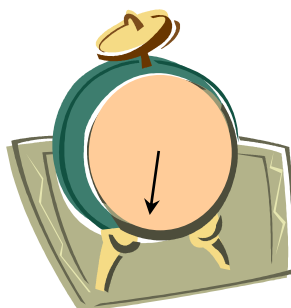
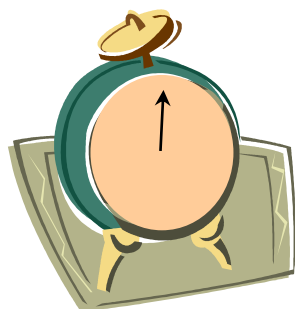
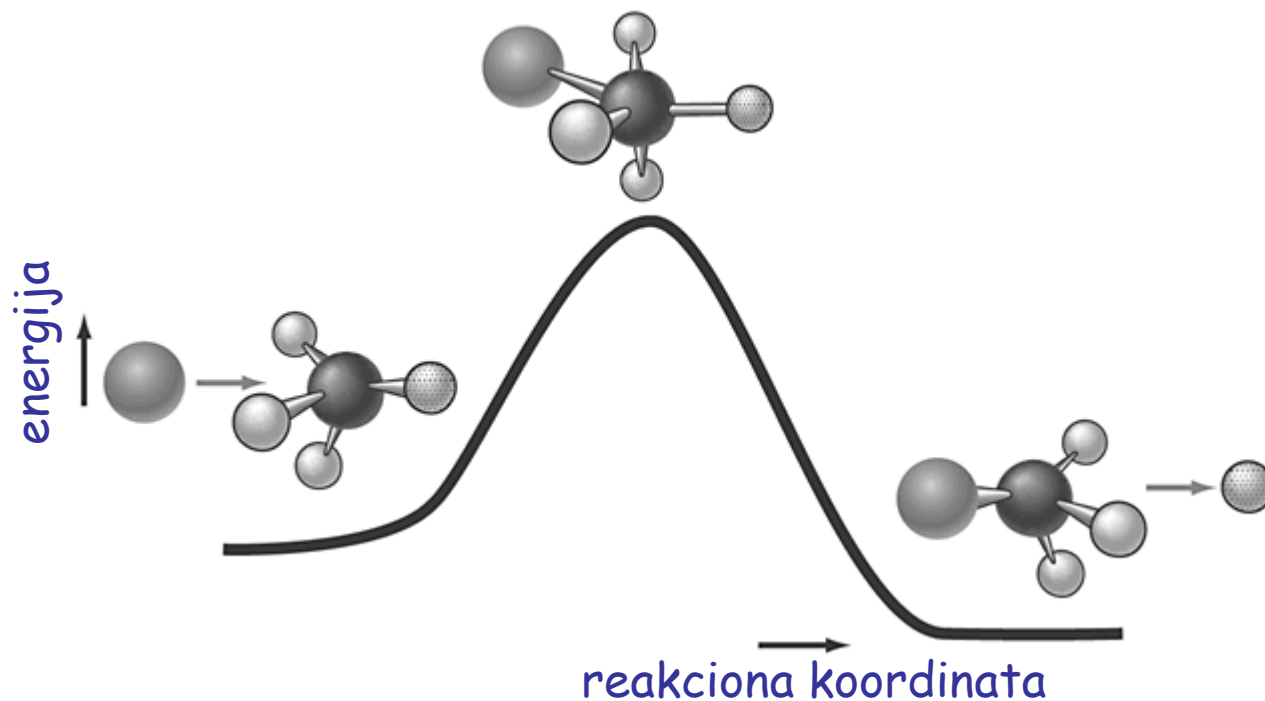


# PRAĆENJE TOKA HEMIJSKE REAKCIJE

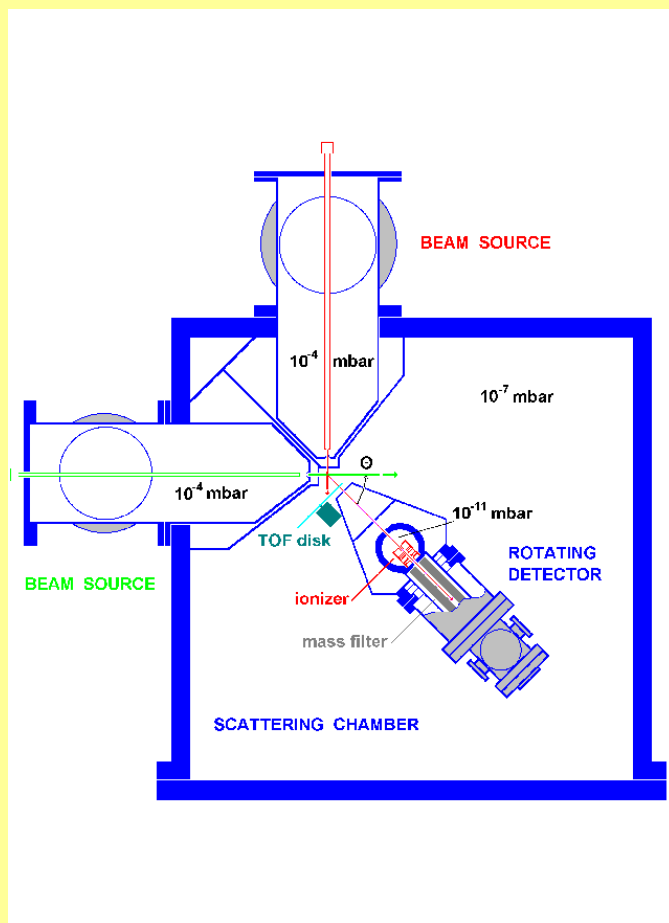


# TEHNOLOGIJA MOLEKULSKIH SNOPOVA

1986 - Nobelova nagrada za hemiju

Dadli Robert Heršbak, Juan T. Li & Džon K. Polanji

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

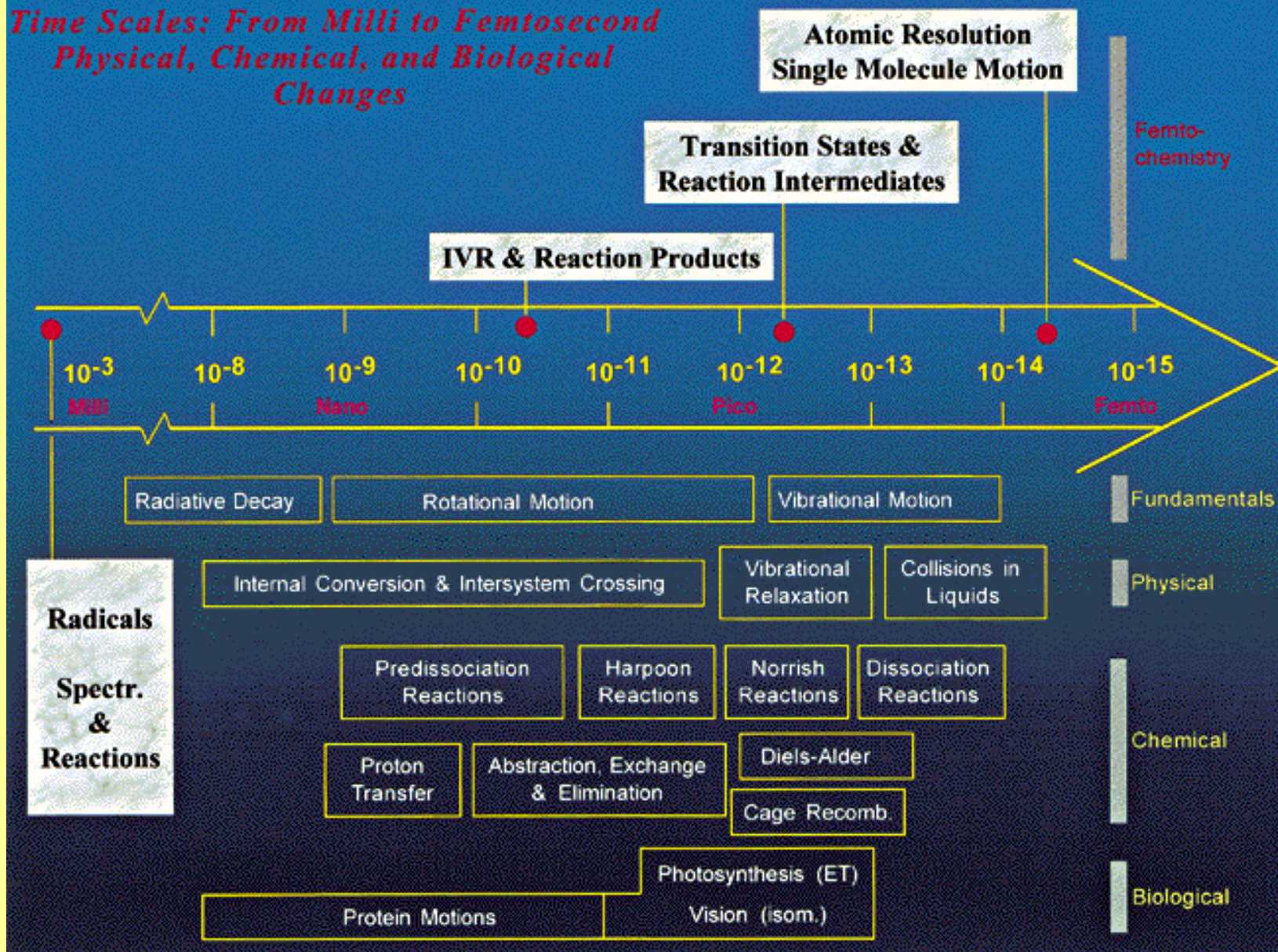


Hamlet!

"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

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



Ahmed Zewail - Nobel lecture



# "Rođenje" ultrabrze tehnologije

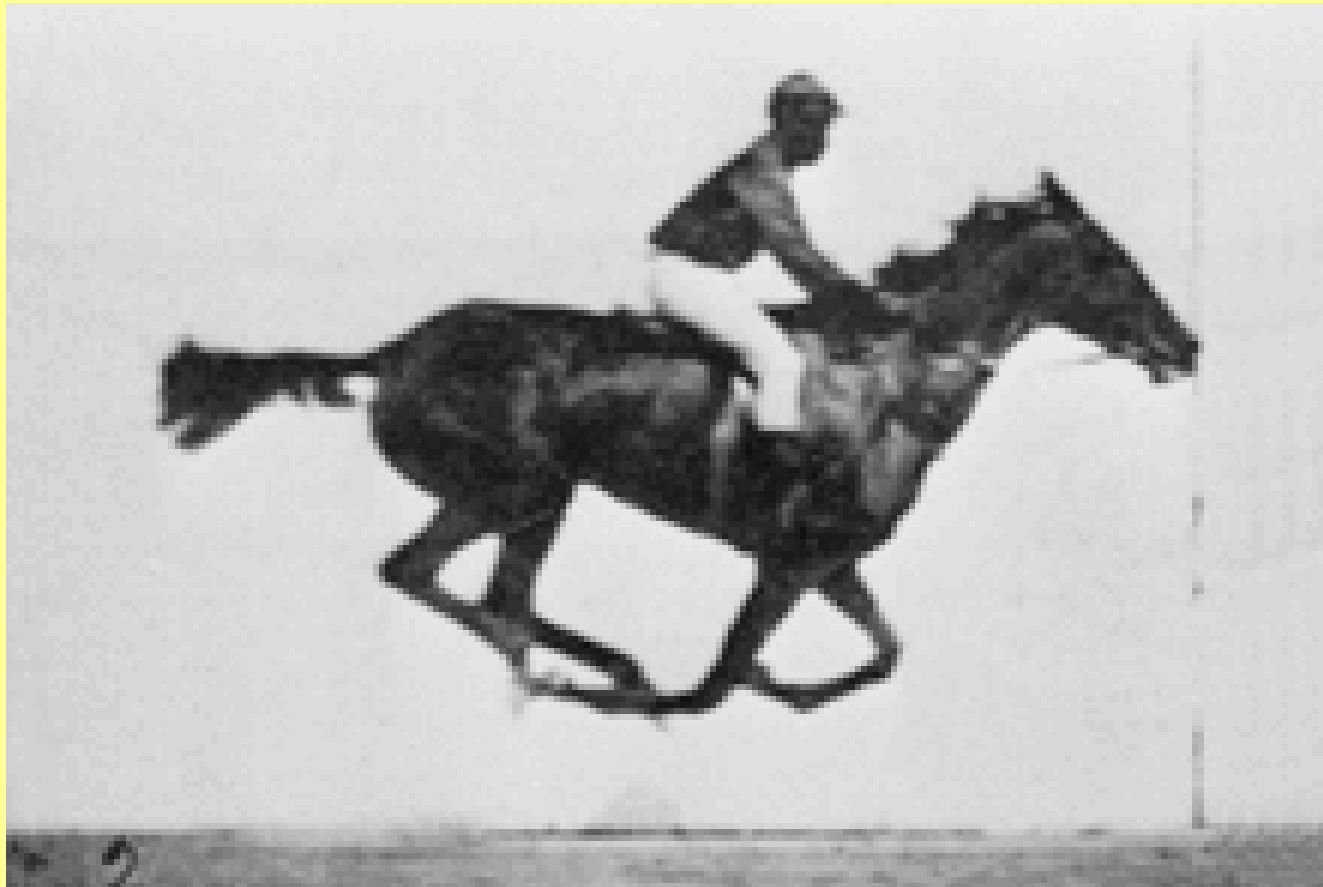


Konj u pokretu (The horse in motion)

Fotograf: Edvard Majbridž (Eadweard Muybridge)

Palo Alto, Kalifornija 1872 → 1878.

