

NOVE FIZIČKOHEMIJSKE METODE

**TEORIJSKA ANALIZA
ULTRABRZIH PROCESA**

MILENA PETKOVIĆ

- **ultrabrzi procesi**
- vremenski nezavisna Šredingerova jednačina
- vremenski zavisna Šredingerova jednačina

ULTRABRZI PROCESI

Ultrabrzim procesima nazivamo procese koji se odvijaju u opsegu od nekoliko atosekundi (10^{-18} s) do nekoliko nanosekundi (10^{-9} s).

- hemijske reakcije inicirane sudarom čestica ili povišenjem temperature
- interakcija čestica sa elektromagnetnim zračenjem: fotofizika i fotohemija

OSNOVNI ALAT TEORETIČARA

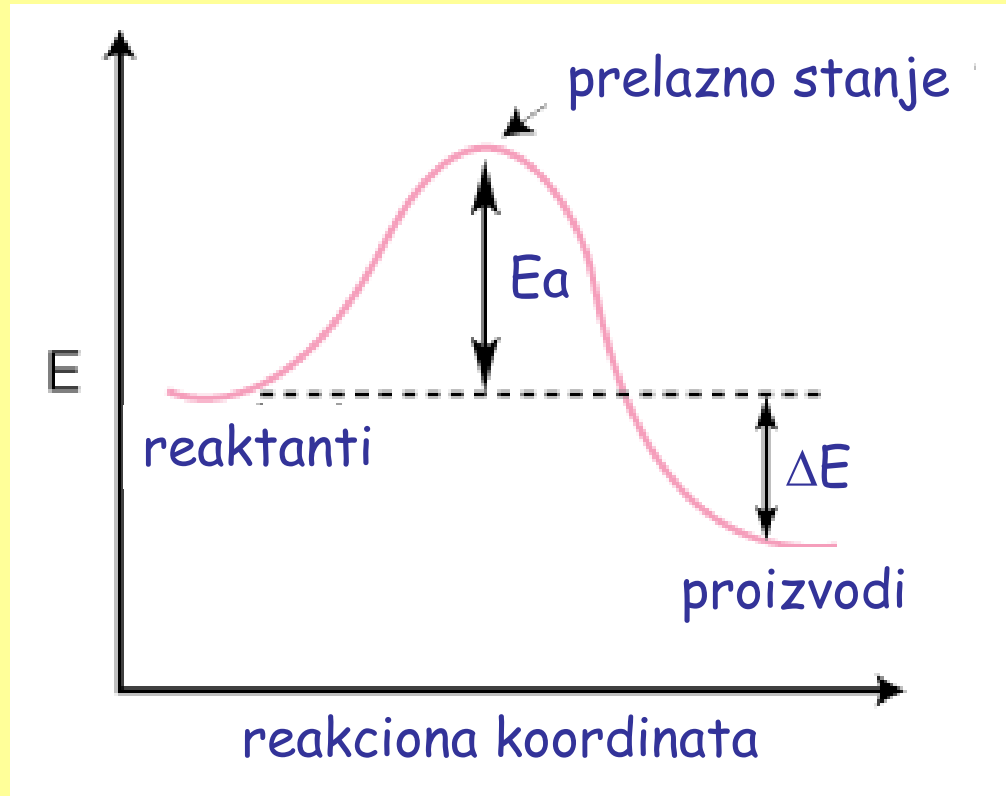
vremenski nezavisna Šredingerova jednačina

$$\hat{H}\Psi = E\Psi$$

vremenski zavisna Šredingerova jednačina

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

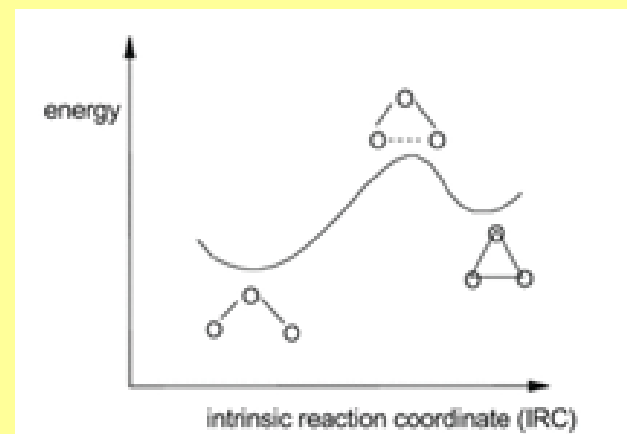
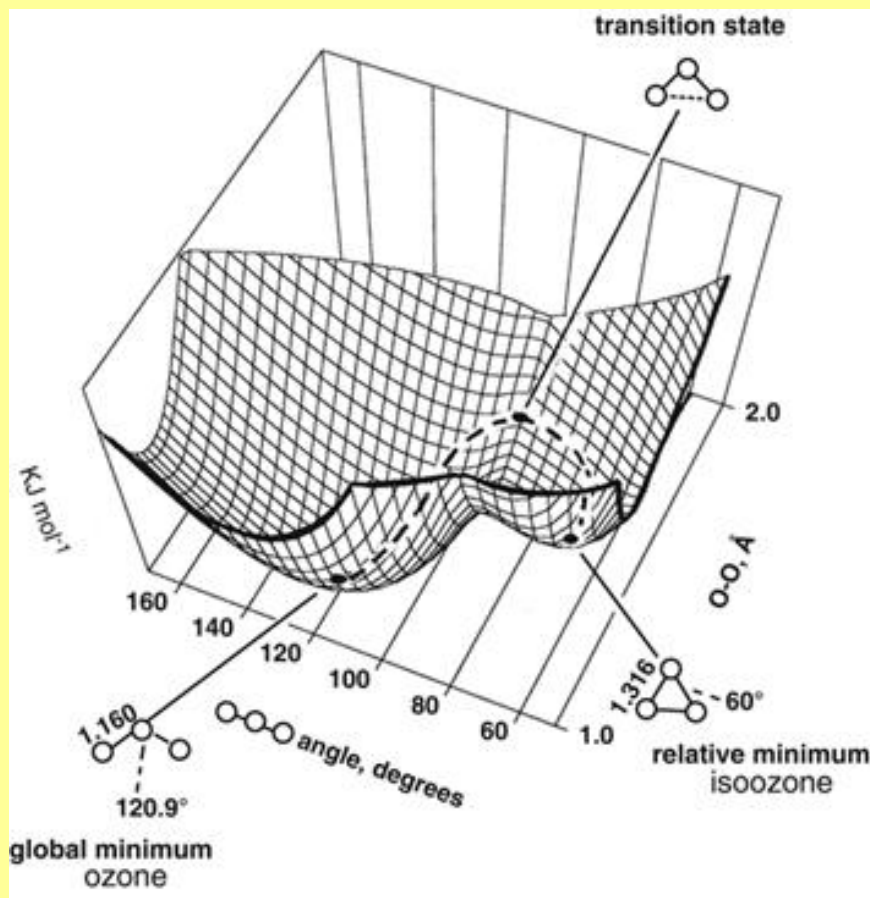
PRELAZNO STANJE



