

Object: spirochromenes

- ✓ Class of organic light-driven **molecular switches**
- ✓ Exhibit fast, reversible and stable **bond cleavage** processes^[1]
- ✓ Studied group has **an outlier** (different absorption, 20× lifetime)

Goal

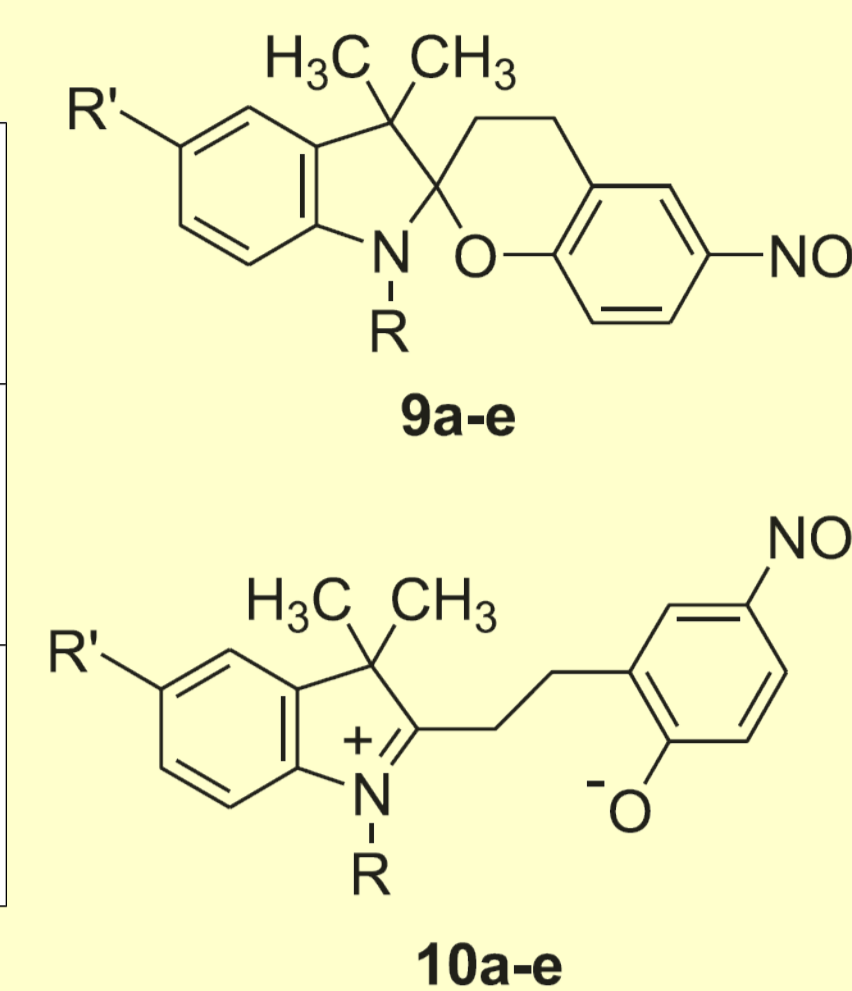
- ✓ Compare properties of the compounds and explain the outlier

Tools

- ✓ Potential energy surface (**PES**) **model** for ground and excited electronic states (successful for similar compounds^[2])
 - ✓ Including excited-to-ground-state *conic intersection* search
- ✓ Ground-state and time-dependent **DFT** (basis: *cc-pVDZ*)
 - ✓ *B3LYP*, *CAM-B3LYP*, *LC-BLYP*, *PBE0* functionals
 - ✓ *PCM* solvent model for acetonitrile
 - ✓ *Gaussian09*^[3] and *GAMESS*^[4] packages

Experiments: group of 5 compounds^[1]