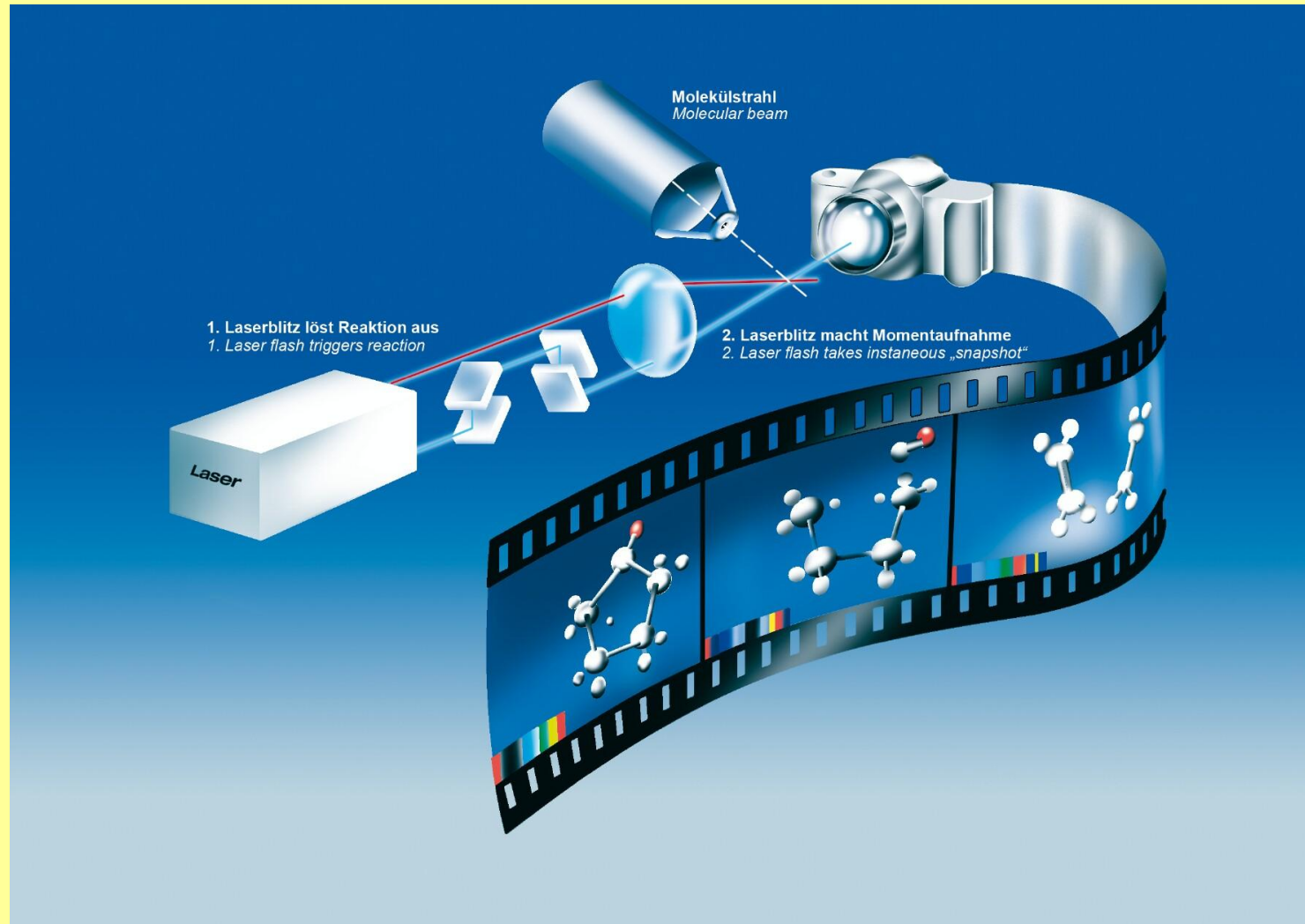
# "Rođenje" ultrabrze tehnologije

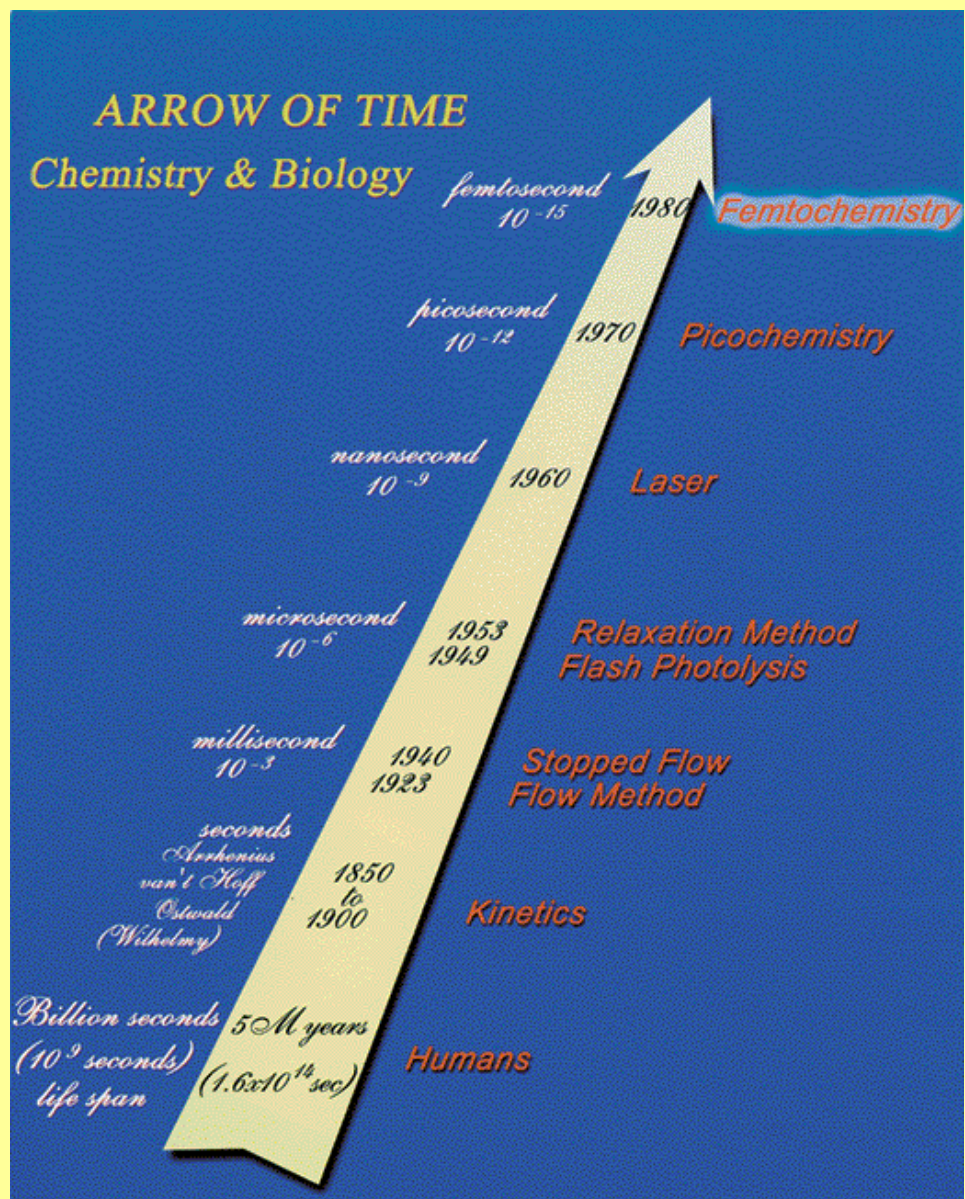


Seli Gardner u galopu - animirano 2006.  
na osnovu Majbridžovih fotografija

# Cilj:

“film” koji prikazuje položaj jezgara  
u toku hemijske reakcije





Ahmed Zewail - Nobel lecture





# The Nobel Prize in Chemistry 1999

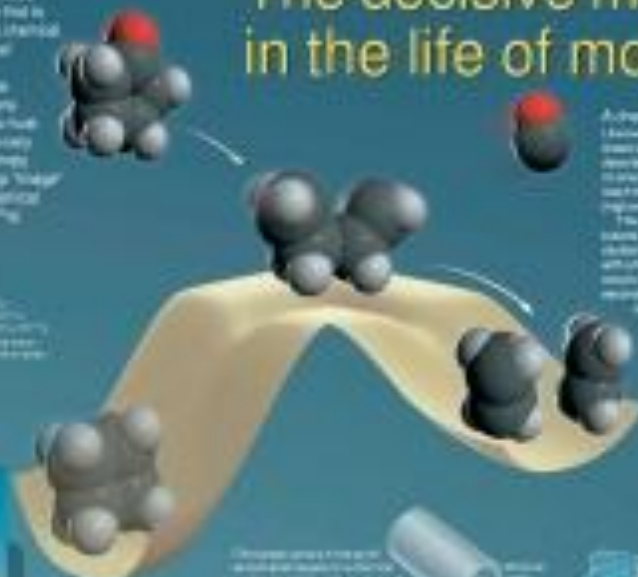
The Royal Swedish Academy of Sciences has awarded the 1999 Nobel Prize in Chemistry to Professor Arvid E. Jönsson for his studies of transition metal complexes and their catalytic activity.

**A**rrived Jönsson receives the 1999 Nobel Prize in Chemistry for being the first to reveal the decisive moments in chemical reactions – the moments when chemical bonds are broken and formed.

Jönsson's technique uses what can be thought of as a molecular camera. The "molecular camera" consists of a series of extremely high-speed molecular spectroscopy experiments (up to 10<sup>12</sup> and 10<sup>13</sup> times) rapidly (1000 times) to obtain a sharp "snapshot" of the molecules in the course of a chemical reaction. This requires a femtosecond laser.

- 1. Jönsson, A. E. J.
- 2. Jönsson, A. E. J.
- 3. Jönsson, A. E. J.
- 4. Jönsson, A. E. J.
- 5. Jönsson, A. E. J.
- 6. Jönsson, A. E. J.
- 7. Jönsson, A. E. J.
- 8. Jönsson, A. E. J.
- 9. Jönsson, A. E. J.
- 10. Jönsson, A. E. J.

## The decisive moments in the life of molecules



Arvid Jönsson's work is up to the point where the reaction is complete. The reaction is complete when the reaction is complete. The reaction is complete when the reaction is complete.

The reaction is complete when the reaction is complete. The reaction is complete when the reaction is complete. The reaction is complete when the reaction is complete.

The reaction is complete when the reaction is complete. The reaction is complete when the reaction is complete. The reaction is complete when the reaction is complete.



Jönsson – King of Femtosecond

Arvid E. Jönsson is a Swedish chemist and physicist. He is known for his work on the reaction coordinate of chemical reactions. He received the Nobel Prize in Chemistry in 1999.



### The Nobel Prize

The Nobel Prize is awarded annually to the person or persons who have made the most important discovery or discoveries in the field of chemistry.



