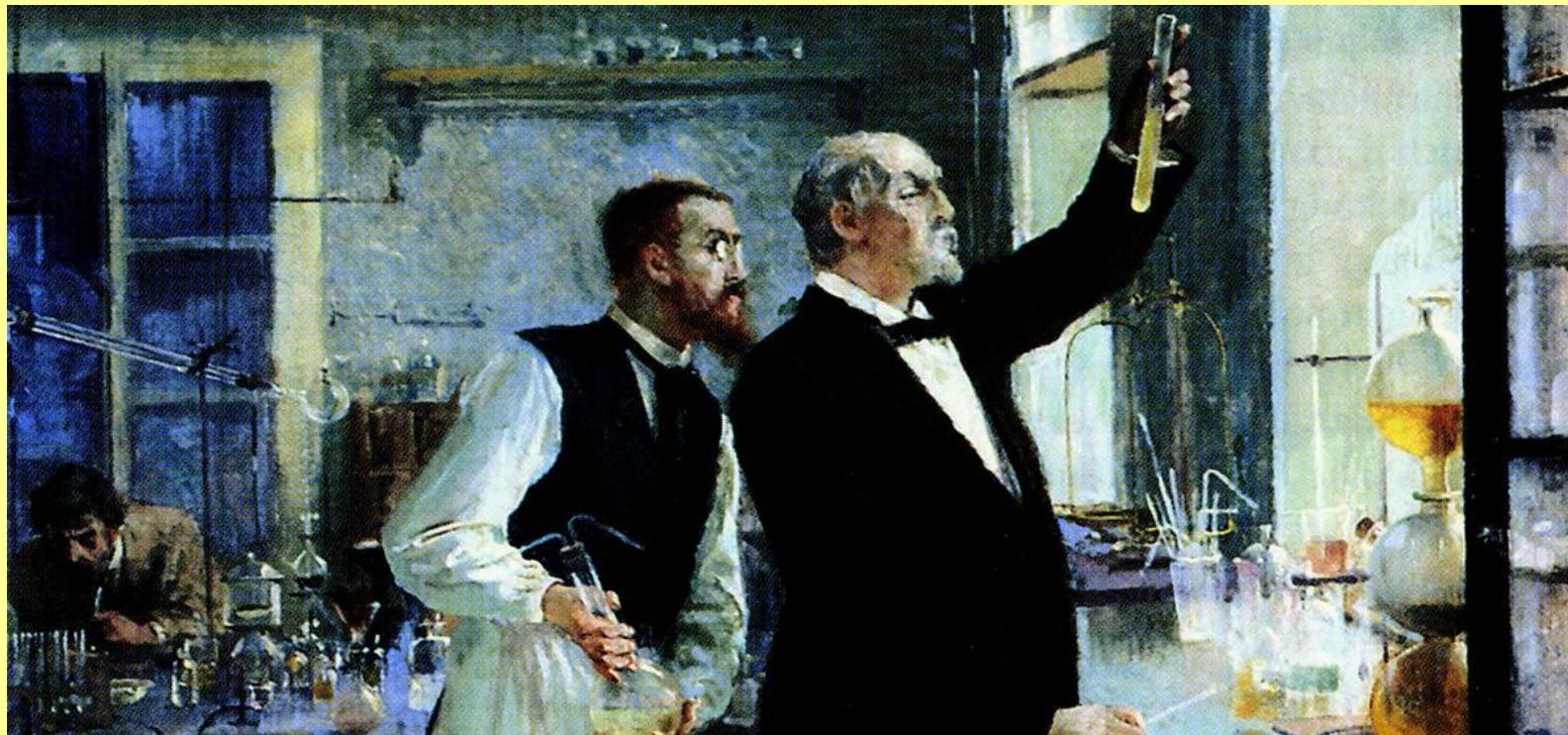


NOVE FIZIČKOHEMIJSKE METODE

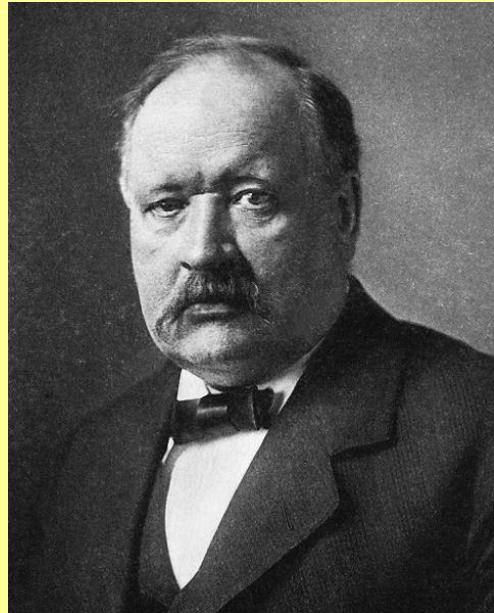
FEMTOHEMIJA

MILENA PETKOVIĆ

ANALIZA HEMIJSKIH REAKCIJA (1)



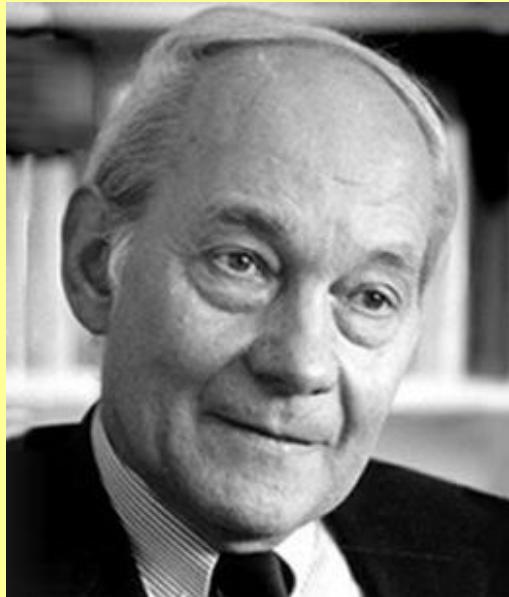
ANALIZA HEMIJSKIH REAKCIJA (2)



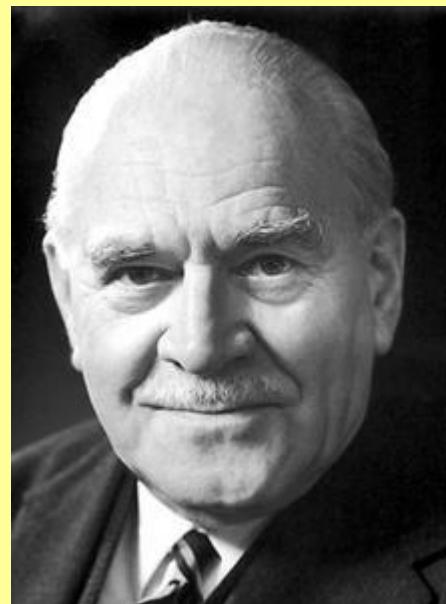
Svante Arenijus

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

ANALIZA HEMIJSKIH REAKCIJA (3)



Manfred Ajgen



Ronald G. V. Noriš



Džordž Porter

Fleš fotoliza
Nobelova nagrada za hemiju 1967.

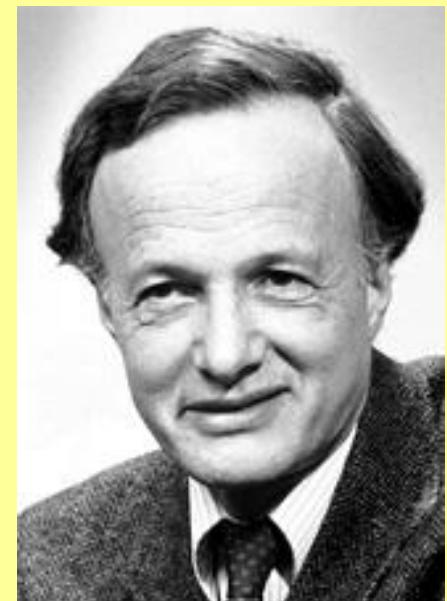
ANALIZA HEMIJSKIH REAKCIJA (4)



Dadli R. Heršbah



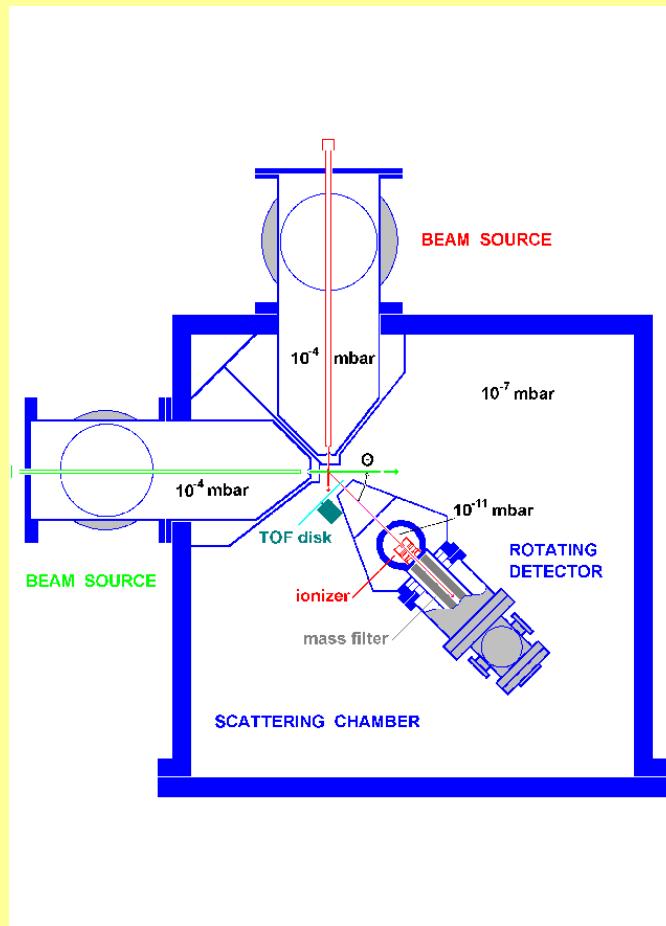
Jan T. Li



Džon Č. Polani

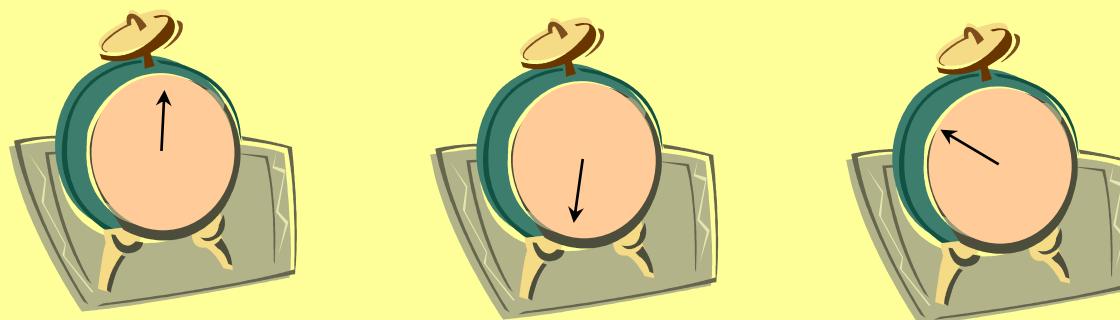
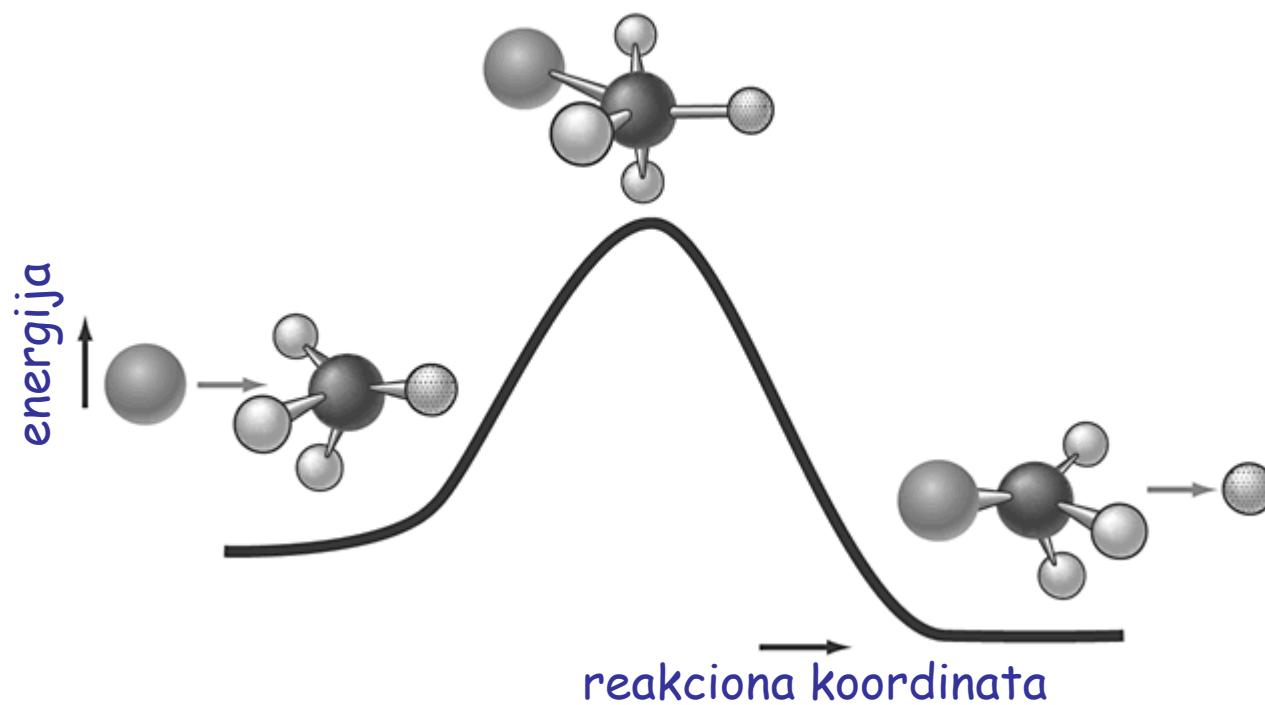
Molekulski snopovi
Nobelova nagrada za hemiju 1986.

