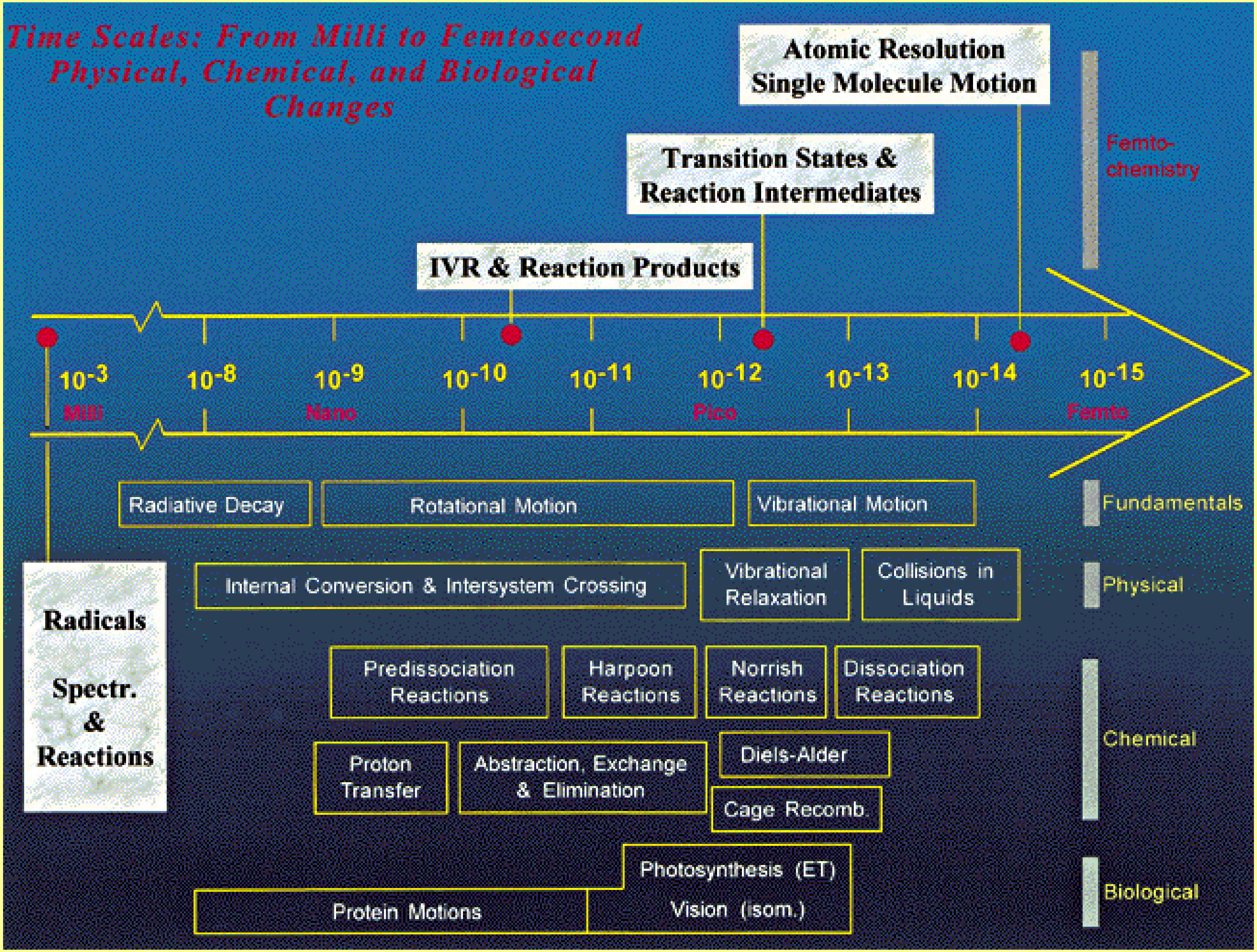
NOVE FIZIČKOHEMIJSKE METODE

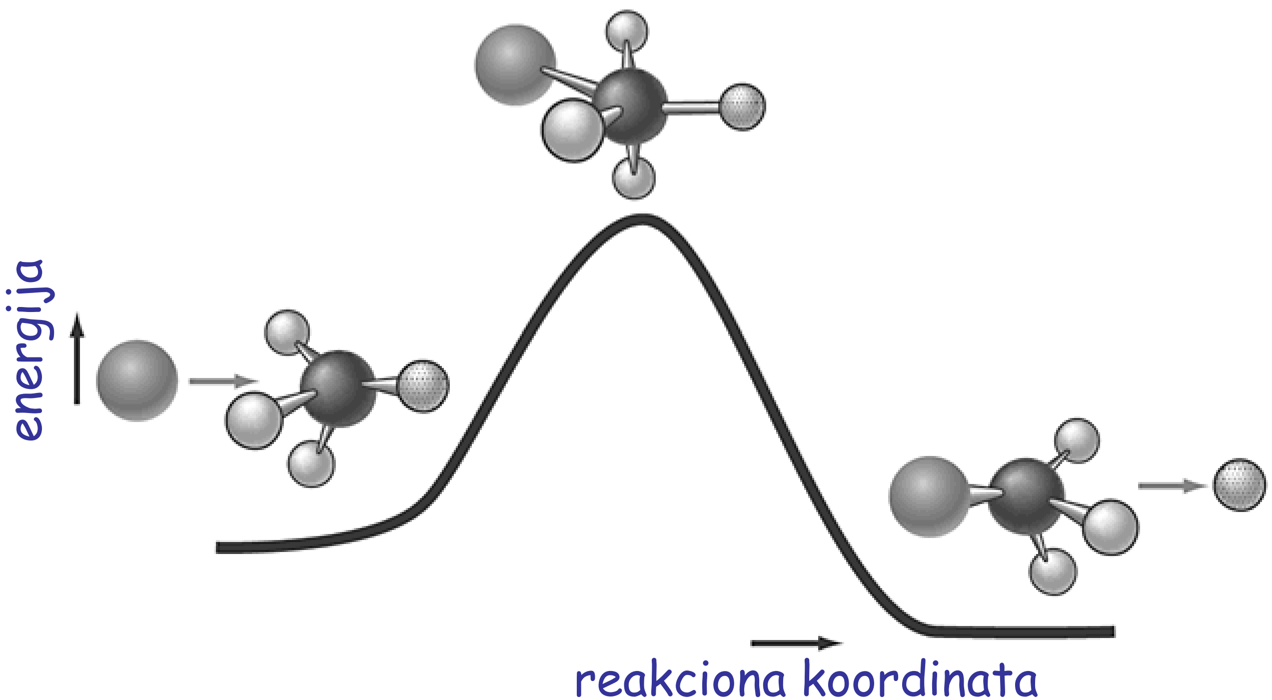
FEMTOHEMIJA

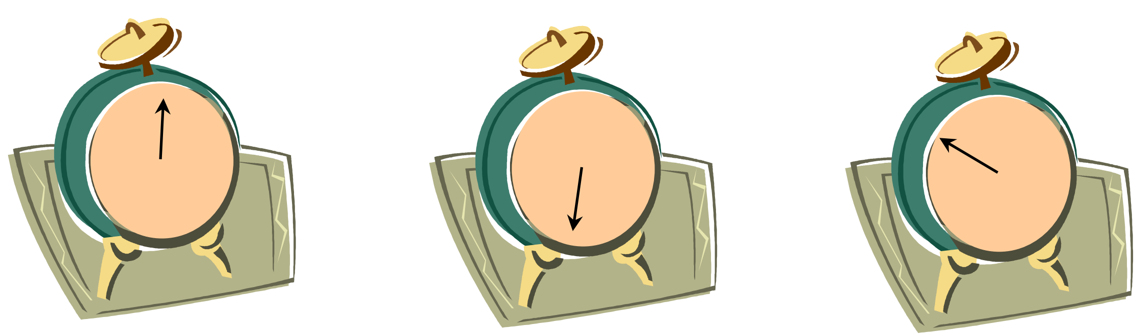
MILENA PETKOVIĆ



Time Scales: From Milli to Femtosecond
Physical, Chemical, and Biological Changes
Atomic Resolution Single Molecule Motion
Transition States & Reaction Intermediates
IVR & Reaction Products
Femto-chemistry
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
Proton Transfer
Abstraction, Exchange & Elimination
Diels-Alder
Cage Recomb.
Chemical
Photosynthesis (ET)
Vision (isom.)
Protein Motions
Biological

PRAĆENJE TOKA HEMIJSKE REAKCIJE





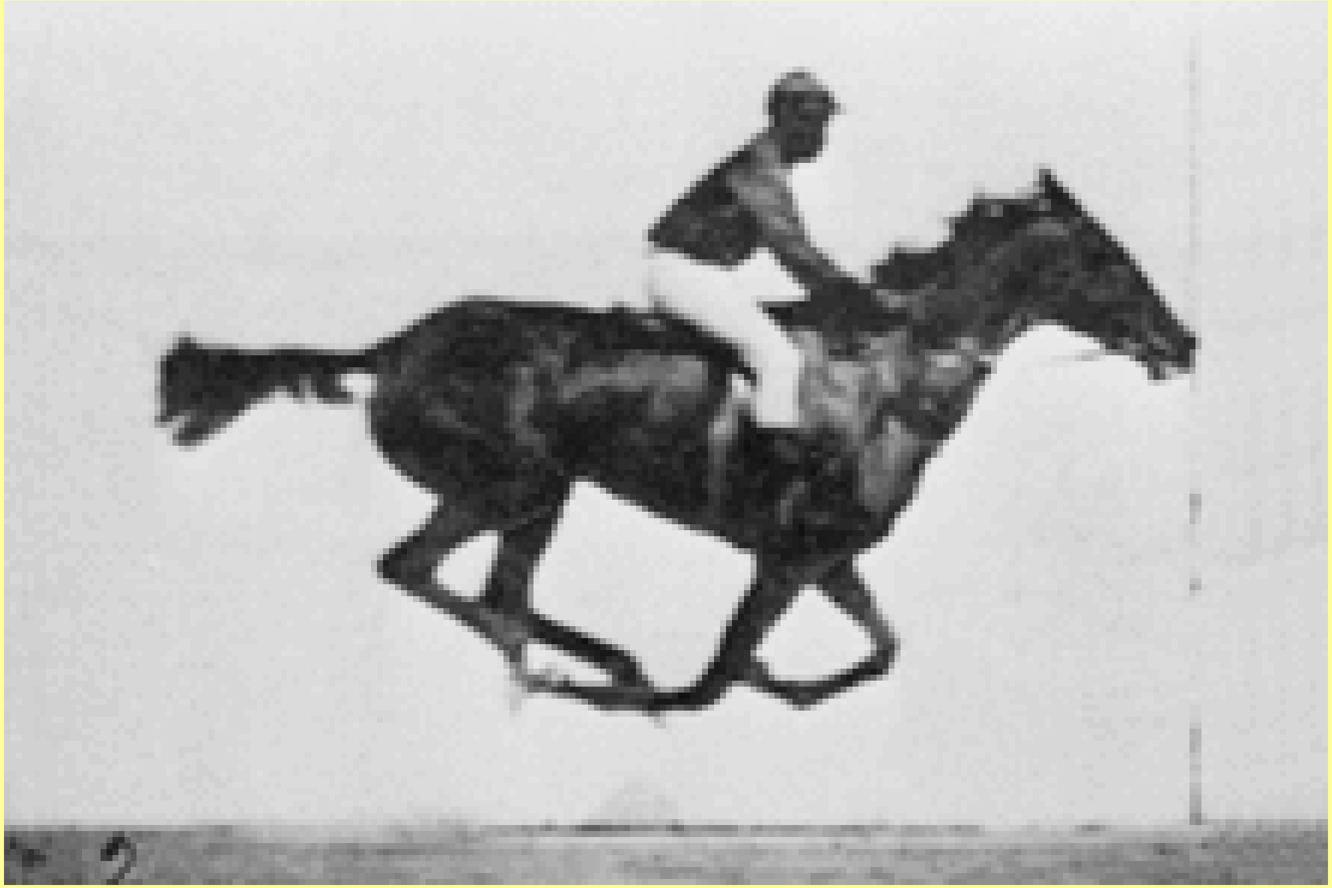
"Rođenje" ultrabrze tehnologije

Konj u pokretu (The horse in motion)

Fotograf: Edvard Majbridž (Eadweard Muybridge)

Palo Alto, Kalifornija 1872 → 1878.