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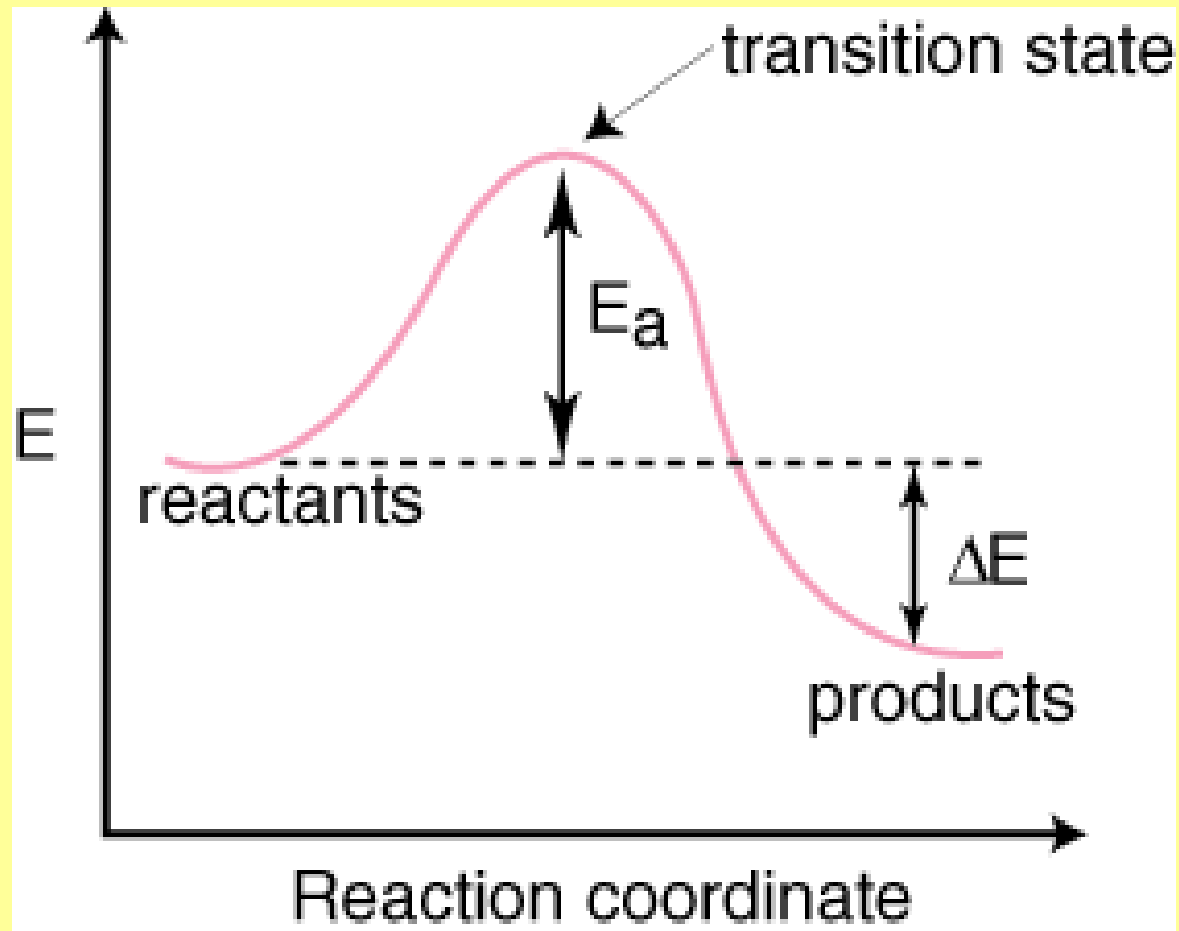


Kungliga Vetenskapsakademien  
The Royal Swedish Academy of Sciences

The Nobel Prize is awarded annually to the person or persons who have made the most important discovery or discoveries in the field of chemistry.

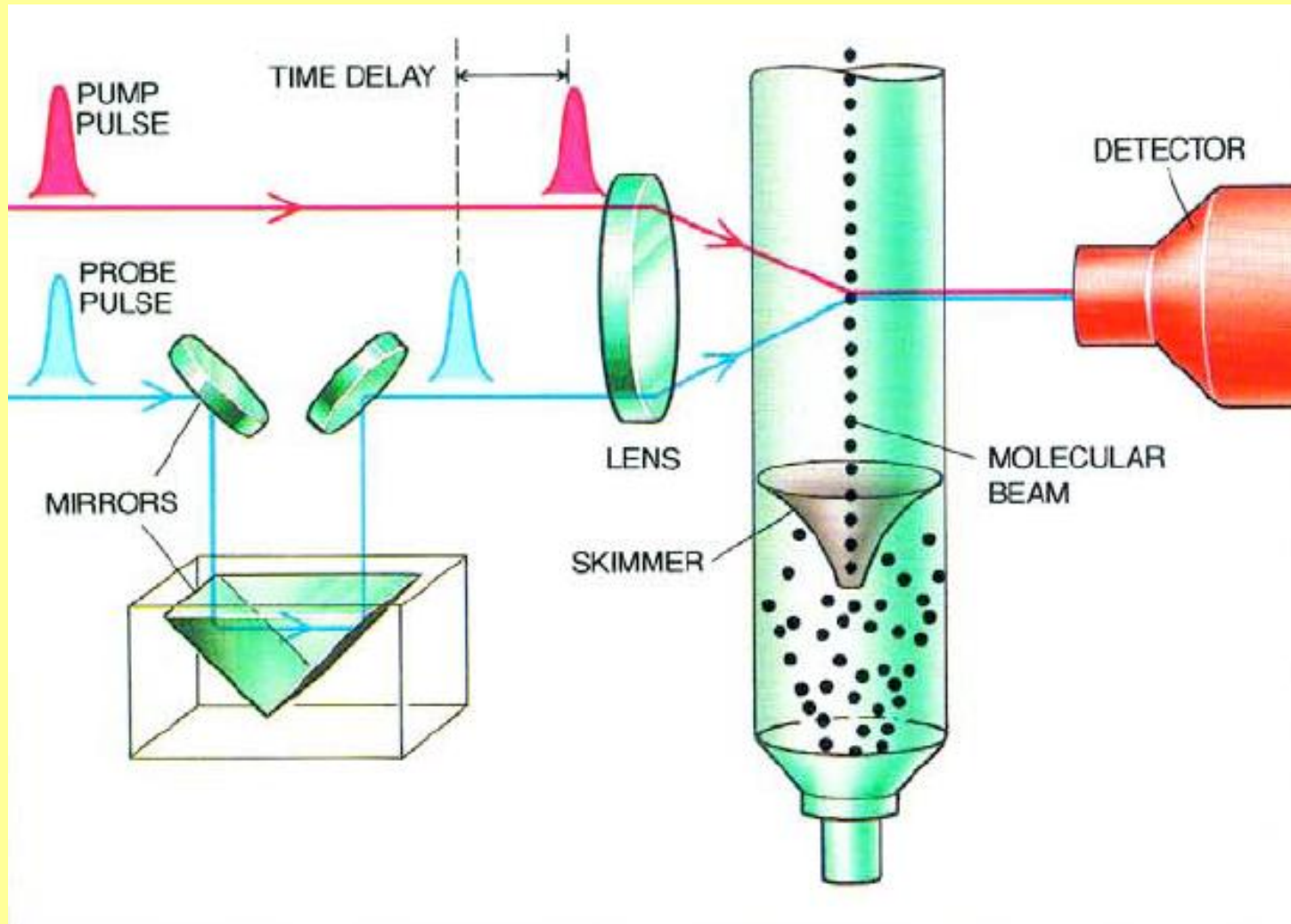
The Nobel Prize is awarded annually to the person or persons who have made the most important discovery or discoveries in the field of chemistry.

# PRELAZNO STANJE



vreme žīvota  $\approx 10 - 100$  fs

# FEMTOSECOND LASER



# KAŠNJENJE PROBA PULSA

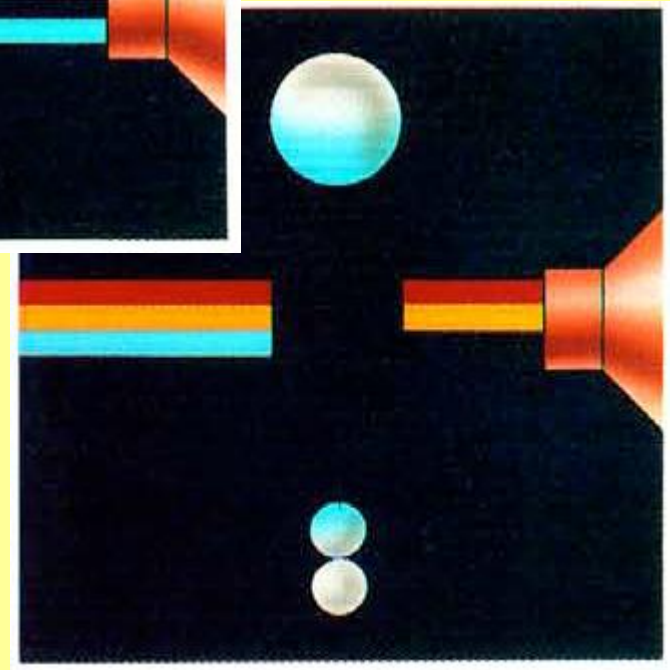
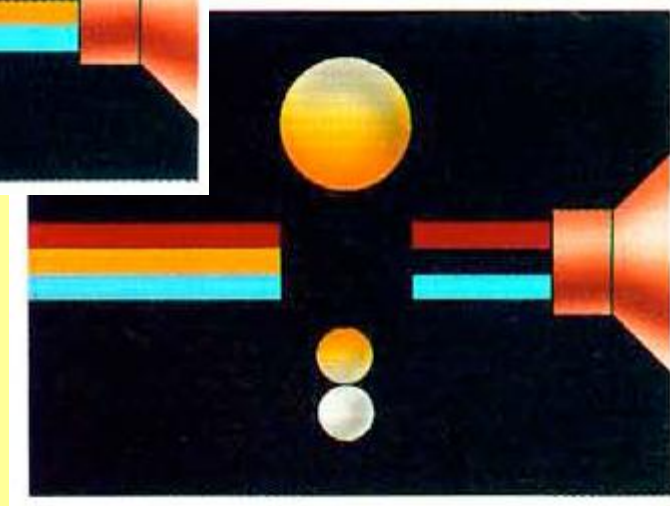
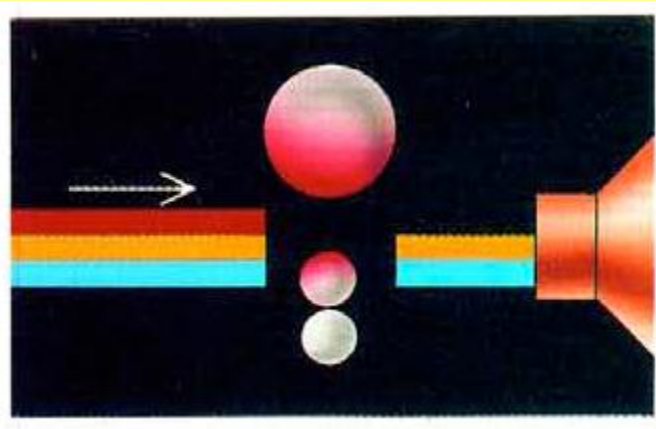
$$c = 3 \cdot 10^8 \text{ m/s}$$

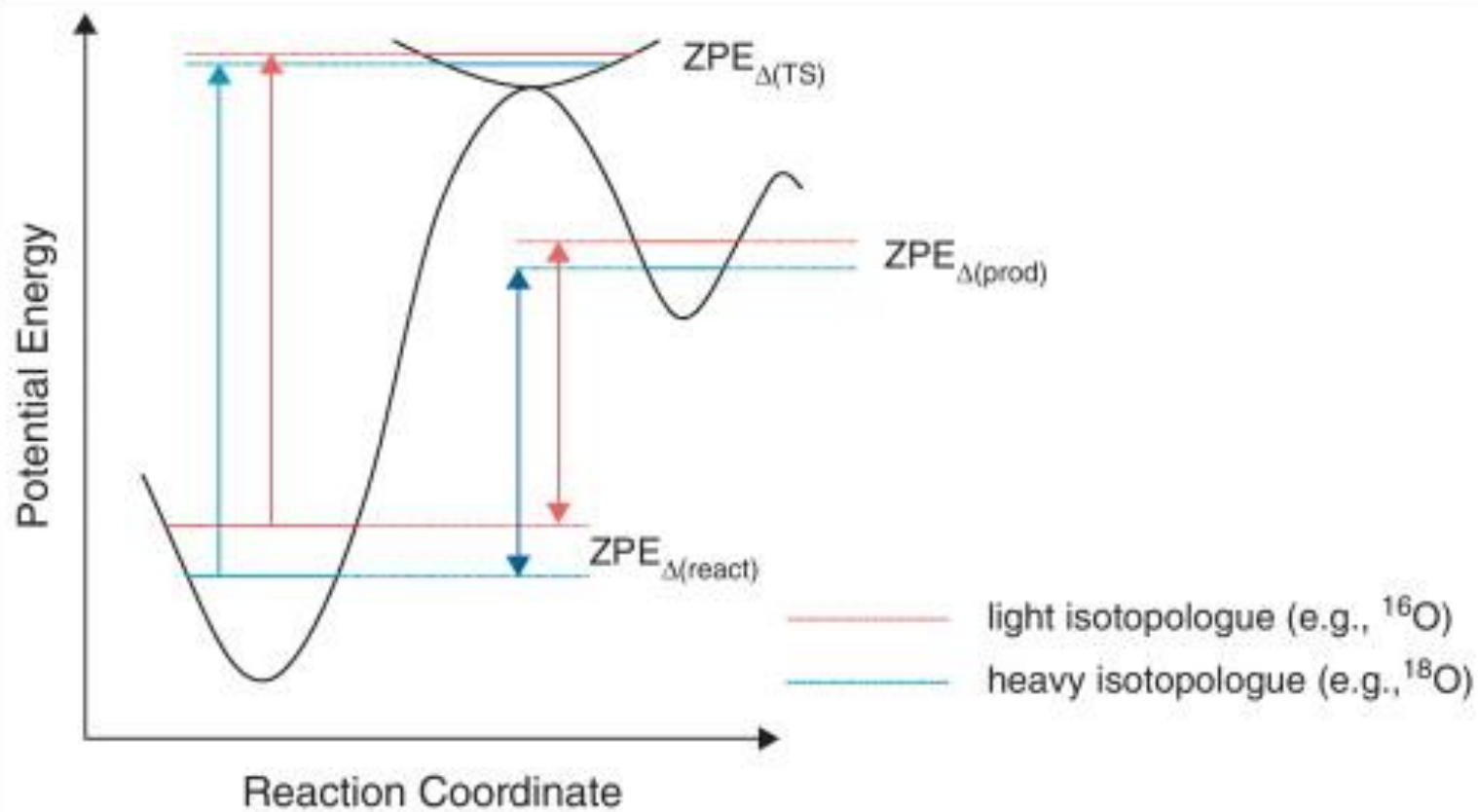
$$\Delta l = 1 \text{ } \mu\text{m} \rightarrow \Delta t = (1 \cdot 10^{-6} \text{ m}) / (3 \cdot 10^8 \text{ m/s}) = 3,33 \cdot 10^{-15} \text{ s} \\ = 3,33 \text{ fs}$$