ANALIZA HEMIJSKIH REAKCIJA (4)

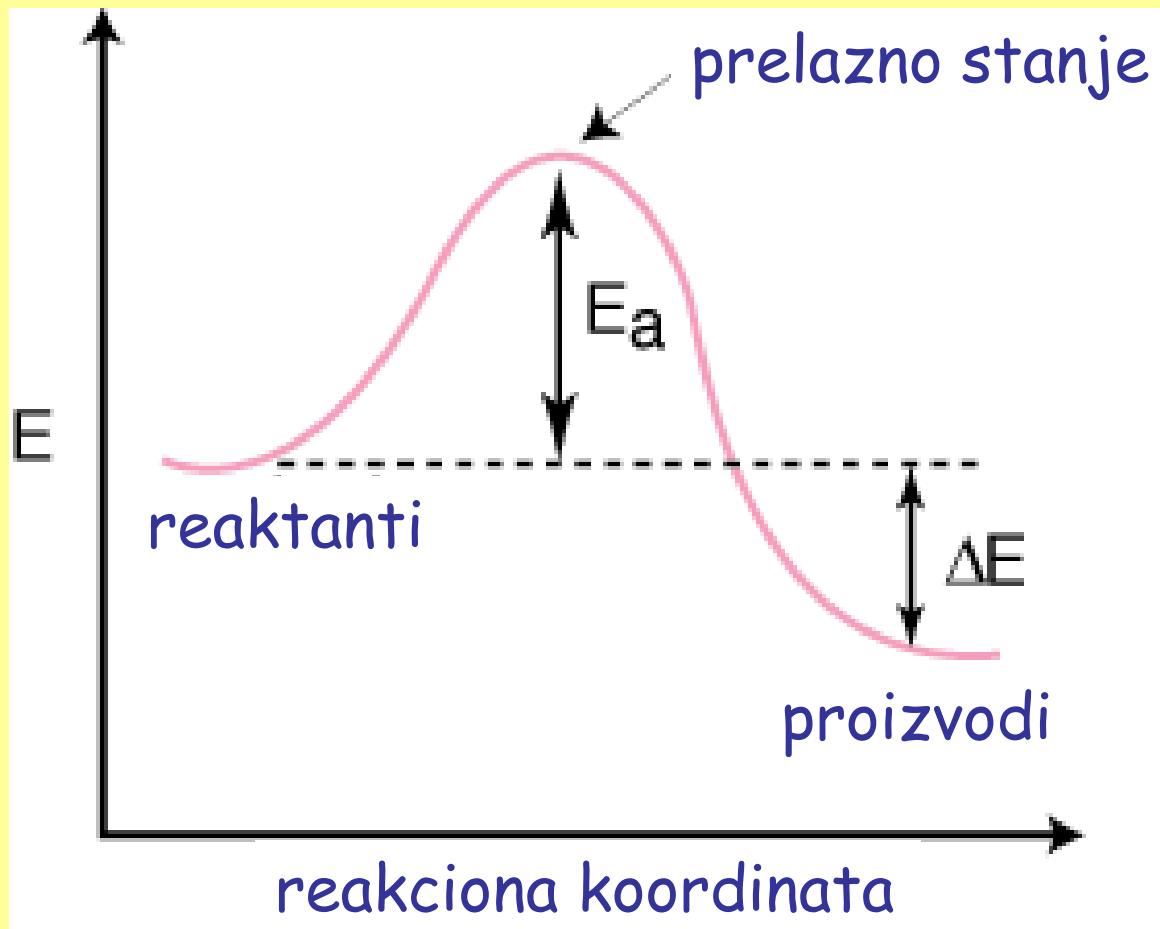


Hamlet!

PRAĆENJE TOKA HEMIJSKE REAKCIJE



PRELAZNO STANJE



vreme života $\approx 10 - 100$ fs

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

Atomic Resolution Single Molecule Motion

Transition States & Reaction Intermediates

IVR & Reaction Products



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

"ROĐENJE" ULTRABRZE TEHNOLOGIJE

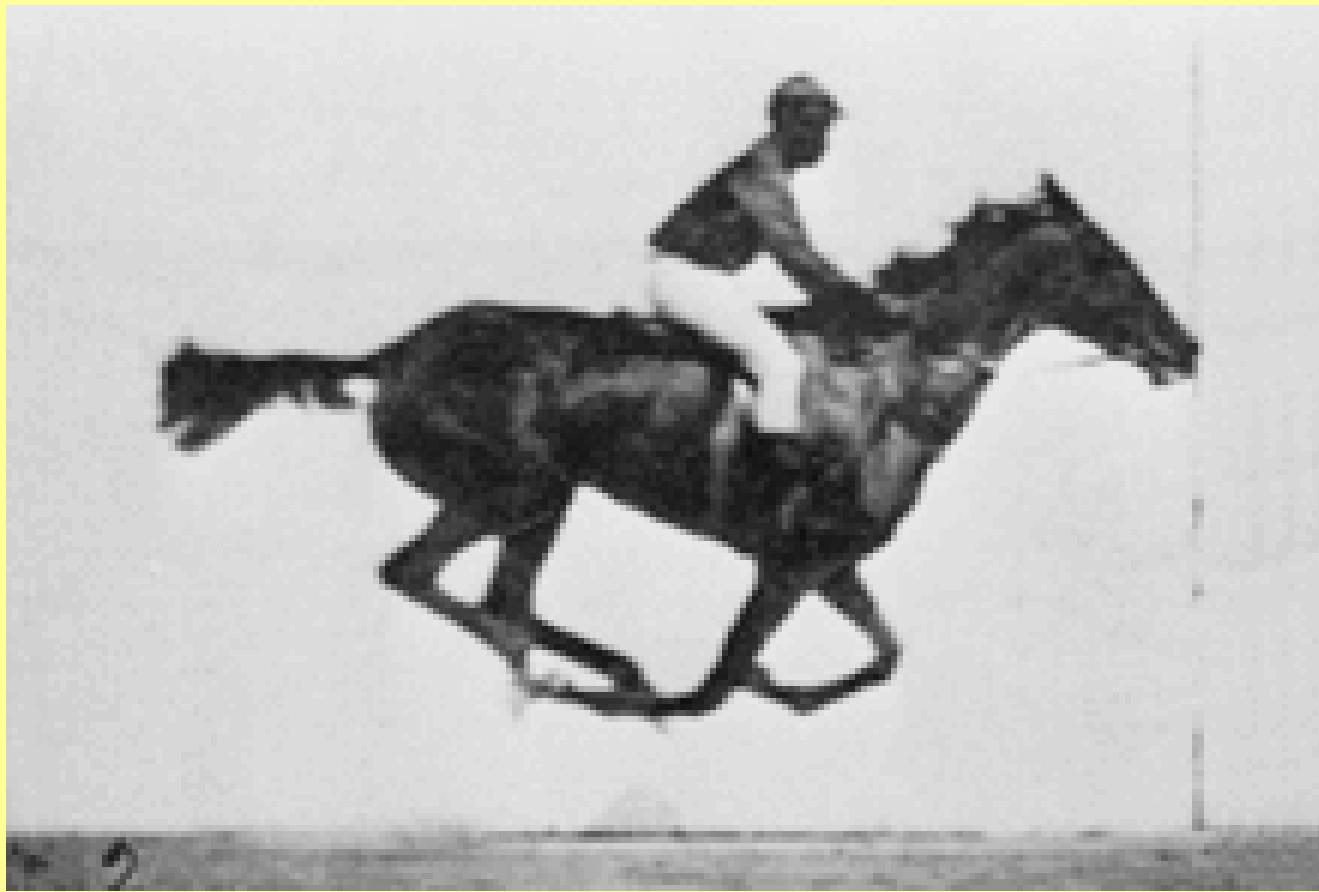


Konj u pokretu (The horse in motion)

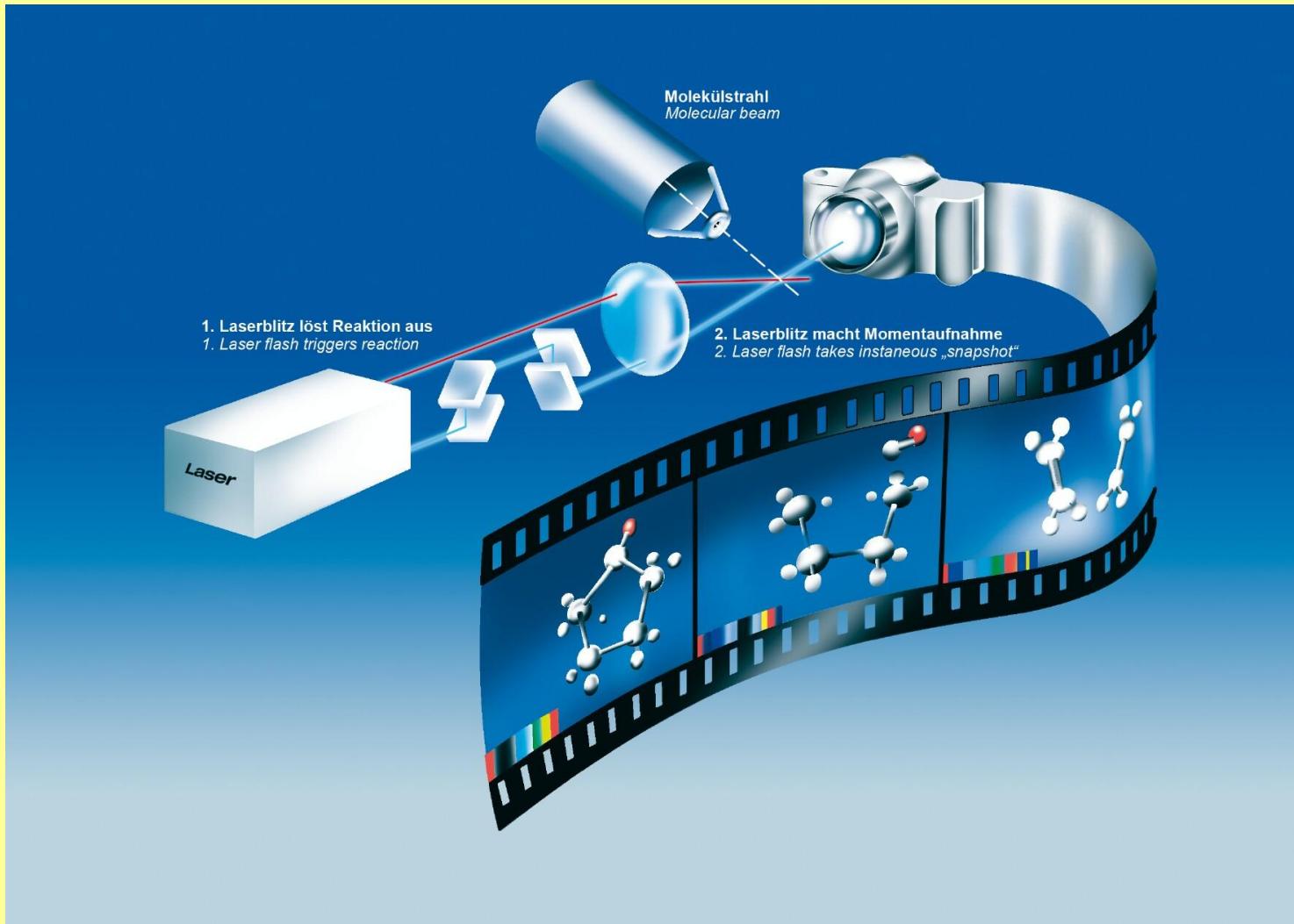
Fotograf: Edvard Majbridž

Palo Alto, Kalifornija 1872 → 1878.