vreme života prelaznog stanja $\approx 10 - 100$ fs

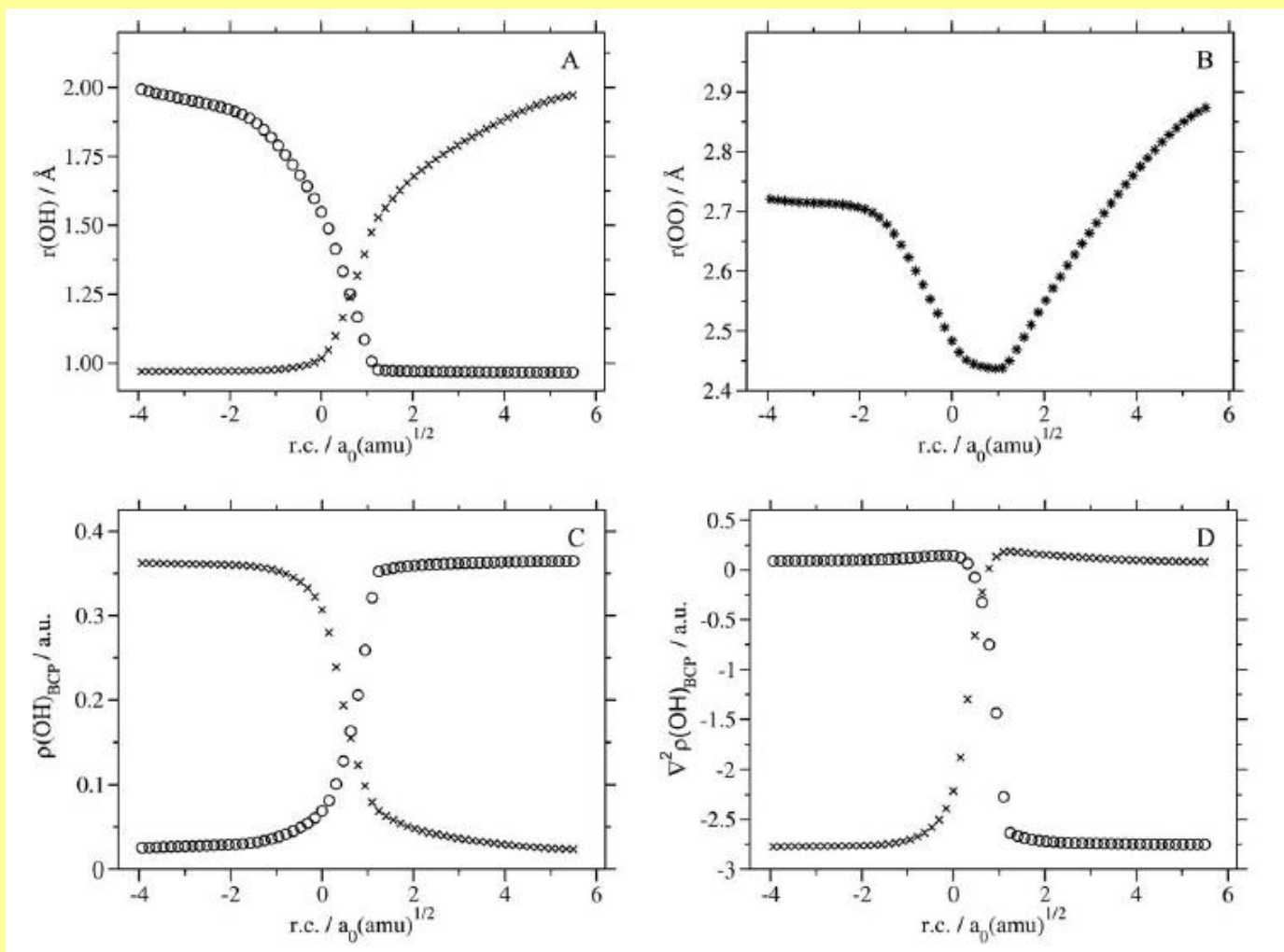
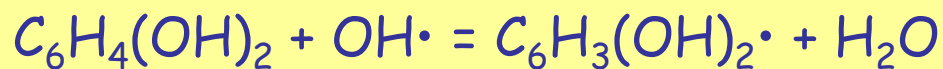
- ultrabrzi procesi
- **vremenski nezavisna Šredingerova jednačina**
- vremenski zavisna Šredingerova jednačina

PROMENE DUŽ PUTA MINIMALNE ENERGIJE

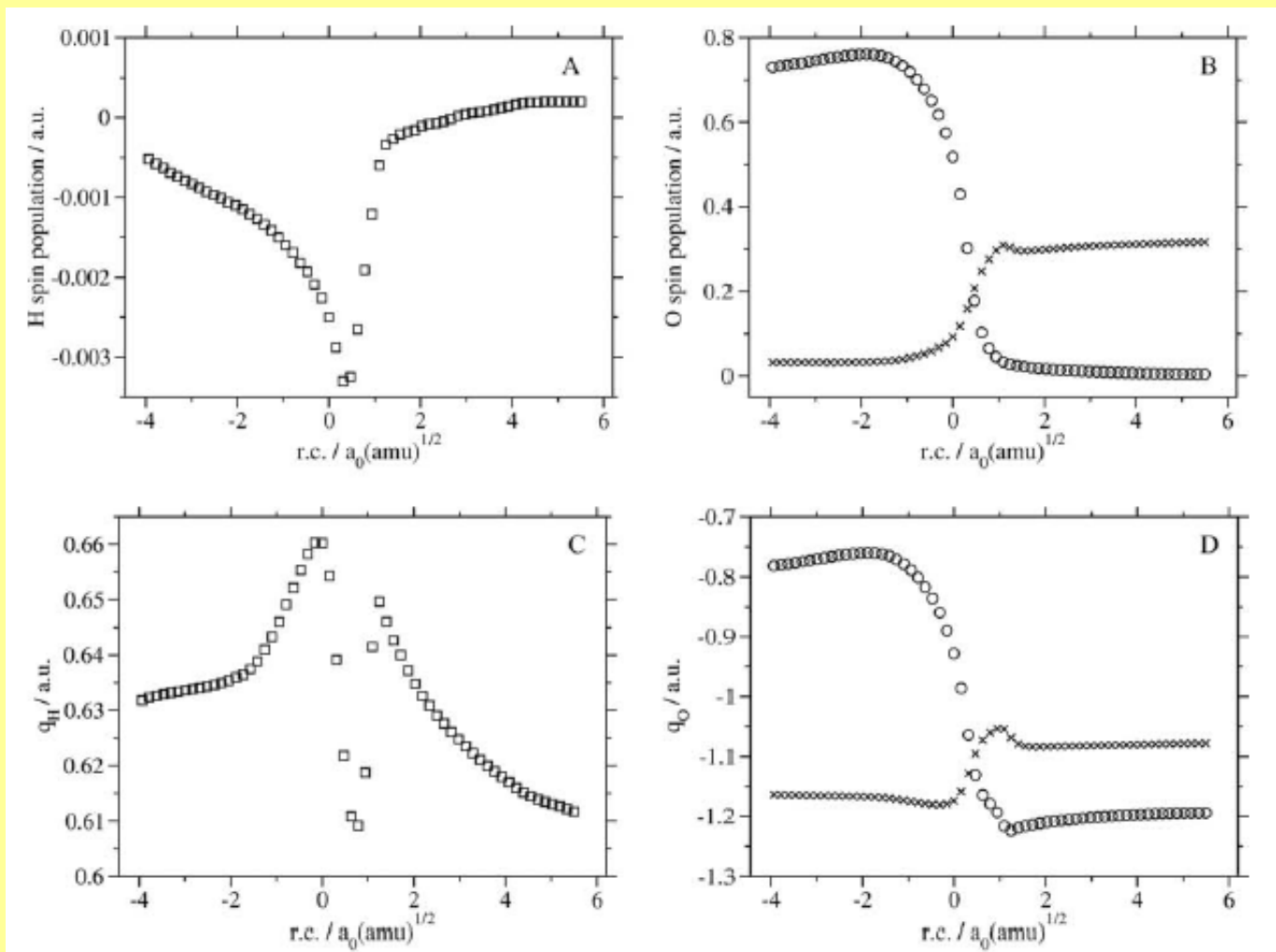
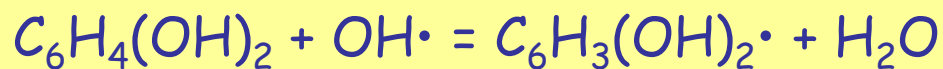