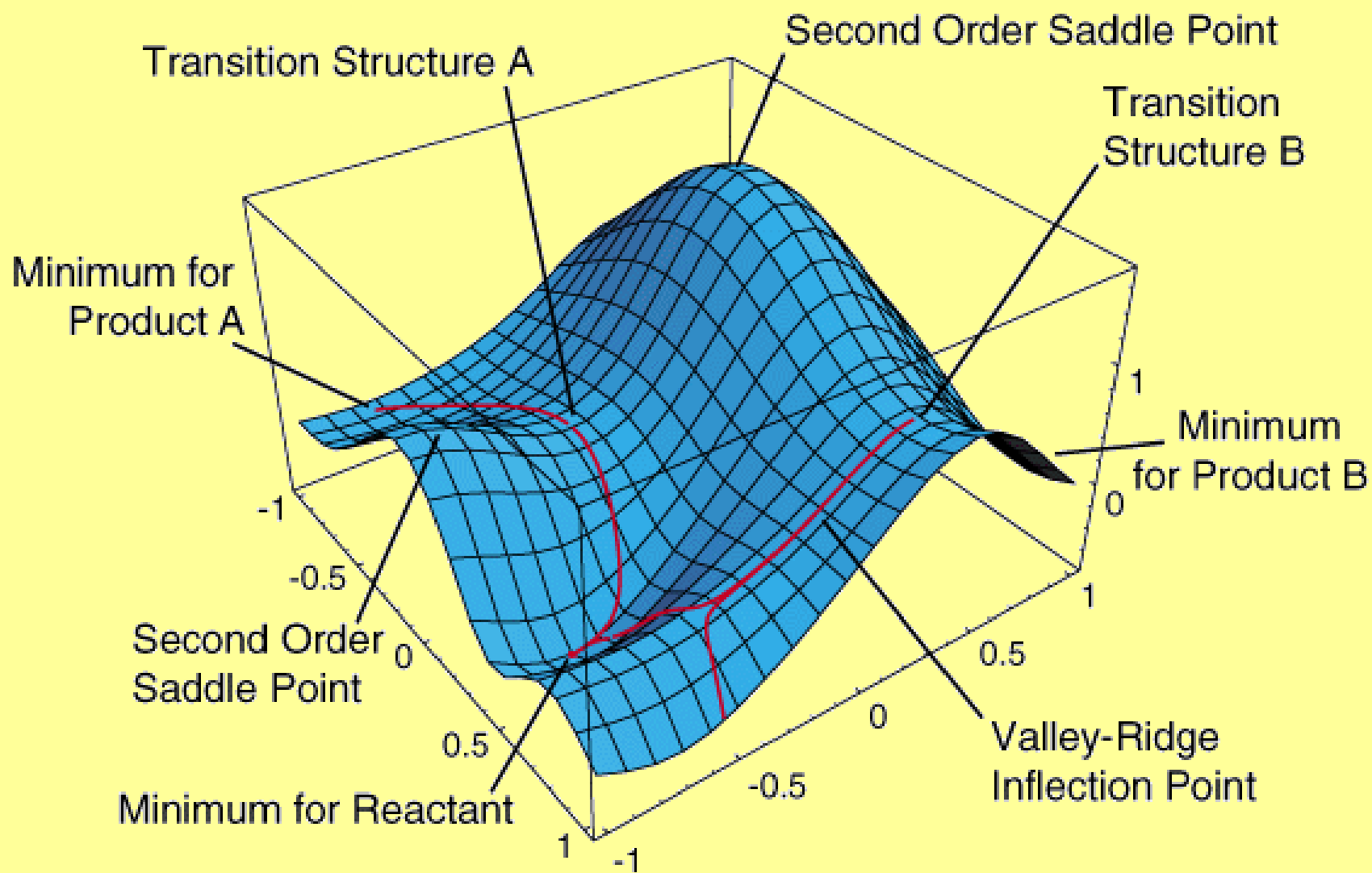
$$\Delta l = 100 \text{ } \mu\text{m} \rightarrow \Delta t = (1 \cdot 10^{-4} \text{ m}) / (3 \cdot 10^8 \text{ m/s}) = 3,33 \cdot 10^{-13} \text{ s} \\ = 333 \text{ fs}$$



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



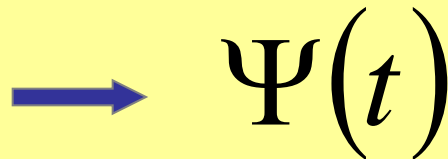
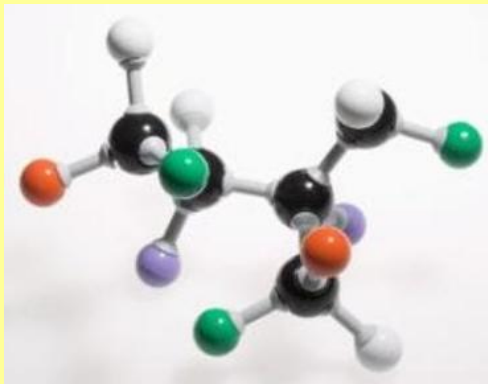




# TEORIJSKI PRISTUP

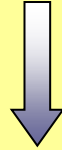
vremenski zavisna Šredingerova jednačina

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





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



## PERTURBACIONI RAČUN

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

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

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

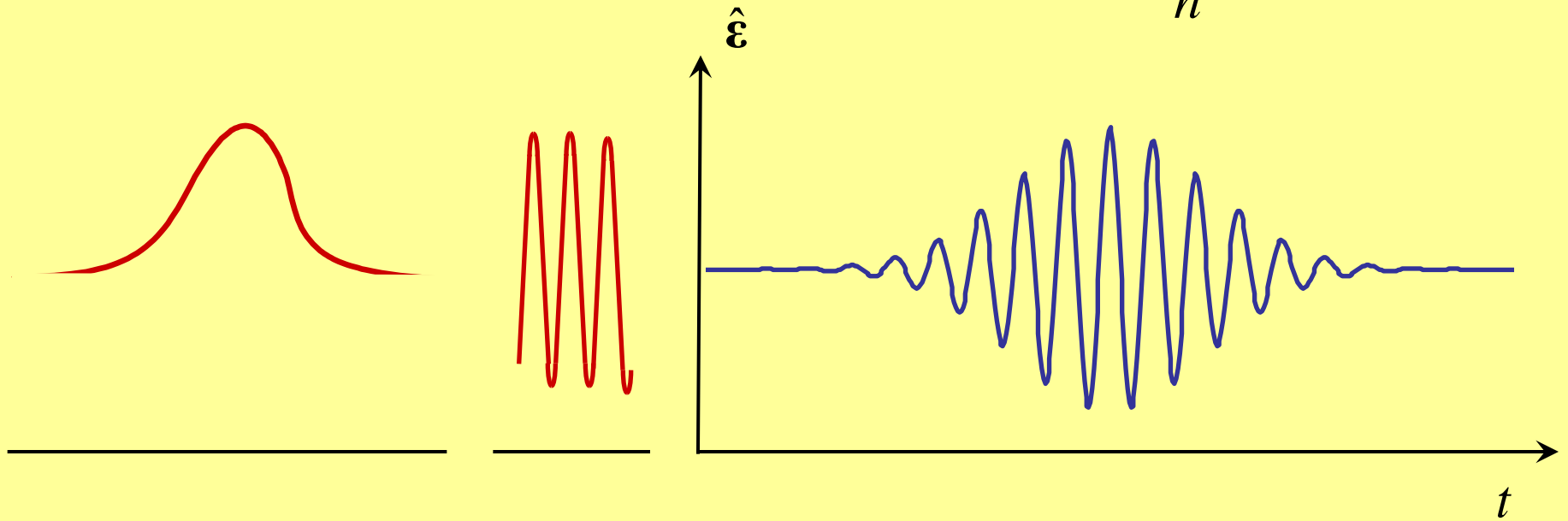
perturbacija  
(laserski puls)

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

# ULTRAKRATKI LASERSKI PULS

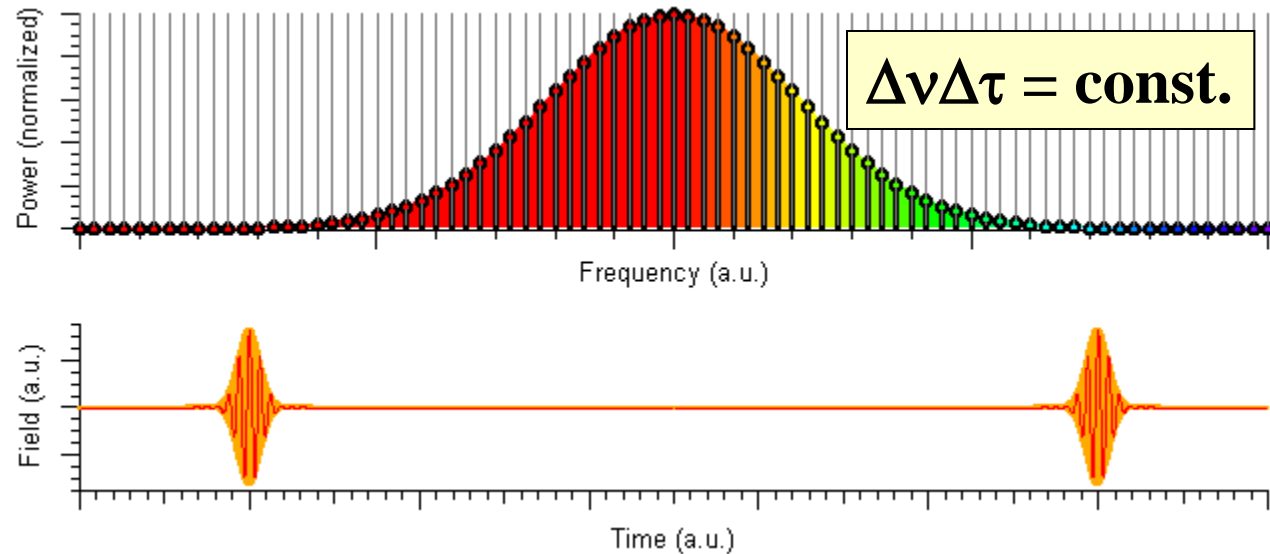
$$\hat{\mathbf{\epsilon}}(t) = \hat{\mathbf{\epsilon}}_0 e^{-\frac{t^2}{\alpha T^2}} \cos(\omega t)$$

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



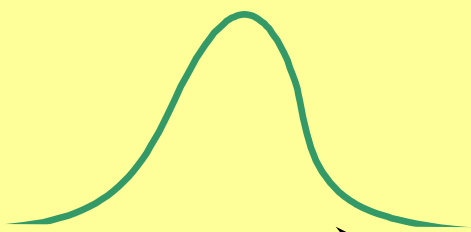
$$\hat{V}(t) = -\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{\epsilon}}(t)$$