"ROĐENJE" ULTRABRZE TEHNOLOGIJE

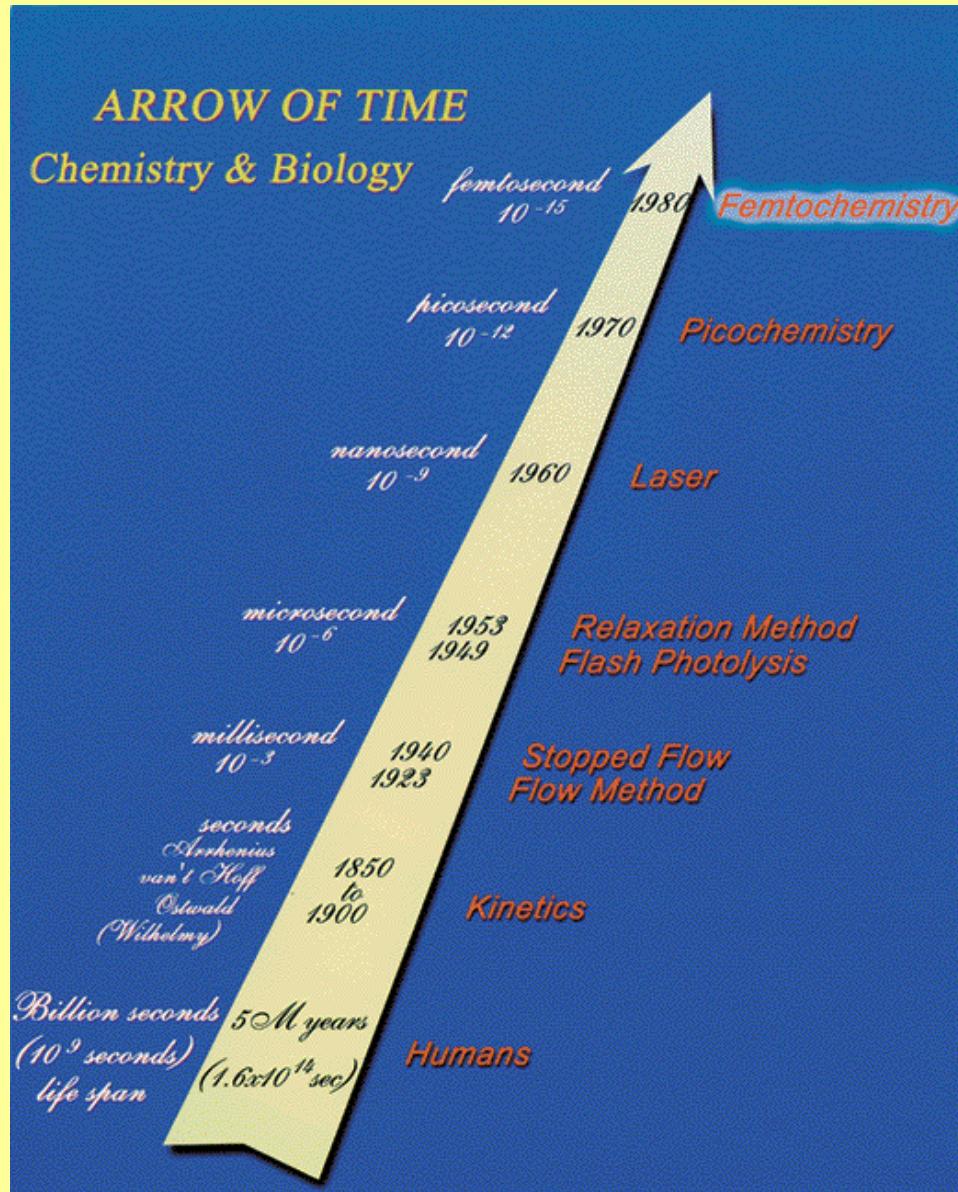


*Seli Gardner u galopu - animirano 2006. godine
na osnovu Majbridžovih fotografija*



CILJ:

“film” koji prikazuje položaj jezgara
u toku hemijske reakcije

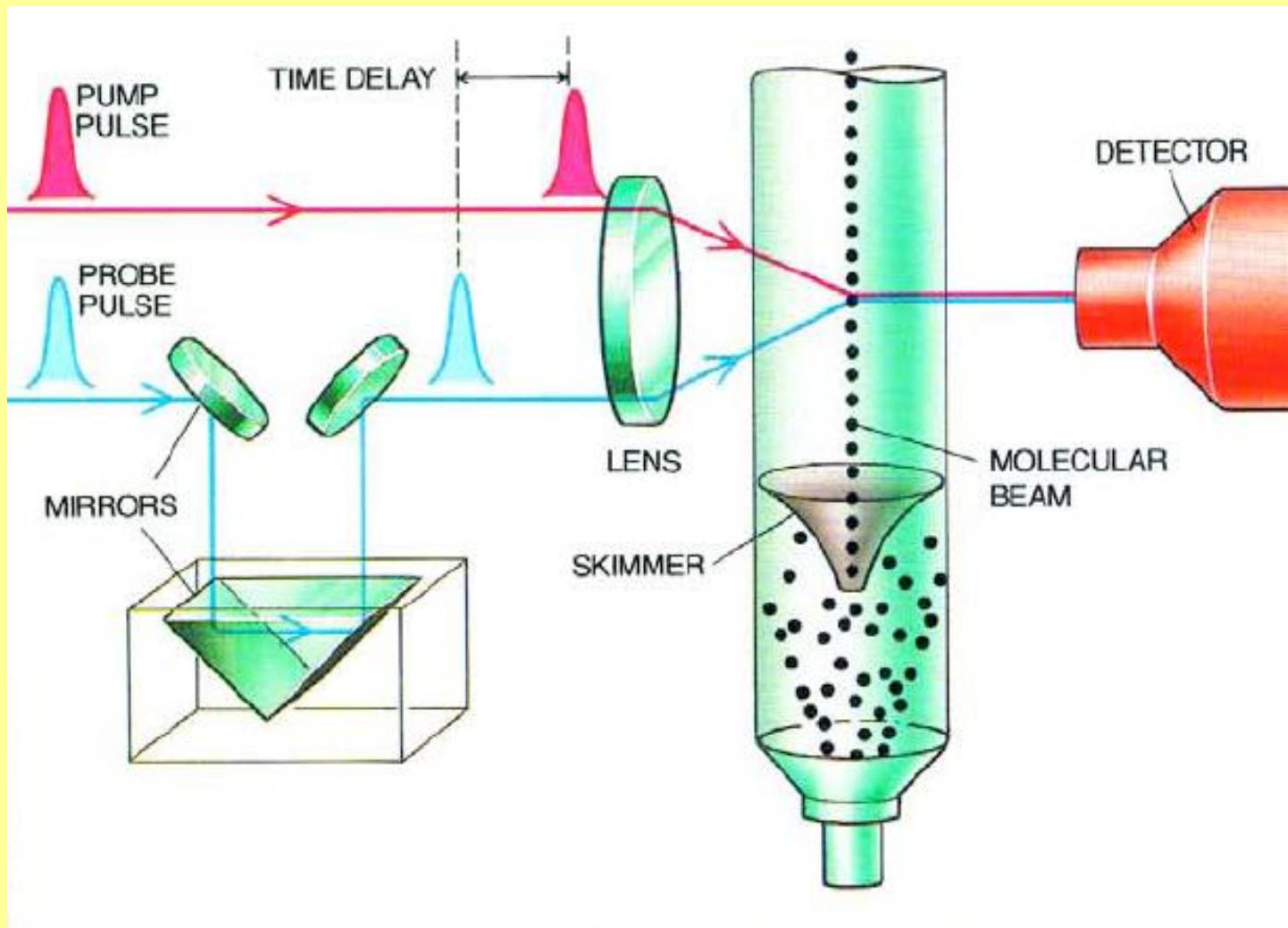




Ahmed Zewail

"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."

FEMTOSEKUNDNI LASERI



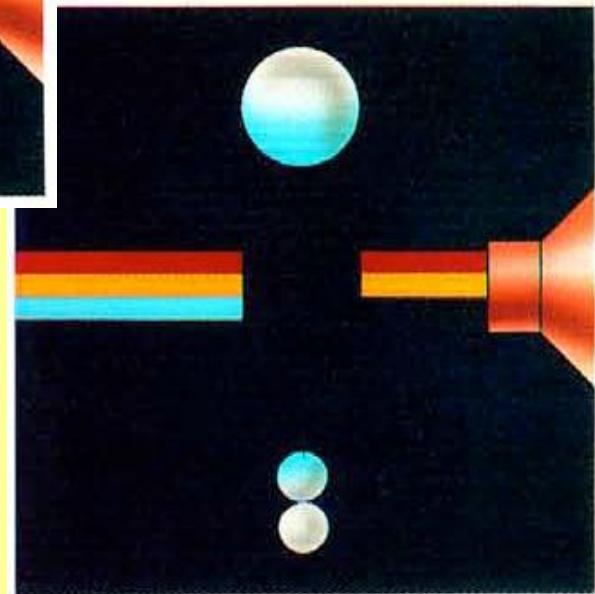
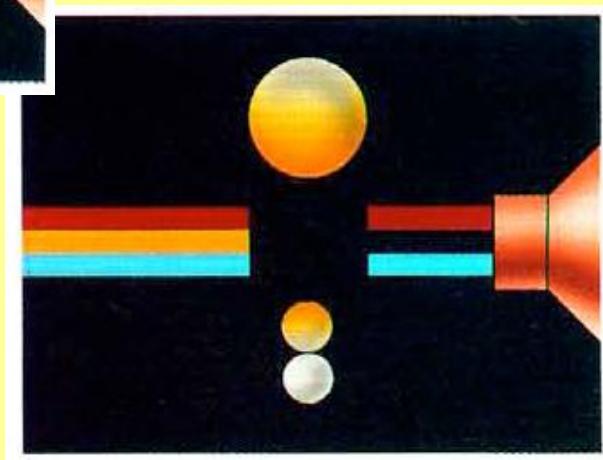
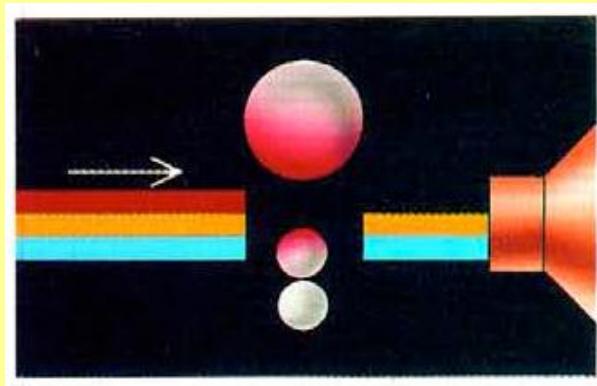
KAŠNJENJE PROBA PULSA

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

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

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

"OTISAK PRSTIJIU" ATOMA U POKRETU



Elementarni fenomeni:

- prelazna stanja
- preraspodela energije
- brzine hemijskih reakcija

Hemijske veze:

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

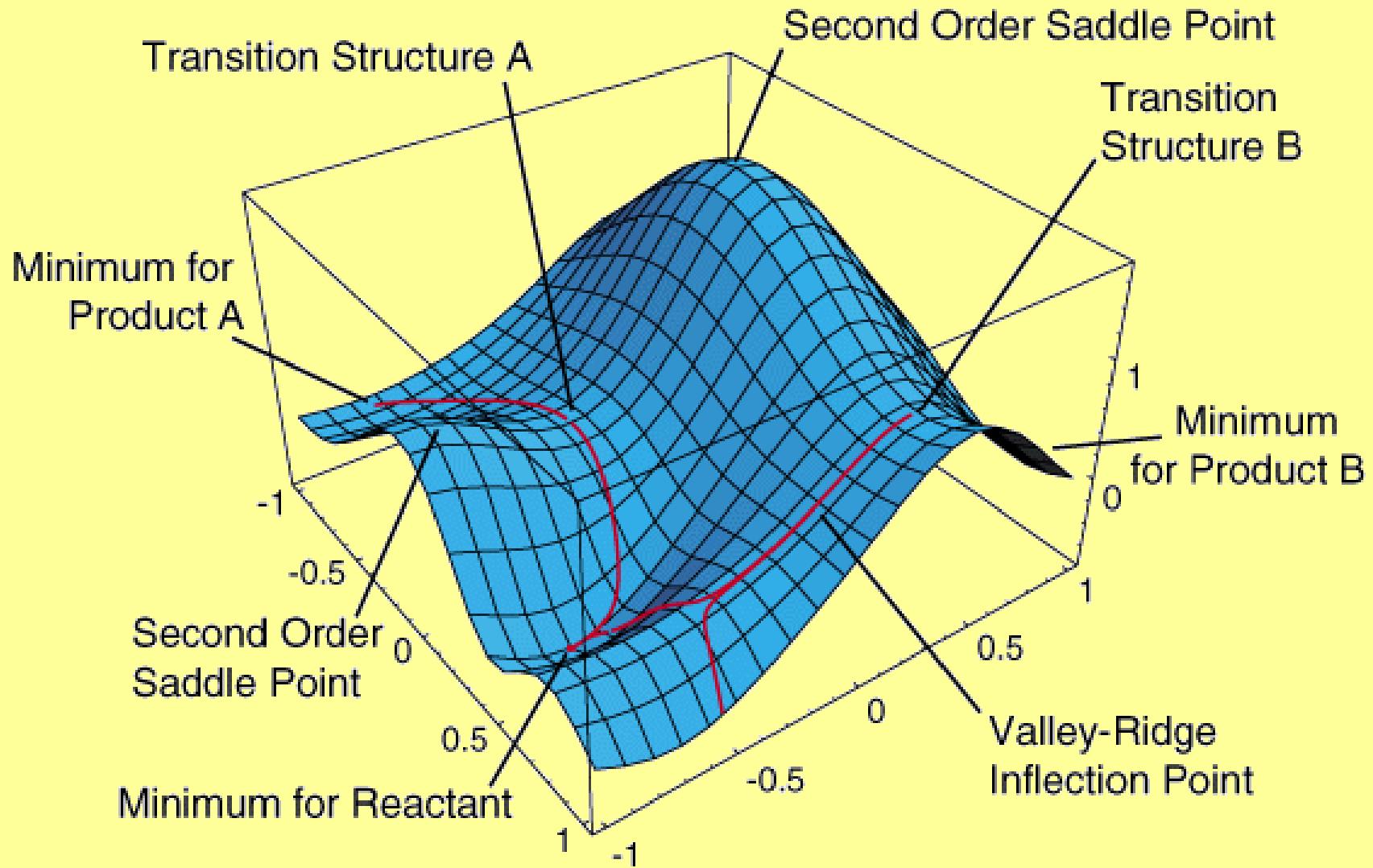
Stanja molekula:

- osnovno i pobuđena stanja
- neutralne čestice i joni

Sistemi različitih dimenzija:

- dvoatomski molekuli
- ...
- DNK i proteini

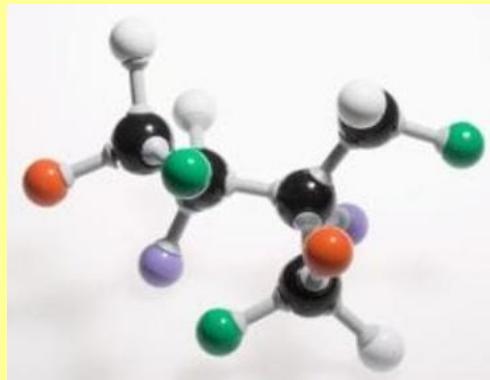
TEORIJSKI PRISTUP



TEORIJSKI PRISTUP

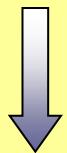
vremenski zavisna Šredingerova jednačina

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



$$\Psi(t)$$

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



PERTURBACIONI RAČUN

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

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

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

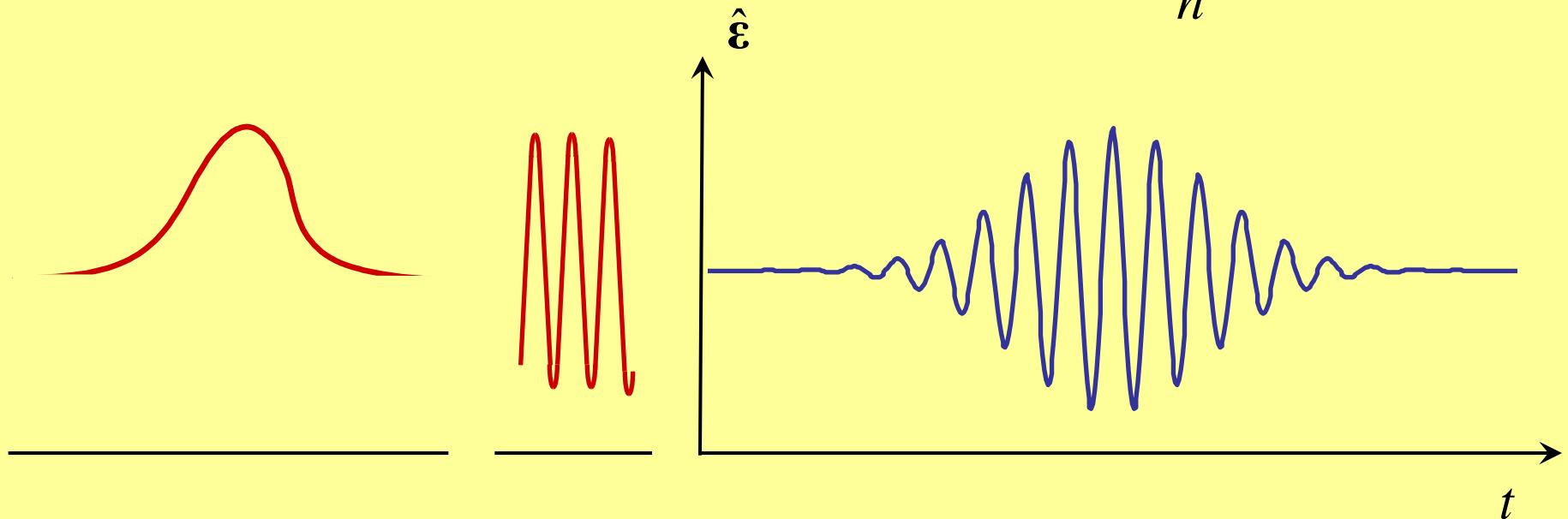
perturbacija
(laserski puls)

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

ULTRAKRATKI LASERSKI PULS

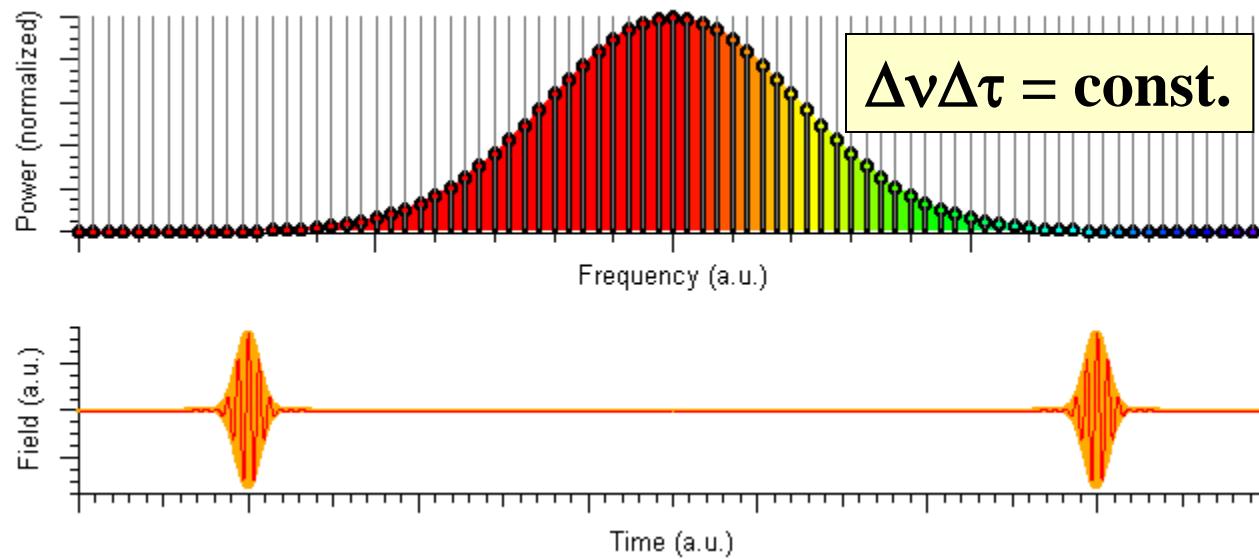
$$\hat{\epsilon}(t) = \hat{\epsilon}_0 e^{-\frac{t^2}{\alpha T^2}} \cos(\omega t)$$

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



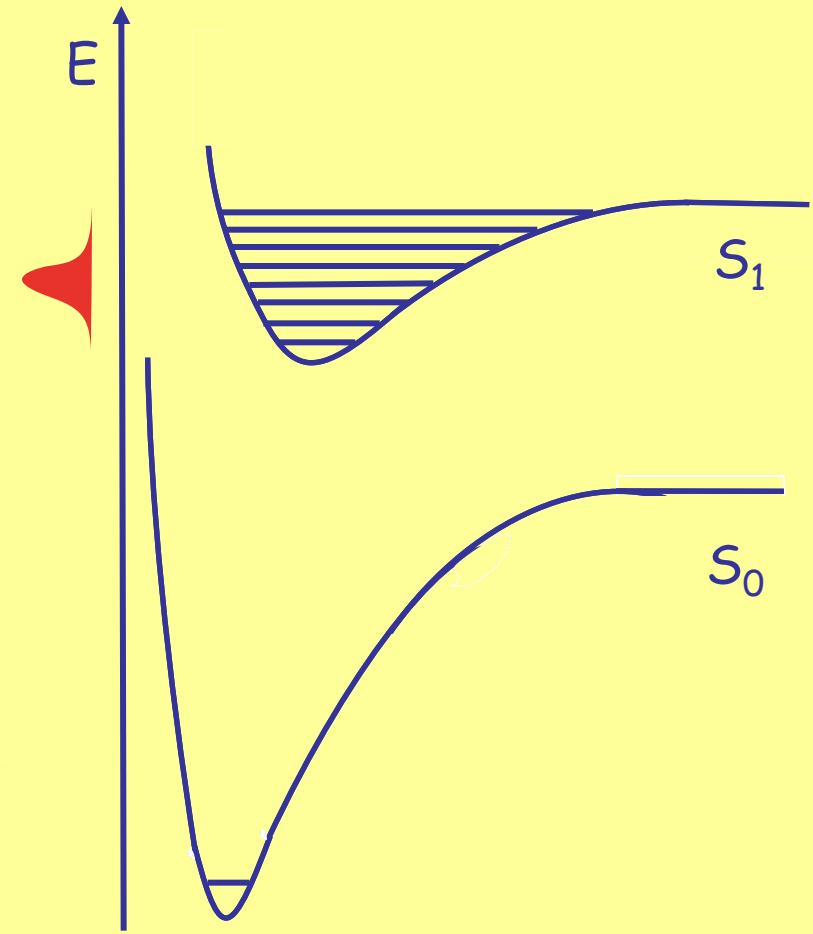
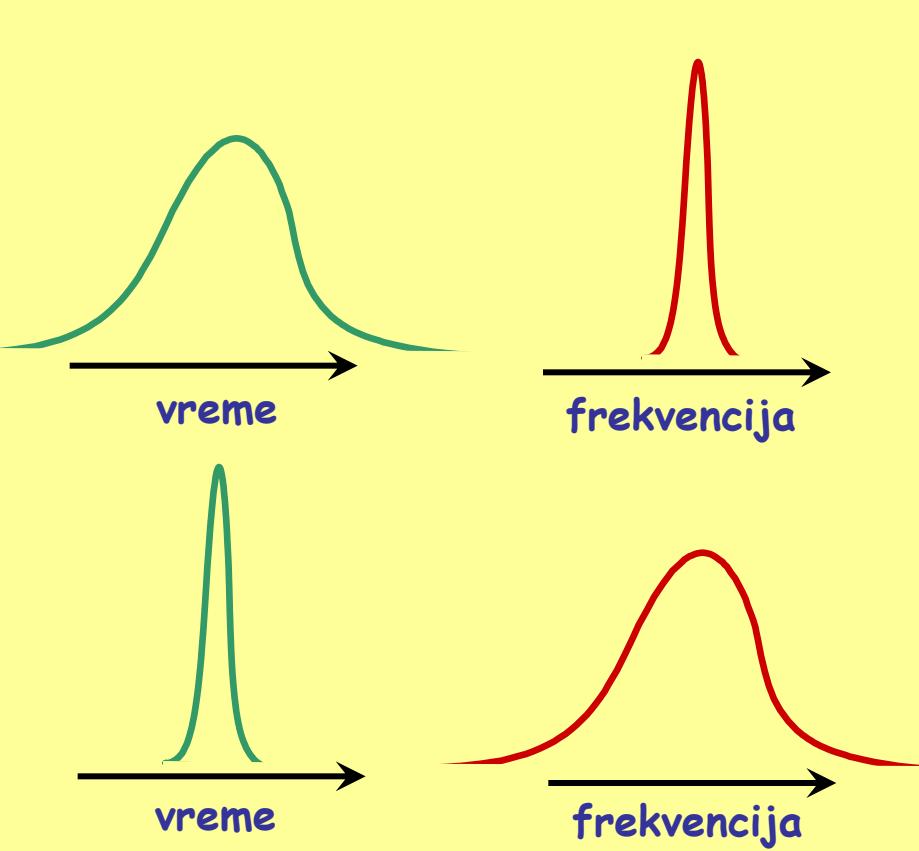
$$\hat{V}(t) = -\hat{\mu} \cdot \hat{\epsilon}(t)$$