E. G. Lewars, *The concept of the Potential Energy Surface in Computational Chemistry* (Springer, Cham, 2016)

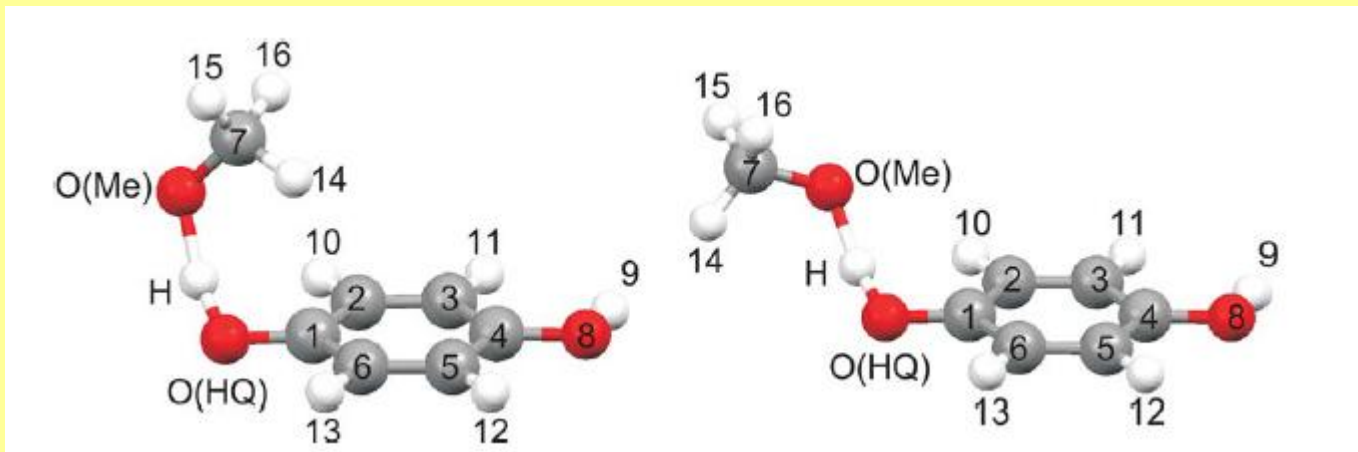
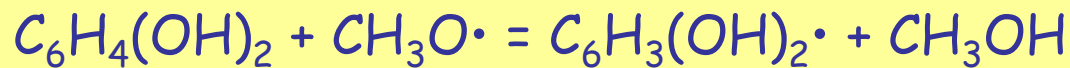
PROMENE DUŽ PUTA MIN. ENERGIJE (1)



PROMENE DUŽ PUTA MIN. ENERGIJE (2)



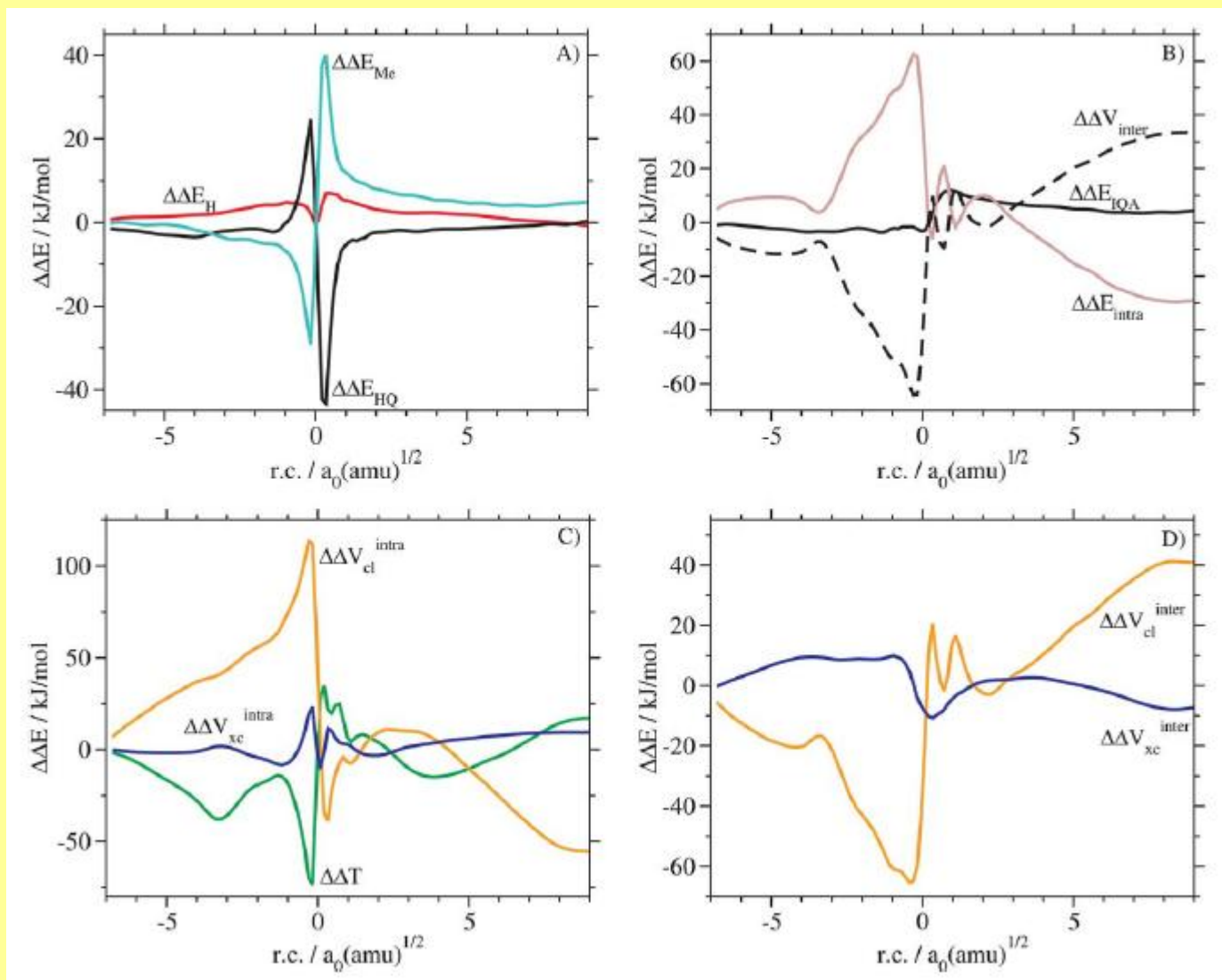
RAZLIČITI REAKCIONI PUTEVI (1)



$E_a = 23 \text{ kJ/mol}$

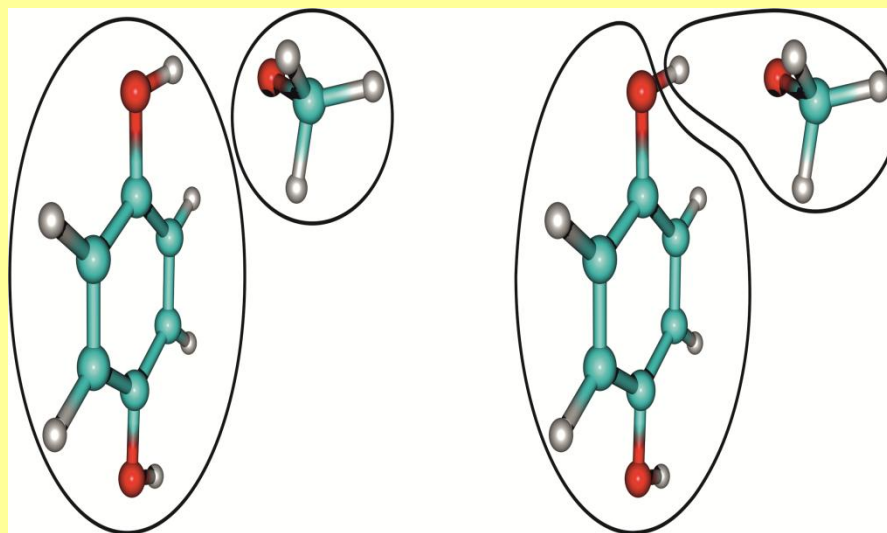
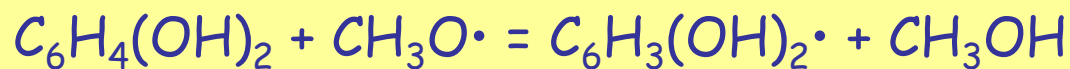
$E_a = 25 \text{ kJ/mol}$