# OSNOVNI PRINCIPI ULTRABRZIH LASERA

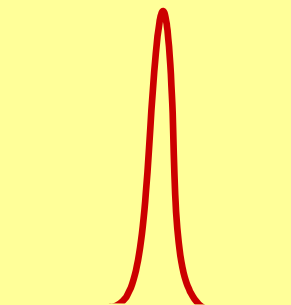


# HAJZENBERGOVA RELACIJA NEODREĐENOSTI

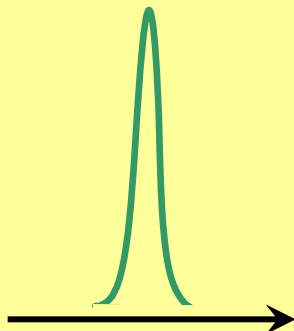
$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$



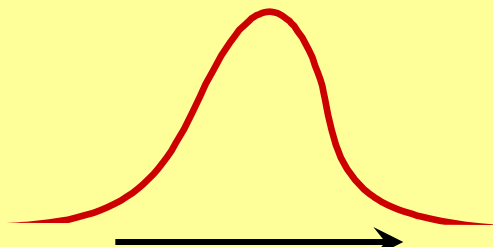
vreme



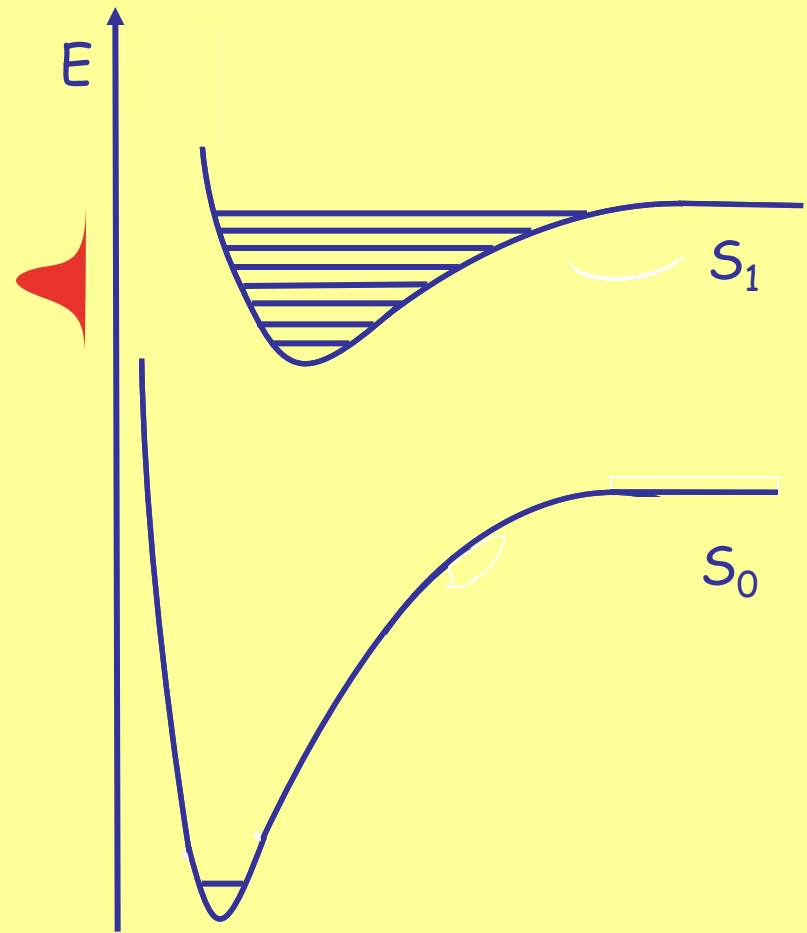
frekvencija



vreme



frekvencija





# 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

# ULTRABRZA SPEKTROSKOPIJA

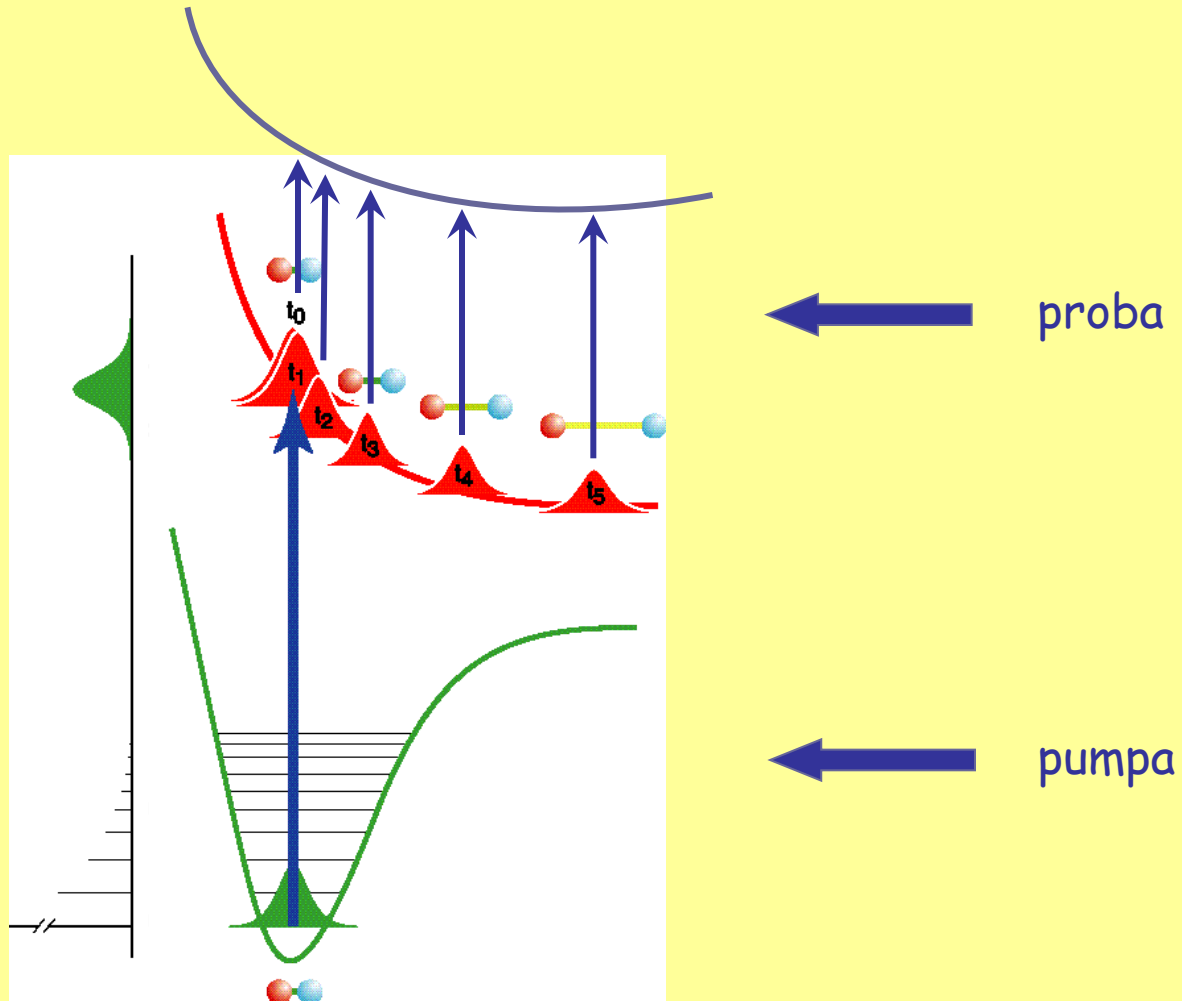
$$\Psi(t) = \sum_k c_k \psi_k e^{-\frac{i}{\hbar} E_k t}$$

talasni paket

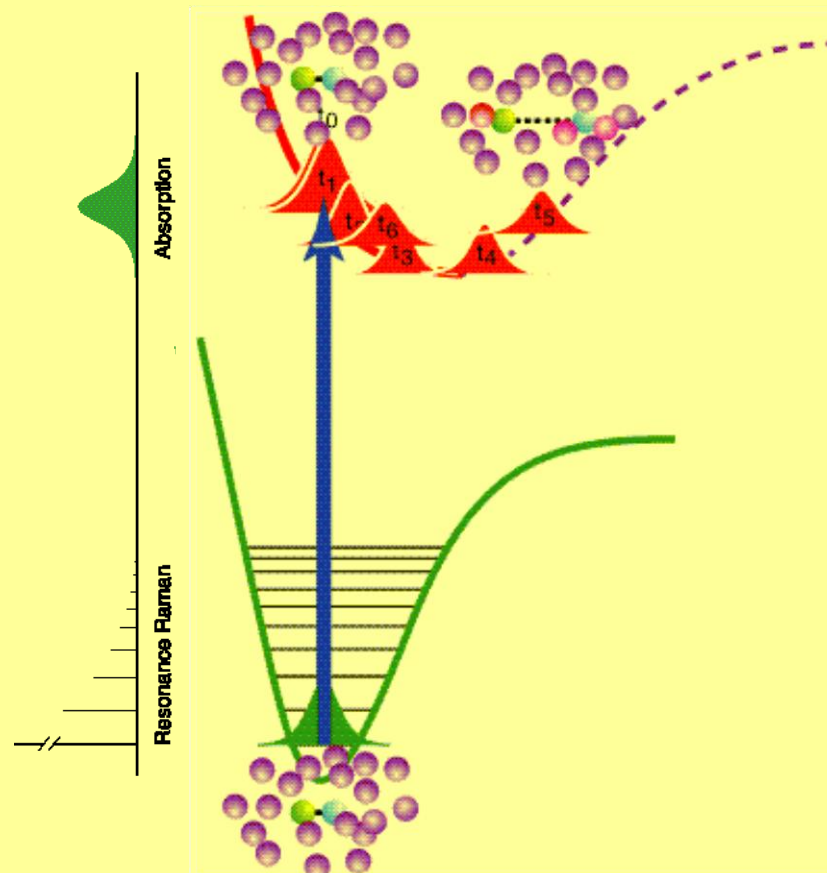
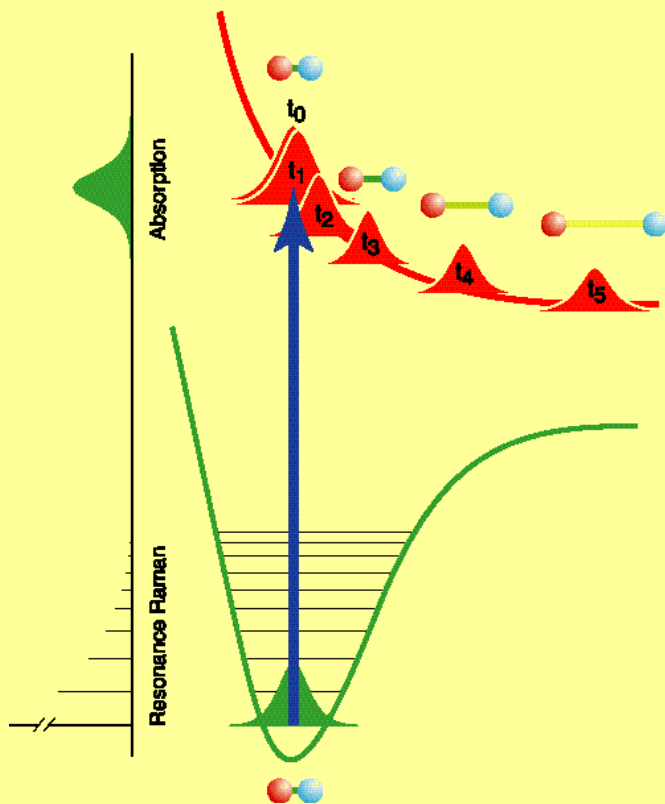
$$\begin{aligned} \Psi(t) \Psi^*(t) &= \left[ \sum_k c_k \psi_k e^{-\frac{i}{\hbar} E_k t} \right] \left[ \sum_l c_l^* \psi_l^* e^{\frac{i}{\hbar} E_l t} \right] = \\ &= \sum_k \sum_l c_k c_l^* \psi_k \psi_l^* e^{-\frac{i}{\hbar} (E_k - E_l) t} \end{aligned}$$

DINAMIKA!