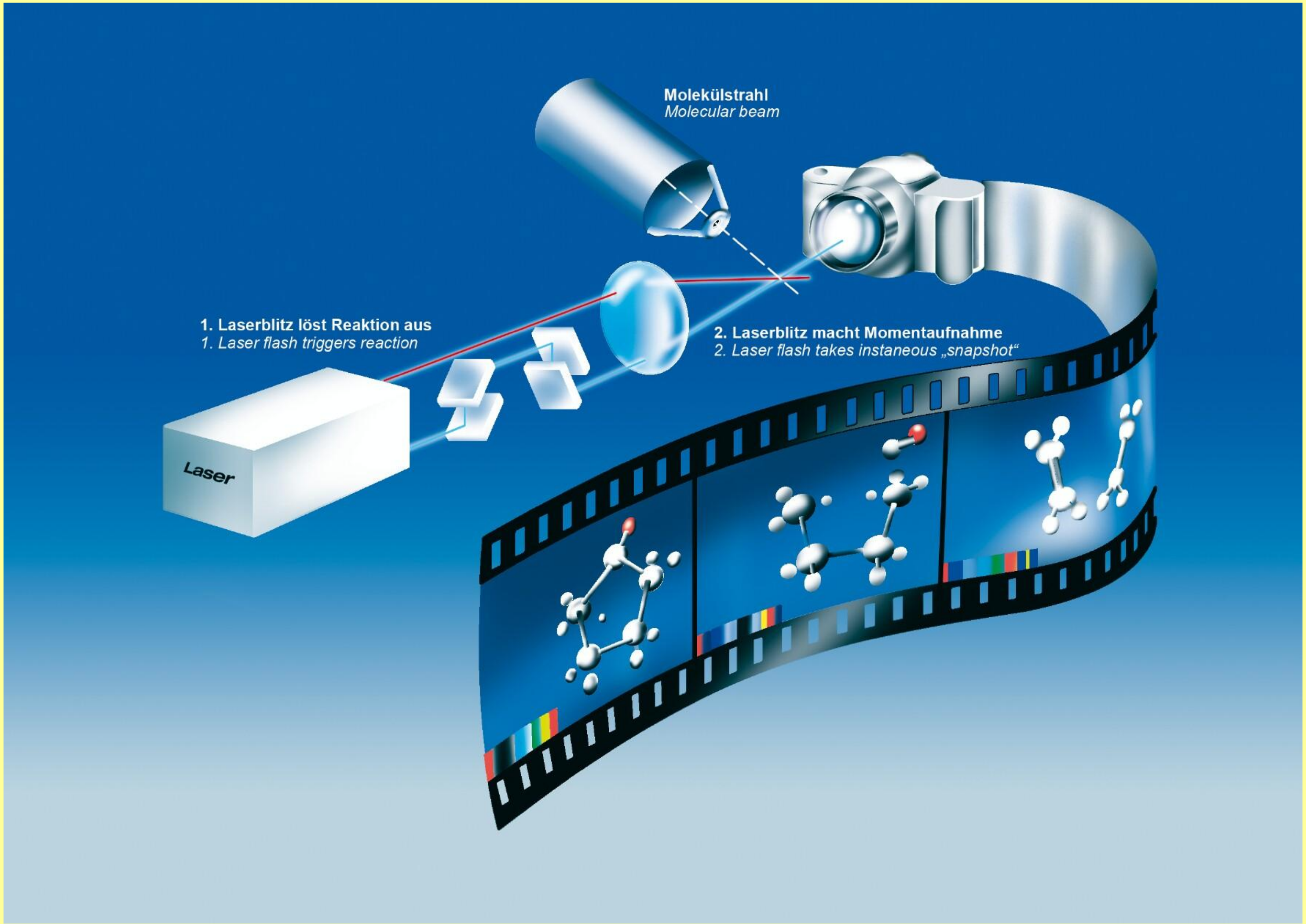
“Rođenje” ultrabrze tehnologije



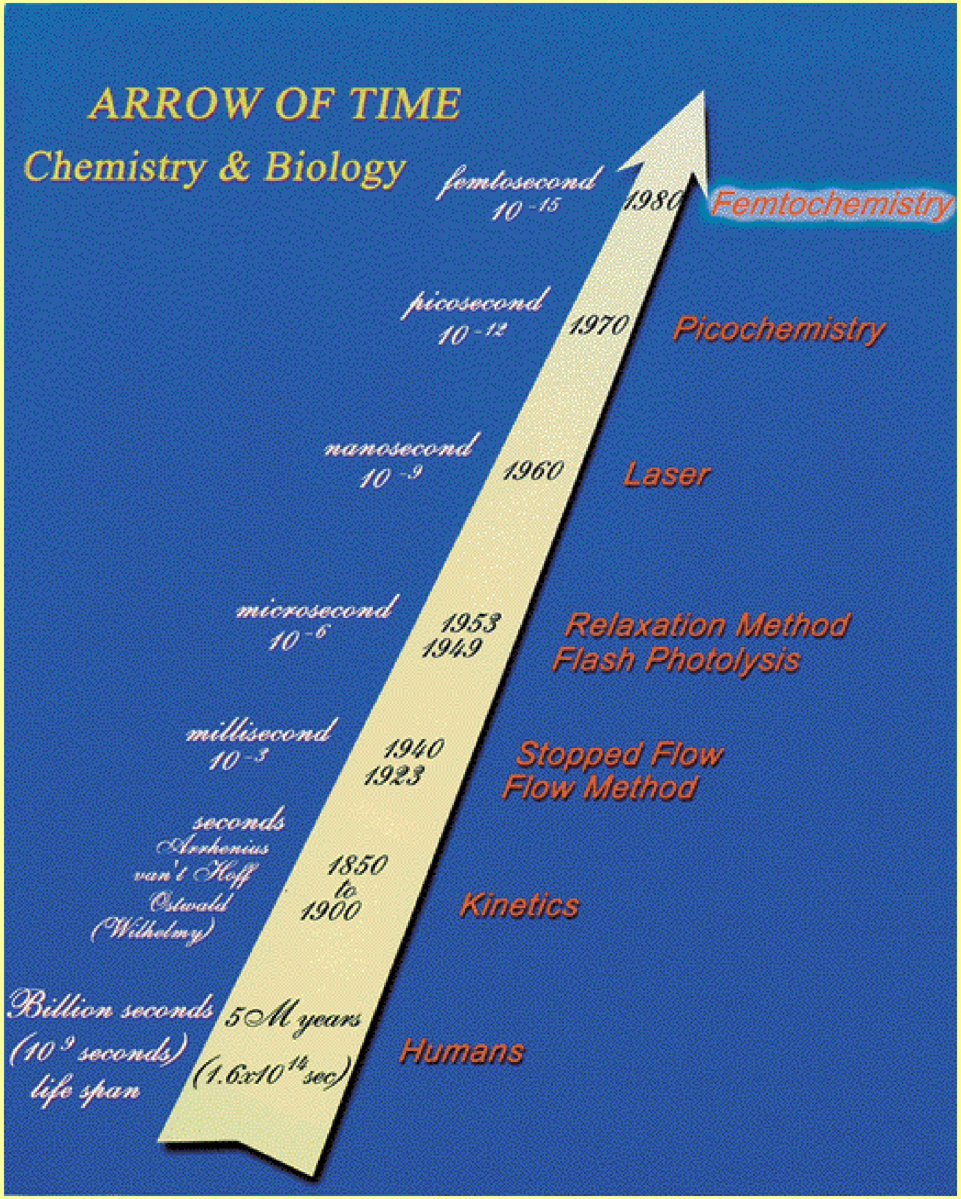
Seli Gardner u galopu - animirano 2006.

na osnovu Majbridžovih fotografija

Cilj:
"film" koji prikazuje položaj jezgara u toku hemijske reakcije



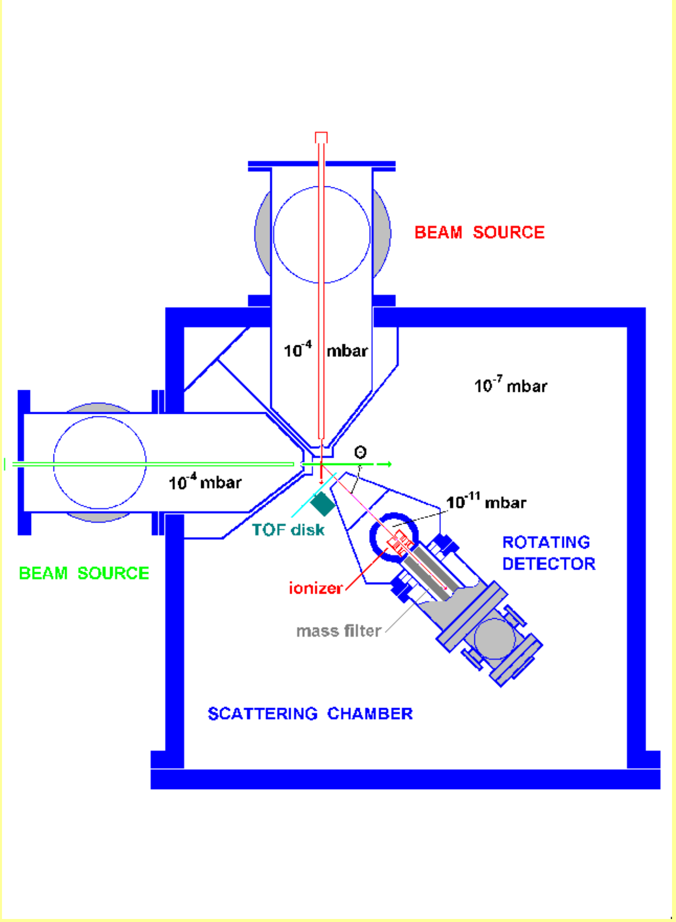
http://www.xfel.eu/media/



Ahmed Zewail – Nobel lecture

TEHNOLOGIJA MOLEKULSKIH SNOPOVA

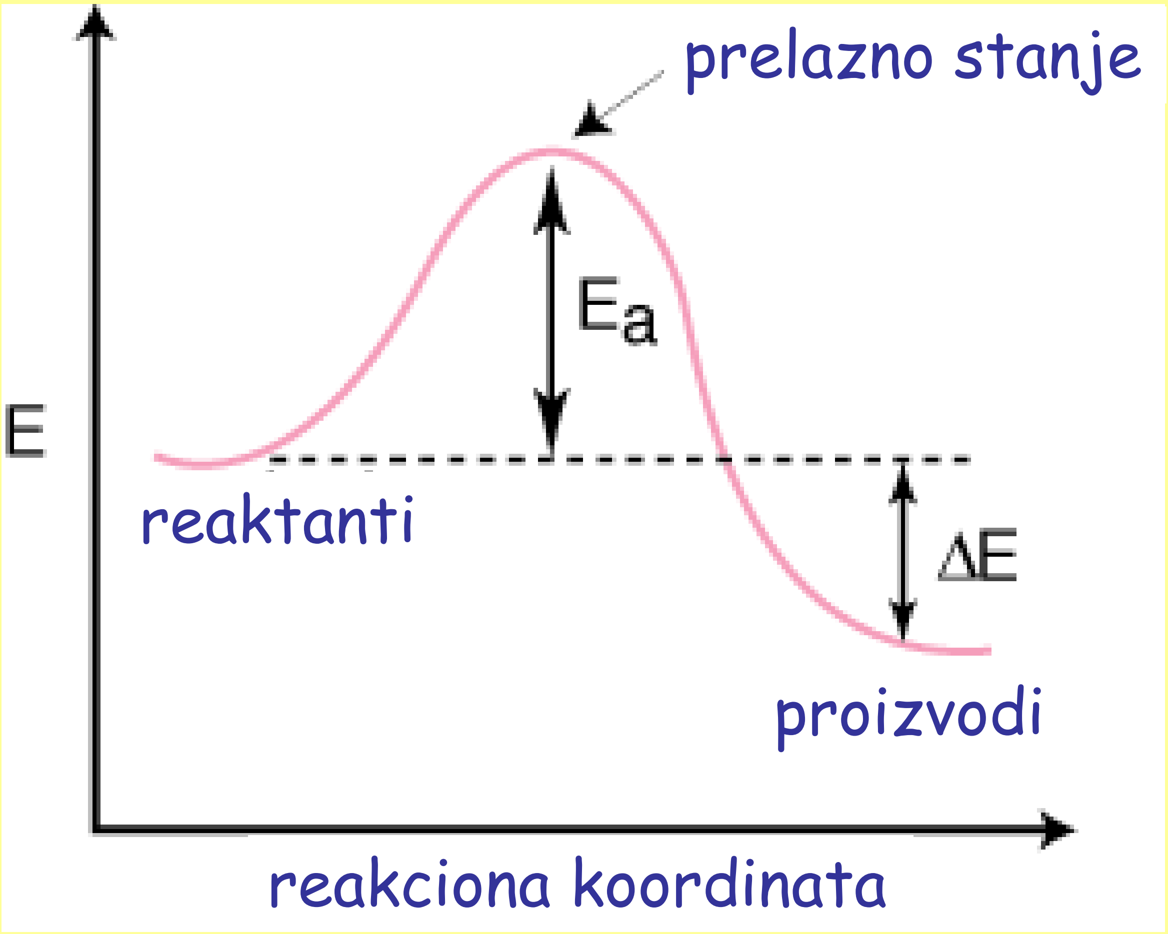
1986 – Nobelova nagrada za hemiju
Dudley Robert Herschbach, Yan T. Lee & John C. Polanyi