RAZLIČITI REAKCIONI PUTEVI (2)



M. Petković, Đ. Nakarada, M. Etinski, J. Comp. Chem. 39 (2018) 1868

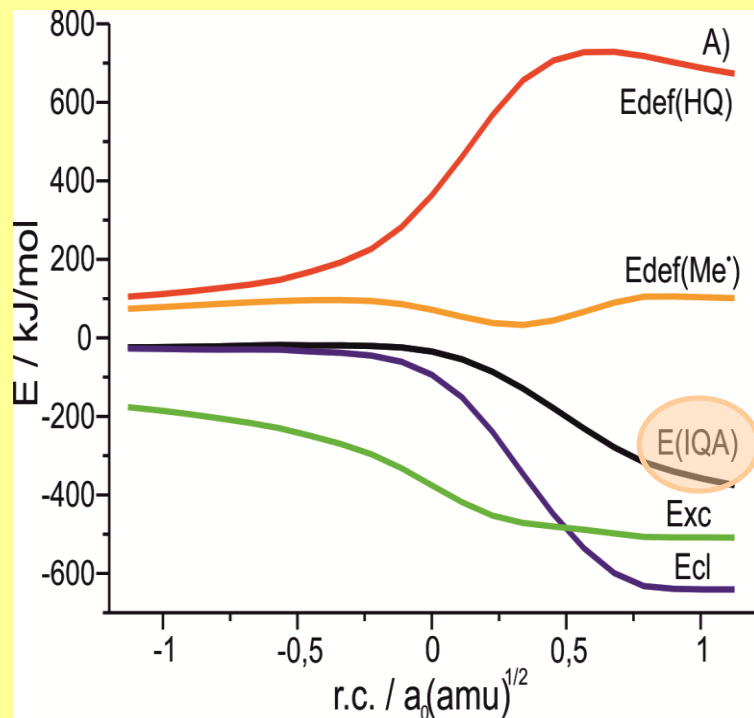
NASTANAK I KIDANJE HEM. VEZE (1)



B. Milovanović, M. Etinski, M. Petković, J. Serb. Chem. Soc. (2019) in press

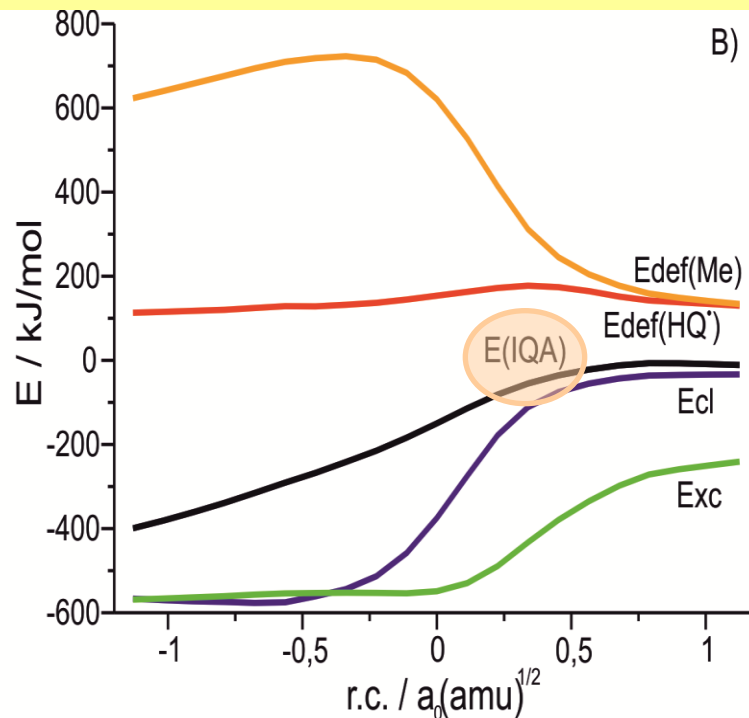
NASTANAK I KIDANJE HEM. VEZE (2)

fragmenti reaktanti:
 $C_6H_4(OH)_2 + CH_3O\cdot$



informacije o vezi
koja nastaje

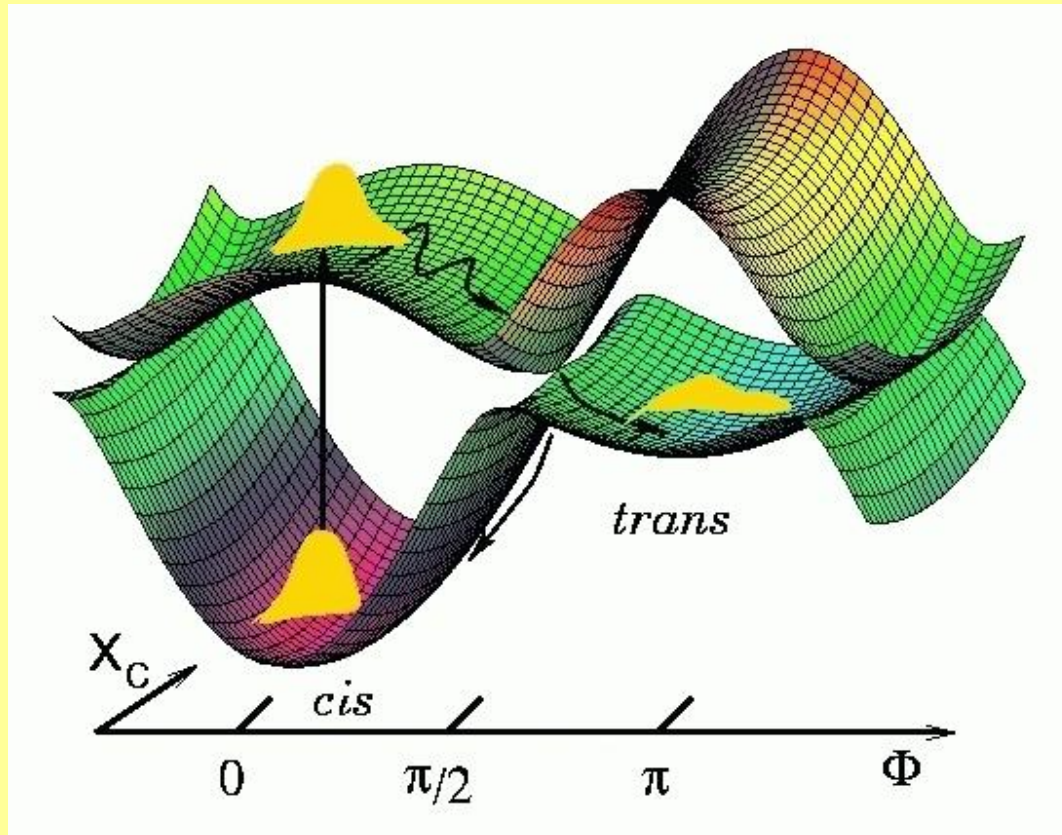
fragmenti proizvodi:
 $C_6H_3(OH)_2\cdot + CH_3OH$



