

PRIRODOSLOVNO-MATEMATIČKI FAKULTET

Kemijski odsjek



Sveučilište u Zagrebu

MODELIRANJE KINETIČKE SELEKTIVNOSTI FOTOINDUCIRANE REAKCIJE

Manuel Martinović

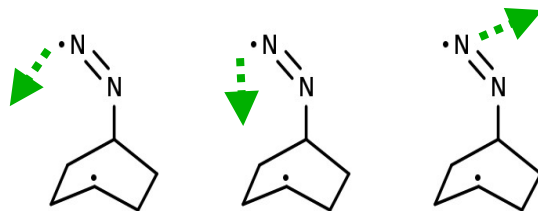
prema članku:

Feng Z, Guo W, Kong WY, Chen D, Wang S, Tantillo DJ. Analogies between photochemical reactions and ground-state post-transition-state bifurcations shed light on dynamical origins of selectivity. *Nat Chem.* **16**, 615–623 (2024).

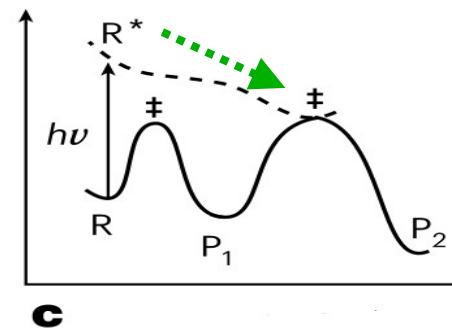
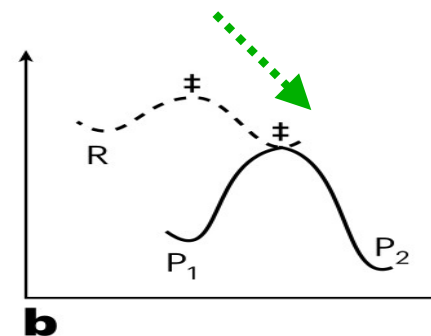
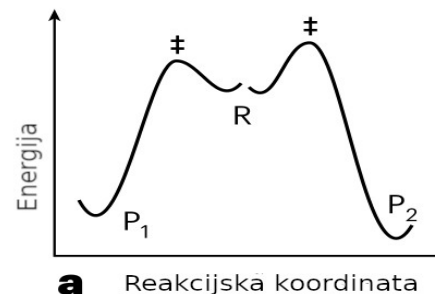
1. UVOD

- Reakcijske plohe potencijalne energije (PPE) i prijelazna stanja (a)
- Ambimodalna prijelazna stanja (APS) – složenost prijelaznih stanja “van idealnog” (kompeticija prijelaznih stanja) (b)

→ Selektivnost uvjetovana **nestatističkim dinamičkim efektima**

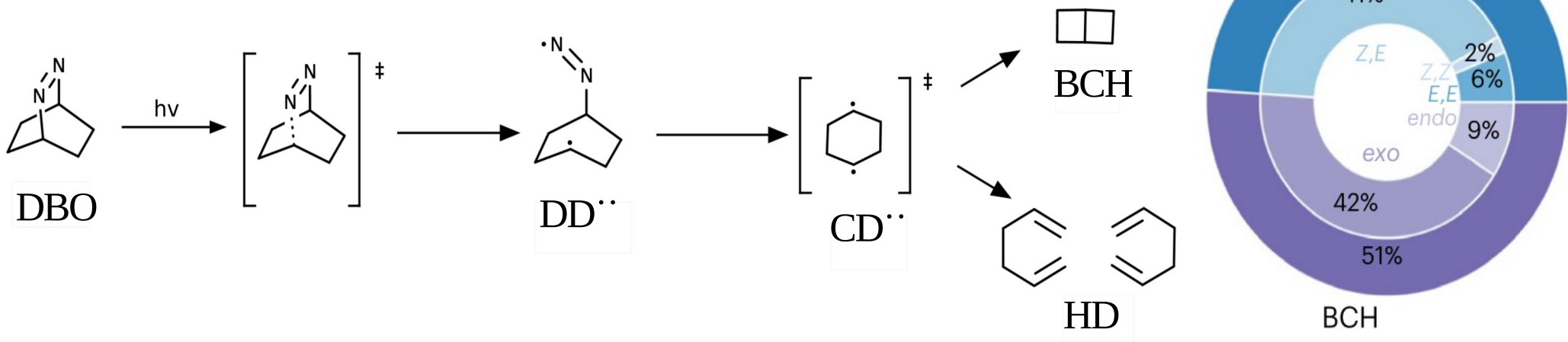


- Sličnost sa fotokemijskom reakcijom sa APS (c)



1. UVOD

- Fotoinducirana reakcija sa APS : deazetizacija 2,3-diazobiciklo[2.2.2]okt-2-ena



- 2,3-diazobiciklo[2.2.2]okt-2-en(**DBO**) \rightarrow diazini diradikal(**DD^{••}**) \rightarrow 1-4-cikloheksandiil radikal(**CD^{••}**)
- [2+2]cikloadicija = bicikloheksan (**BCH**) [3,3]pregradnja = heksadien (**HD**)

2. METODE : 2.1. ELEKTRONSKA STRUKTURA

- Elektronski Hamiltonijan (vremenski neovisna Schrödingerova jednačba + Born-Oppenheimerova aproksimacija)

$$\hat{H}_e \psi_e(\mathbf{r}_{i,j \dots \rightarrow n}; \mathbf{R}_{A,B \dots \rightarrow N}) = \sum_A^N \sum_i^n E_e(\mathbf{R}_A) \psi_e(\mathbf{r}_i; \mathbf{R}_A)$$

$$\left[- \sum_i^n \frac{1}{2} \nabla_i^2 + \sum_{i,A=1} \frac{Z_A}{r_{iA}} + \sum_{A,B=1}^N \frac{Z_A Z_B}{R_{AB}} + \sum_{i,j=1}^n \frac{1}{r_{ij}} \right] \psi_e(\mathbf{r}_i; \mathbf{R}_A)$$

- Statička i dinamička elektronska korelacija

- Slaterova determinanta

$$\Psi_{SD}(\mathbf{r}_i \dots \mathbf{r}_n) = \frac{1}{\sqrt{N_n!}} \begin{vmatrix} \psi_{\uparrow}(\mathbf{r}_i) & \psi_{\downarrow}(\mathbf{r}_i) & \cdots & \psi_{\downarrow}(\mathbf{r}_i) \\ \psi_{\uparrow}(\mathbf{r}_j) & \psi_{\downarrow}(\mathbf{r}_j) & \cdots & \psi_{\downarrow}(\mathbf{r}_j) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{\uparrow}(\mathbf{r}_n) & \psi_{\downarrow}(\mathbf{r}_n) & \cdots & \psi_{\downarrow}(\mathbf{r}_n) \end{vmatrix} = \det \frac{1}{\sqrt{N_n!}} |\psi_i \dots \psi_n|$$

2. METODE : 2.1. ELEKTRONSKA STRUKTURA

- **Hartree-Fock (HF):**

$$\left[- \sum_i^n \frac{1}{2m_i} \nabla_i^2 + \sum_{i,A=1} \frac{Z_A}{r_{iA}} + \sum_{A,B=1}^N \frac{Z_A Z_B}{R_{AB}} + \frac{1}{2} \sum_{i,j=1}^n (\hat{j}_{i,j} - \hat{k}_{i,j}) \right] \psi_{HF,i}(\mathbf{r}_i; \mathbf{R}_A)$$

- Elektronska korelacija:

- **Statička:** 1 Slaterova determinanta (nema korelacije među više mol.el.struktura)
- **Dinamička:** J+K: uprosječeno Coulombovo polje (svi elektroni međudjeluju jednako)
- **Post Hartree-Fock metode**