HAJZENBERGOVA RELACIJA



HAJZENBERGOVA RELACIJA

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



TRADICIONALNA I ULTRABRZA SPEKTROSKOPIJA

tradicionalna spektroskopija

$$T \rightarrow \infty$$

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

monohromatsko zračenje

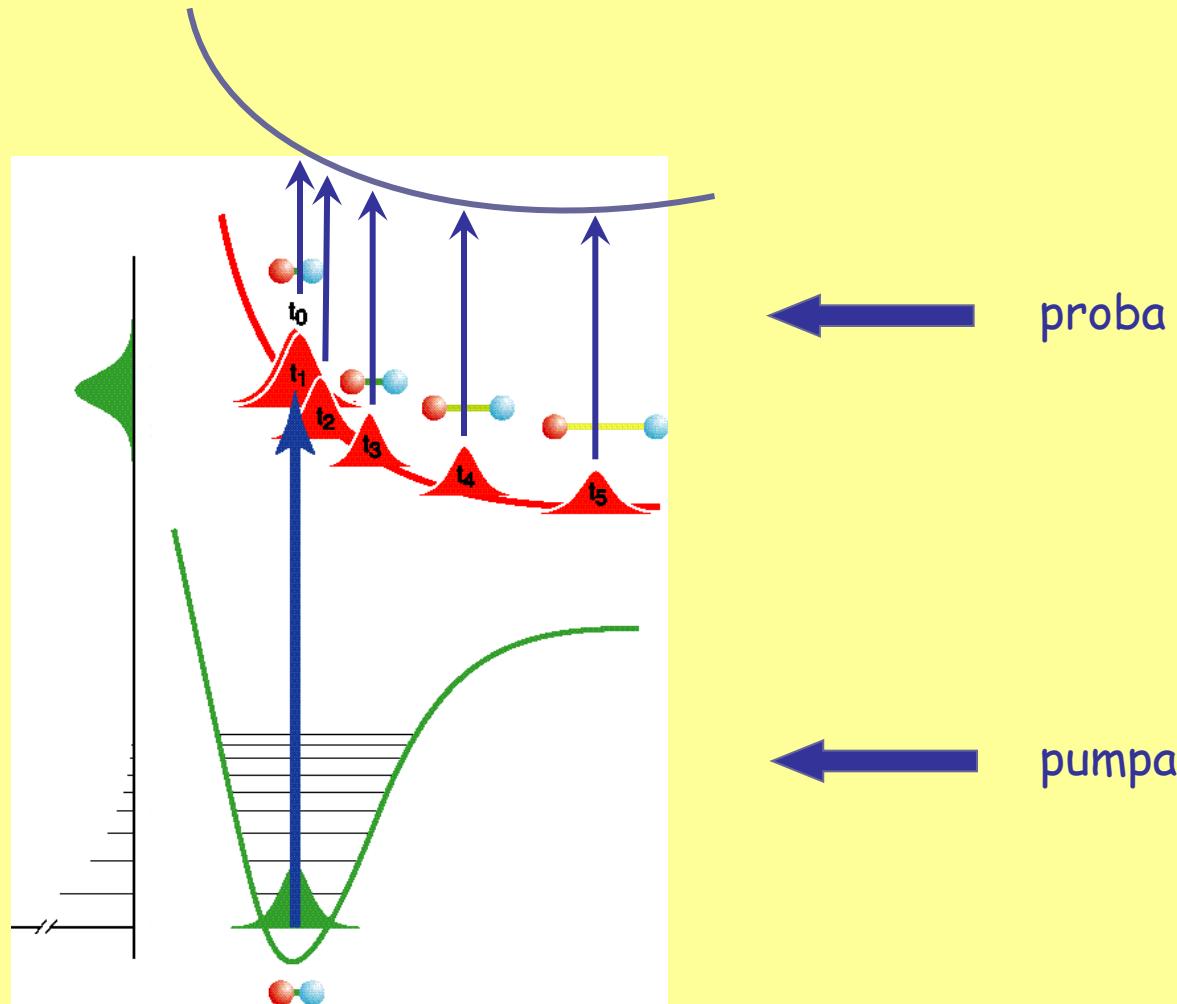
ultrabrza spektroskopija

$$T \rightarrow 0$$

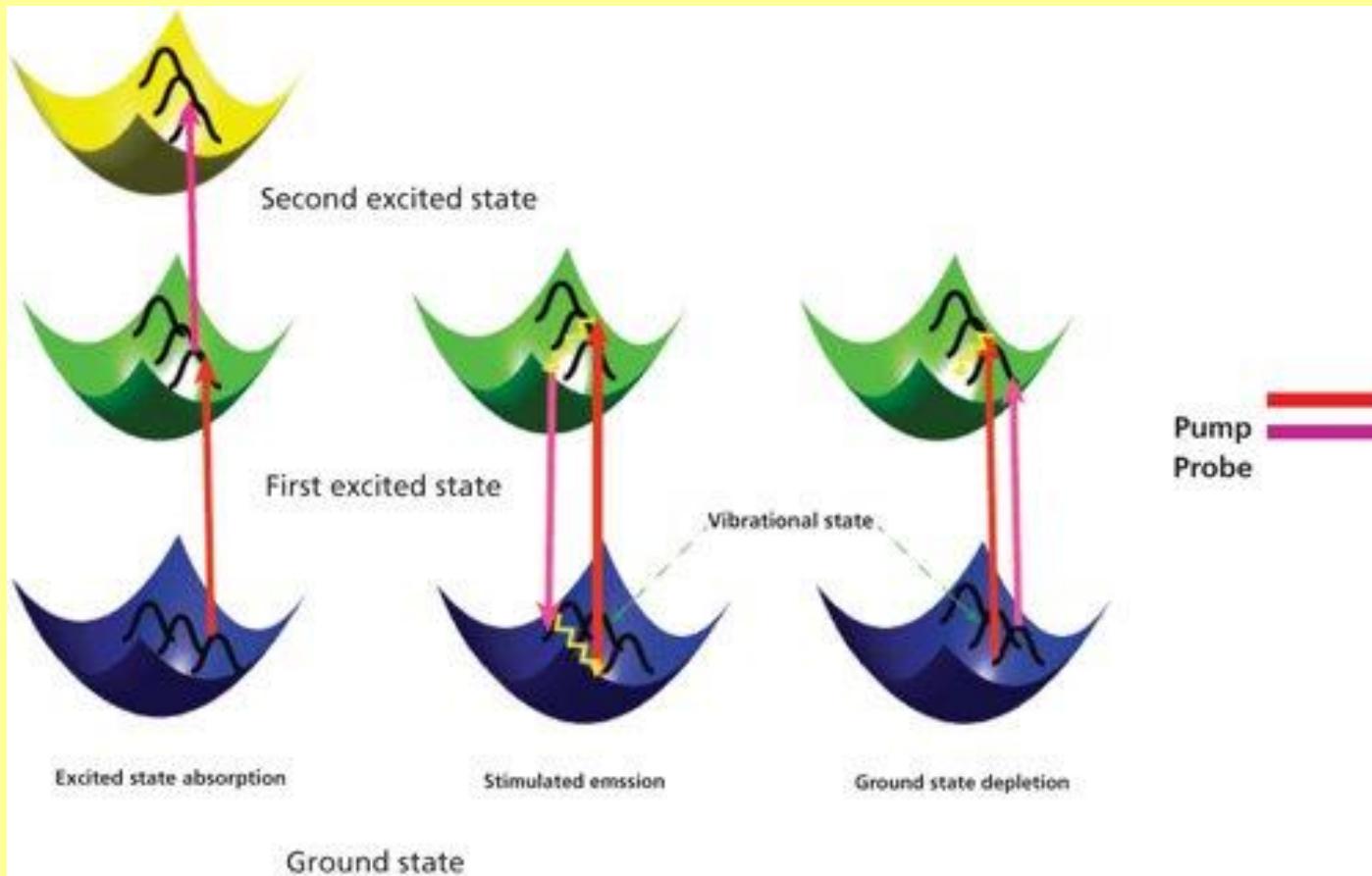
$$\varepsilon(t) = \varepsilon_0 e^{-\frac{t^2}{\alpha T^2}} \cos(\omega t)$$