informacije o vezi
koja se kida

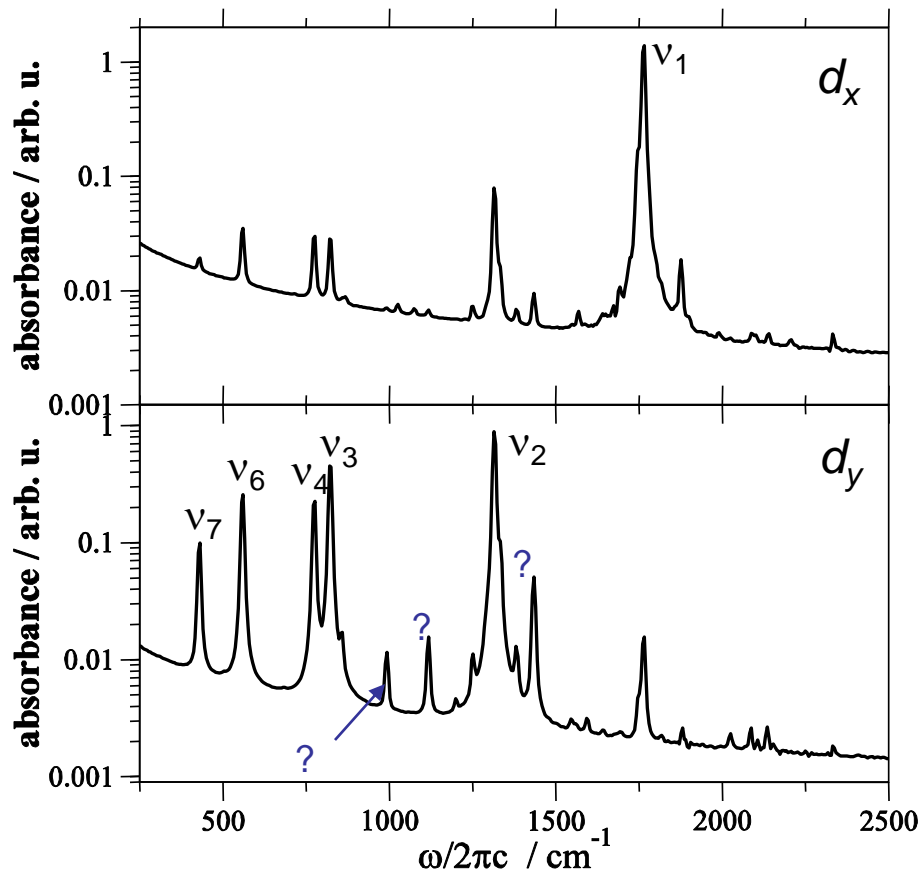
- ultrabrzi procesi
- vremenski nezavisna Šredingerova jednačina
- **vremenski zavisna Šredingerova jednačina**

ANALIZA DINAMIKE SISTEMA



G. Stock, W. Domcke, *Conical Intersections in Femtosecond time-resolved spectroscopy of the dynamics at conical intersections* (World Scientific Singapore, 2003)

IC SPEKTRI I ASIGNACIJA TRAKA (1)



stepen 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

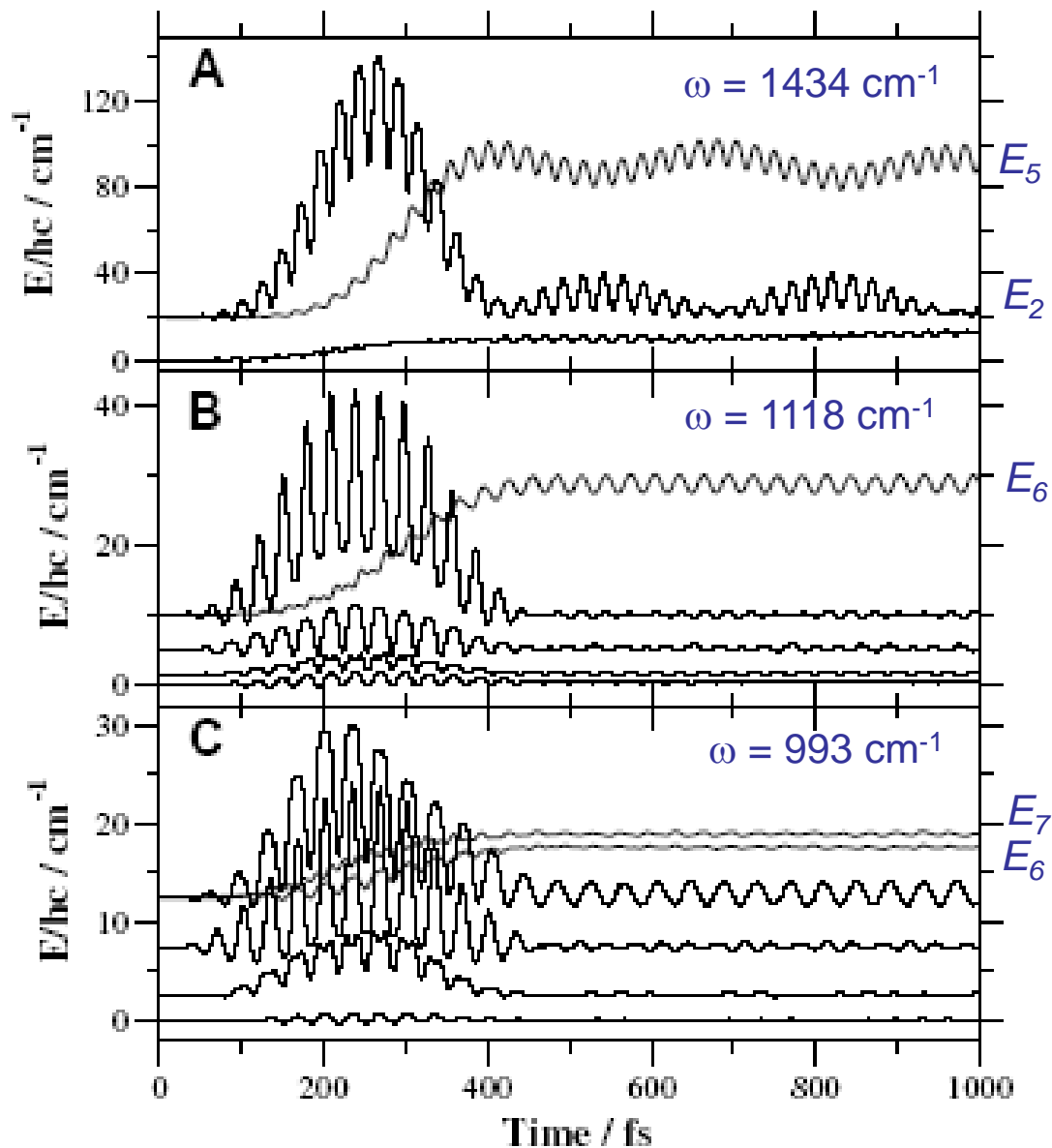
prelaz	frekvencija / cm ⁻¹	
	izr.	eksp. ^b
?	1434	1424
?	1118	1119
?	993	988

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

IC SPEKTRI I ASIGNACIJA TRAKA (2)