Sustavno bolji opisi statičke i dinamičke e. korelacije

$$\Psi_{Multikonfiguracijski-sustav} = \sum_{\alpha} c_{\alpha} \Psi_{SD}$$

2. METODE : 2.1. ELEKTRONSKA STRUKTURA

- **Teorija funkcionala elektronske gustoće (DFT) :**
- opis sustava sa \mathbf{g} (3 · prostorna rezolucija) umjesto sa \mathbf{r}_i (3 · n)
- Hohenberg-Kohn teoremi:
 - Totalna energija višeelektronskog sustava u osnovnom stanju, funkcional je elektronske gustoće tog sustava, na kojeg djeluje potencijal

$$\rho(\mathbf{g}) = N \int |\Psi(\mathbf{r}_1 \dots \mathbf{r}_n)|^2 d\mathbf{r}_1 \dots d\mathbf{r}_n$$

$$E_{e,0}[\rho] = \overbrace{E_{kin}[\rho] + V_{eff_{i \rightarrow n}}[\rho]}^{F_{HK}[\rho]} + \overbrace{V_{ext}[\rho]}^{V_{ext}[\rho] = \int \rho(\mathbf{g}) V_{ext}(\mathbf{g}) d\mathbf{g}} + V_{eff_{A \rightarrow N}}[\rho]$$

2. METODE : 2.1. ELEKTRONSKA STRUKTURA

- **Teorija funkcionala elektronske gustoće (DFT):**
- Kohn-Sham formalizam DFT-a:
 - Dijelovi HF formalizma : Slaterova determinanta, modelni elektronski Hamiltonijan → orbitale i svojstva kao u valno-funkcijskim metodama

$$\left[- \sum_i^n \frac{1}{2m_i} \nabla_i^2 + v_{EFF}(\mathbf{g}) \right] \psi_{ksm,i}(\rho(\mathbf{g}), \mathbf{r}_i; \mathbf{R}_A)$$

$$v_{EFF}(\mathbf{g}) = \int \rho(\mathbf{g}) V_{ext}(\mathbf{g}) + \frac{dJ[\rho]}{d\rho(\mathbf{g})} + \frac{dE_{xc}[\rho]}{d\rho(\mathbf{g})}$$

- Elektronska korelacija:

- **Statička** i **dinamička** : E_{XC} funkcional

$$E_{XC}[\rho] = E_{kin}[\rho] - \hat{H}_{ksm}[\rho] - J[\rho] + V_{eff_{i \rightarrow n}}[\rho]$$

2. METODE : 2.1. ELEKTRONSKA STRUKTURA

- Teorija Multikonfiguracijskog funkcionala gustoće elektronskog para (MC-PDFT):

$$\Pi(\mathbf{g}_i, \mathbf{g}_j) = \binom{n}{2} \int |\Psi(\mathbf{r}_i \dots \mathbf{r}_n)|^2 d\uparrow_i \dots d\downarrow_n d\mathbf{g}_{j+1} \dots d\mathbf{g}_n$$

$$\left[- \sum_i^n \frac{1}{2m_i} \nabla_i^2 + \sum_{i,A=1} \frac{Z_A}{r_{iA}} + \sum_{A,B=1}^N \frac{Z_A Z_B}{R_{AB}} \right] \psi_{MC,i}(\mathbf{r}_i; \mathbf{R}_A)$$

$$+ [J[\rho] + E_{ot}[\rho, \Pi]] \psi_{MC-PDFT,i}(\rho(\mathbf{g}), \Pi(\mathbf{g}_i, \mathbf{g}_j), \mathbf{r}_i; \mathbf{R}_A)$$

- Elektronska korelacija:

- **Statička** : Multikonfiguracijska valna funkcija ($\sum_{\alpha} c_{\alpha} \Psi_{SD}$; aktivni prostor orbitala)
- **Dinamička** : ... na kojoj se računa dinamička korelacija iz elektronske gustoće (tj .gustoće elektronskog para)

2. METODE : 2.2. NEADIJABATSKA MOLEKULARNA DINAMIKA

(NAMD)

- Born-Huang formalizam vremenski-ovisne Schr.j.

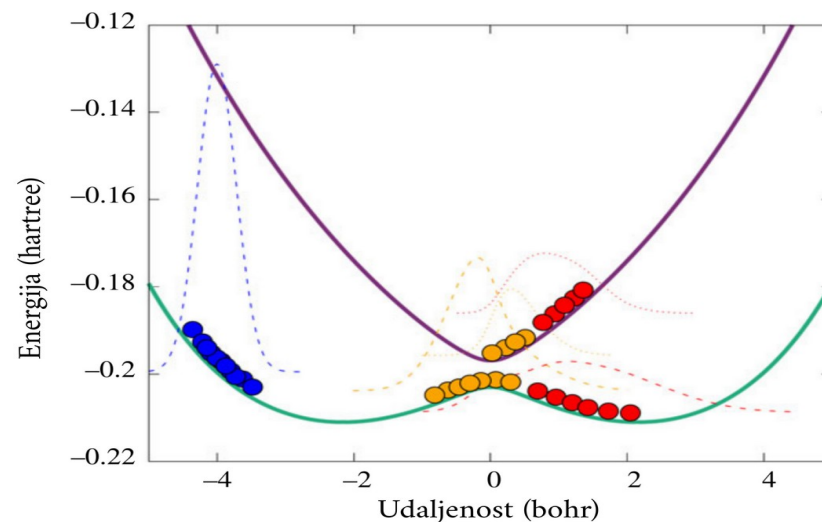
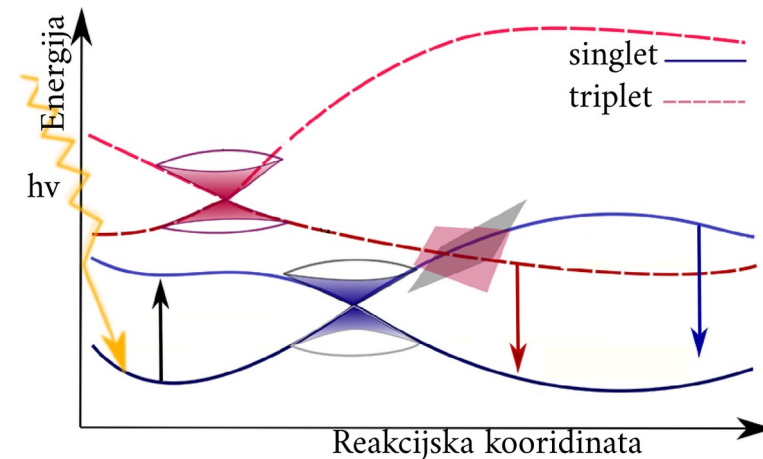
$$\Psi(\mathbf{r}_i; \mathbf{R}_A, t) = \sum_{s0} \chi_e^{(s0)}(\mathbf{R}_A, t) \psi_e^{(s0)}(\mathbf{r}_i; \mathbf{R}_A)$$

- Doprinosi jezgra i elektrona vremenski ovisnoj elektronskoj strukturi

➔ NAMD, tip: preskakanje ploha (eng. Surface hopping)