širok opseg frekvencija

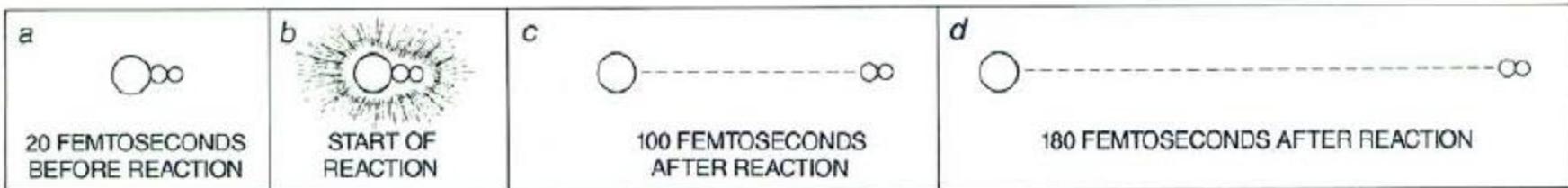
PUMPA - PROBA METODA



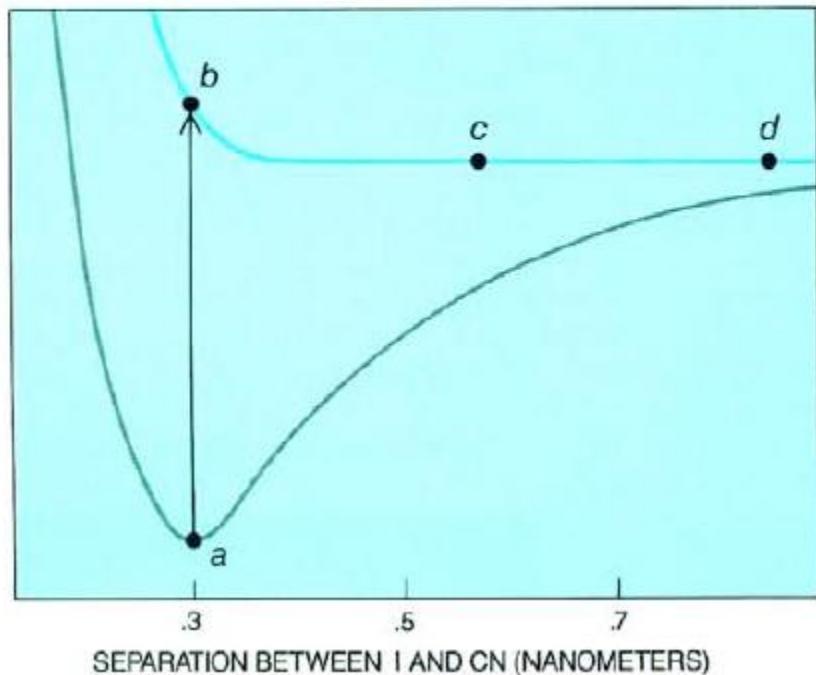
PUMPA - PROBA METODA



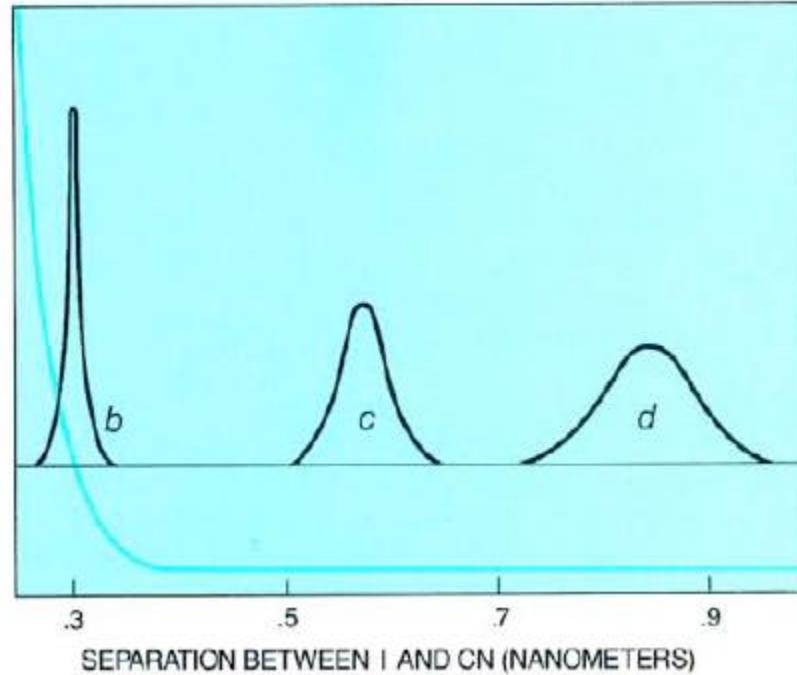
ICN



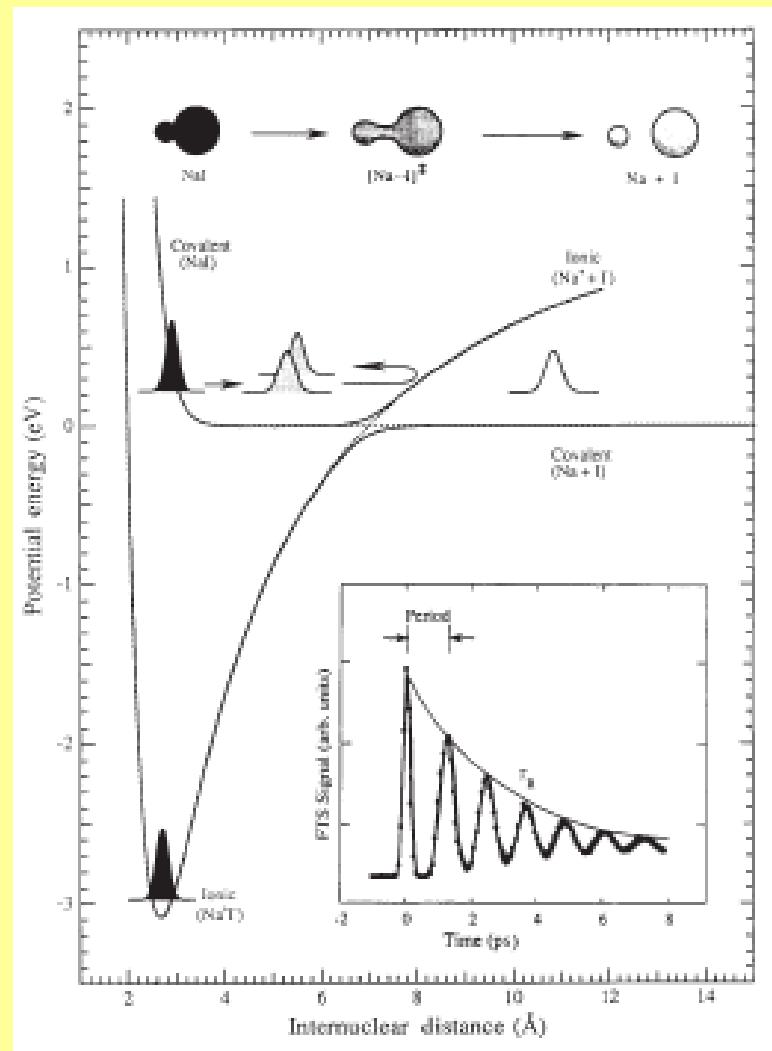
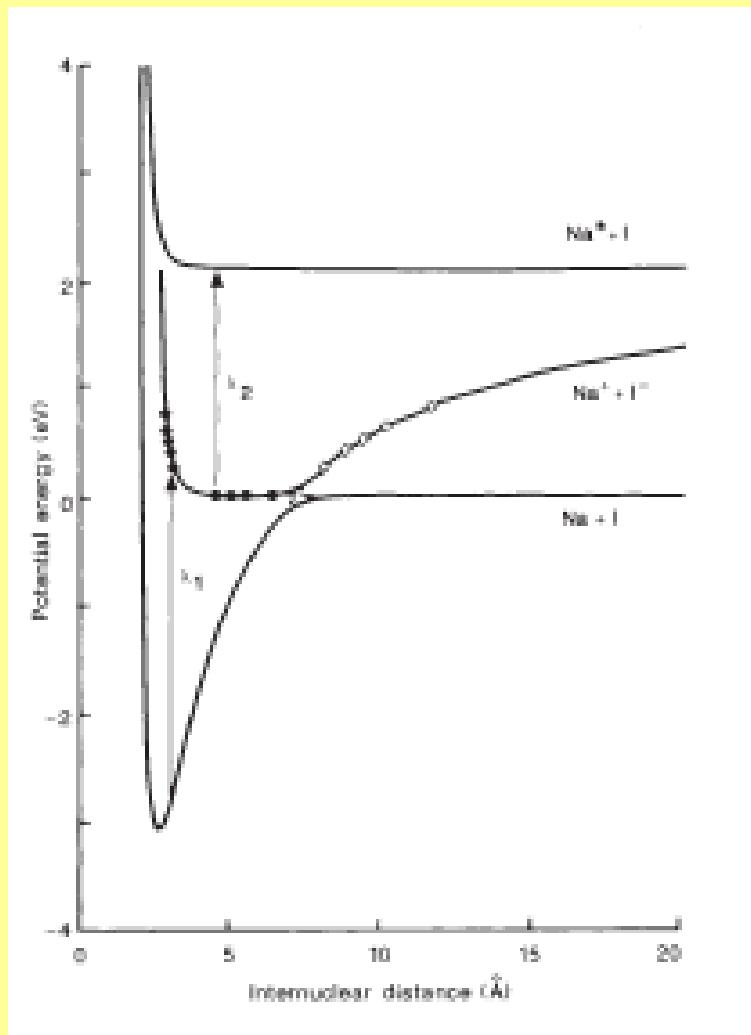
POTENTIAL ENERGY