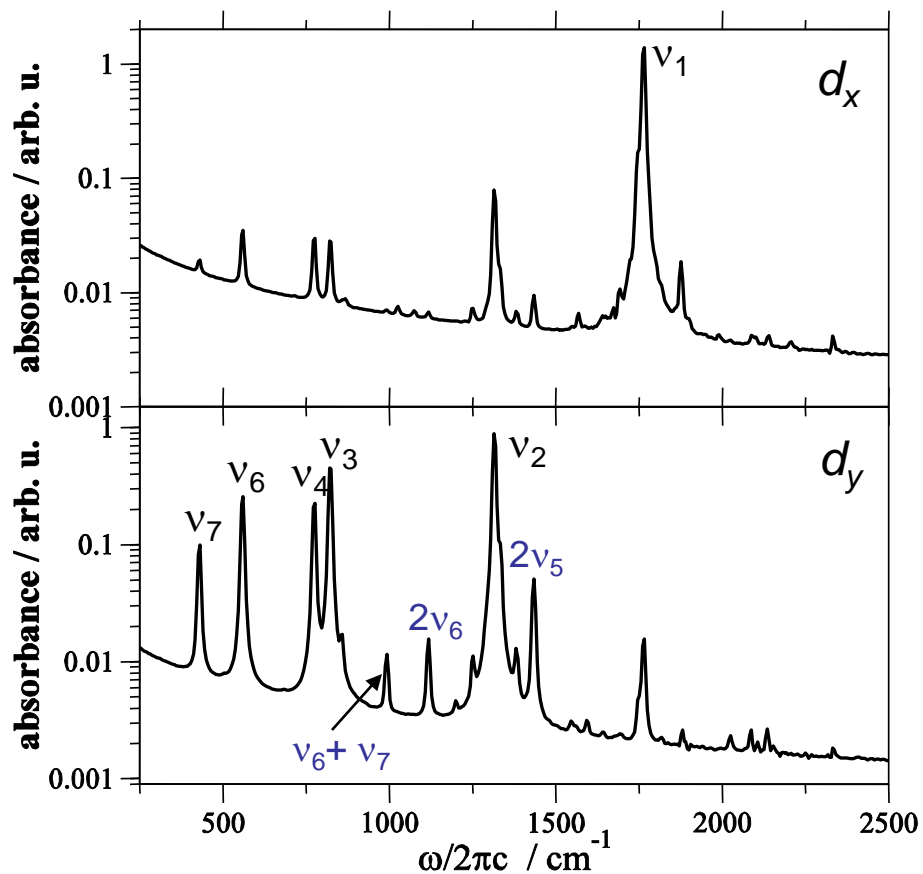


$E_{1,3,4,6-9}$

E_2 E_3
 E_4 $E_{1,5,7-9}$

E_3 E_2
 E_4 $E_{1,5,8,9}$

IC SPEKTRI I ASIGNACIJA TRAKA (3)



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
$2\nu_5$	1434	1424
$2\nu_6$	1118	1119
$\nu_6 + \nu_7$	993	988

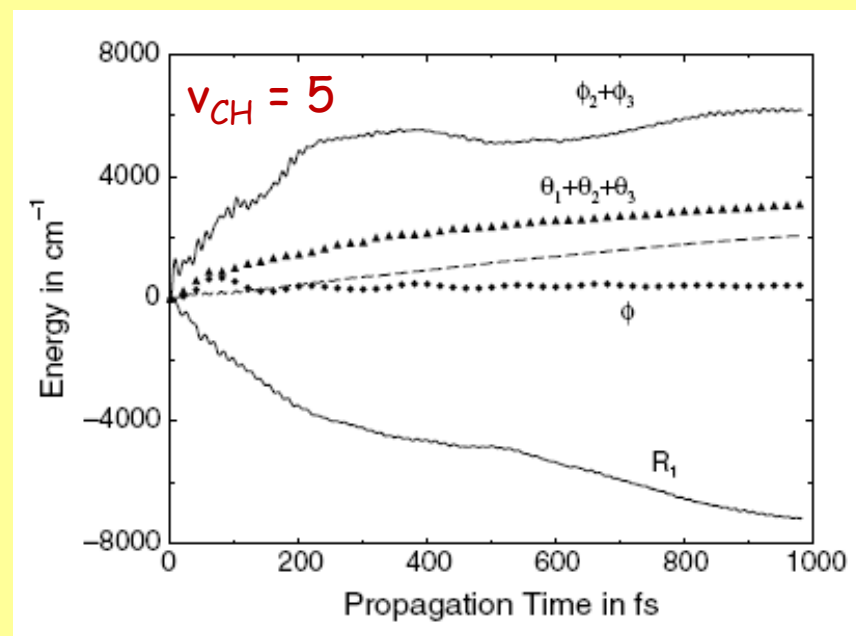
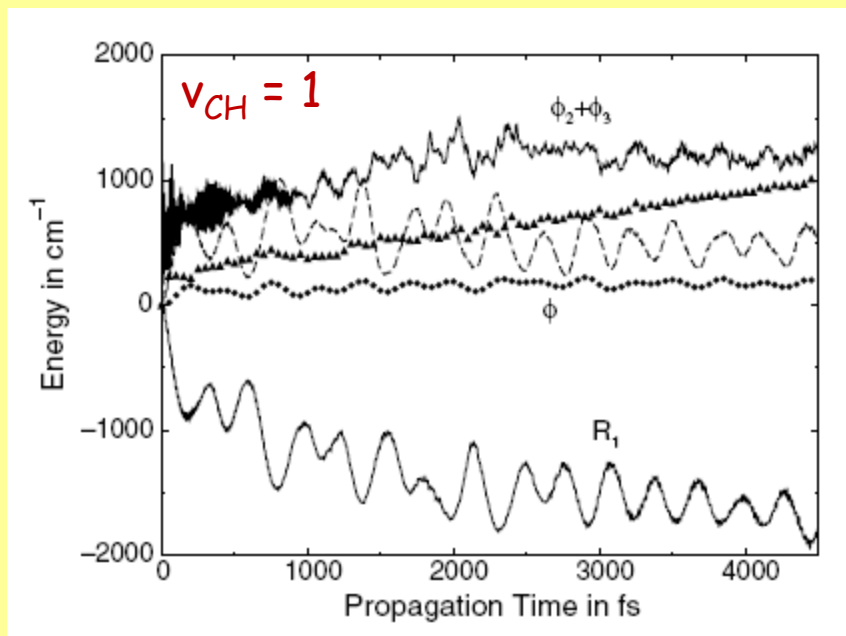
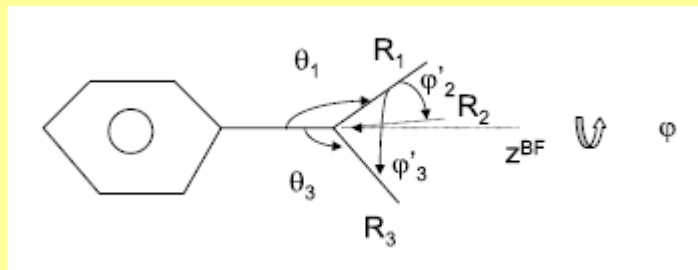
M. Petković, Chem. Phys. 331 (2007) 438

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

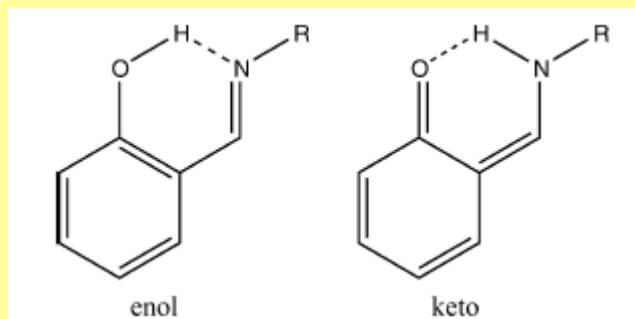
^b Miller et al. Spec. Acta 23A (1967) 223