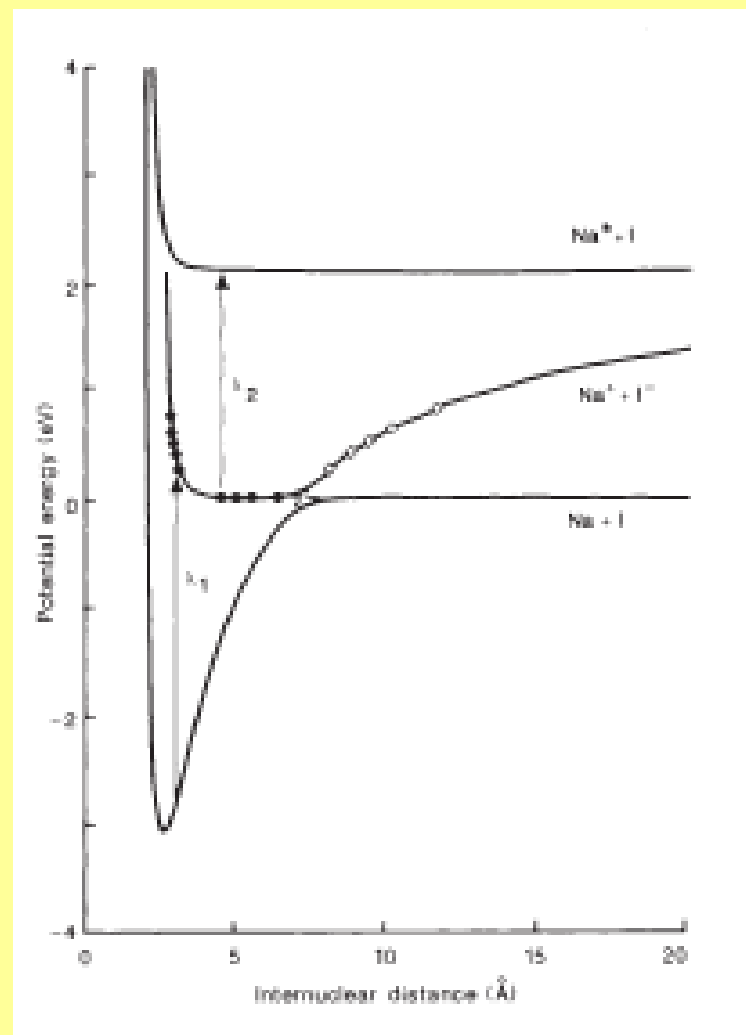
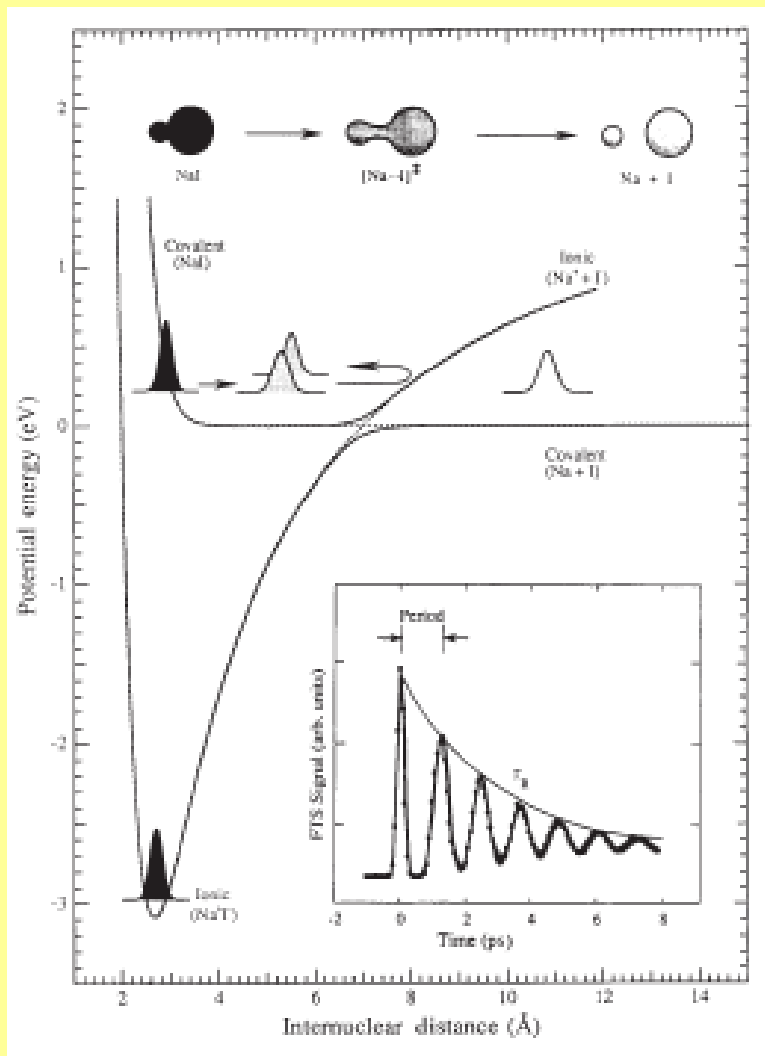
# PUMPA-PROBA METOD



# FOTODISOCIJACIJA DVOATOMSKOG MOLEKULA

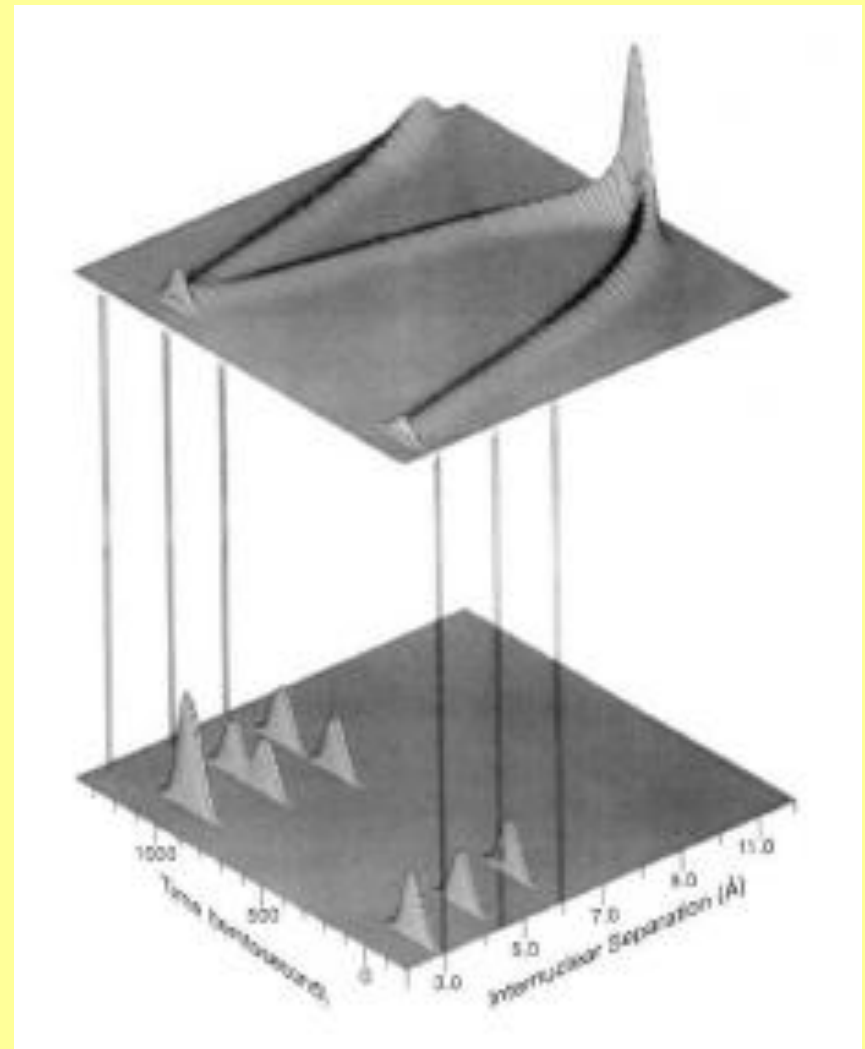
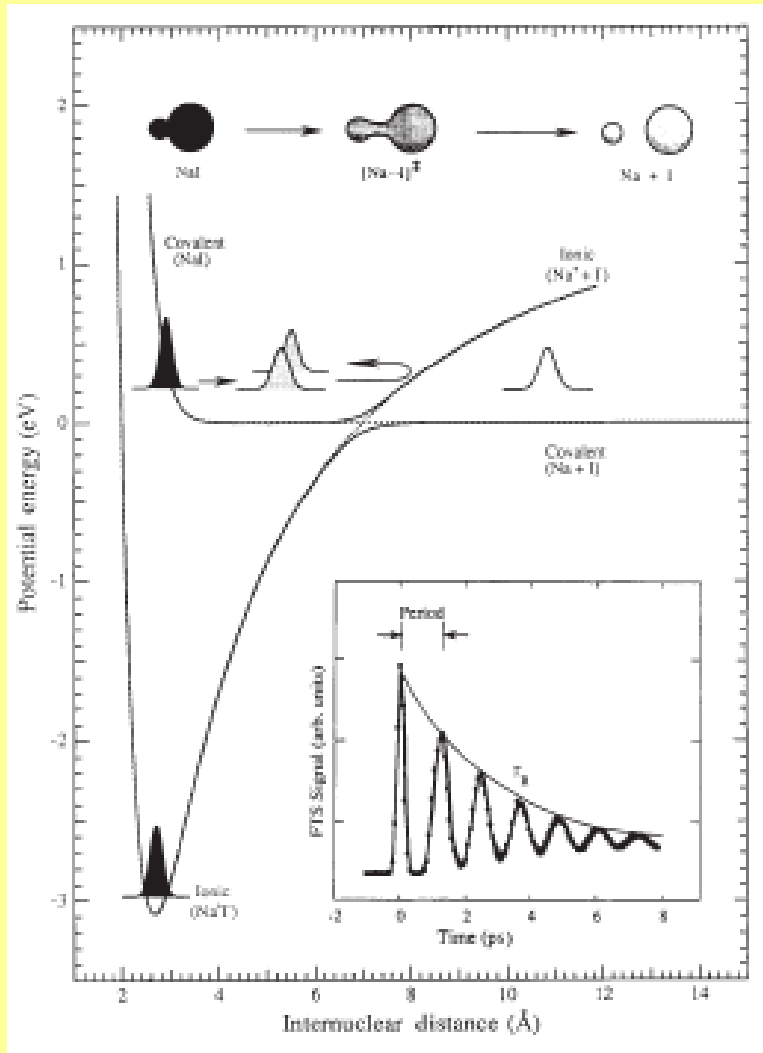