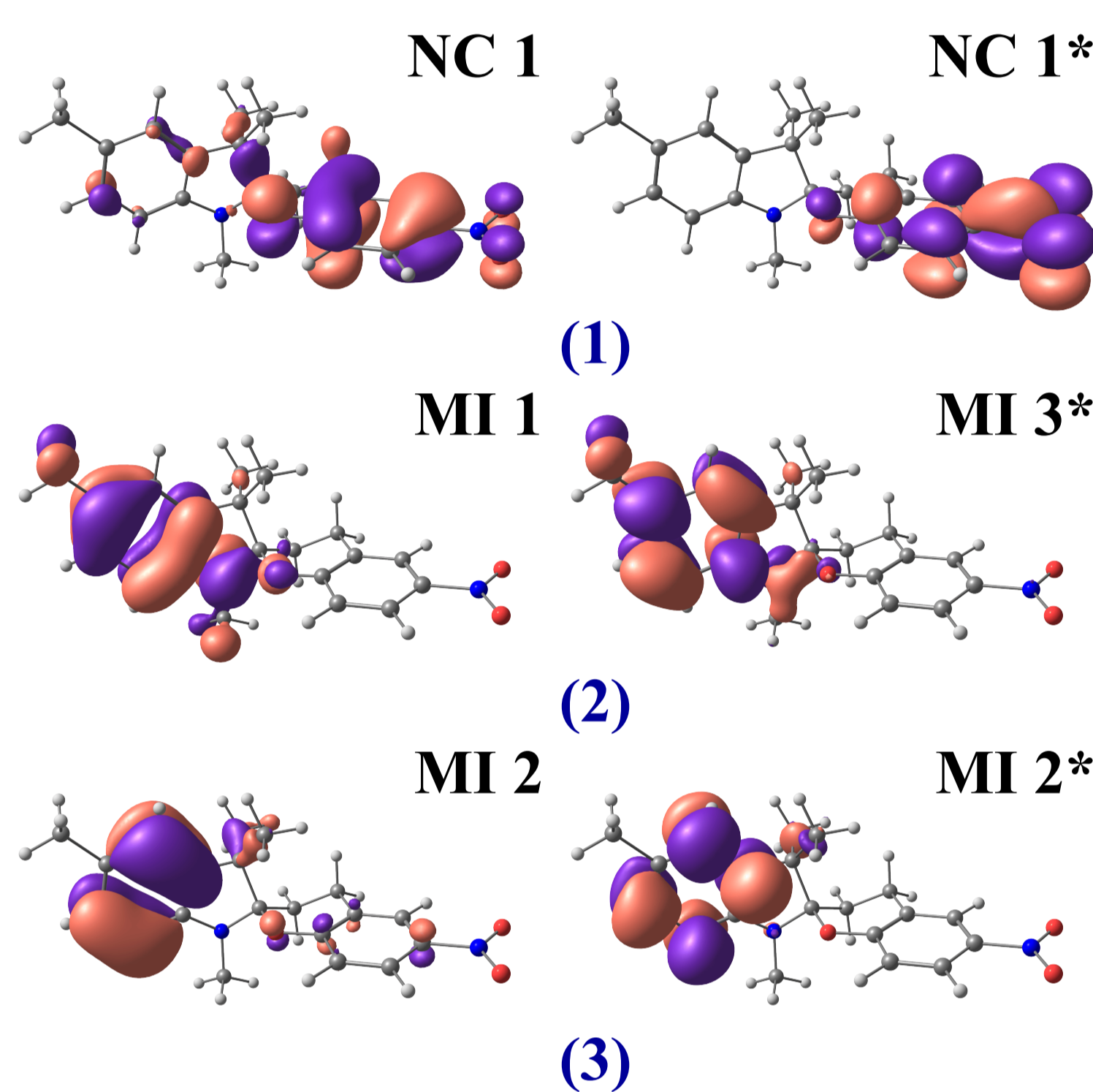
Compound (closed / open)	R	R'	Closed: absorption (nm)	intensity	Open: absorption (nm)	lifetime (ns)
9c / 10c	CH ₃	CH ₃	206	46,3	450	22
			245	15,7		
			313	13,6		
9e / 10e	CH ₂ CH ₃	NO ₂	~230	14,1	420	484
			~330	14,6		
			380	22,1		