- klasične jezgre na PPE koju čini elektronska struktura

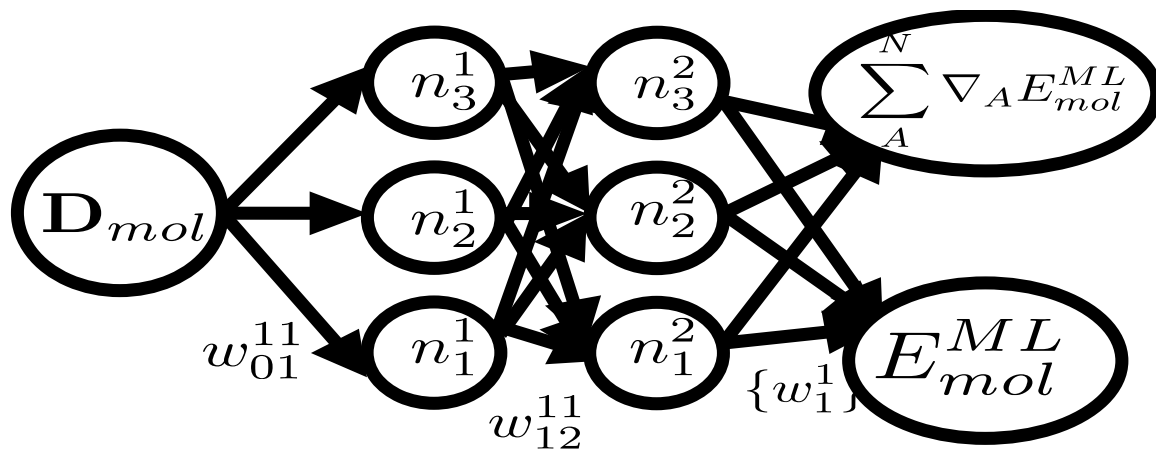
$$\mathbf{F}^{traj.}(t) = -\nabla_{A^{traj.}(t)} E_e^{(s^*)}(\mathbf{R}_A^{traj.}(t))$$



2. METODE : 2.3. STROJNO UČENJE ZA NAMD

- Model Neuralne mreže :

- interpoliranje svojstva iz ulaznih podataka sustavom čvorova(n) i koeficijenata(w),
prateći minimizaciju funkcije gubitka (L)



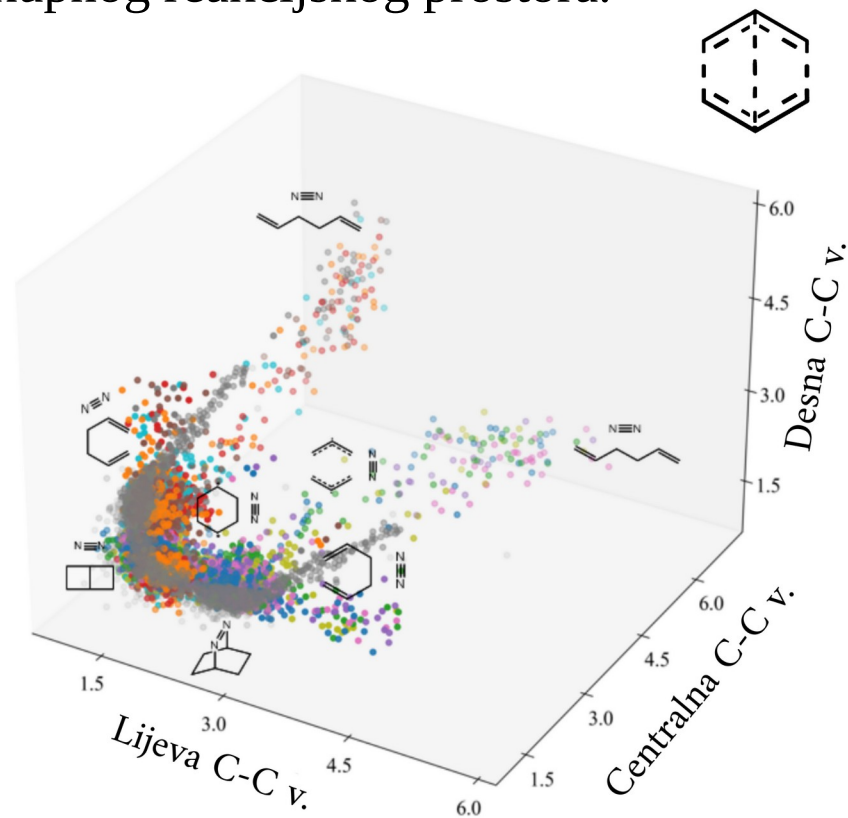
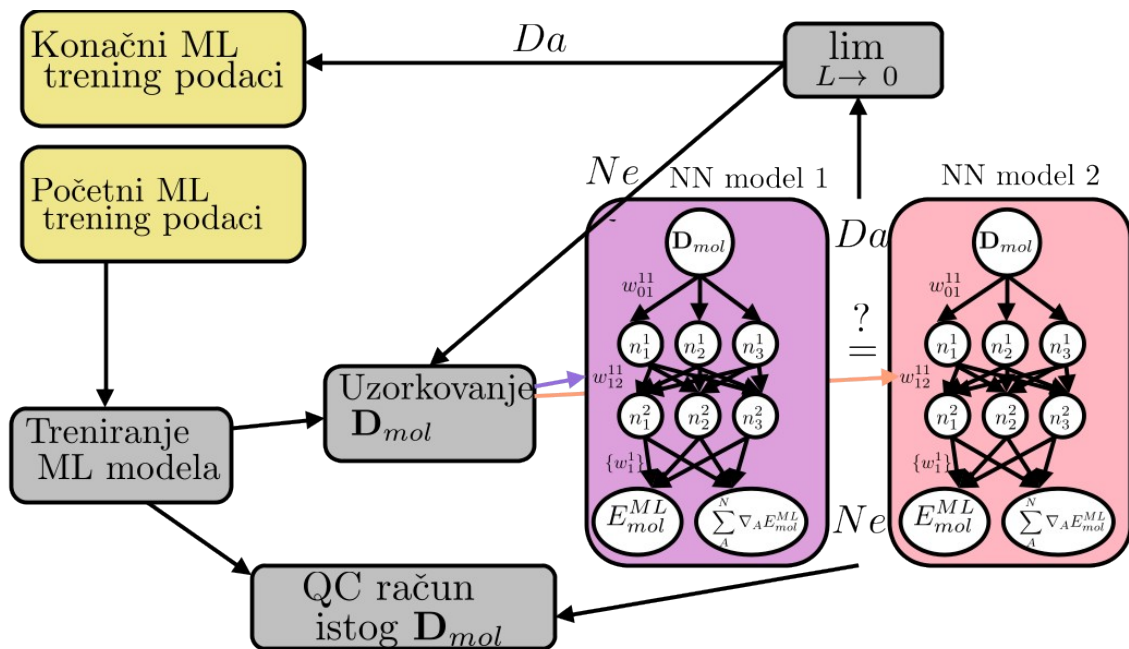
→ interpoliranje PPE (E_{mol} i $\nabla_N E_{mol}$) iz molekularnog deskriptora (D_{mol})

[2] Westermayr J, Marquetand P. Machine learning for excited-state dynamics and spectroscopy. Chem Rev. 2021;121(16):9873–9926.

[8] Li J, Lopez SA. A look inside the black box of machine learning photodynamics simulations. Acc Chem Res. 2022;55(14):1972–1984.

2. METODE : 2.3. STROJNO UČENJE ZA NAMD

- Adaptivno uzorkovanje – uzorkovanje podskupa ukupnog reakcijskog prostora.