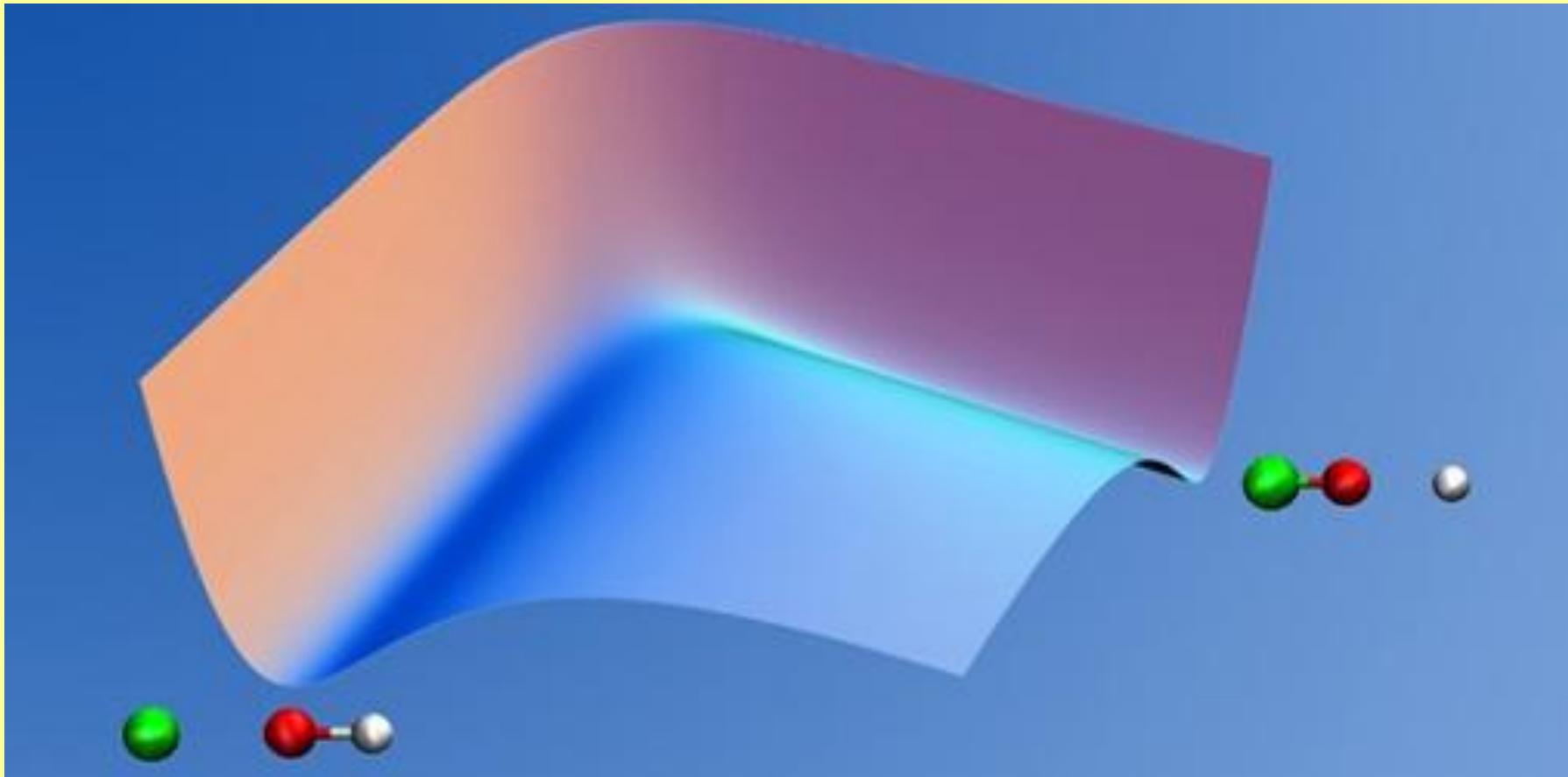
POTENTIAL ENERGY

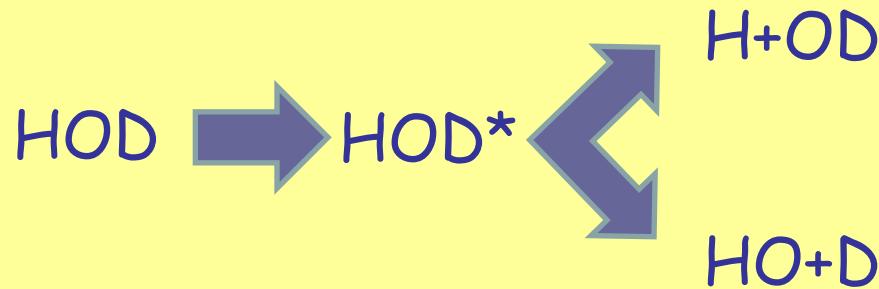


NaI



KONTROLA HEMIJSKE REAKCIJE



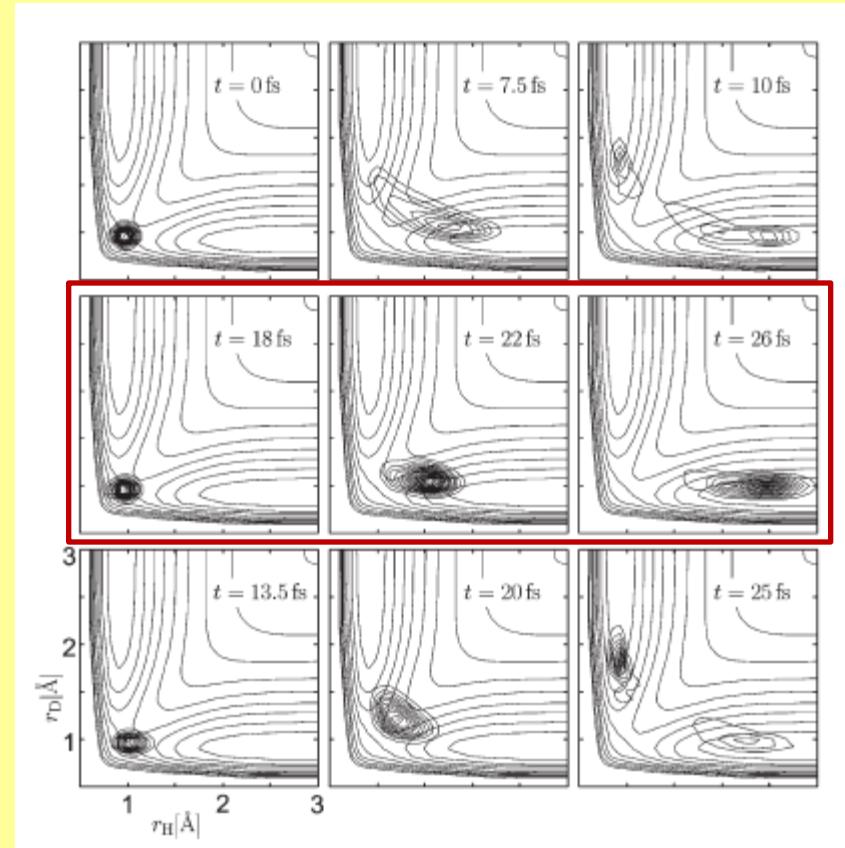
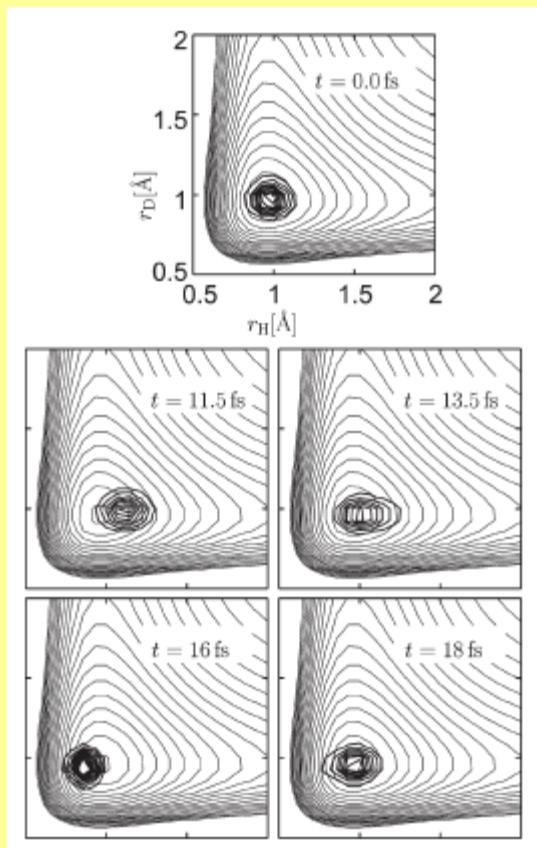
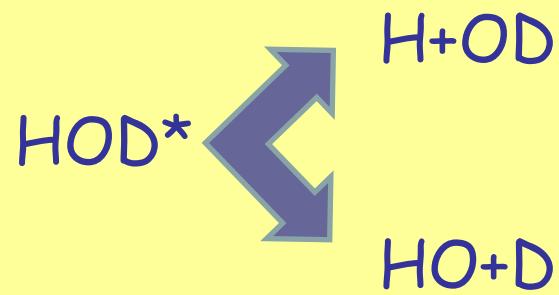


$$HOD(S_0, v=0) \xrightarrow{IR} HOD(S_0, v \neq 0)$$

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

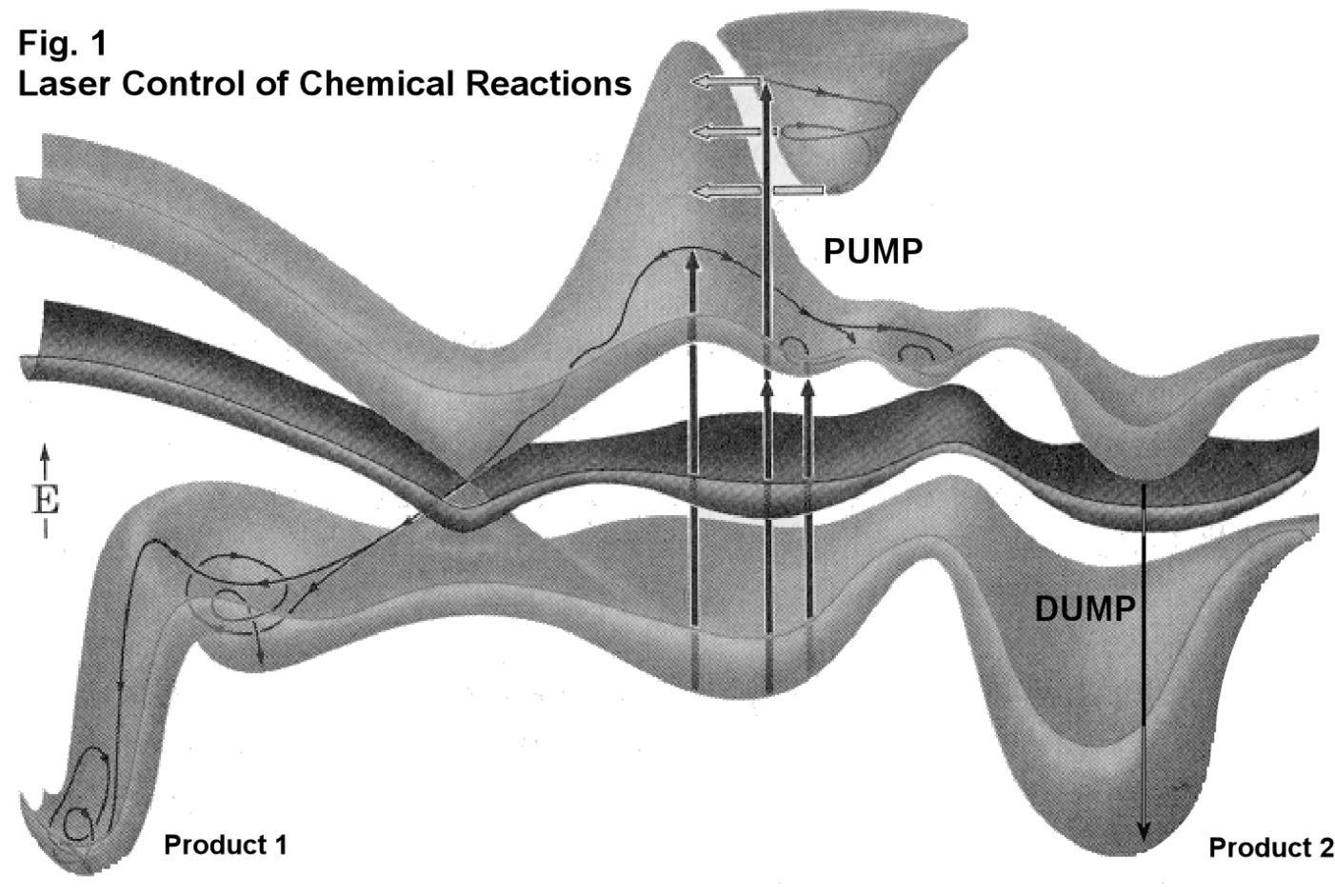
$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} |\Psi_g(t)\rangle \\ |\Psi_e(t)\rangle \end{pmatrix} = \begin{pmatrix} \hat{H}_{gg}(t) & \hat{H}_{ge}(t) \\ \hat{H}_{eg}(t) & \hat{H}_{ee}(t) \end{pmatrix} \begin{pmatrix} |\Psi_g(t)\rangle \\ |\Psi_e(t)\rangle \end{pmatrix}$$

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



KONTROLA HEMIJSKE REAKCIJE

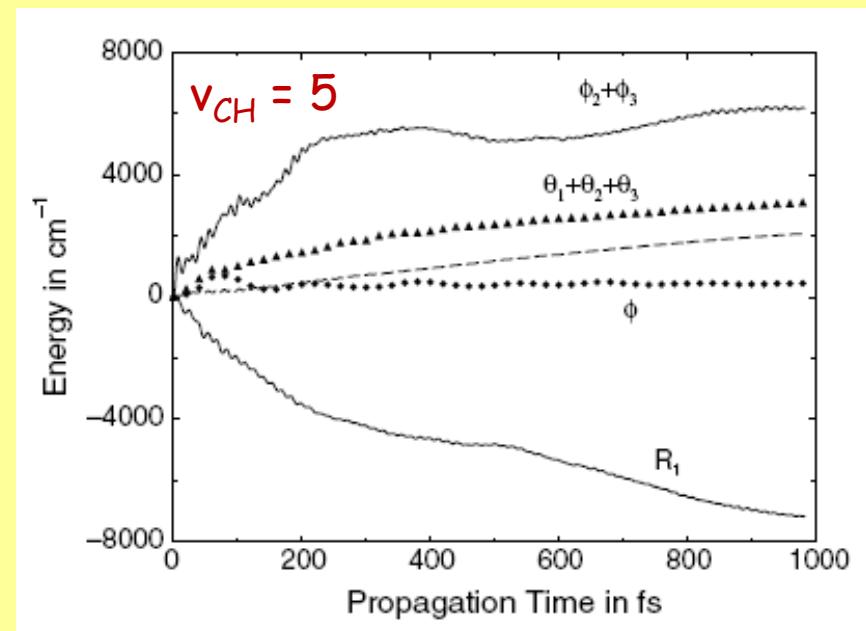
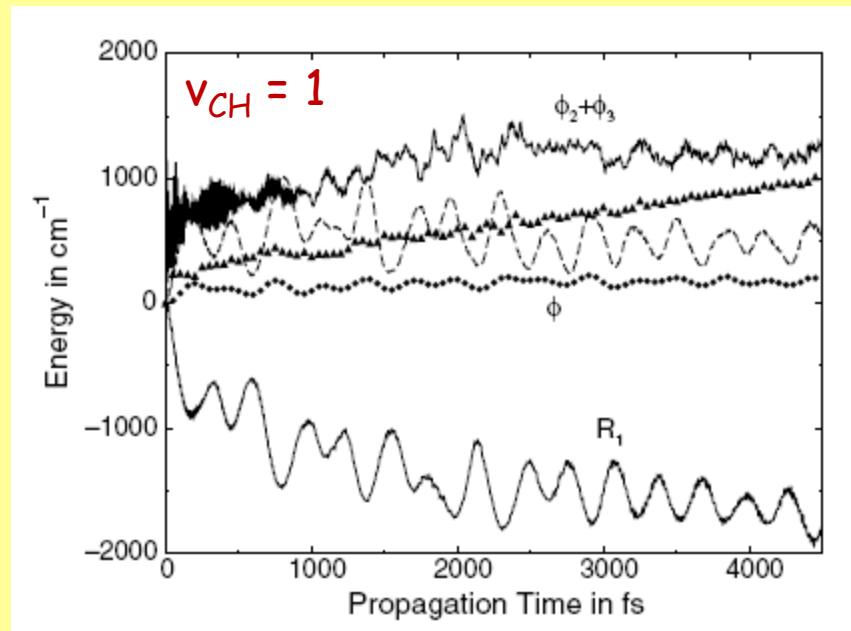
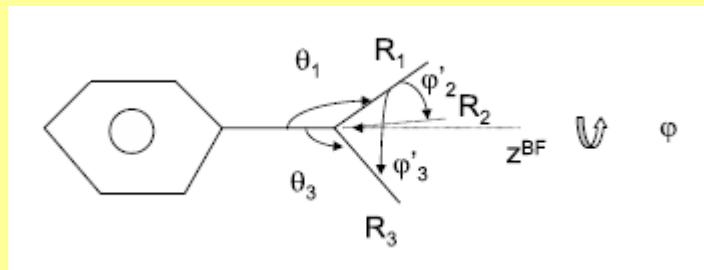
Fig. 1
Laser Control of Chemical Reactions



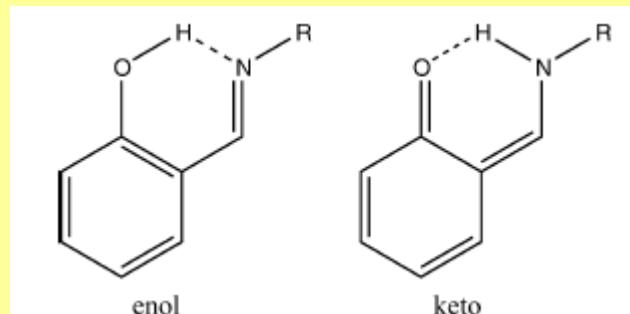
J. Michl and V. Bonačić-Koutecky, Electronic aspects of organic Photochemistry,
John Wiley & Sons: New York, 1990

INTRAMOLEKULSKA PRERASPODELA VIBRACIONE ENERGIJE

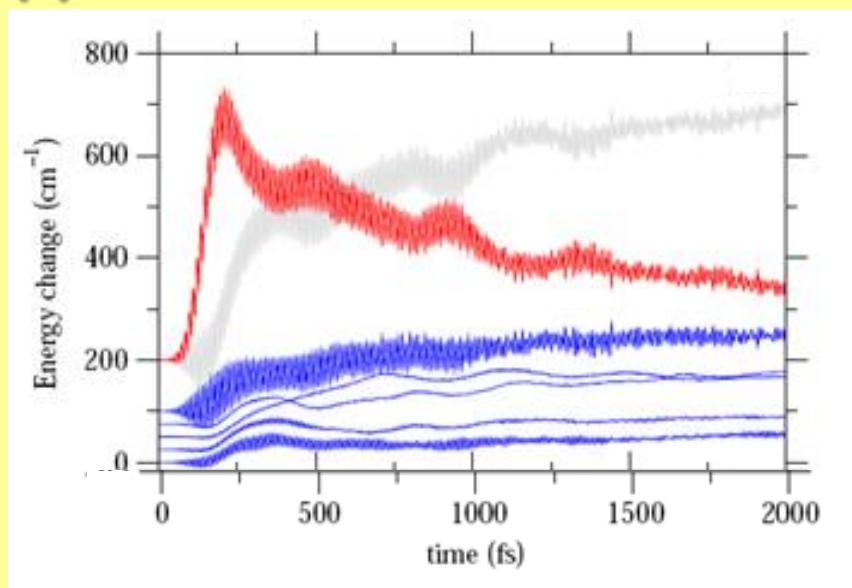
IVR - intramolecular vibrational energy redistribution