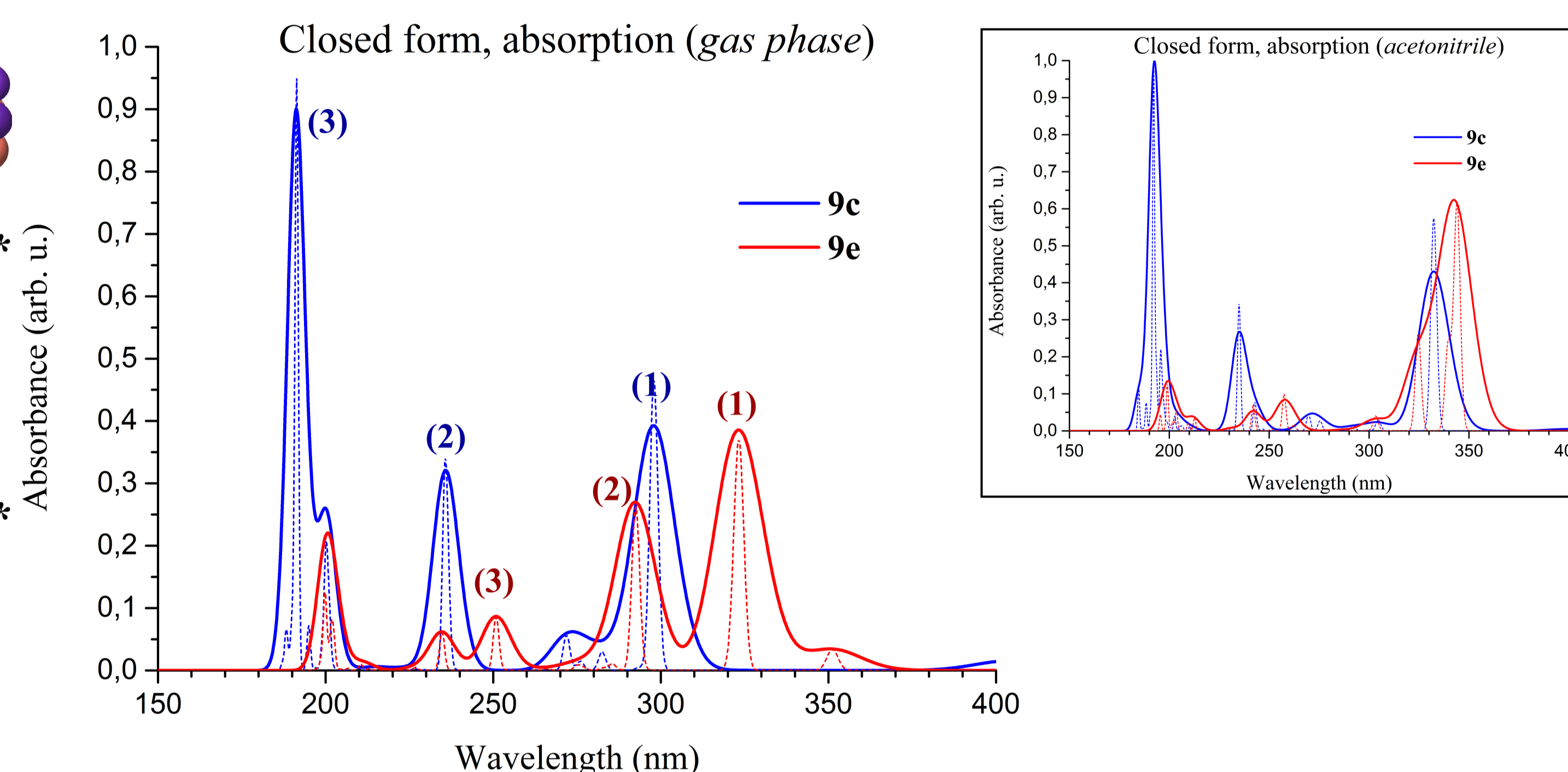
Study: 2 compounds

9c: methylindole (MI) + nitroisochroman (NC), 9e: nitroindole (NI) + nitroisochroman
9 and 9* – closed ring conformers (cf. ^[5]), 9e± – ethyl group (R) conformers
TS – transition state (barrier), CI – conic intersection, 10^o – ground-state intermediate