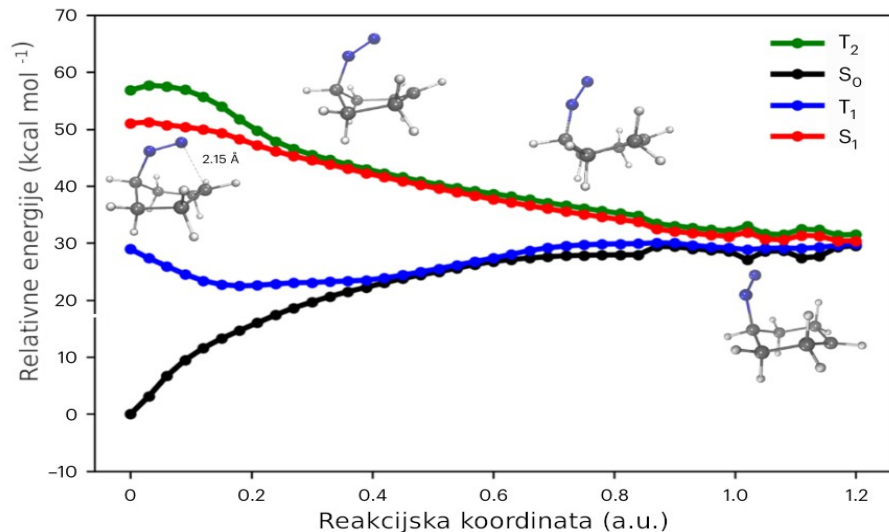
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3. RAČUNALNO MODELIRANJE REAKCIJE

- Pobuđena stanja

 Energija kidanja prve C-N veze

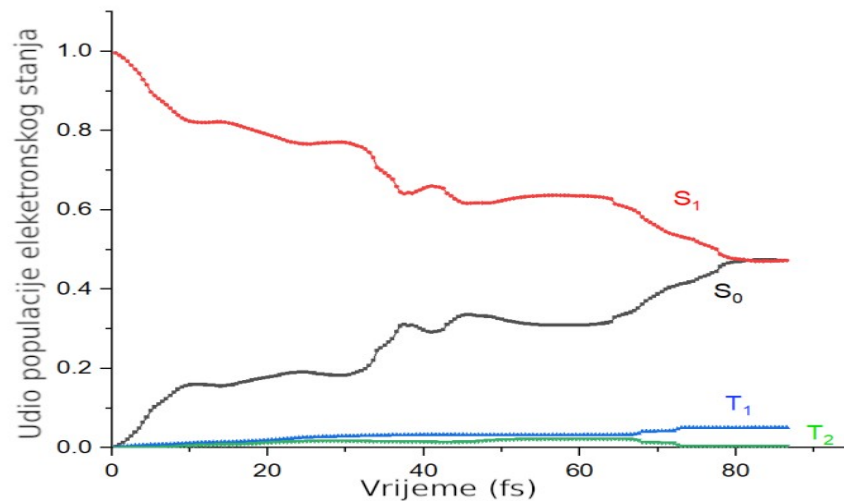


- dobro podudaranje sa eksperimentom i drugim razinama teorije (CASPT2)

Glavno pobuđeno stanje?

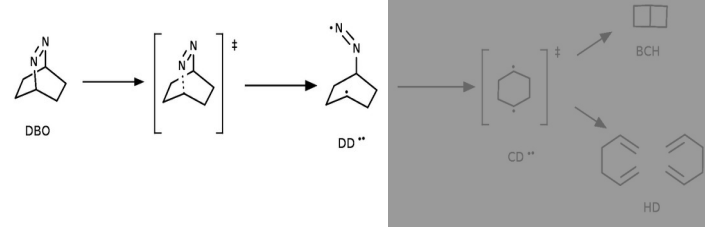


 NAMD



- glavno pobuđeno stanje je S₁

- prelazak S₁-S₀ tijekom kidanja prve C-N veze, u DD^{••}



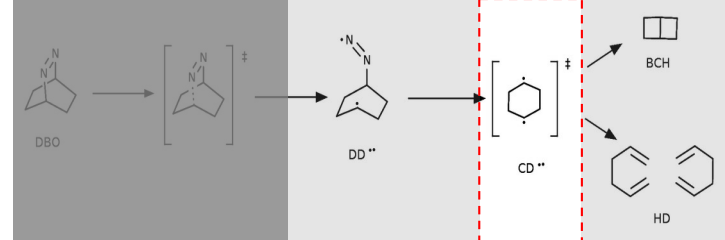
3. RAČUNALNO MODELIRANJE REAKCIJE

- Ambimodalno prijelazno stanje

- Kidanje druge C-N veze (prije APS), ima puno nižu energiju od prve.



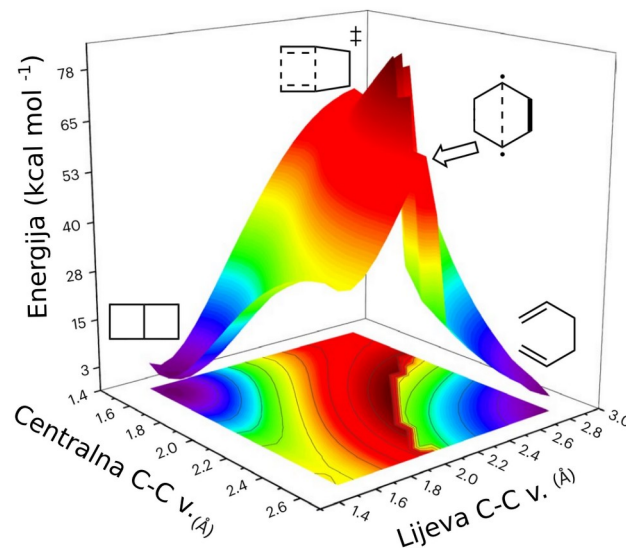
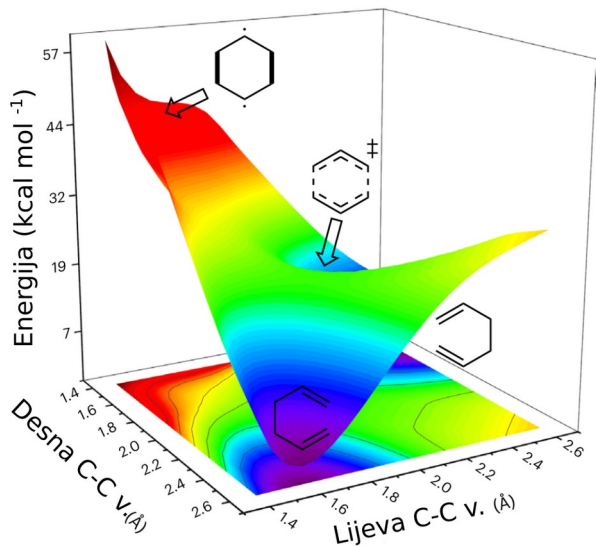
utjecaj **nestatističkih dinamičkih efektata** kidanja prve C-N u samom APS



 Reaktivnost APS, razne razine teorije



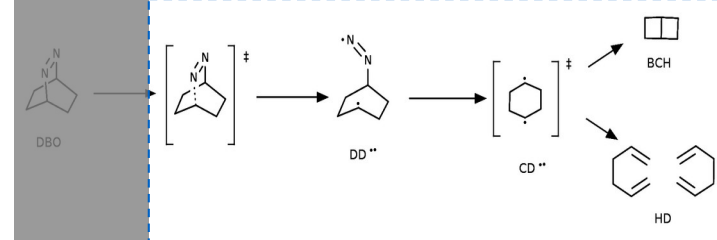
osjetljiva PPE na razine teorije (CASSCF, CASPT2, B3LYP, M06X)



[1] Feng Z, Guo W, Kong WY, Chen D, Wang S, Tantillo DJ. Analogies between photochemical reactions and ground-state post-transition-state bifurcations shed light on dynamical origins of selectivity. Nat Chem. 2024;16(4):615–623.