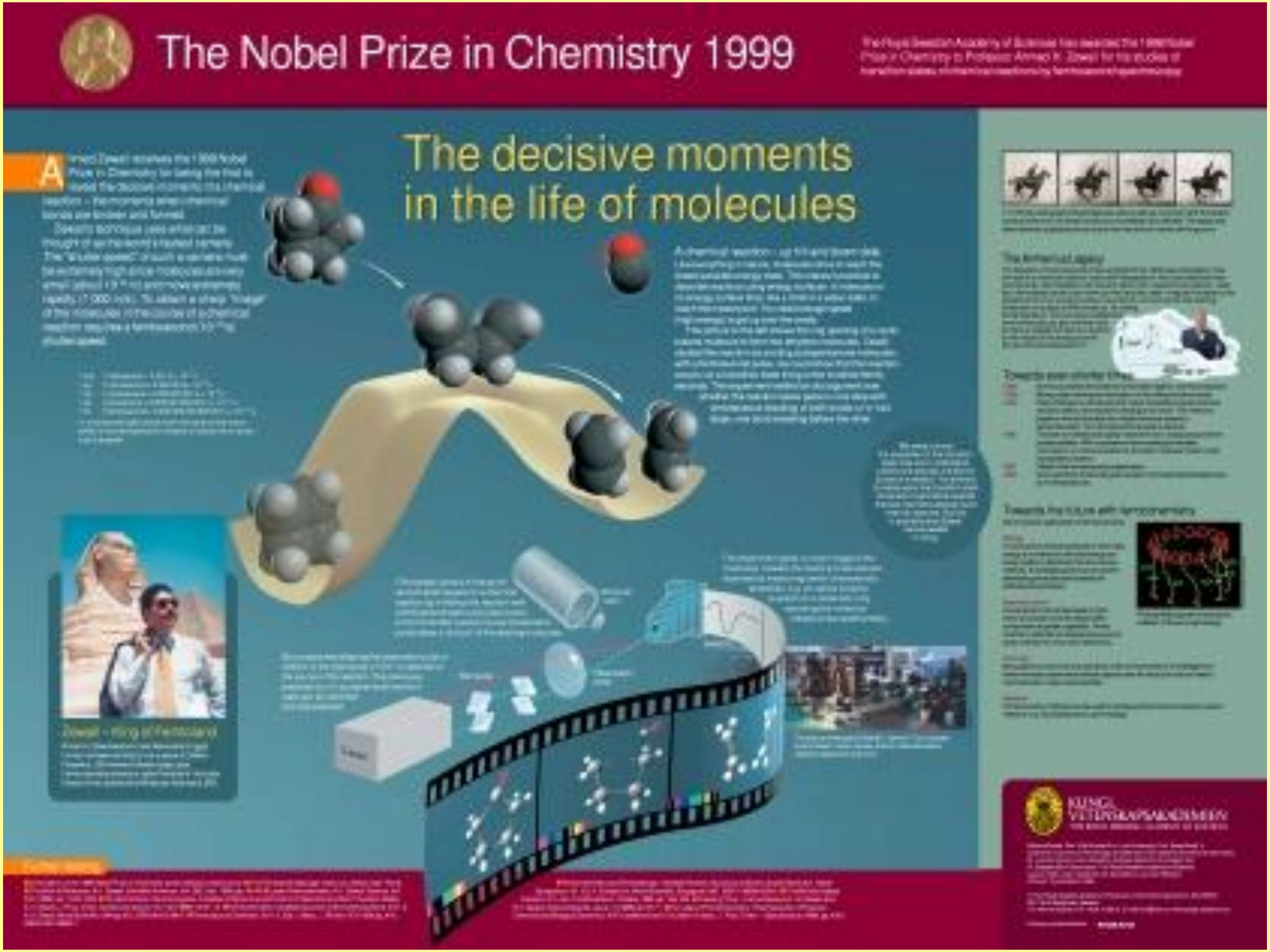
$A + B \rightarrow C$

Hamlet!