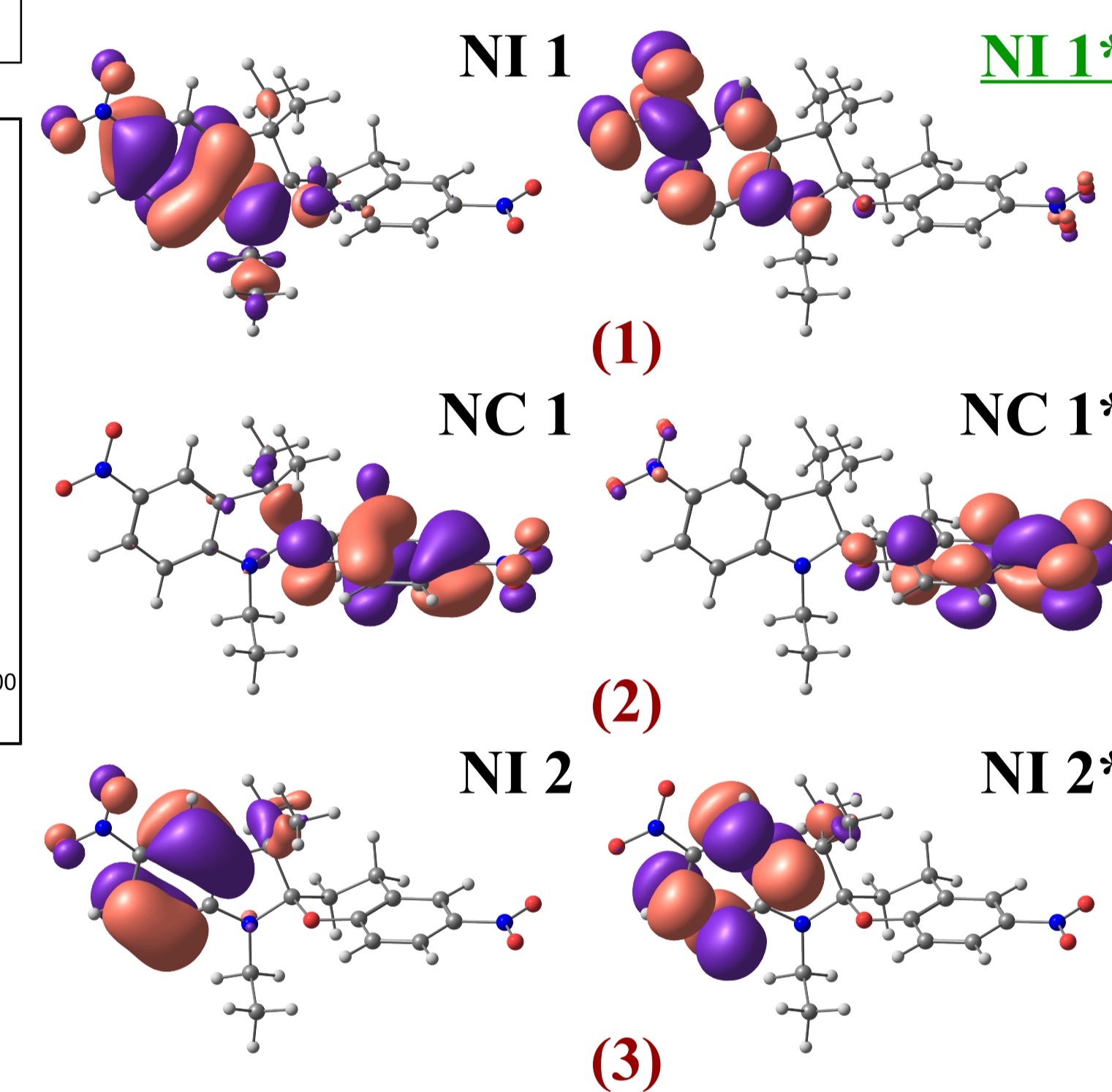
Molecular orbitals of 9c



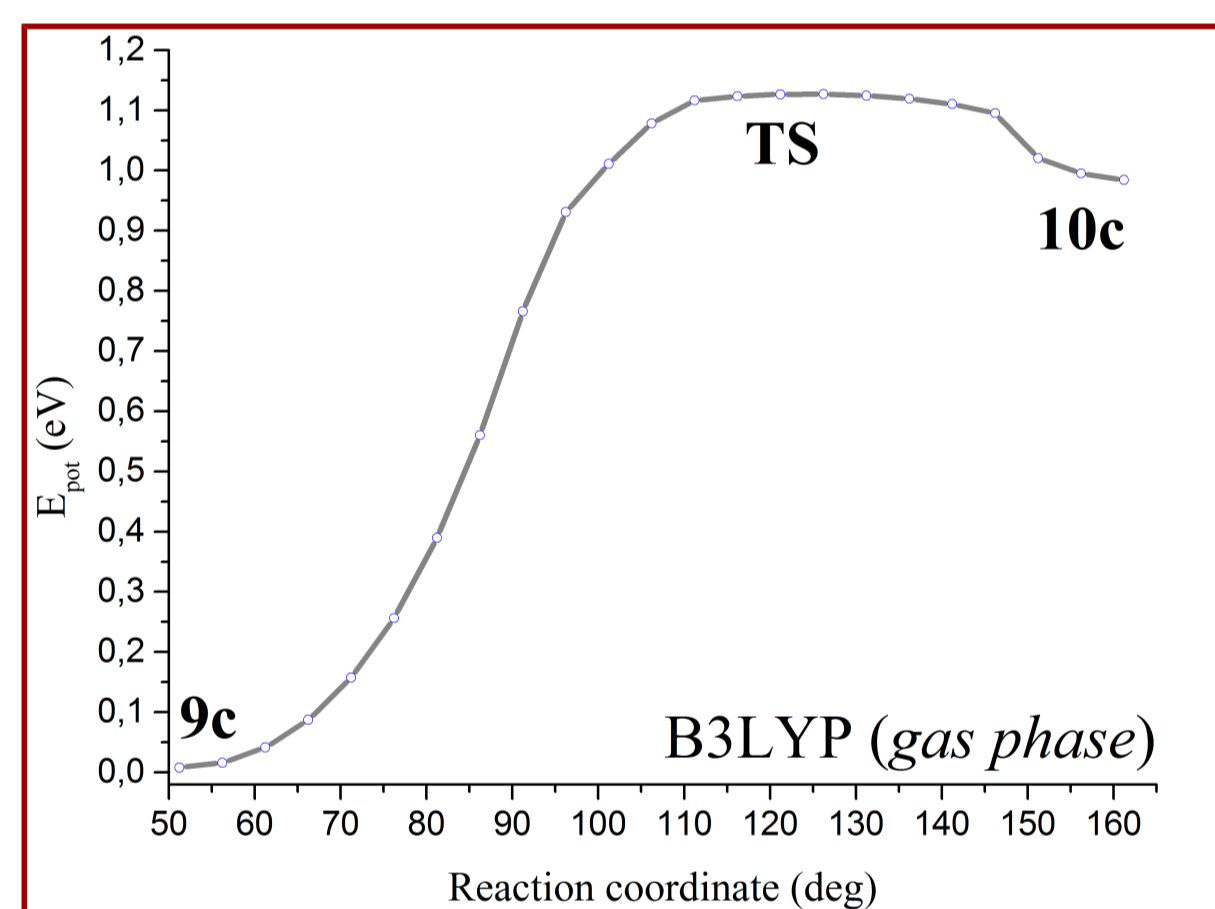
- ✓ Observed shift is caused by the absorption of a **second chromophore** in 9e
- ✓ Calculations correctly reproduce spectral shape and features
- ✓ Accounting for solvent also results in good quantitative agreement