3. RAČUNALNO MODELIRANJE REAKCIJE

-  ML – NAMD sa MC-PDFT



- Kidanje druge C-N veze (prije APS), ima puno nižu energiju od prve.



utjecaj **nestatističkih dinamičkih efektata** kidanja prve C-N u samom APS

- Reaktivnost APS, razne razine teorije



osjetljiva PPE na razine teorije (CASSCF, CASPT2, B3LYP, M06X)

- Raspon elektronskih struktura reakcije



Statička i **dinamička** elektronska korelacija : **MC-PDFT (revPBE//ANO-S-VDZP)**

- prelazak S1-S0 tijekom kidanja prve C-N veze



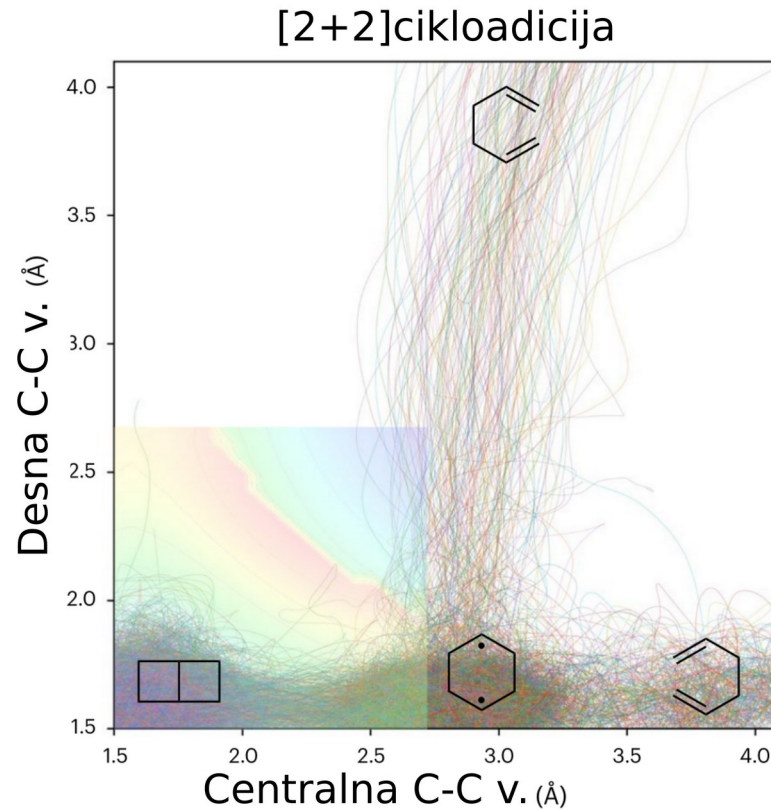
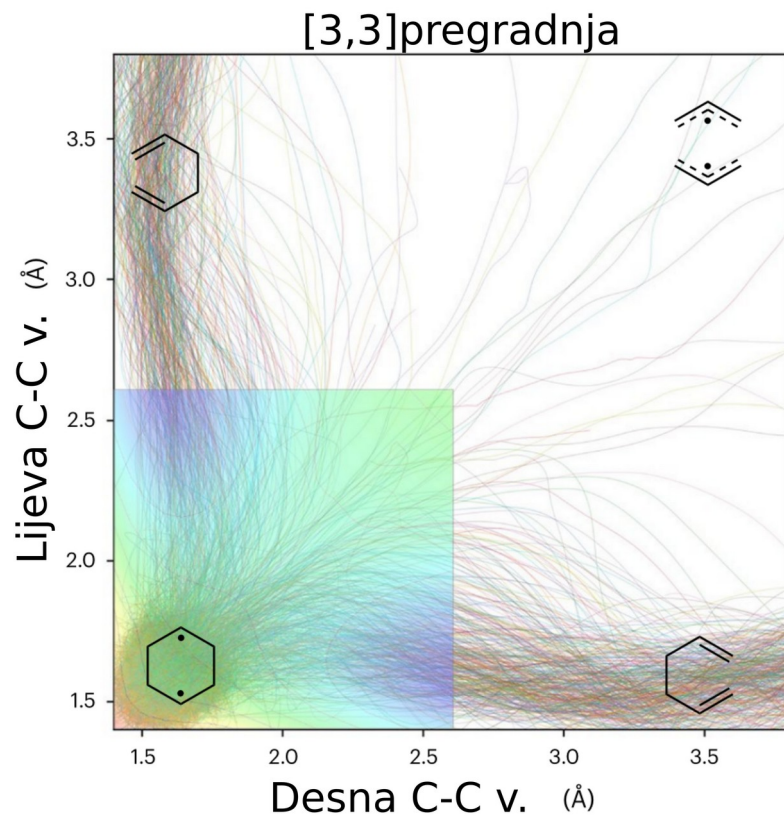
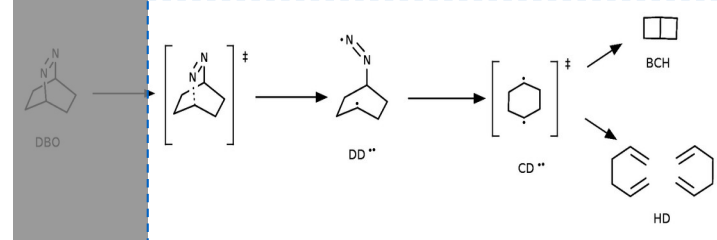
Surface hopping NAMD :

 ML – NAMD:

(PyRAI²MD // SHARC)

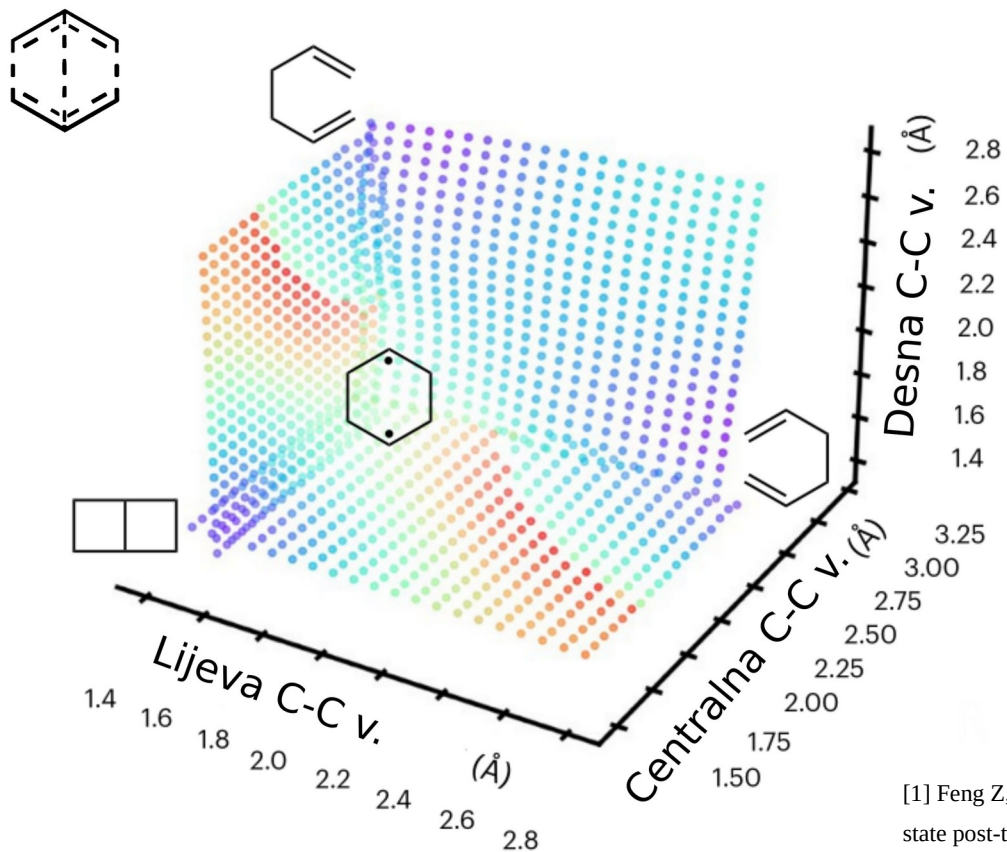
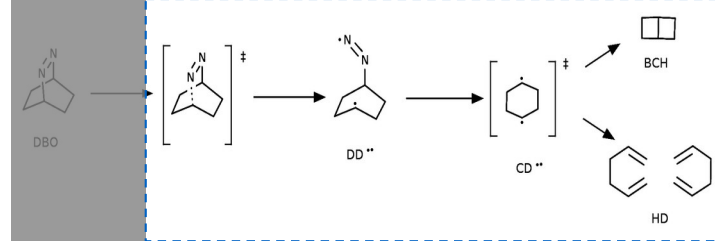
3. RAČUNALNO MODELIRANJE REAKCIJE