# NaI



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

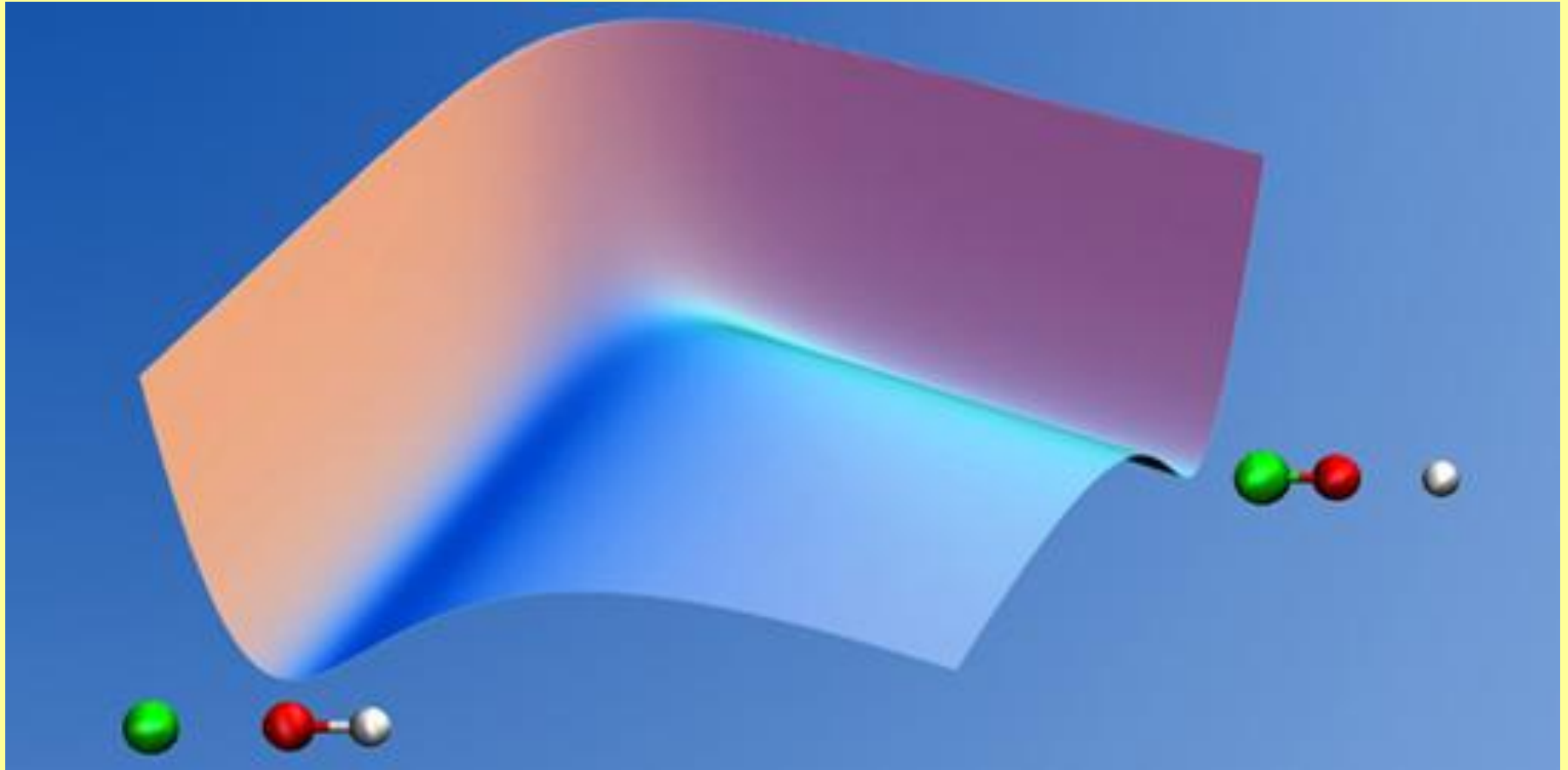
# NaI

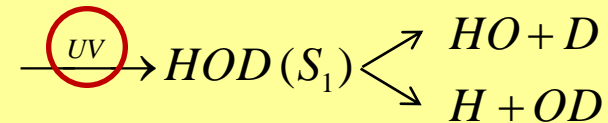
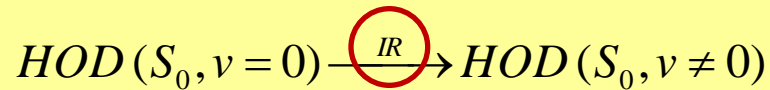
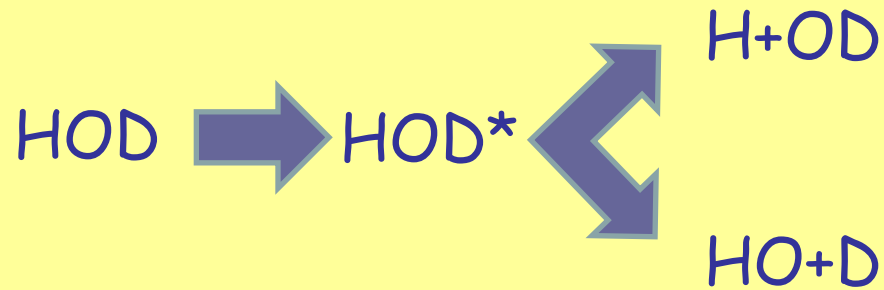


A. Mokhtari, P. Cong, J. L. Herek and A. H. Zewail, Letters to nature, 348 (1990) 225



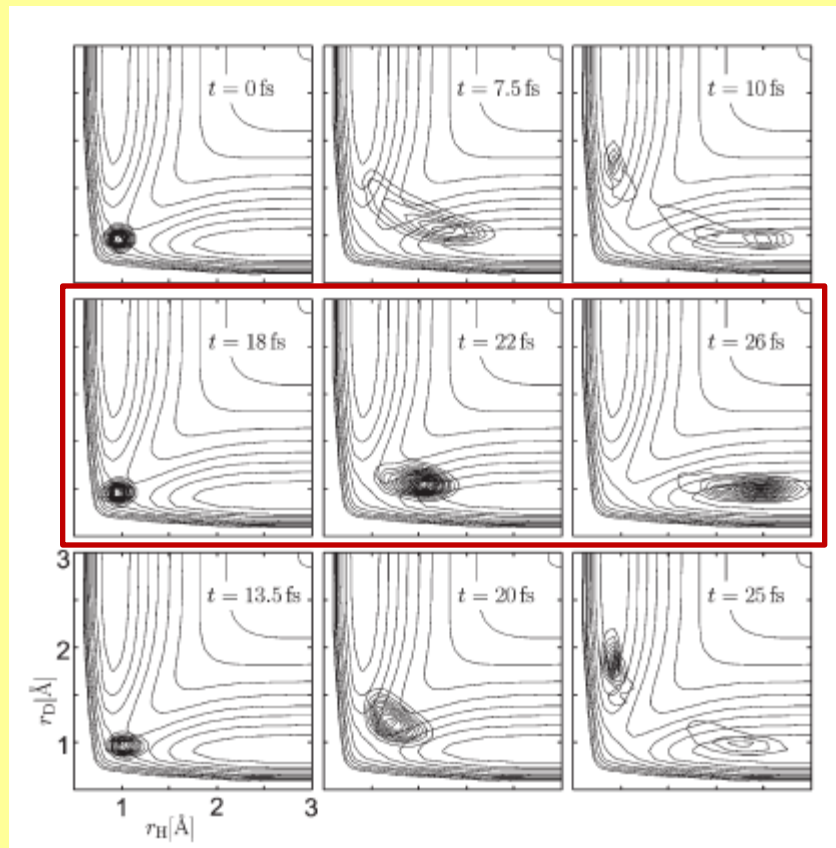
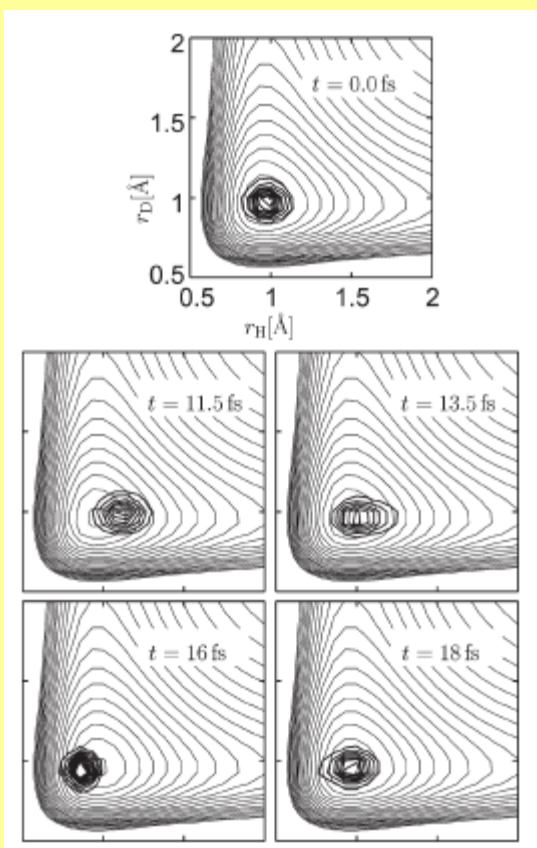
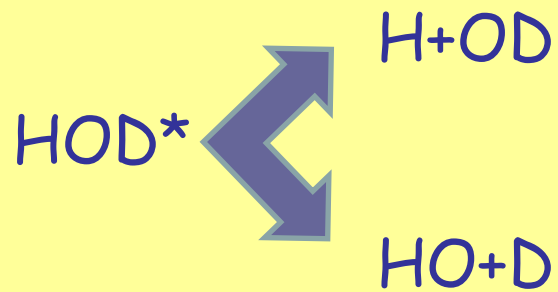
# KONTROLA HEMIJSKE REAKCIJE



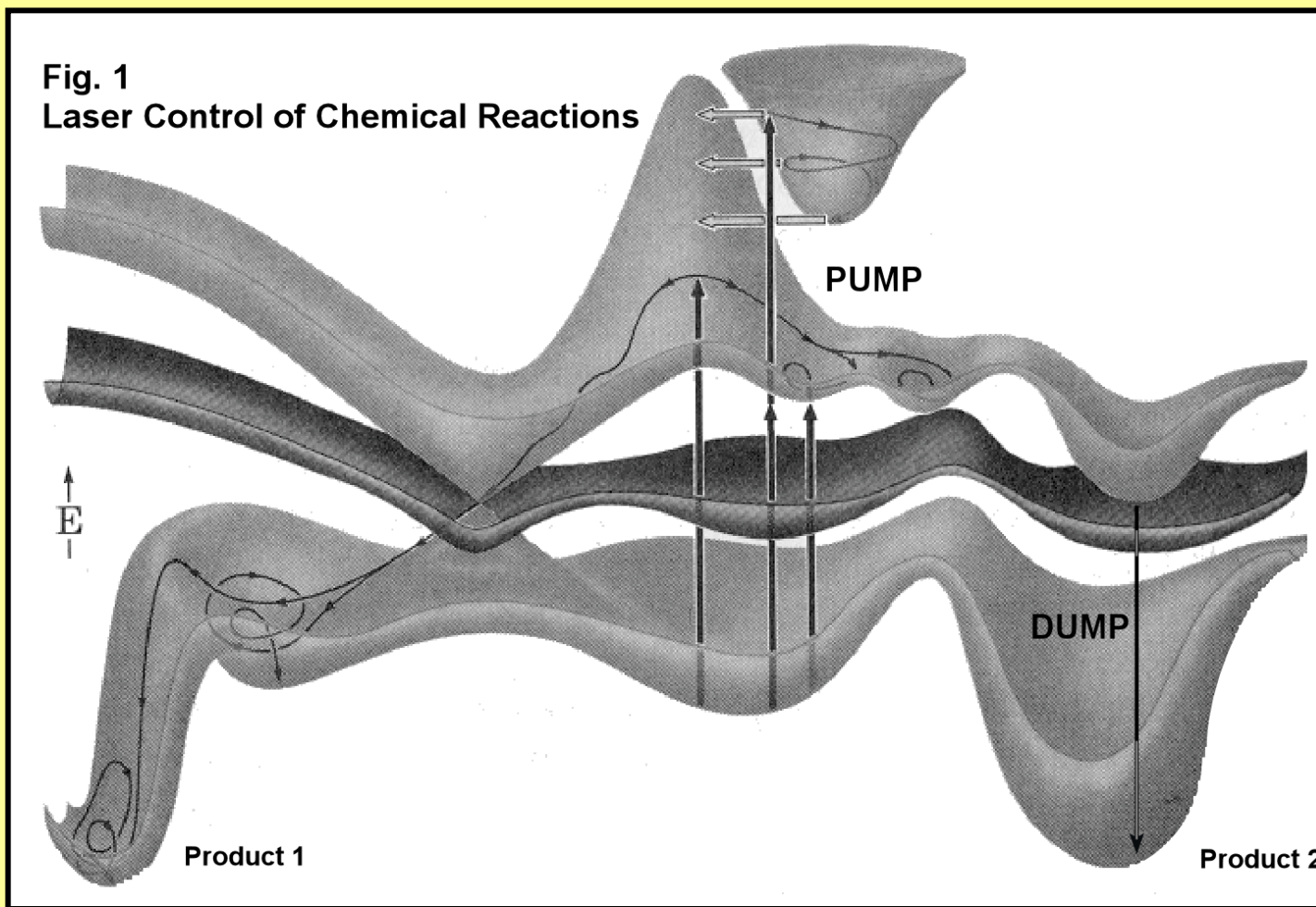


$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} |\Psi_g(t)\rangle \\ |\Psi_e(t)\rangle \end{pmatrix} = \begin{pmatrix} \hat{H}_{gg}(t) & \hat{H}_{ge}(t) \\ \hat{H}_{eg}(t) & \hat{H}_{ee}(t) \end{pmatrix} \begin{pmatrix} |\Psi_g(t)\rangle \\ |\Psi_e(t)\rangle \end{pmatrix}$$