INTRAMOLEKULSKA PRERASPODELA VIBRACIONE ENERGIJE

IVR - intramolecular vibrational energy redistribution

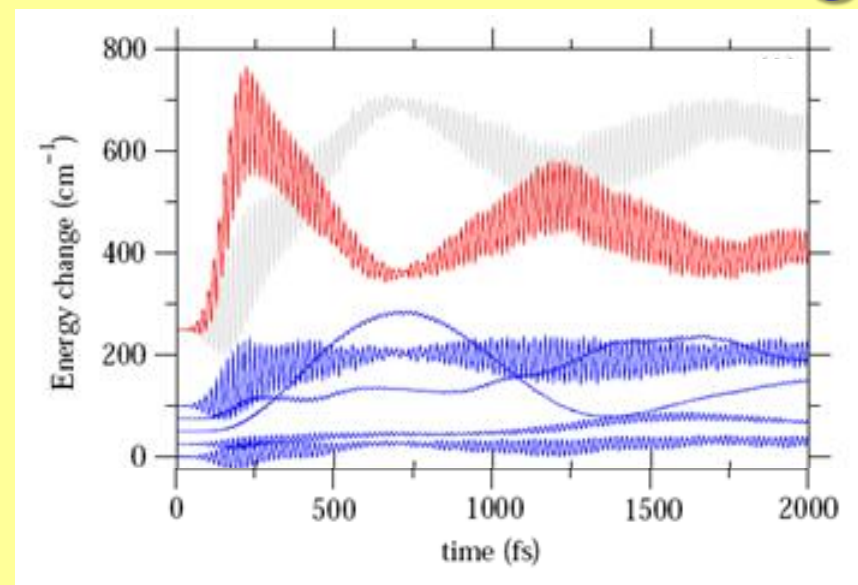
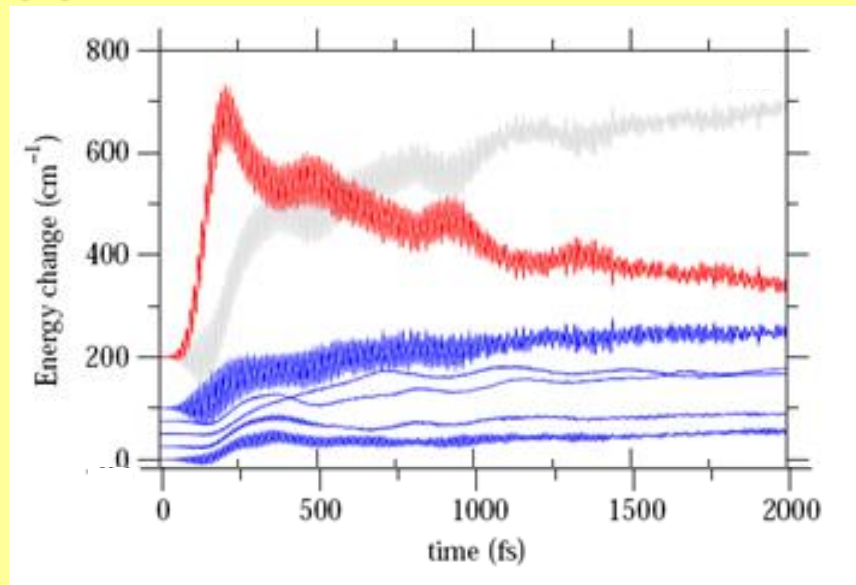


KONTROLA HEMIJSKE REAKCIJE I INTRAMOLEKULSKA PRERASPODELA VIBRACIONE ENERGIJE

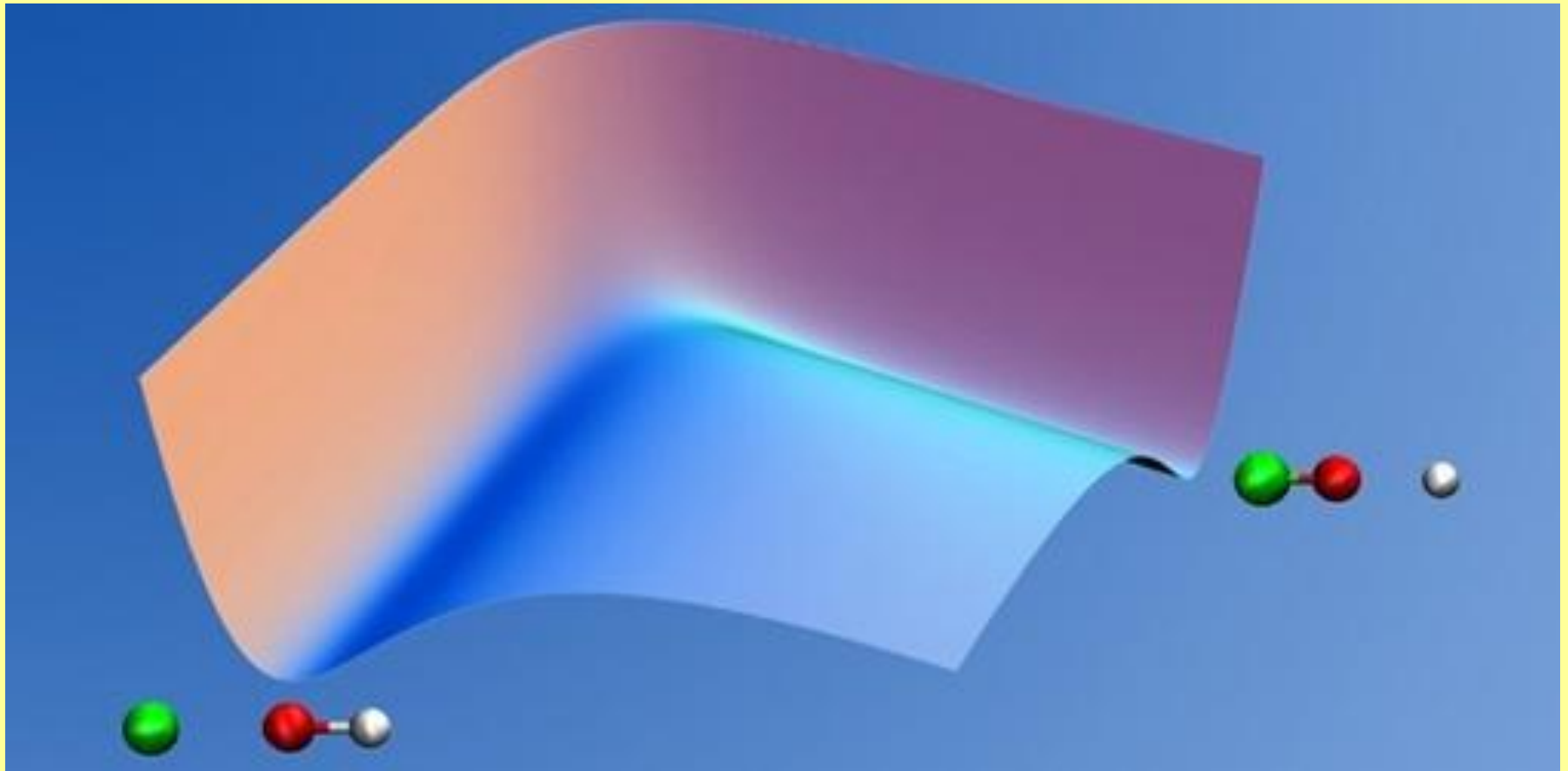


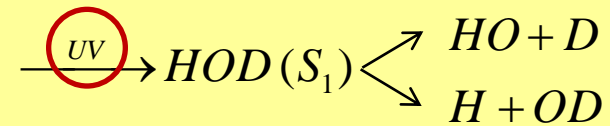
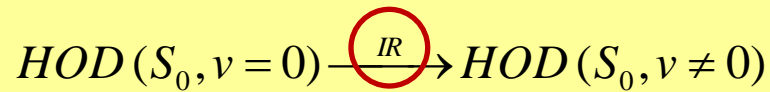
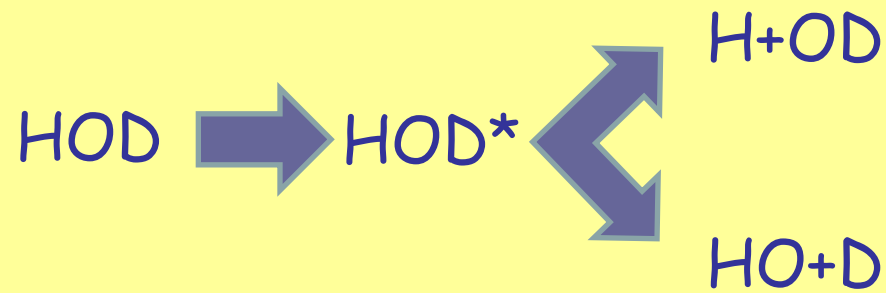
H