- ML – NAMD sa MC-PDFT

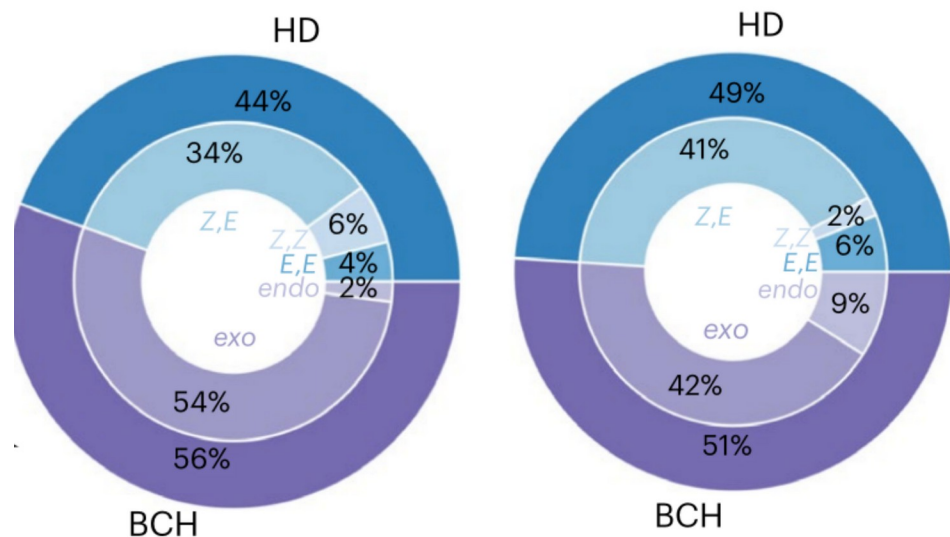


3. RAČUNALNO MODELIRANJE REAKCIJE

- ML – NAMD sa MC-PDFT



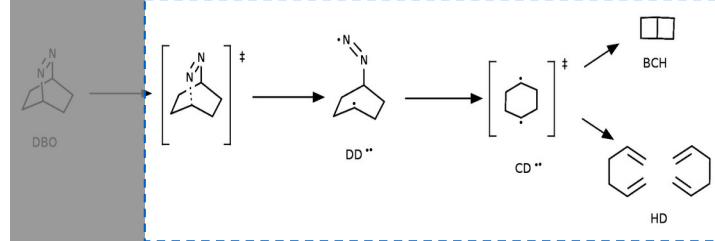
- Usporedba ML-NAMD sa eksperimentom



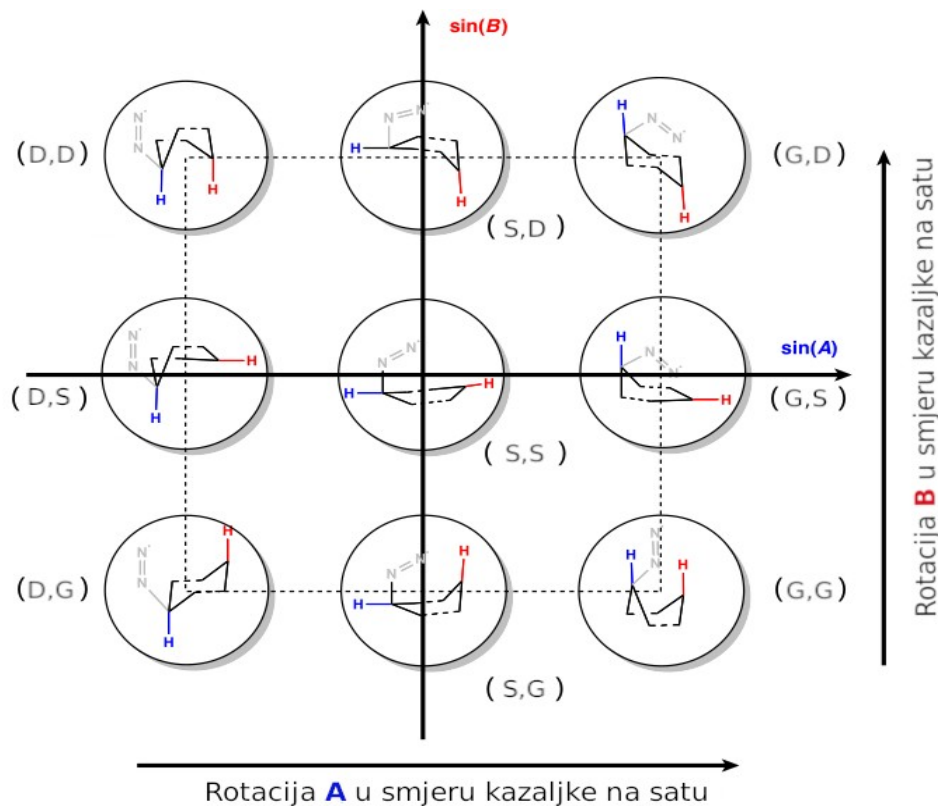
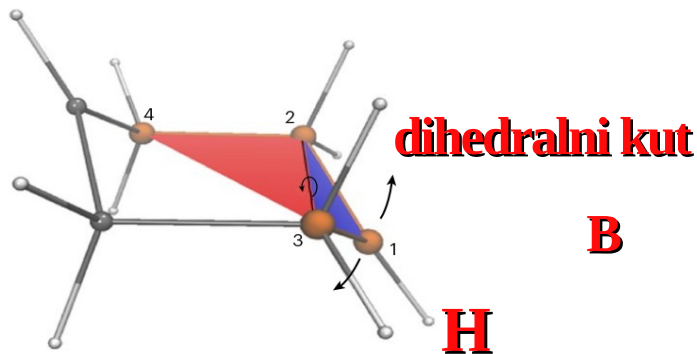
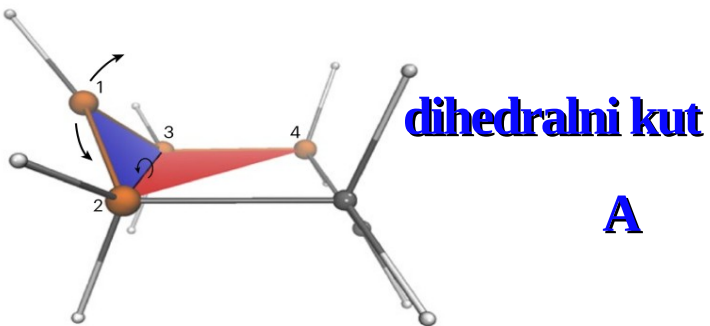
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3. RAČUNALNO MODELIRANJE REAKCIJE