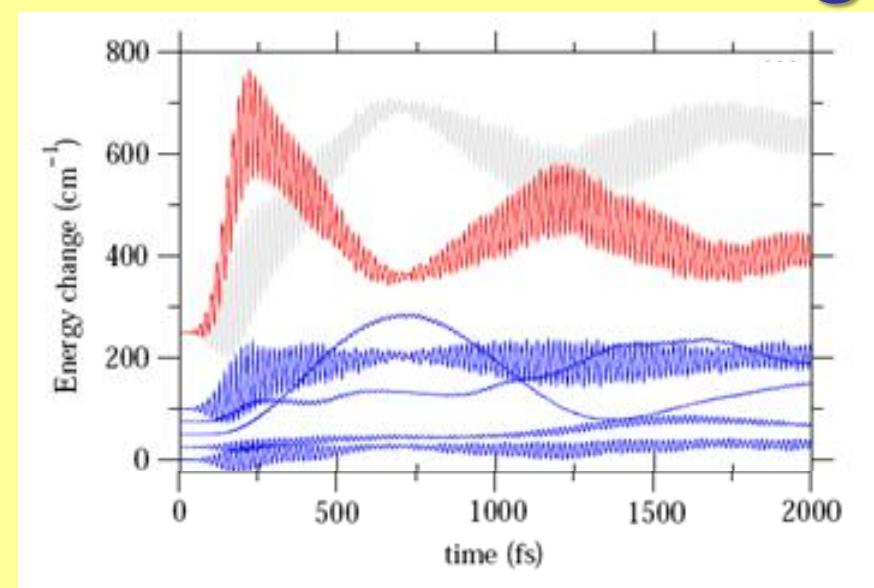
KONTROLA HEMIJSKE REAKCIJE I INTRAMOLEKULSKA PRERASPODELA VIBRACIONE ENERGIJE



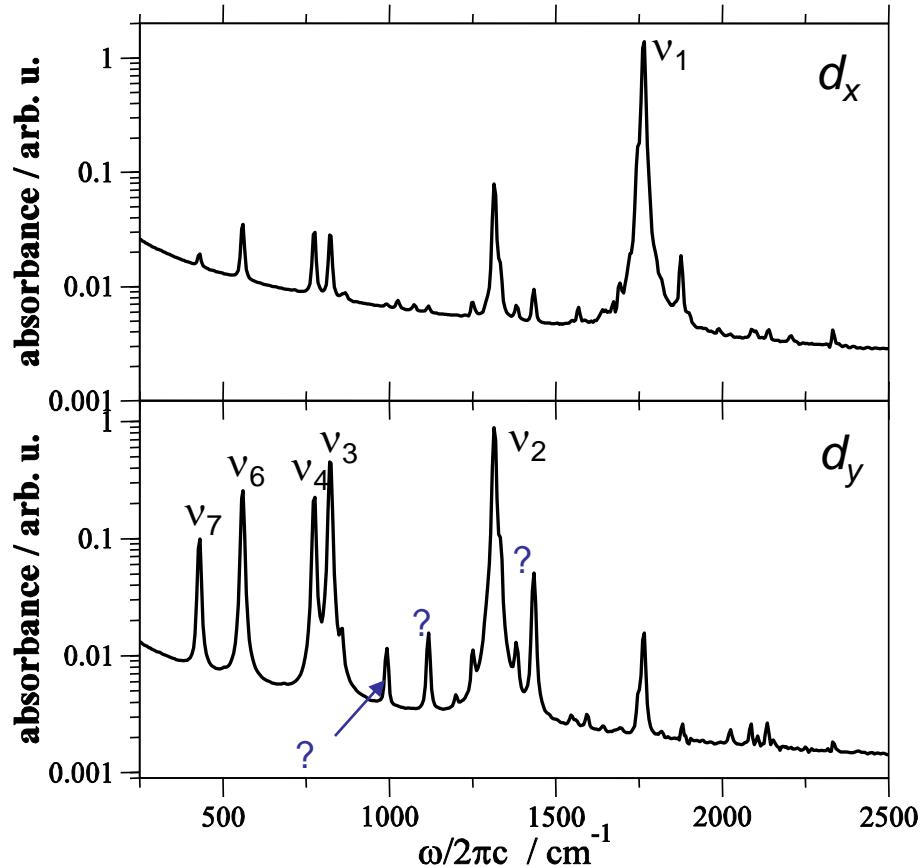
H



D



IC SPEKTRI I ASIGNACIJA TRAKA



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

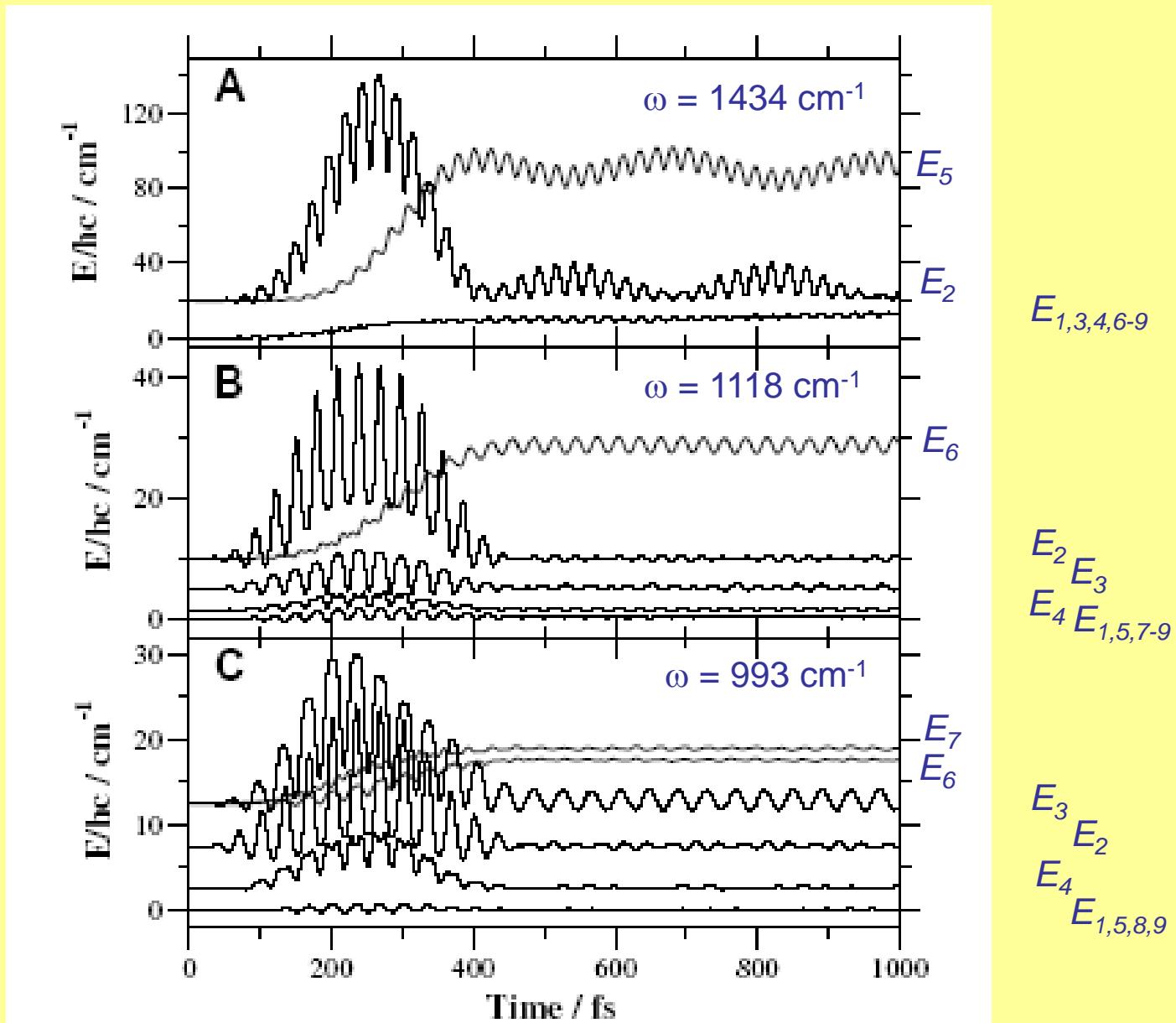
^a Orphal et al. J. Phys. Chem. A 101 (1997) 1062

^b Miller et al. Spec. Acta 23A (1967) 223

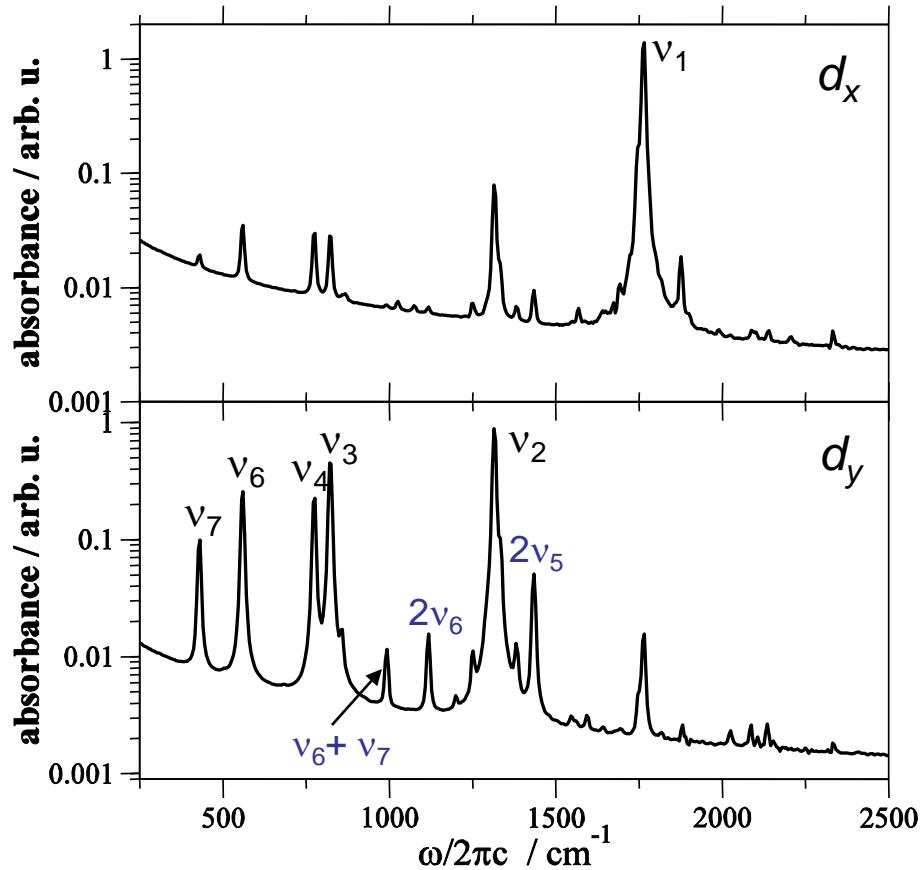
stepen slobode	frekvencija / cm ⁻¹		
	harm.	anh.	eksp. ^a
ν_1	1800	1766	1737
ν_2	1342	1314	1293
ν_3	828	820	809
ν_4	786	777	780
ν_5	731	719	711
ν_6	561	561	563
ν_7	436	431	434
ν_8	250	254	273
ν_9	135	158	122

prelaz	frekvencija / cm ⁻¹	
	izr.	eksp. ^b
?	1434	1424
?	1118	1119
?	993	988

IC SPEKTRI I ASIGNACIJA TRAKA



IC SPEKTRI I ASIGNACIJA TRAKA



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

^a Orphal et al. J. Phys. Chem. A 101 (1997) 1062

^b Miller et al. Spec. Acta 23A (1967) 223

stepon slobode	frekvencija / cm^{-1}		
	harm.	anh.	eksp. ^a
v_1	1800	1766	1737
v_2	1342	1314	1293
v_3	828	820	809
v_4	786	777	780
v_5	731	719	711
v_6	561	561	563
v_7	436	431	434
v_8	250	254	273
v_9	135	158	122

prelaz	frekvencija / cm^{-1}	
	izr.	eksp. ^b
$2v_5$	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
- ...