PRELAZNO STANJE



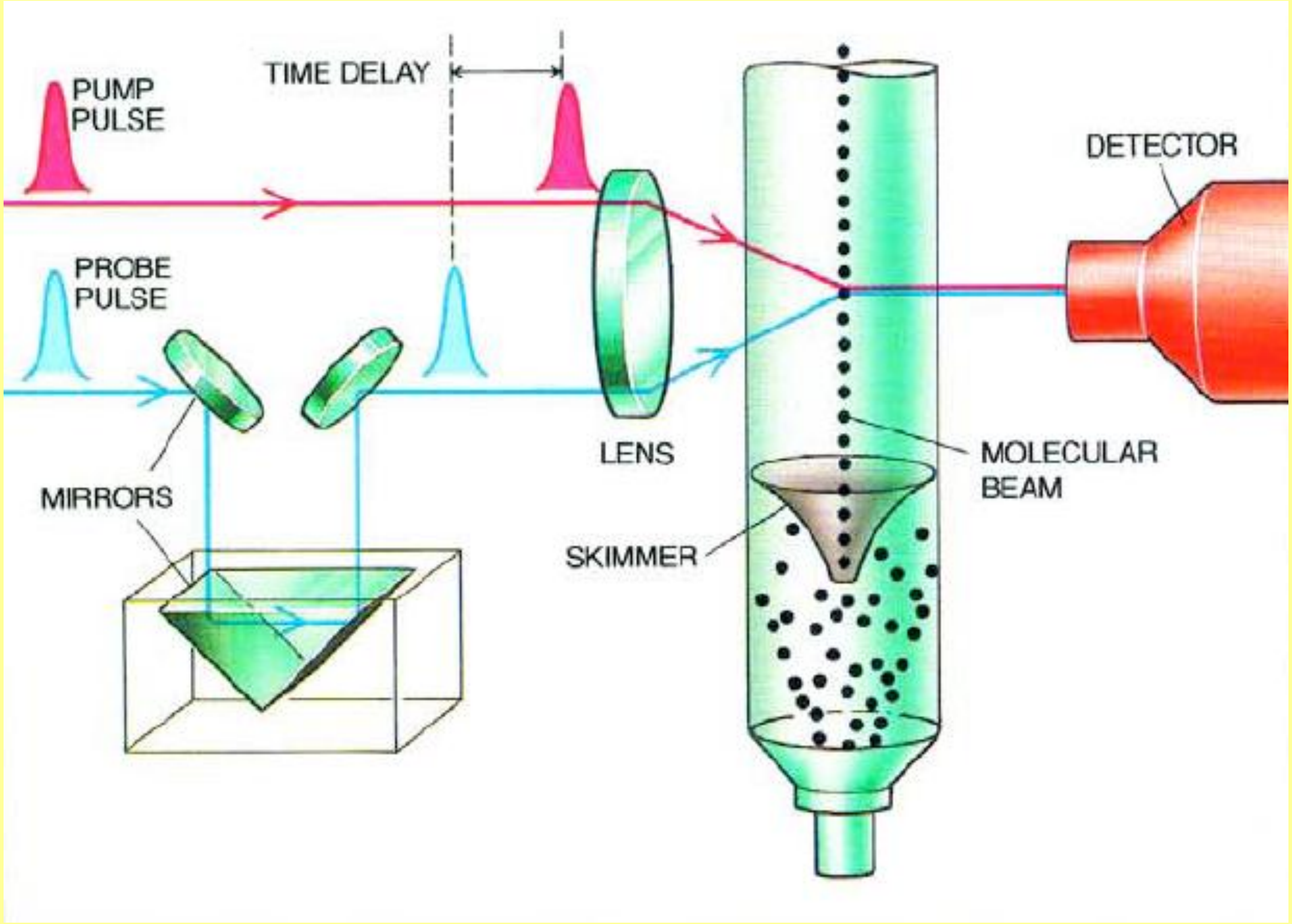
vreme života ≈ 10 - 100 fs


The Nobel Prize in Chemistry 1999
The decisive moments
in the life of molecules

"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



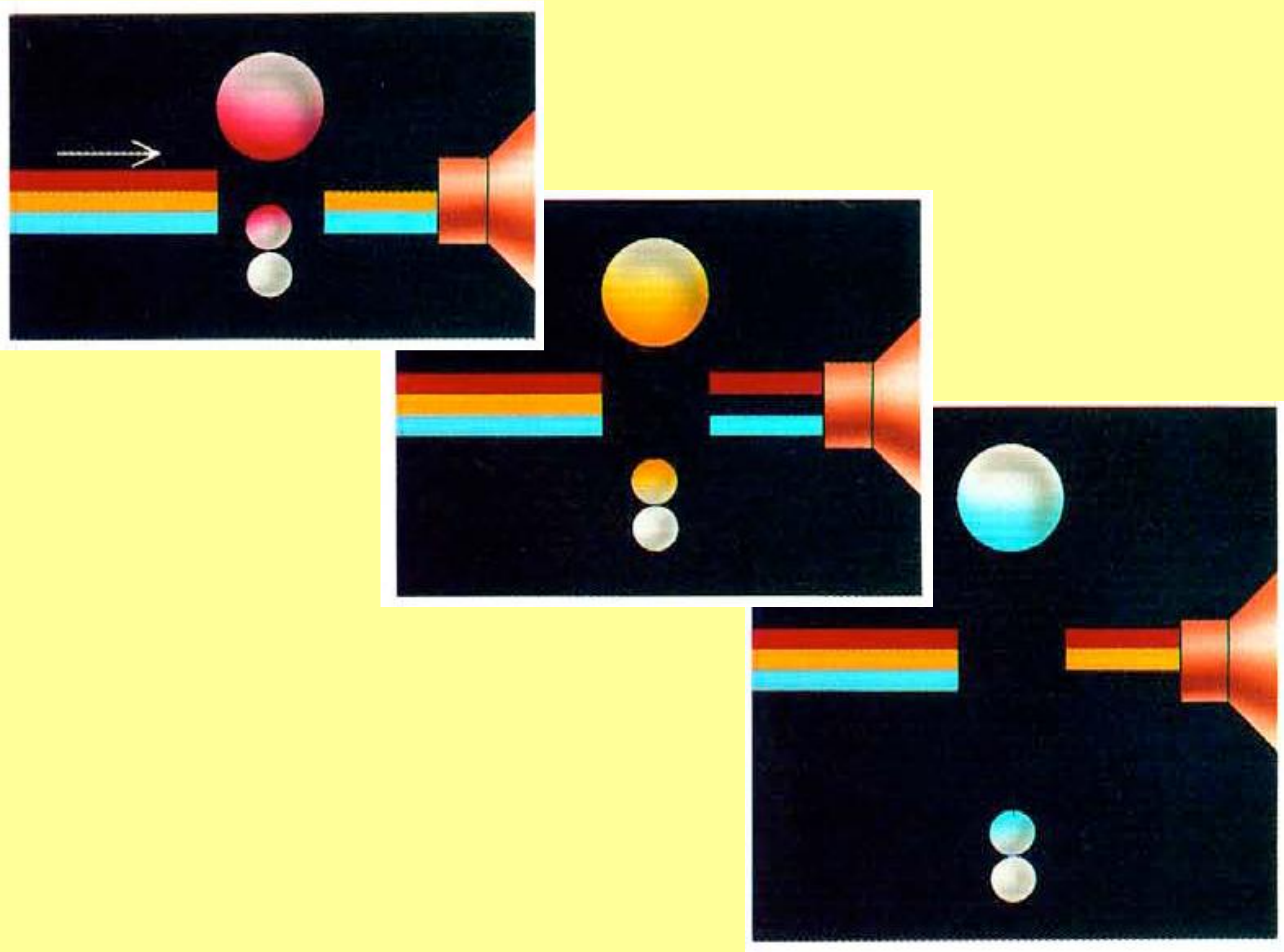
KAŠNJENJE PROBA PULSA

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

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

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

Promena u spektru - “otisak prstiju” atoma u pokretu



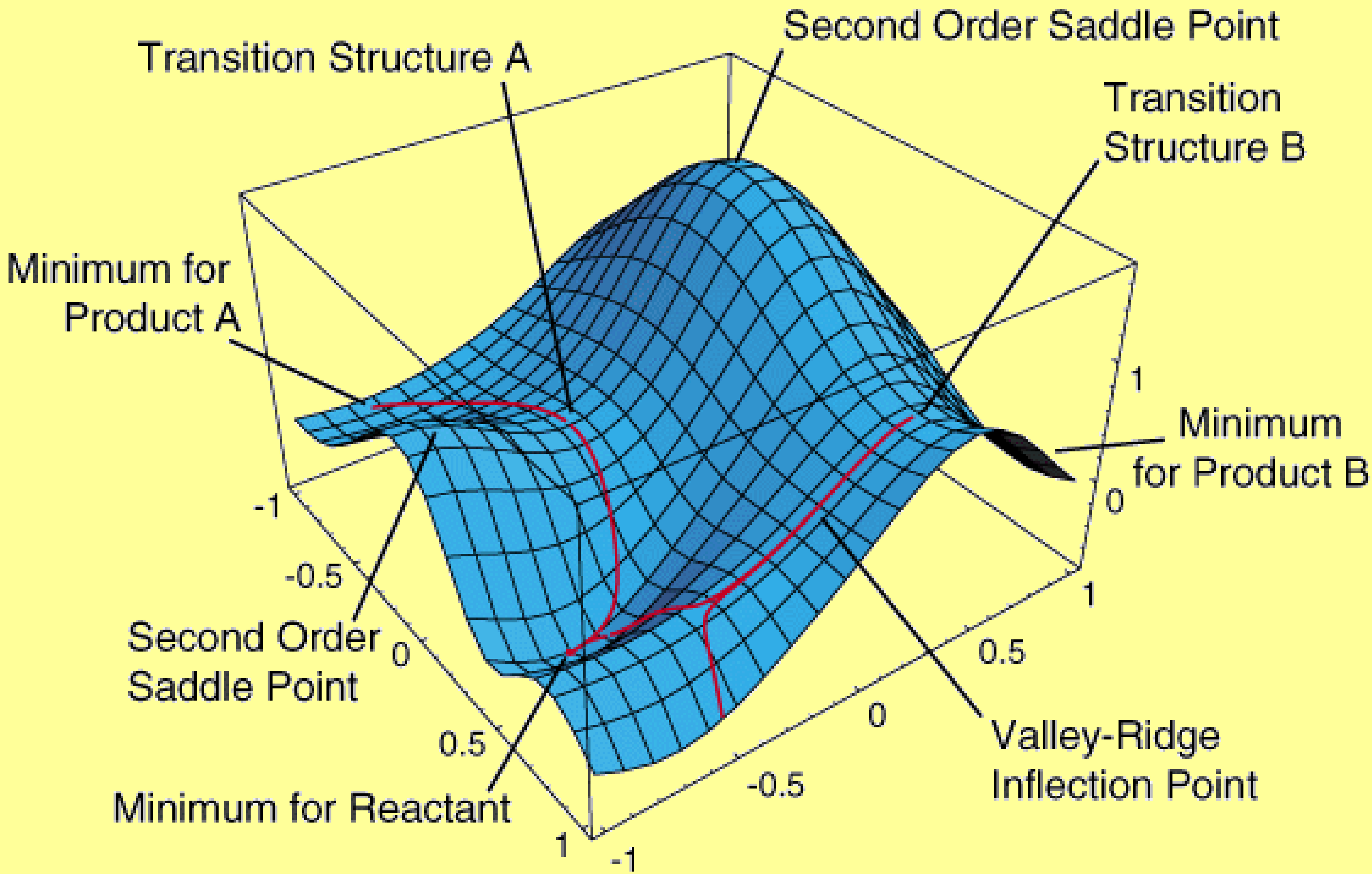
Elementarni fenomeni:
- prelazna stanja
- preraspodela energije
- brzine hemijskih reakcija

Stanja molekula:
- osnovno i pobuđena stanja
- neutralne čestice i joni

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

Dimenzije molekula:
- dvoatomski molekuli
- ...
- DNK i proteini

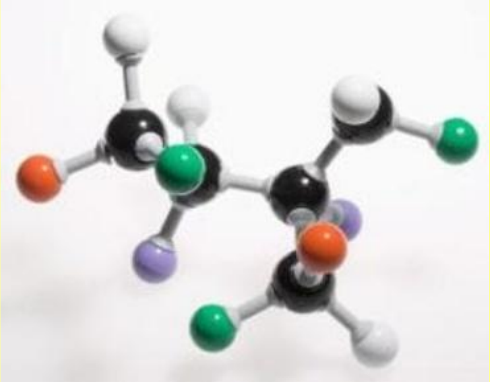
TEORIJSKI PRISTUP



TEORIJSKI PRISTUP

vremenski zavisna Šredingerova jednačina

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



$$\rightarrow \quad \Psi(t)$$

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

PERTURBACIONI RAČUN

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

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

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

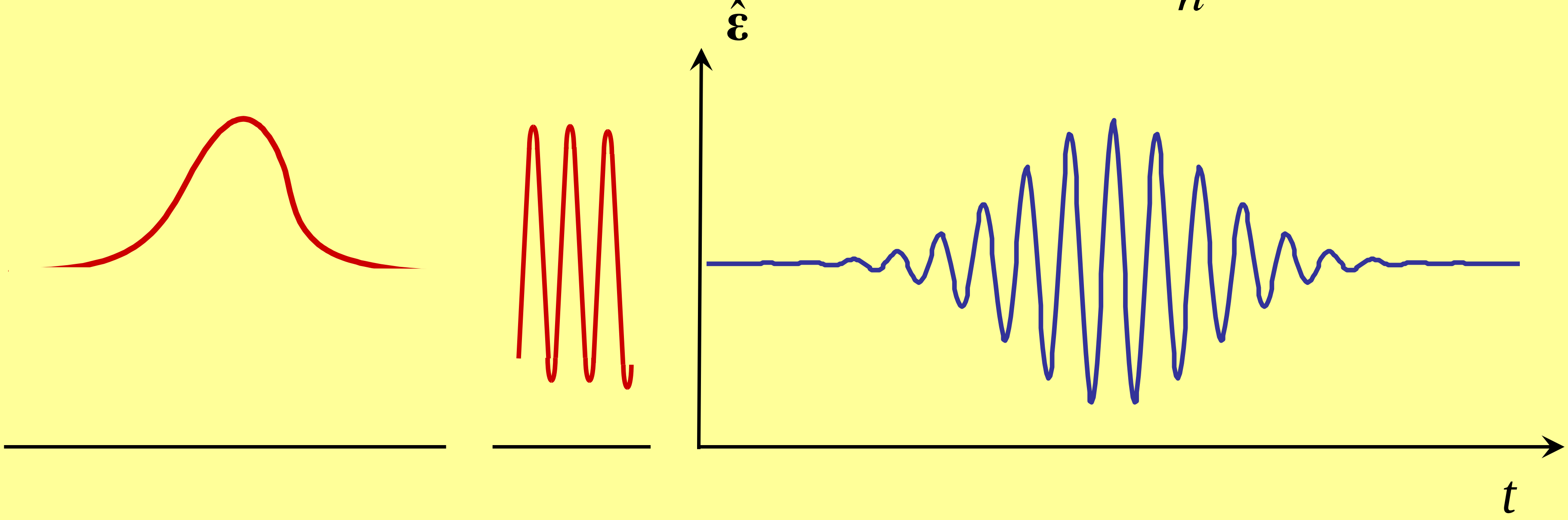
perturbacija
(laserski puls)

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

ULTRAKRATKI LASERSKI PULS

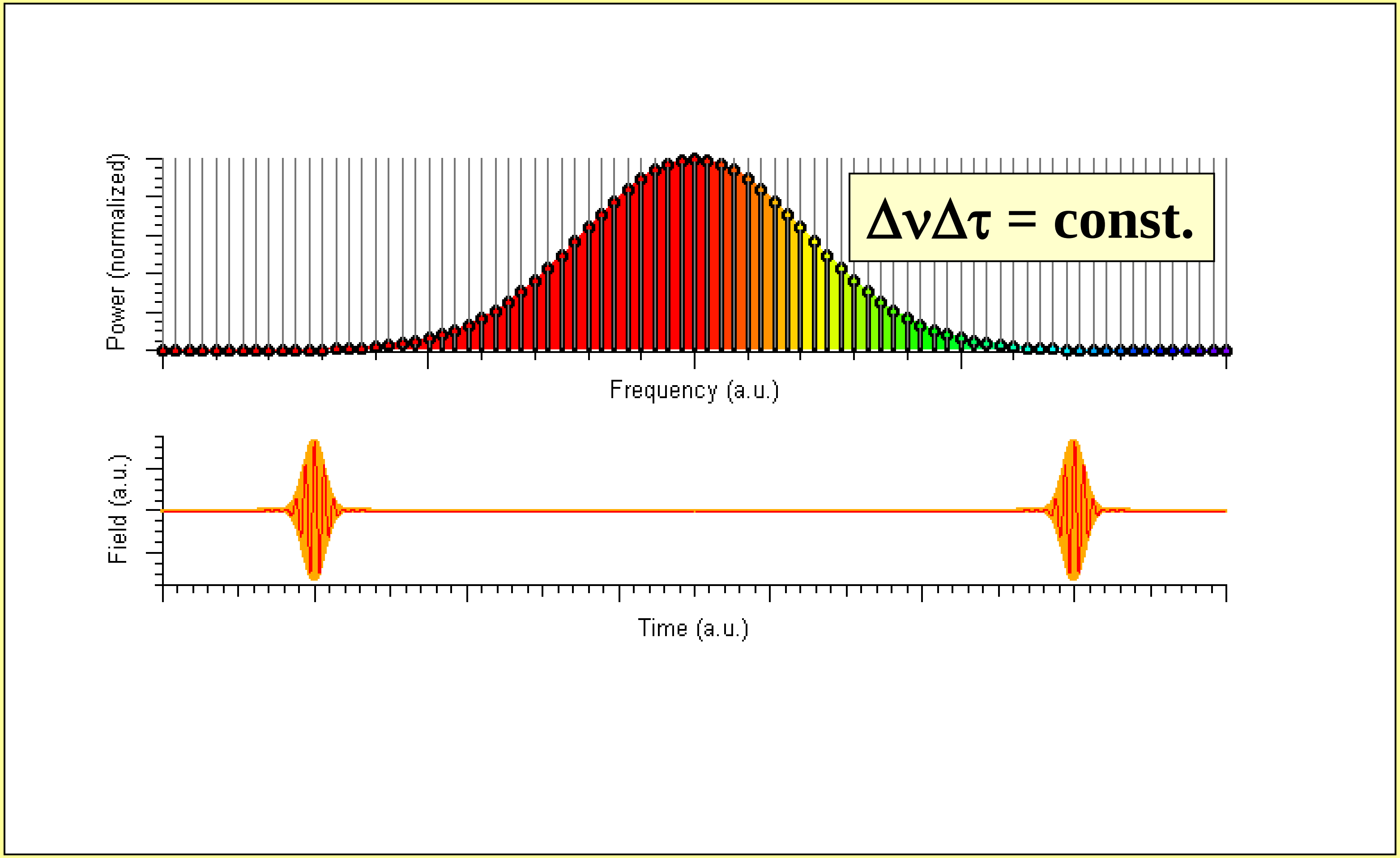
$$\hat{\boldsymbol{\varepsilon}}(t) = \hat{\boldsymbol{\varepsilon}}_{\mathbf{0}} e^{-\frac{t^2}{\alpha T^2}} \cos(\omega t)$$