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



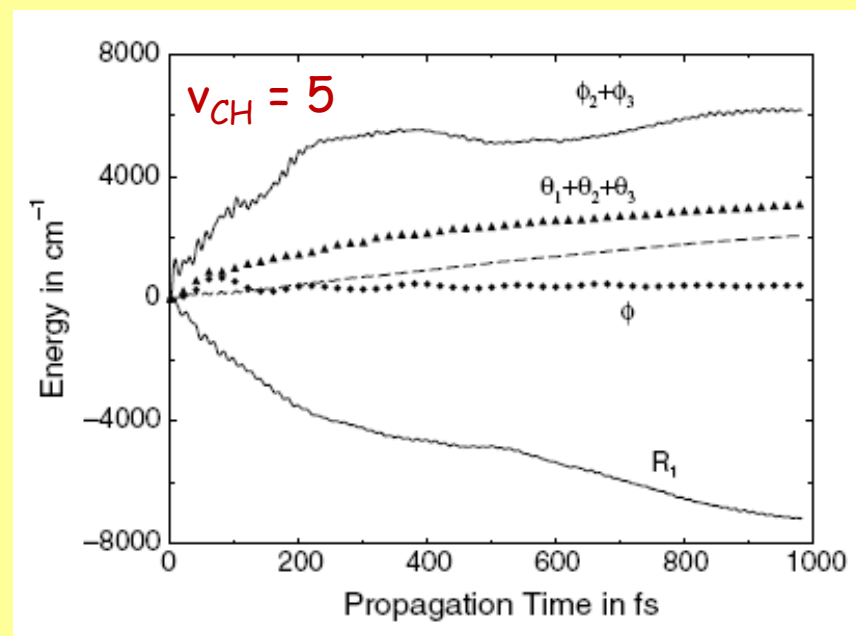
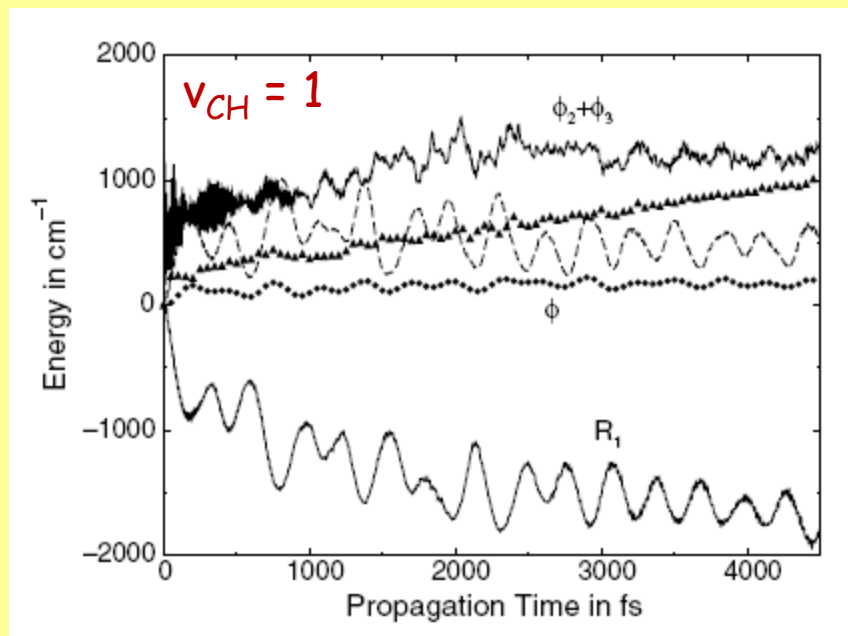
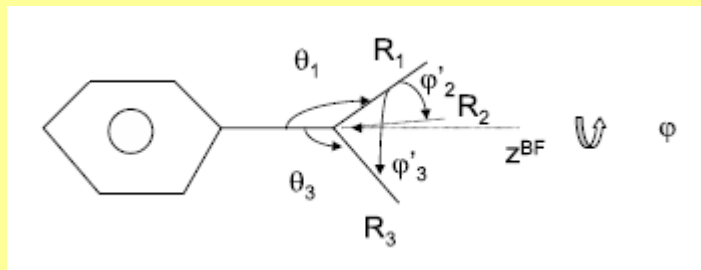
# KONTROLA HEMIJSKE REAKCIJE



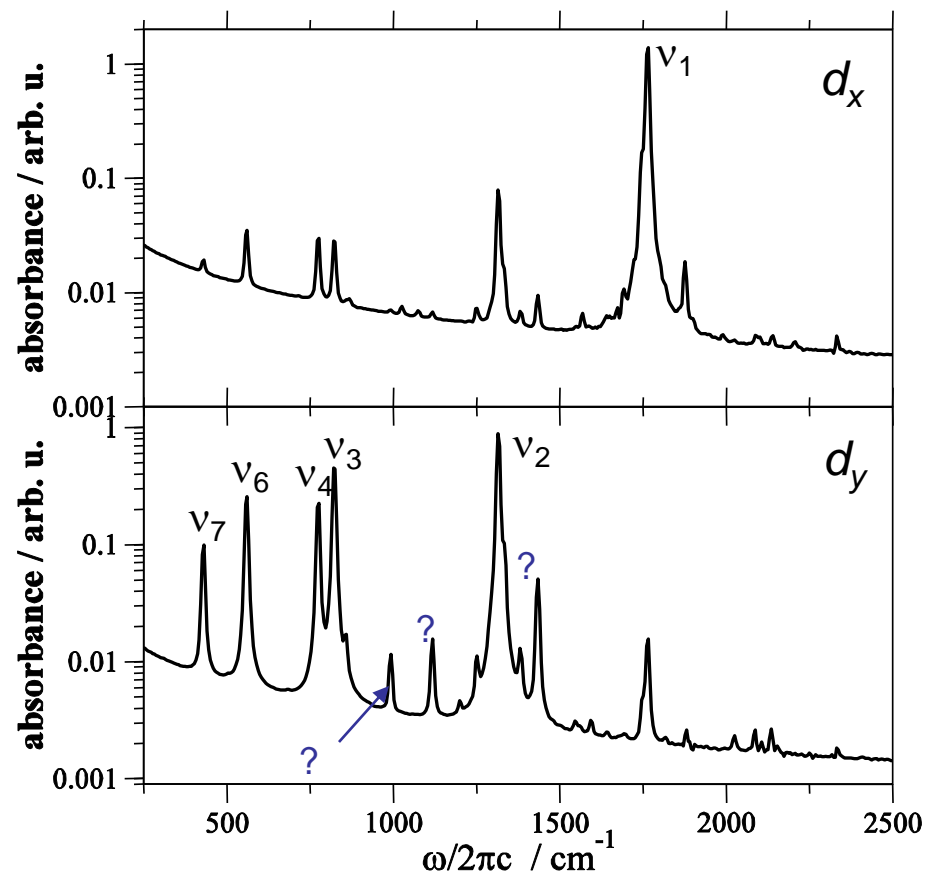
J. Michl and V. Nobačić-Koutecký, *Electronic aspects of organic Photochemistry*,  
John Wiley & Sons: New York, 1990

# INTRAMOLEKULSKA PRERASPODELA VIBRACIONE ENERGIJE

IVR - intramolecular vibrational energy redistribution



# IC SPEKTRI - ASIGNACIJA TRAKA



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

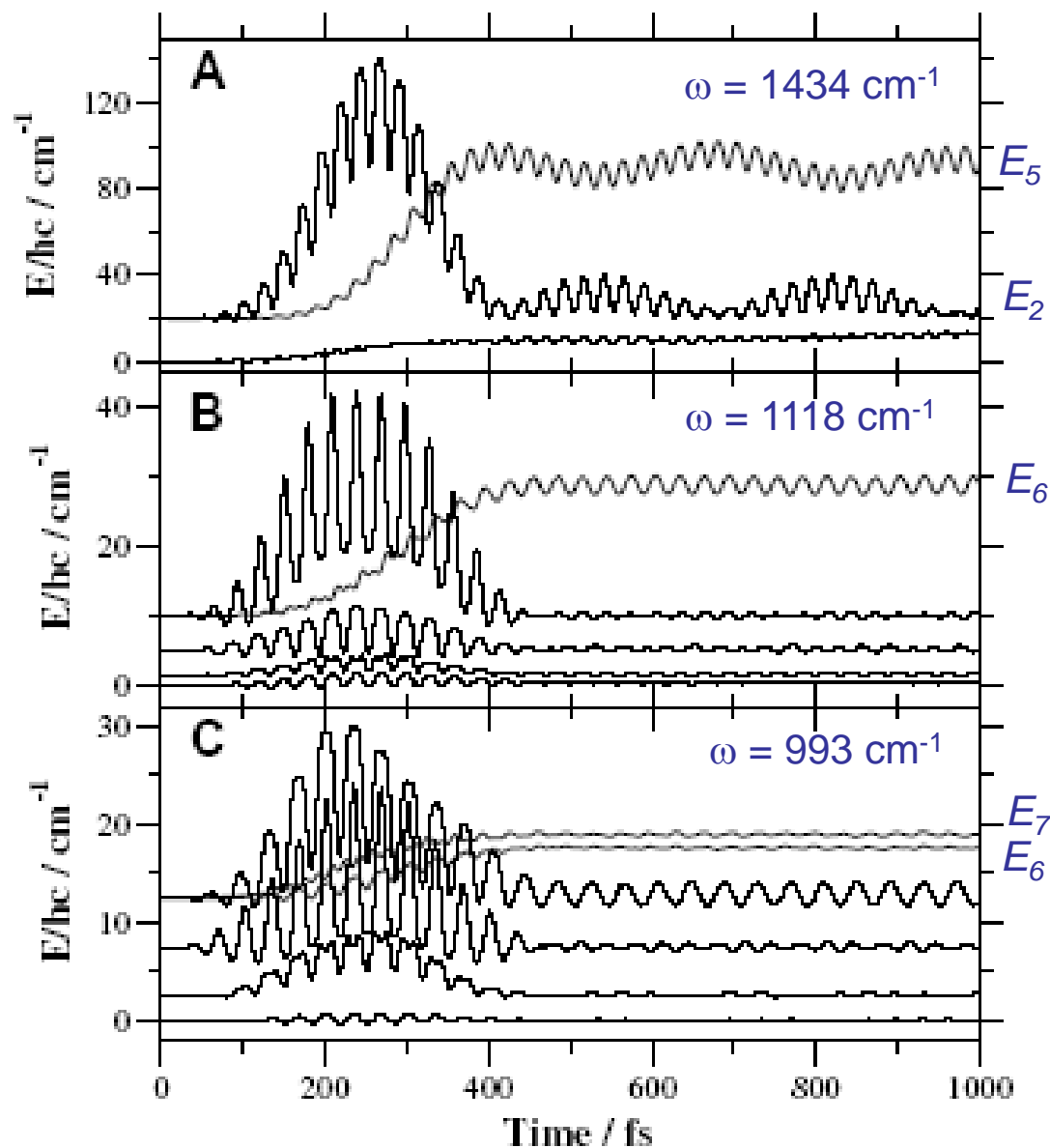
prelaz	frekvencija / $\text{cm}^{-1}$	
	izr.	eksp. <sup>b</sup>
?	1434	1424
?	1118	1119
?	993	988

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

# IC SPEKTRI - ASIGNACIJA TRAKA



$E_{1,3,4,6-9}$

$E_2$

$E_3$

$E_4$

$E_{1,5,7-9}$

$E_3$

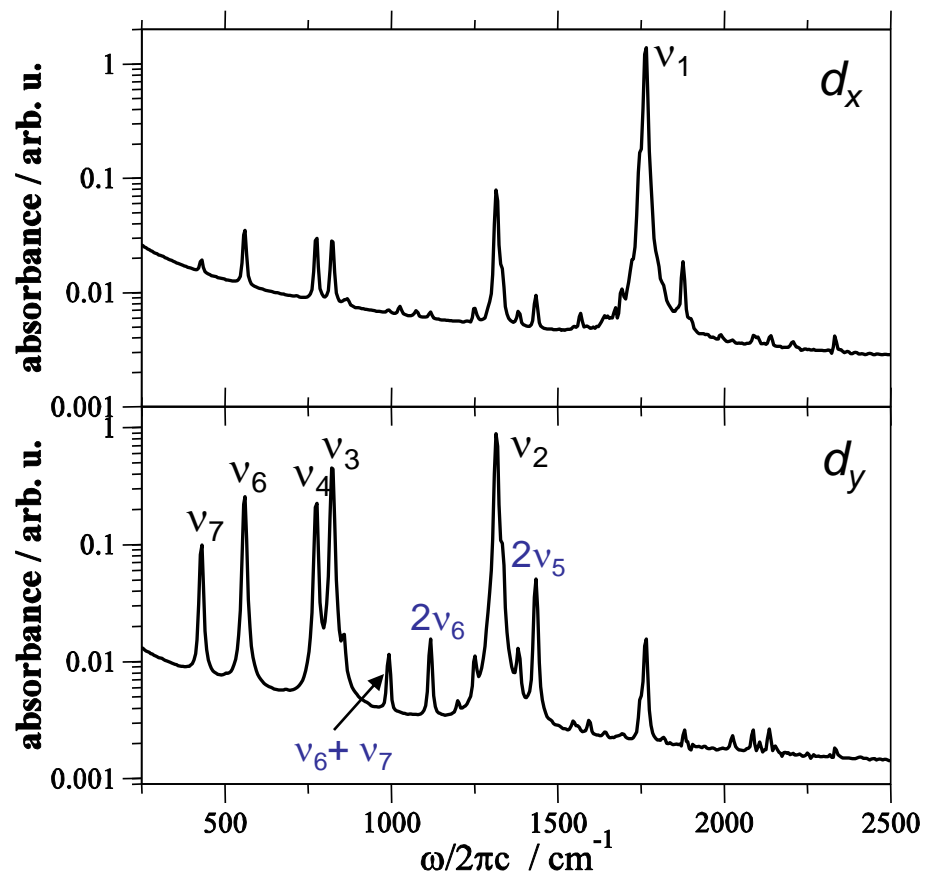
$E_2$

$E_4$

$E_{1,5,8,9}$



# IC SPEKTRI - ASIGNACIJA TRAKA



stepen slobode	frekvencija / $\text{cm}^{-1}$		
	harm.	anh.	eksp. <sup>a</sup>
$v_1$	1800	1766	1737
$v_2$	1342	1314	1293
$v_3$	828	820	809
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$v_5$	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 / $\text{cm}^{-1}$	
	izr.	eksp. <sup>b</sup>
$2v_5$	1434	1424
$2v_6$	1118	1119
$v_6 + v_7$	993	988

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

# 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)
- ...