- Konformacije tijekom  ML-NAMD trajektorija

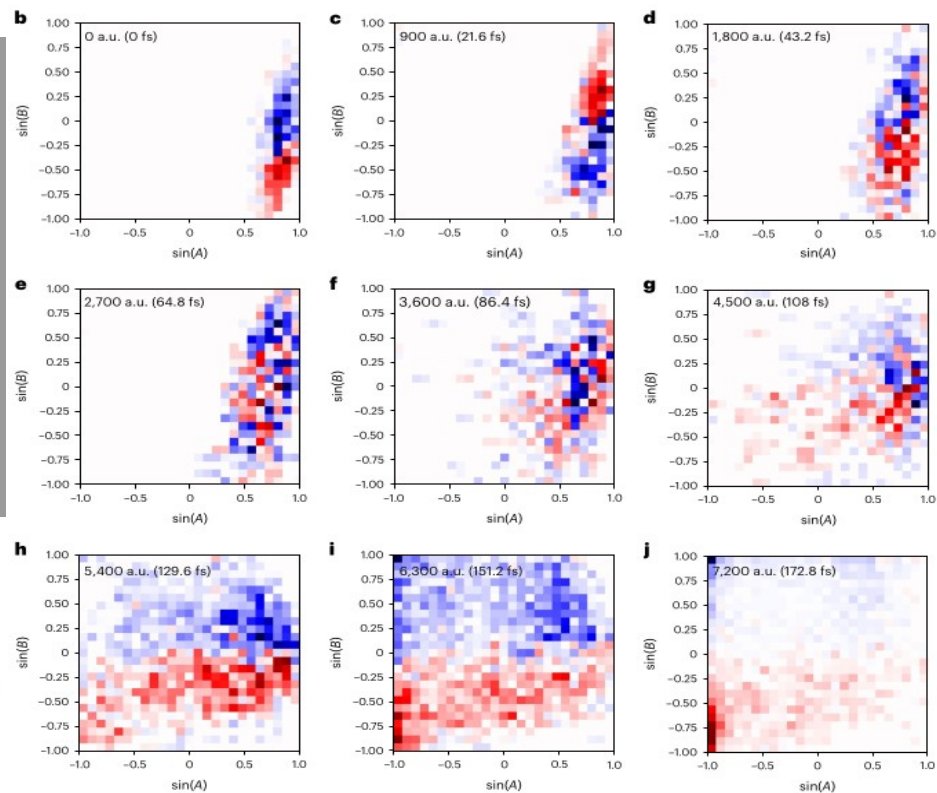
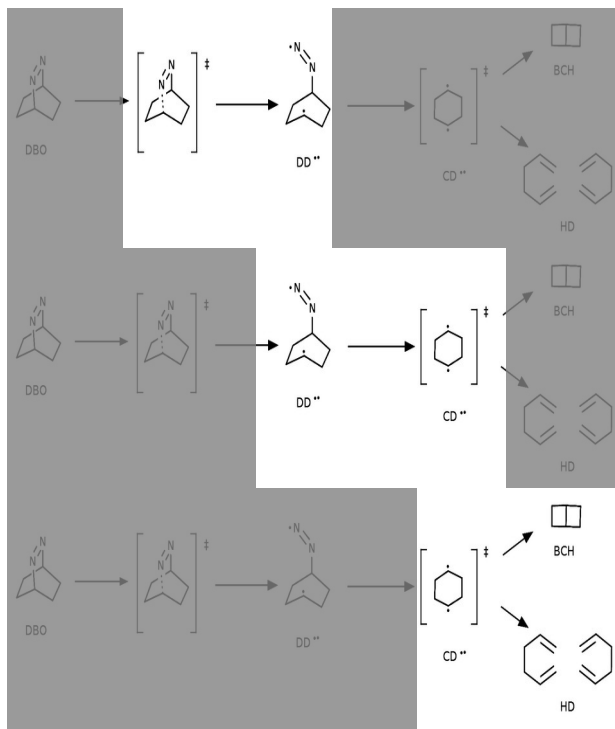
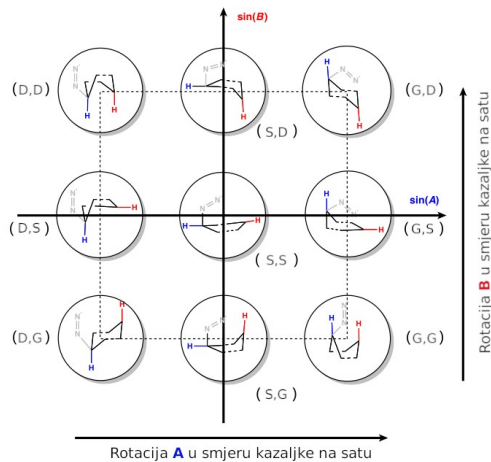
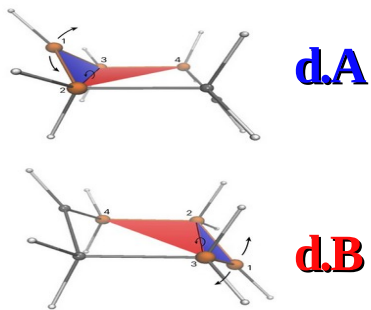
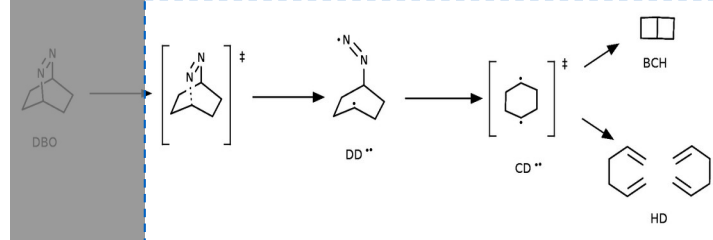


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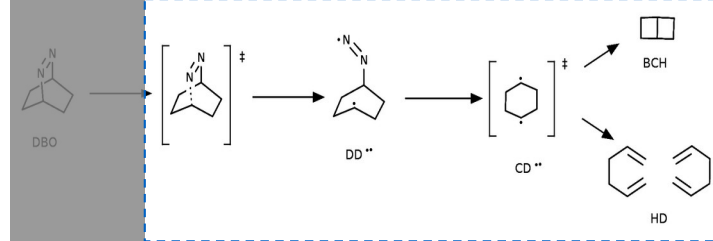


3. RAČUNALNO MODELIRANJE REAKCIJE

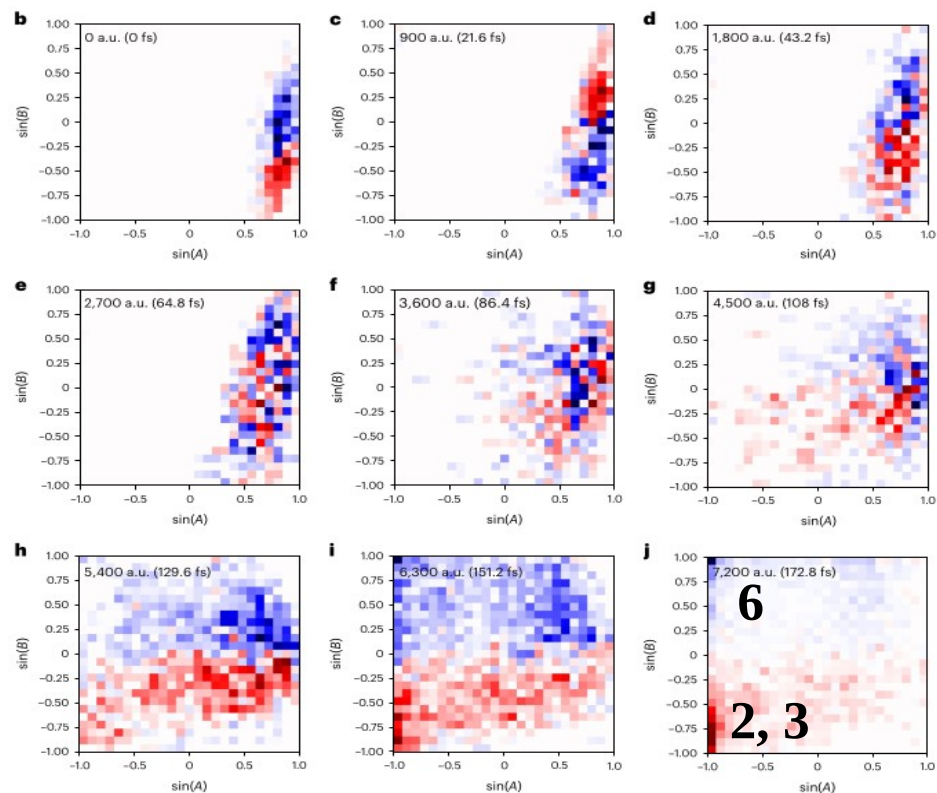
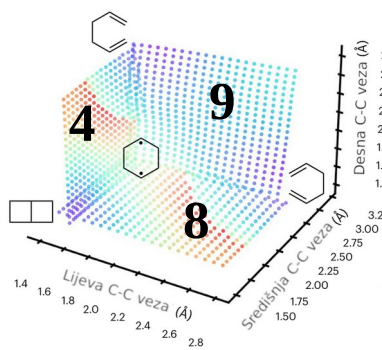
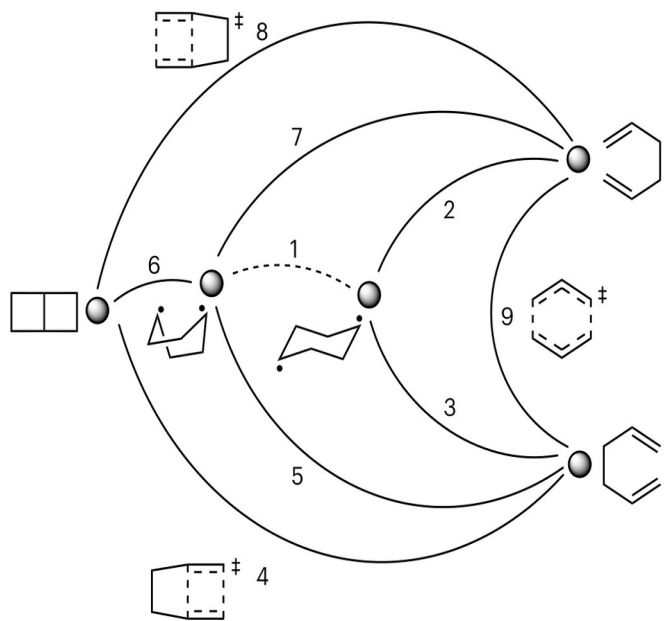
- Konformacije tijekom  ML-NAMD trajektorija