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



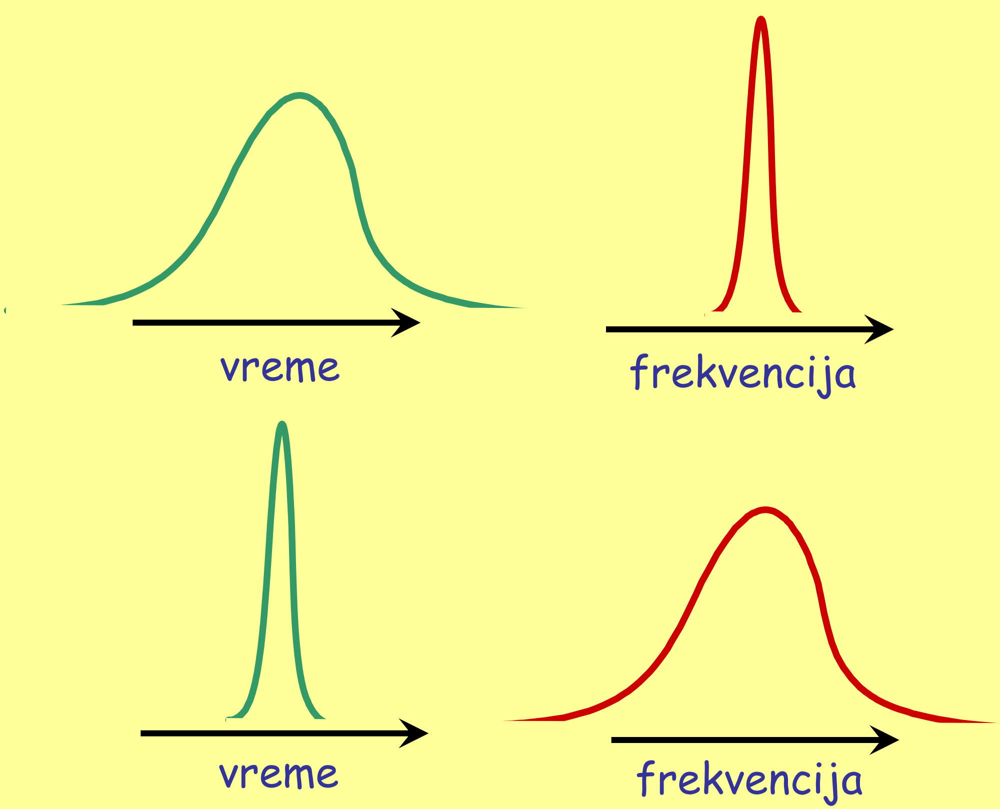
$$\hat{V}(t) = -\hat{\boldsymbol{\mu}} \cdot \hat{\boldsymbol{\varepsilon}}(t)$$

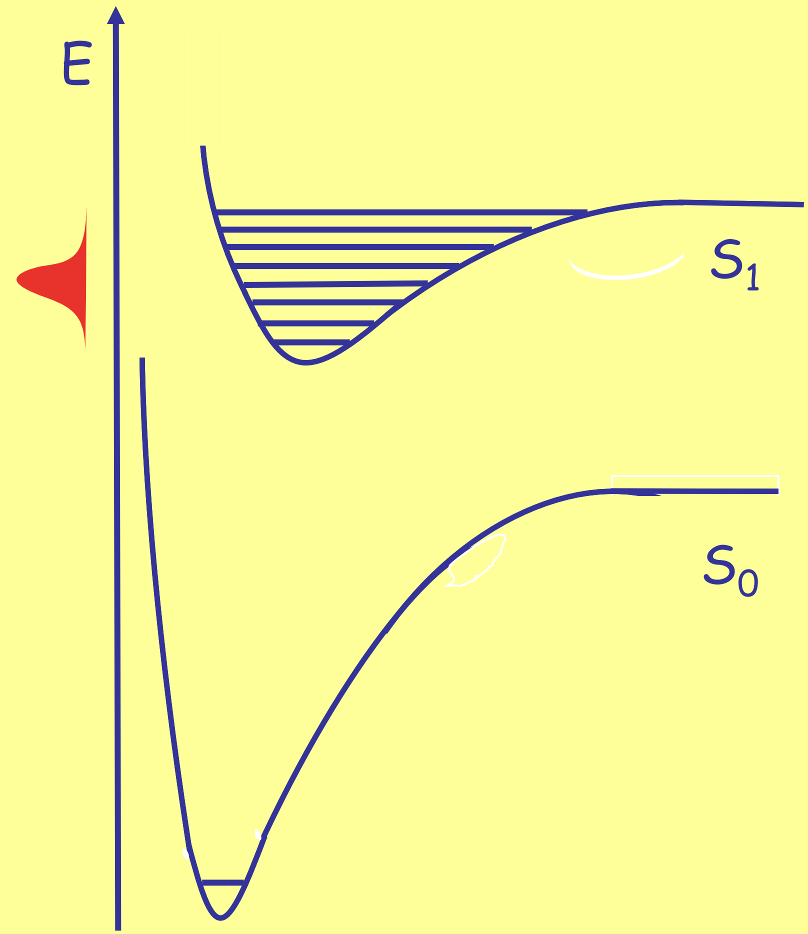
OSNOVNI PRINCIPI ULTRABRZIH LASERA



HAJZENBERGOVA RELACIJA NEODREĐENOSTI

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





TRADICIONALNA I ULTRABRZA SPEKTROSKOPIJA

tradicionalna spektroskopija

$T \to \infty$

$$\boldsymbol{\varepsilon}(t) = \boldsymbol{\varepsilon}_0 \cos(\omega t)$$

monohromatsko zračenje

ultrabrza spektroskopija

$T \to 0$

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

širok opseg frekvencija

ULTRABRZA SPEKTROSKOPIJA (1)

osnovno elektronsko stanje

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

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

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

pobuđeno elektronsko stanje

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

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

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

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

ULTRABRZA SPEKTROSKOPIJA (2)

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

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

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

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

ULTRABRZA SPEKTROSKOPIJA (3)

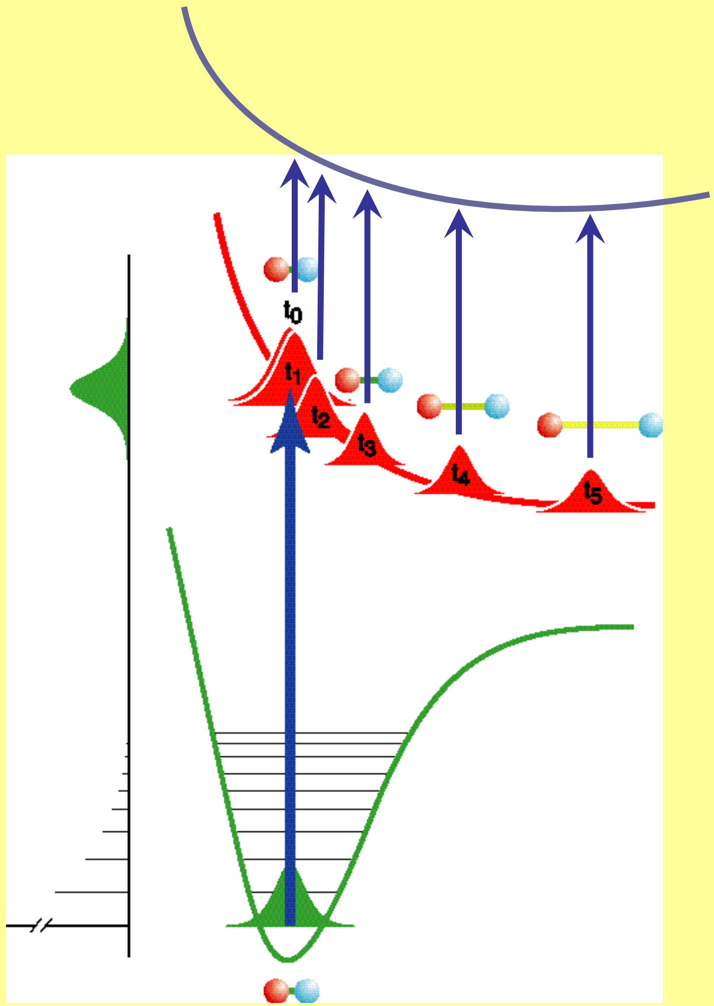
$$\left|\Psi(t)\right\rangle = \sum_n \left\langle \phi_n(0) \middle| \varphi_0(0) \right\rangle \left|\phi_n(0)\right\rangle e^{-\frac{i}{\hbar}E_n t}$$

$$\left\langle x \right\rangle = \left\langle \Psi(t) \middle| x \middle| \Psi(t) \right\rangle$$

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

DINAMIKA!