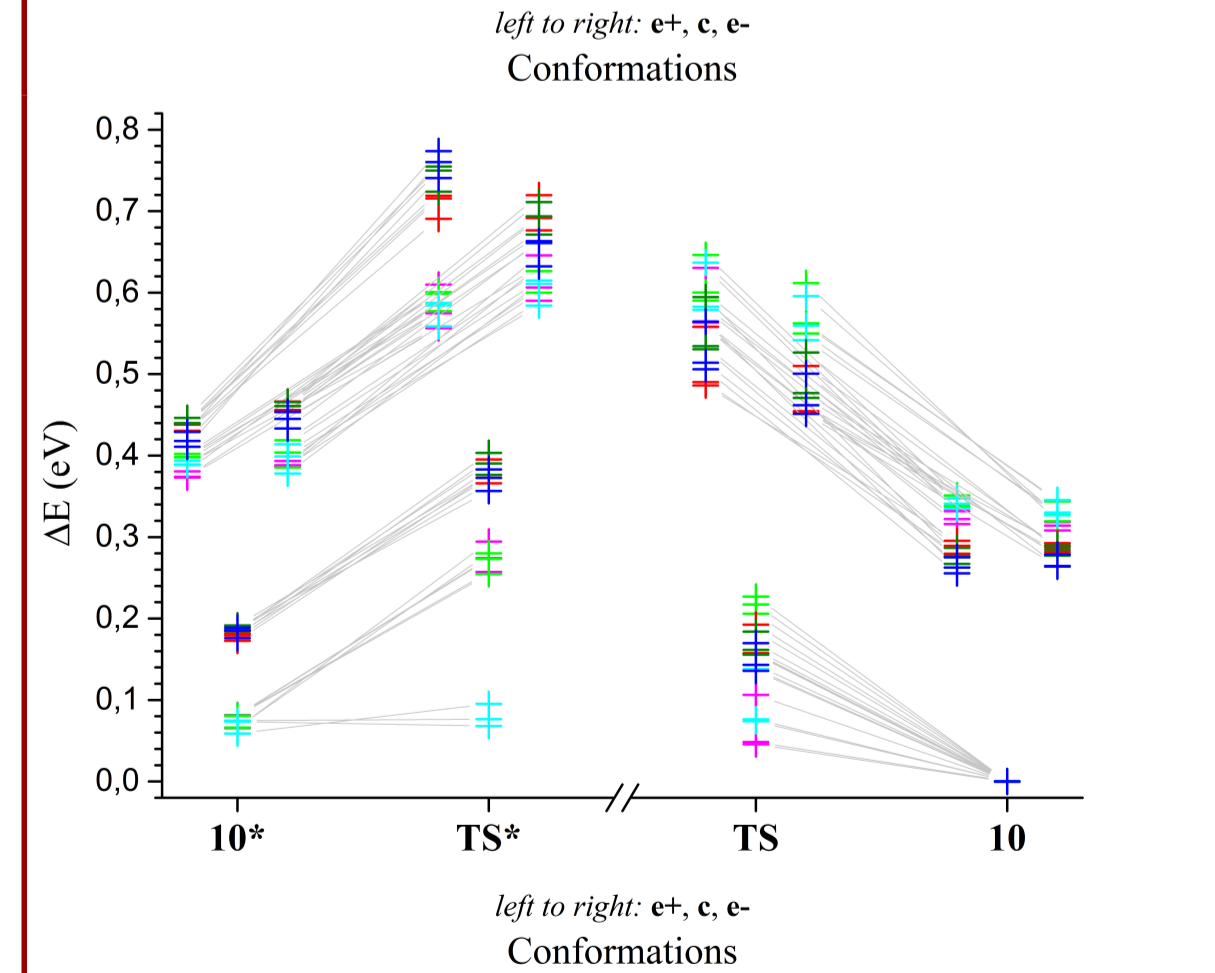