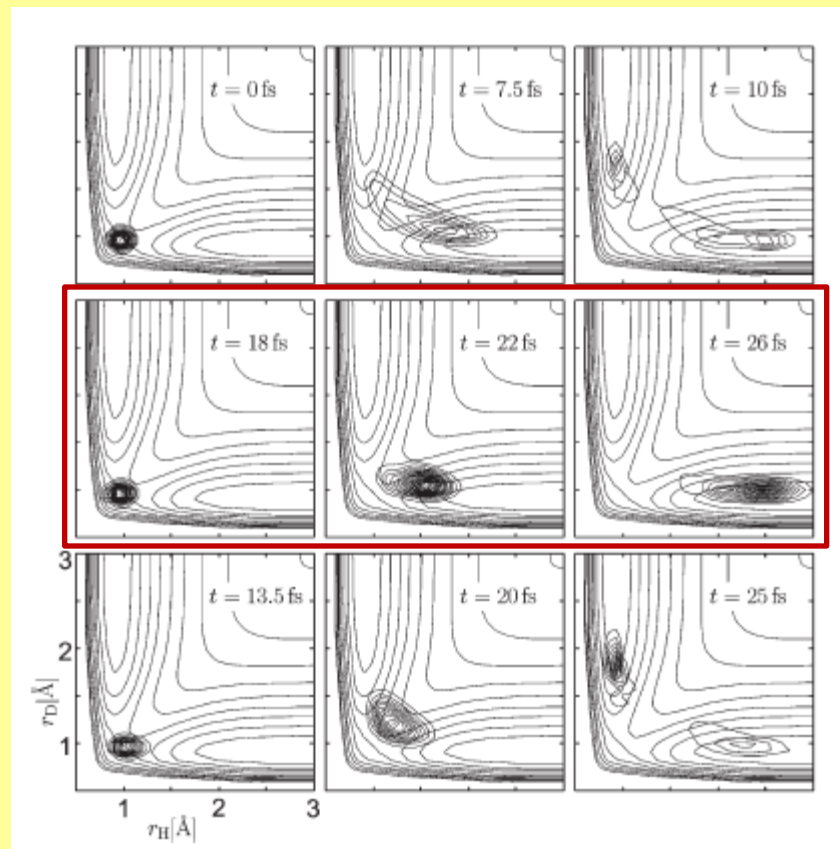
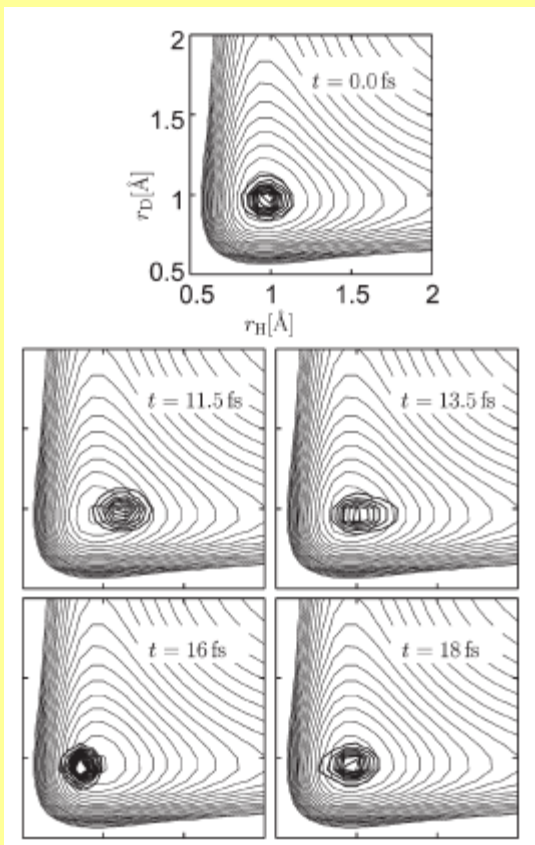
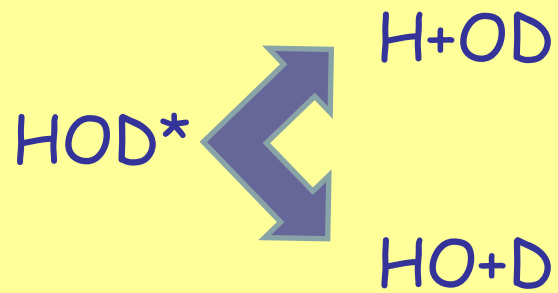
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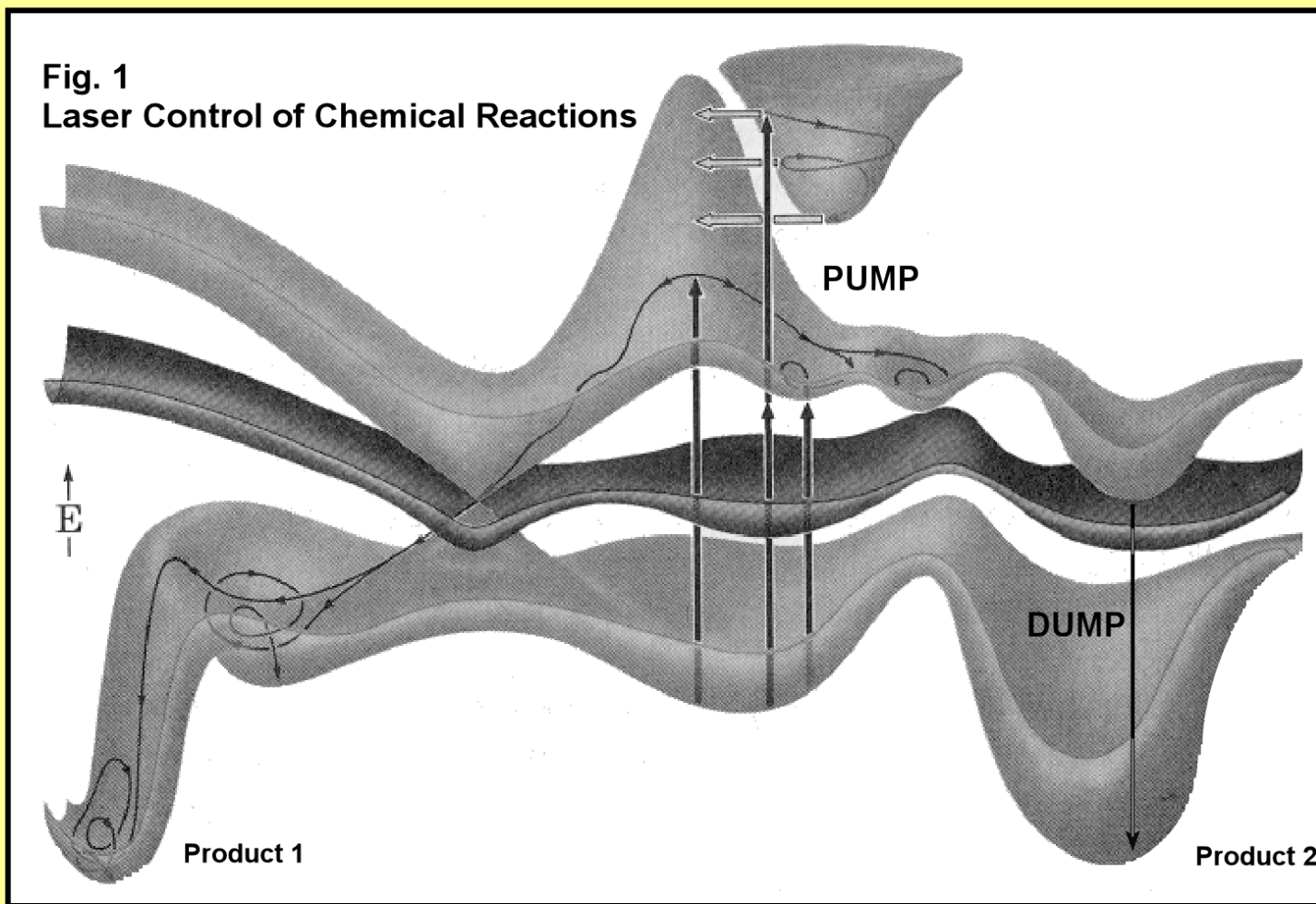
KONTROLA HEMIJSKE REAKCIJE







KONTROLA HEMIJSKE REAKCIJE



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

REZIME

- ultrabrzi procesi (atosekundna - nanosekundna skala)
- vremenski nezavisna Šredingerova jednačina
(analiza svojstava sistema duž puta minimalne energije,
asignacija spektralnih traka)
- vremenski zavisna Šredingerova jednačina
(vremenska evolucija sistema, kontrola hemijske
reakcije)