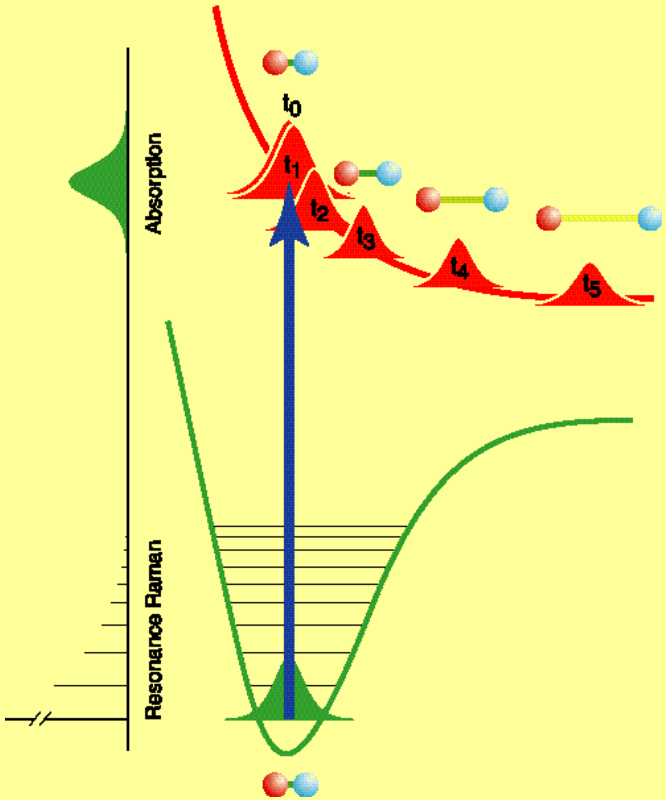
PUMPA-PROBA METOD

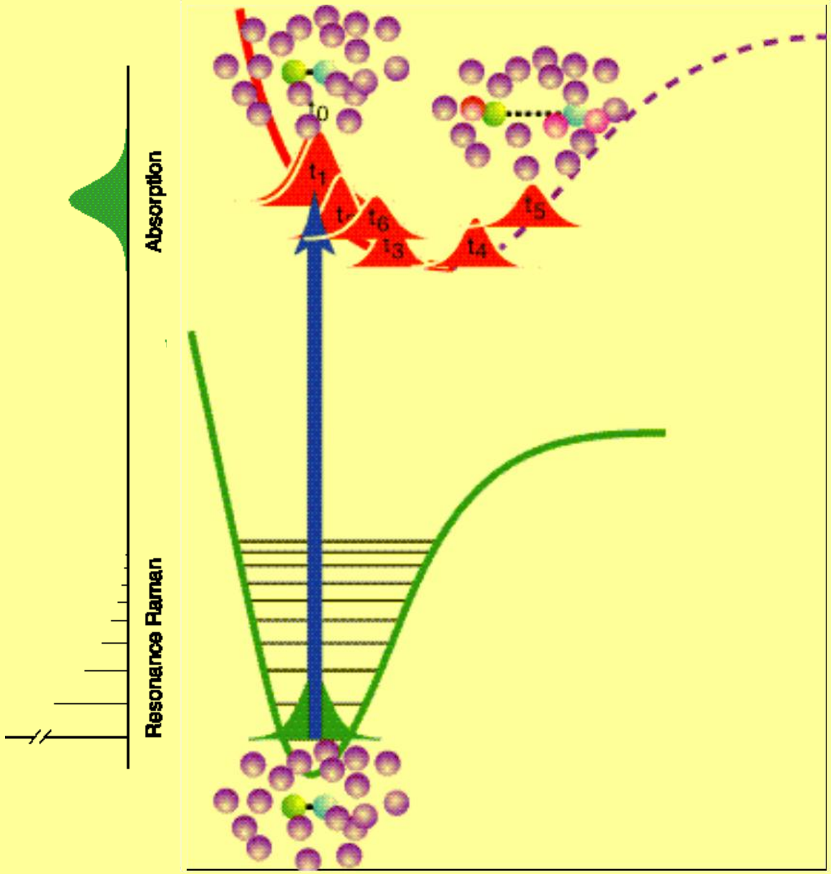


proba

pumpa

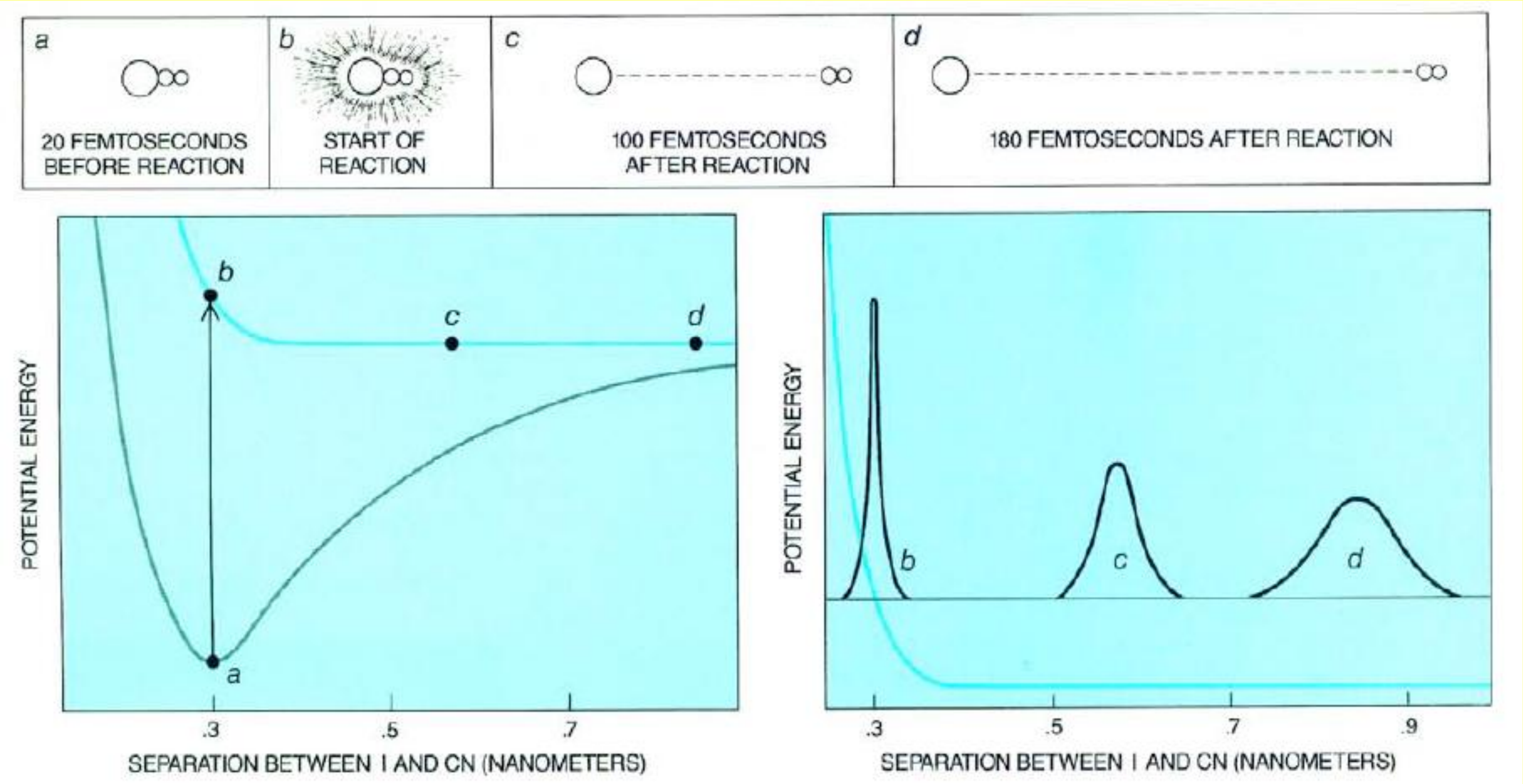
FOTODISOCIJACIJA DVOATOMSKOG MOLEKULA



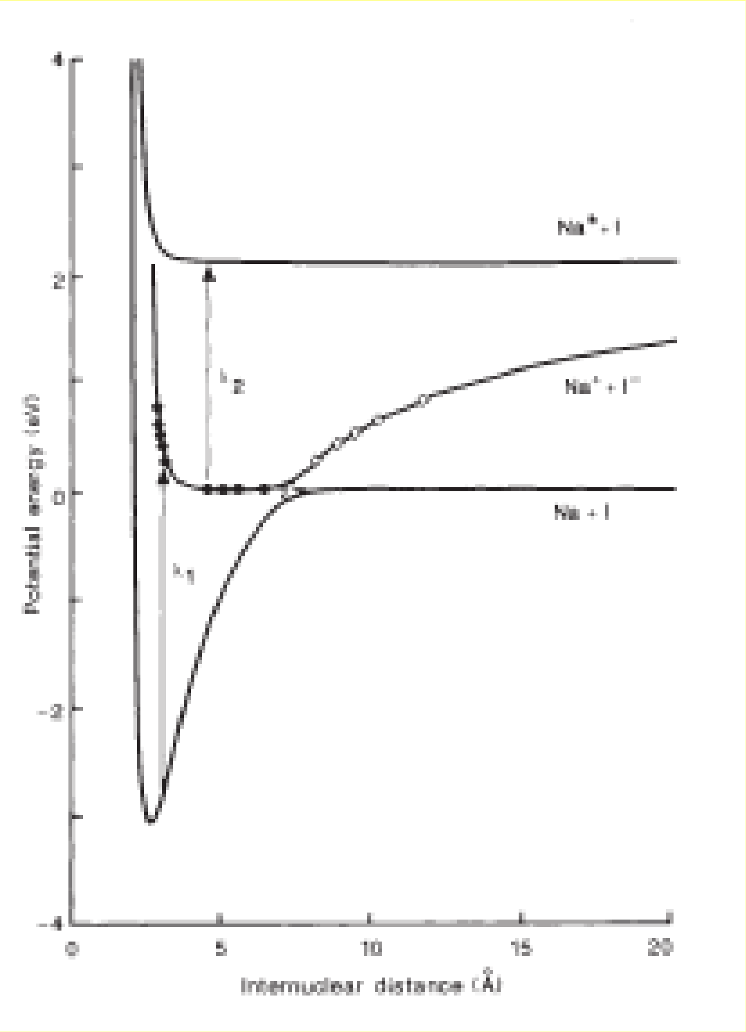


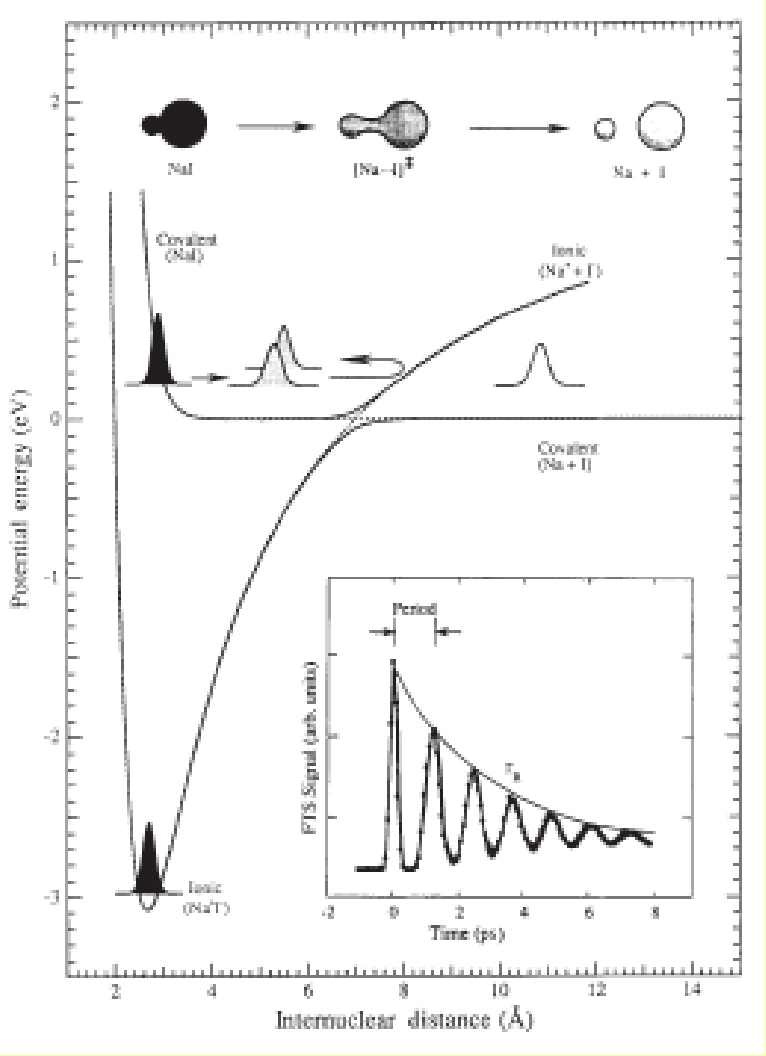
ICN

$$ICN \rightarrow I \cdots CN \rightarrow I + CN$$



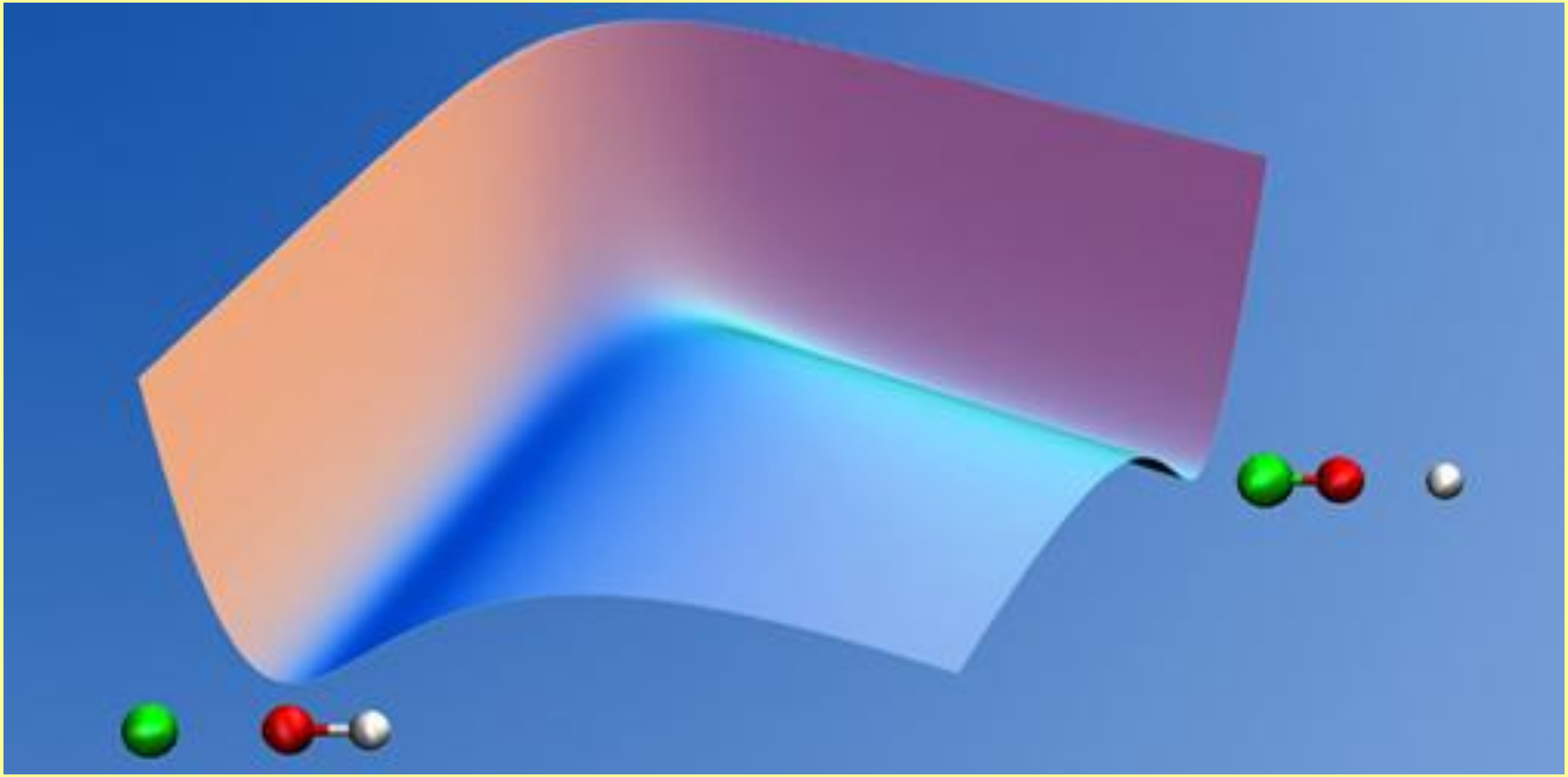
NaI



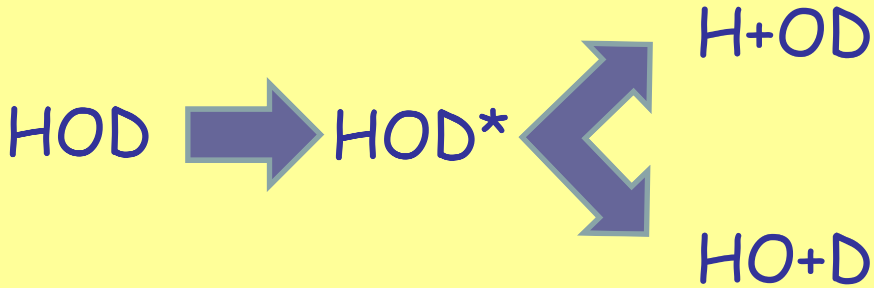


A. Mokhtari, P. Cong, J. L. Herek and A. H. Zewail, Letters to nature, 348 (1990) 225

KONTROLA HEMIJSKE REAKCIJE



http://www. biofysisk.kemi.dtu.dk/Research/Physical/crd.aspx



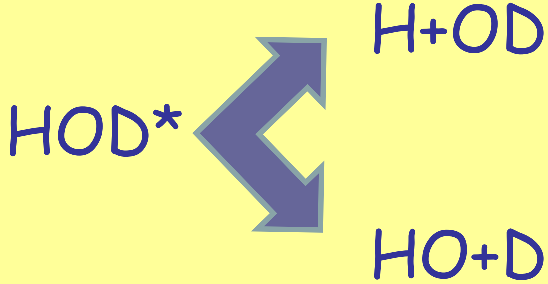
$$HOD\left(S_0, v=0\right) \xrightarrow{IR} HOD\left(S_0, v\neq 0\right)$$