3. RAČUNALNO MODELIRANJE REAKCIJE



- Konformacije tijekom  ML-NAMD trajektorija



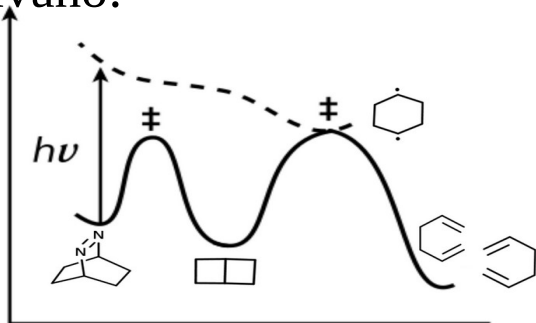
- Glavni reakcijski putevi:

6 (BCH) i 2, 3 (HD)

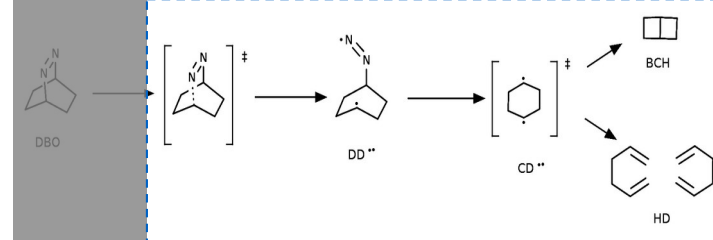
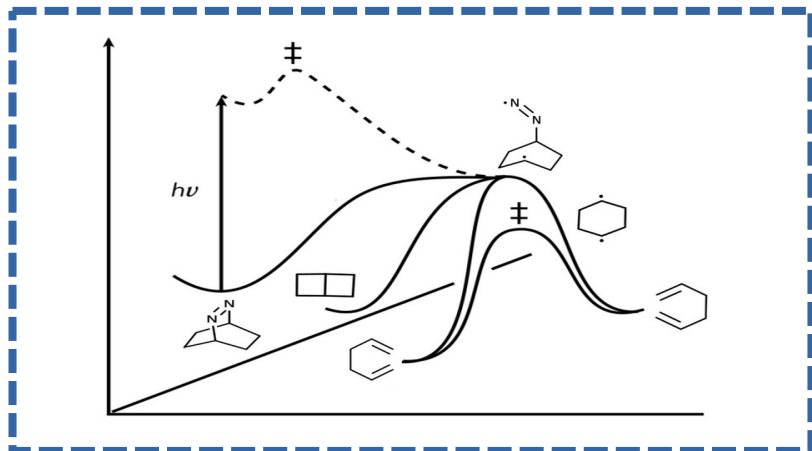
3. RAČUNALNO MODELIRANJE REAKCIJE

- PPE modelirane reakcije

Očekivano:

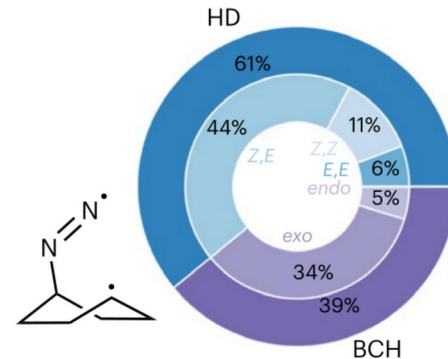
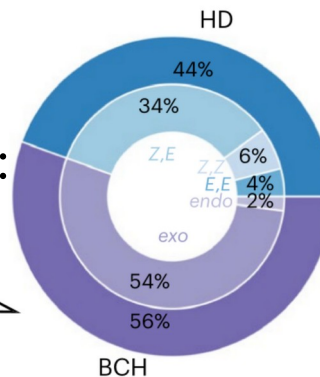
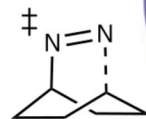


ML-NAMD:

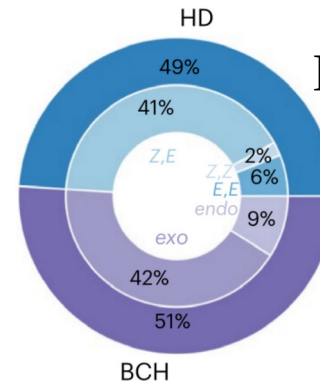


- Usporedba ML-NAMD sa eksperimentom

Početak
ML-NAMD:



→ Ključno:
kidanje prve
C-N veze na
prijelazu
S1-S0 stanja.



Eksperiment

4. ZAKLJUČAK

Za modeliranje reakcije bilo je potrebno :

1. Multireferentna elektronska struktura, dinamična elektronska korelacija (**MC-PDFT**)
2. Nestatistički dinamički efekti fotokemijske reakcije sa APS, modelirani sa neadijabatskom dinamikom (**NAMD**)
3. **Strojno učenje** omogućilo stvaranje računalno-efikasnog modela reakcije (**ML-NAMD**)

5. LITERATURA

- [1] Feng Z, Guo W, Kong WY, Chen D, Wang S, Tantillo DJ. Analogies between photochemical reactions and ground-state post-transition-state bifurcations shed light on dynamical origins of selectivity. *Nat Chem*. 2024;16(4):615–623.
- [2] Westermayr J, Marquetand P. Machine learning for excited-state dynamics and spectroscopy. *Chem Rev*. 2021;121(16):9873–9926.
- [3] Agostini F, Curchod BFE. Review of nonadiabatic molecular dynamics methods. *WIREs Comput Mol Sci*. 2019;9(1):e1417.
- [4] Chen H, Li S. Theoretical study on the photolysis mechanism of 2,3-diazabicyclo[2.2.2]oct-2-ene. *J Am Chem Soc*. 2005;127(38):13190–13199.
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