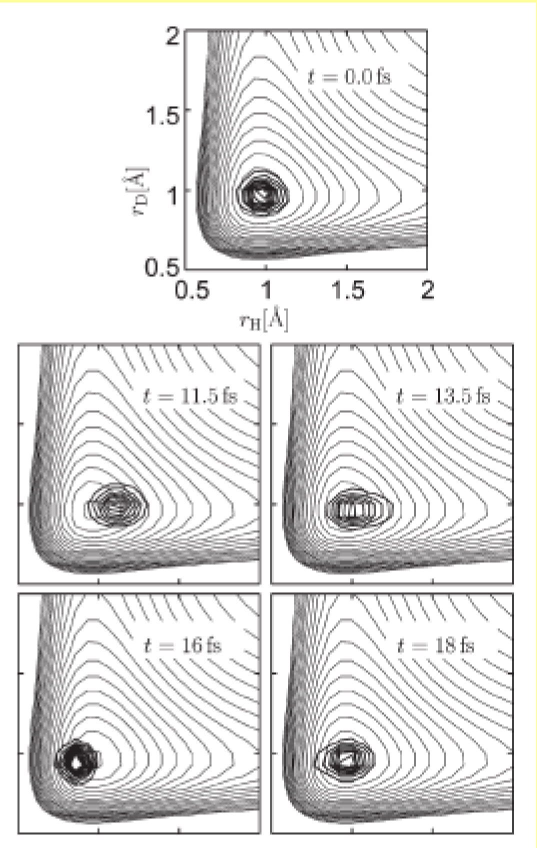
$$\xrightarrow{UV} HOD\left(S_1\right) \begin{cases} HO + D \\ H + OD \end{cases}$$

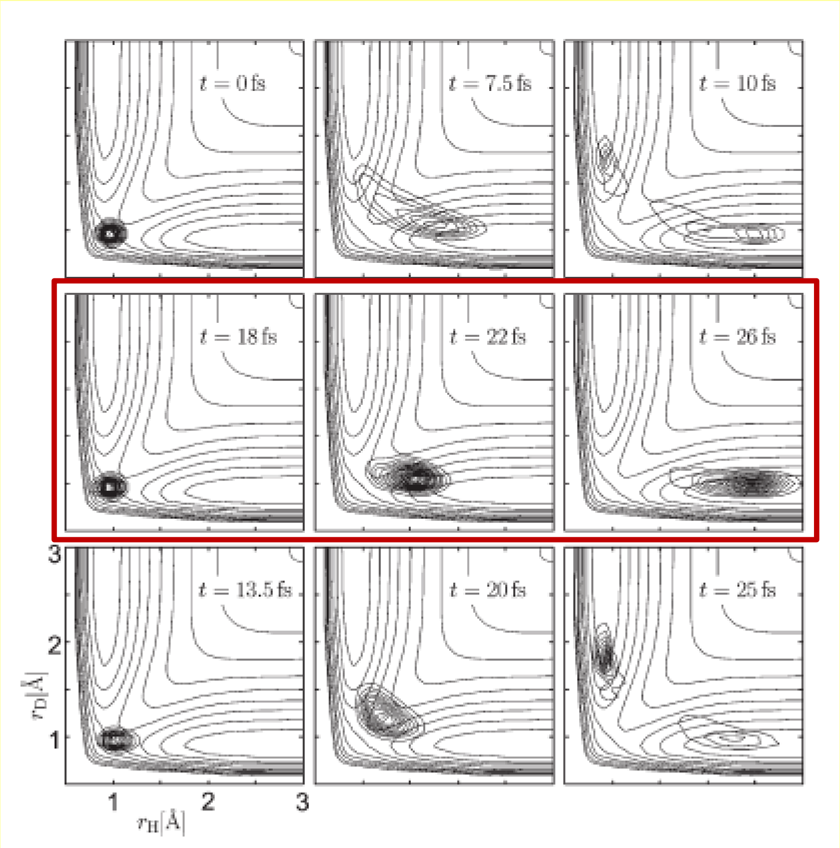
$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \left|\Psi_g(t)\right\rangle \\ \left|\Psi_e(t)\right\rangle \end{pmatrix} = \begin{pmatrix} \hat{H}_{gg}(t) & \hat{H}_{ge}(t) \\ \hat{H}_{eg}(t) & \hat{H}_{ee}(t) \end{pmatrix} \begin{pmatrix} \left|\Psi_g(t)\right\rangle \\ \left|\Psi_e(t)\right\rangle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

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

N. Elghobashi, P. Krause, J. Manz and M. Oppel, PCCP, 5 (2003) 4806



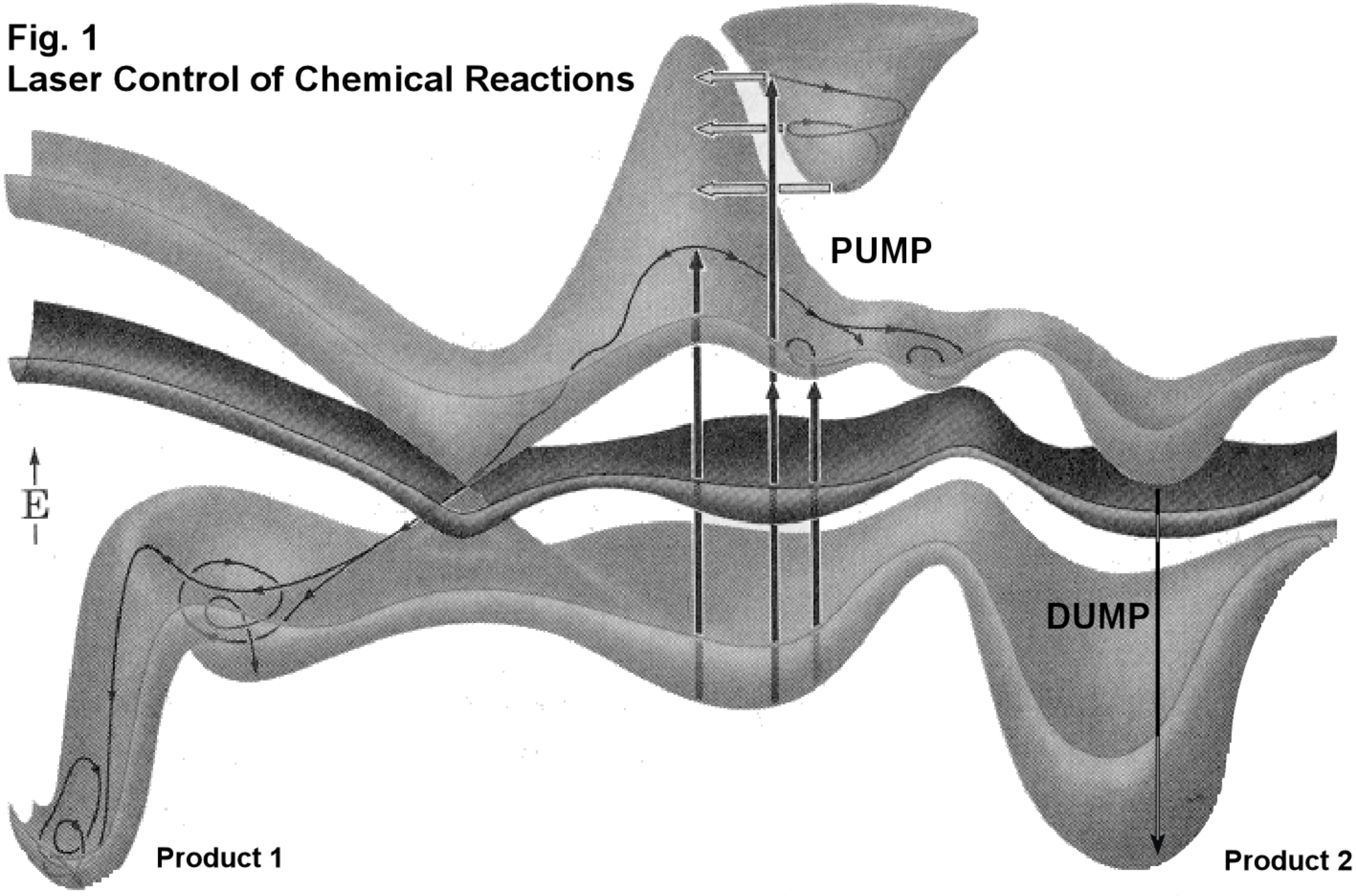




N. Elghobashi, P. Krause, J. Manz and M. Oppel, PCCP, 5 (2003) 4806

KONTROLA HEMIJSKE REAKCIJE

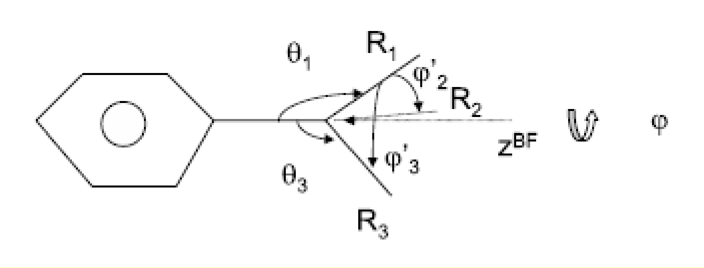
Fig. 1
Laser Control of Chemical Reactions

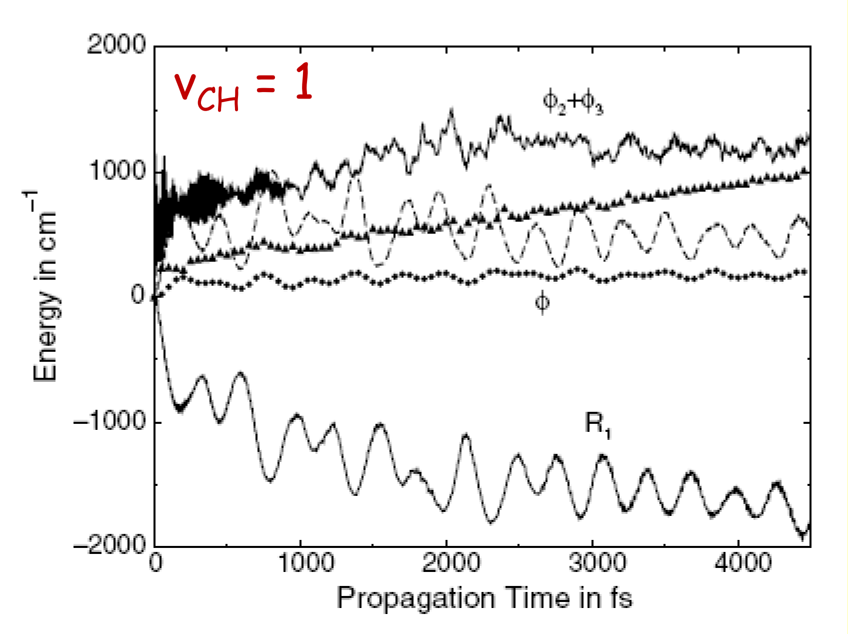


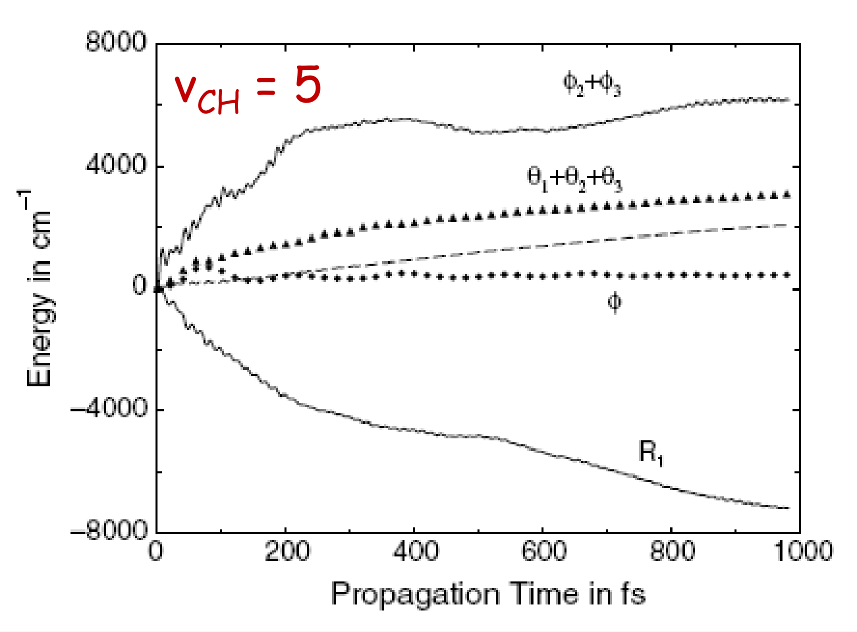
J. Michl and V. Nobačić-Koutecky, Electronic aspects of organic Photochemistry, John Wiley & Sons: New York, 1990

INTRAMOLEKULSKA PRERASPODELA VIBRACIONE ENERGIJE

IVR – intramolecular vibrational energy redistribution

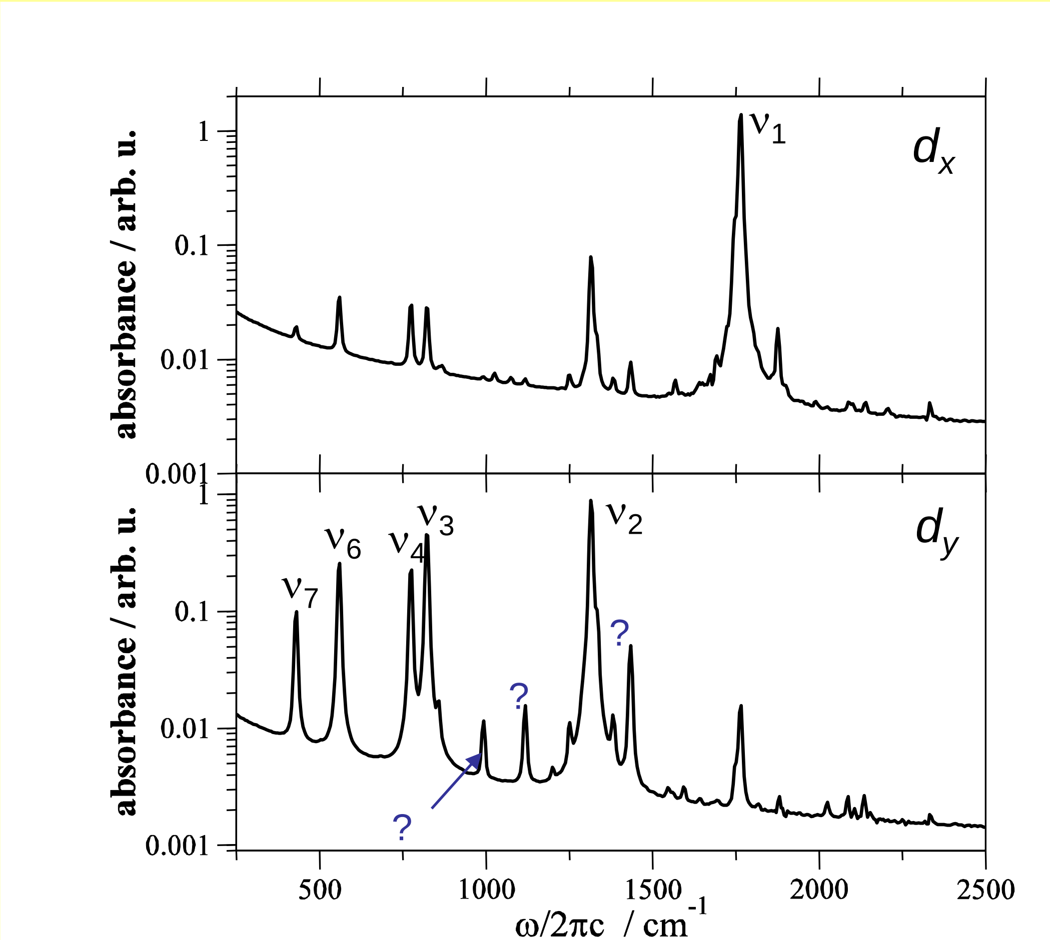






F. Gatti and H-D. Meyer, Chem. Phys. 301 (2004) 3

IC SPEKTRI - ASIGNACIJA TRAKA



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

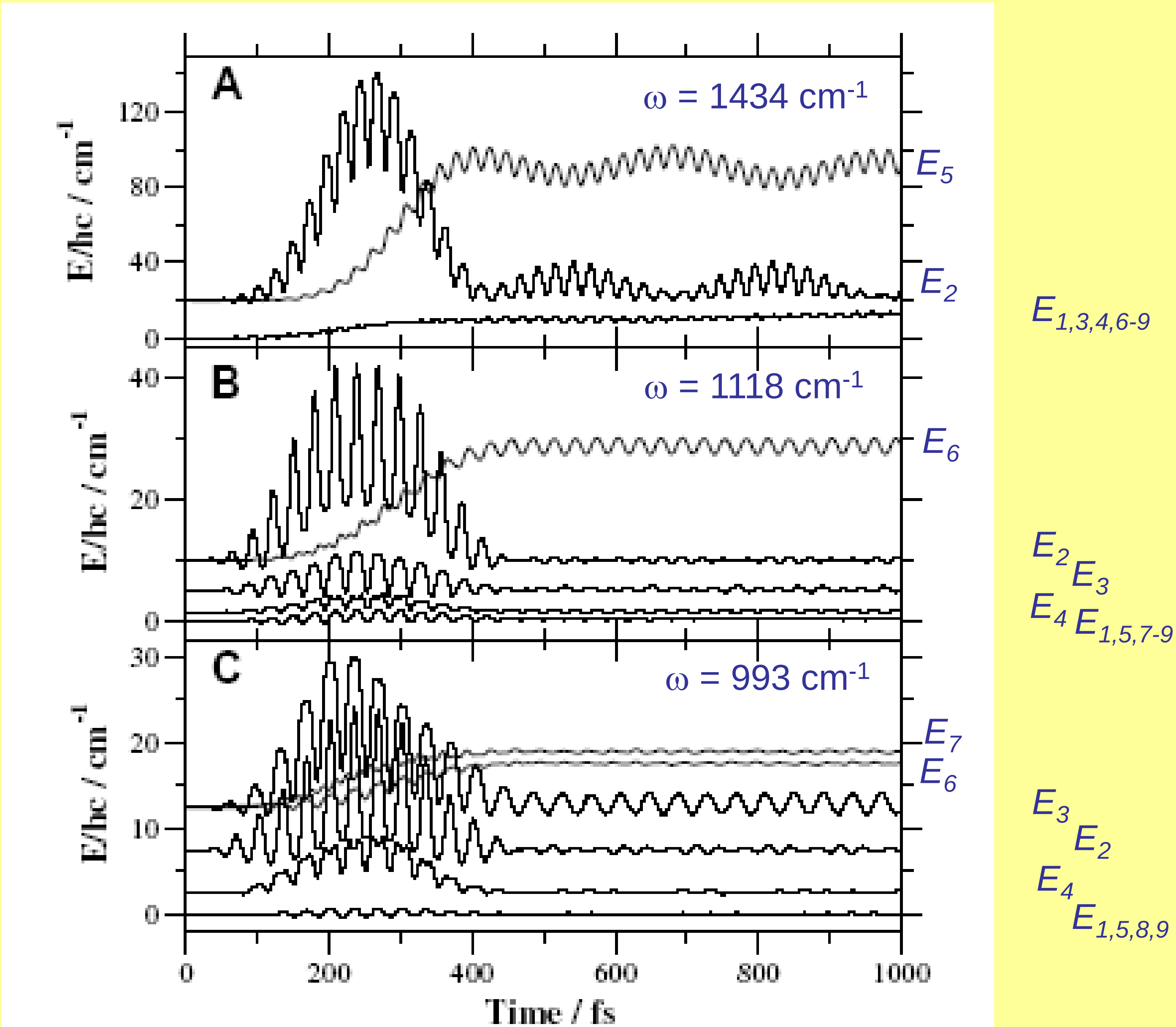
[a] Orphal et al. J. Phys. Chem. A 101 (1997) 1062

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

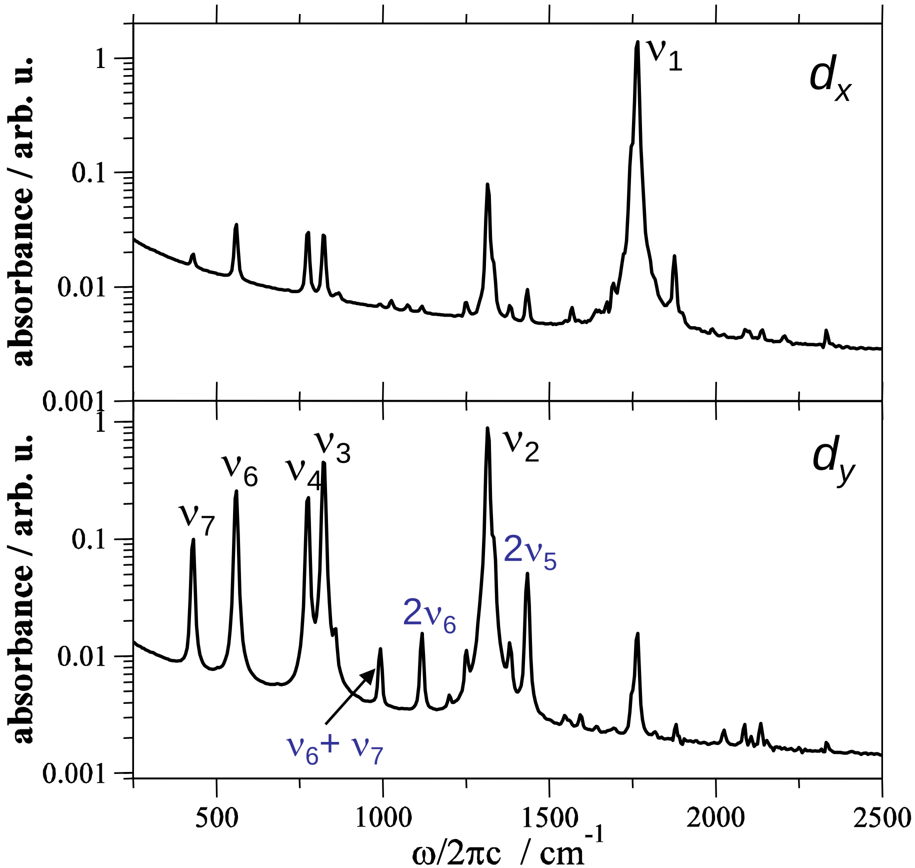
stepen slobode	frekvencija / cm^{-1} harm.	anh.	eksp.[a]
ν_1	1800	1766	1737
ν_2	1342	1314	1293
ν_3	828	820	809
ν_4	786	777	780
ν_5	731	719	711
ν_6	561	561	563
ν_7	436	431	434
ν_8	250	254	273
ν_9	135	158	122

prelaz	frekvencija / cm^{-1} izr.	eksp.[b]
?	1434	1424
?	1118	1119
?	993	988

IC SPEKTRI – ASIGNACIJA TRAKA



IC SPEKTRI – ASIGNACIJA TRAKA



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

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

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ν_7	436	431	434
ν_8	250	254	273
ν_9	135	158	122

prelaz	frekvencija / cm^{-1} izr.	eksp.[b]
$2\nu_5$	1434	1424
$2\nu_6$	1118	1119
$\nu_6 + \nu_7$	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
- ...