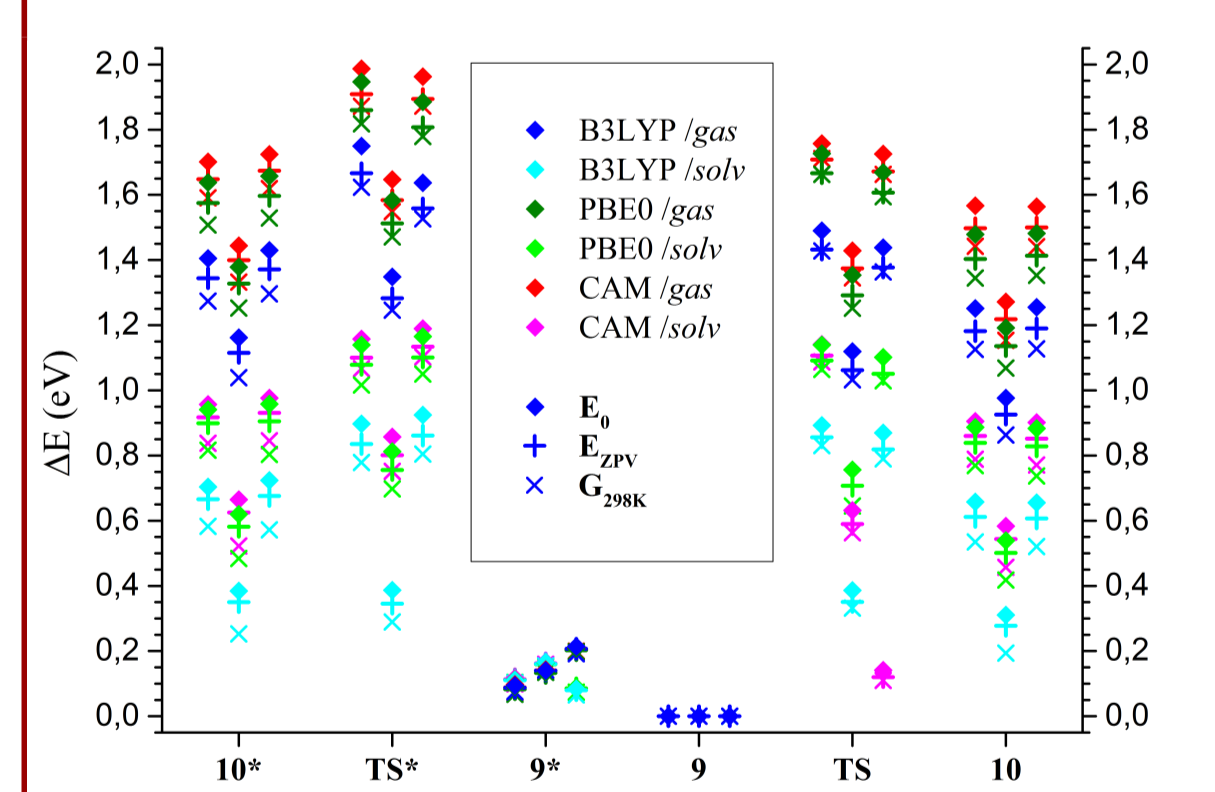
Molecular orbitals of 9e



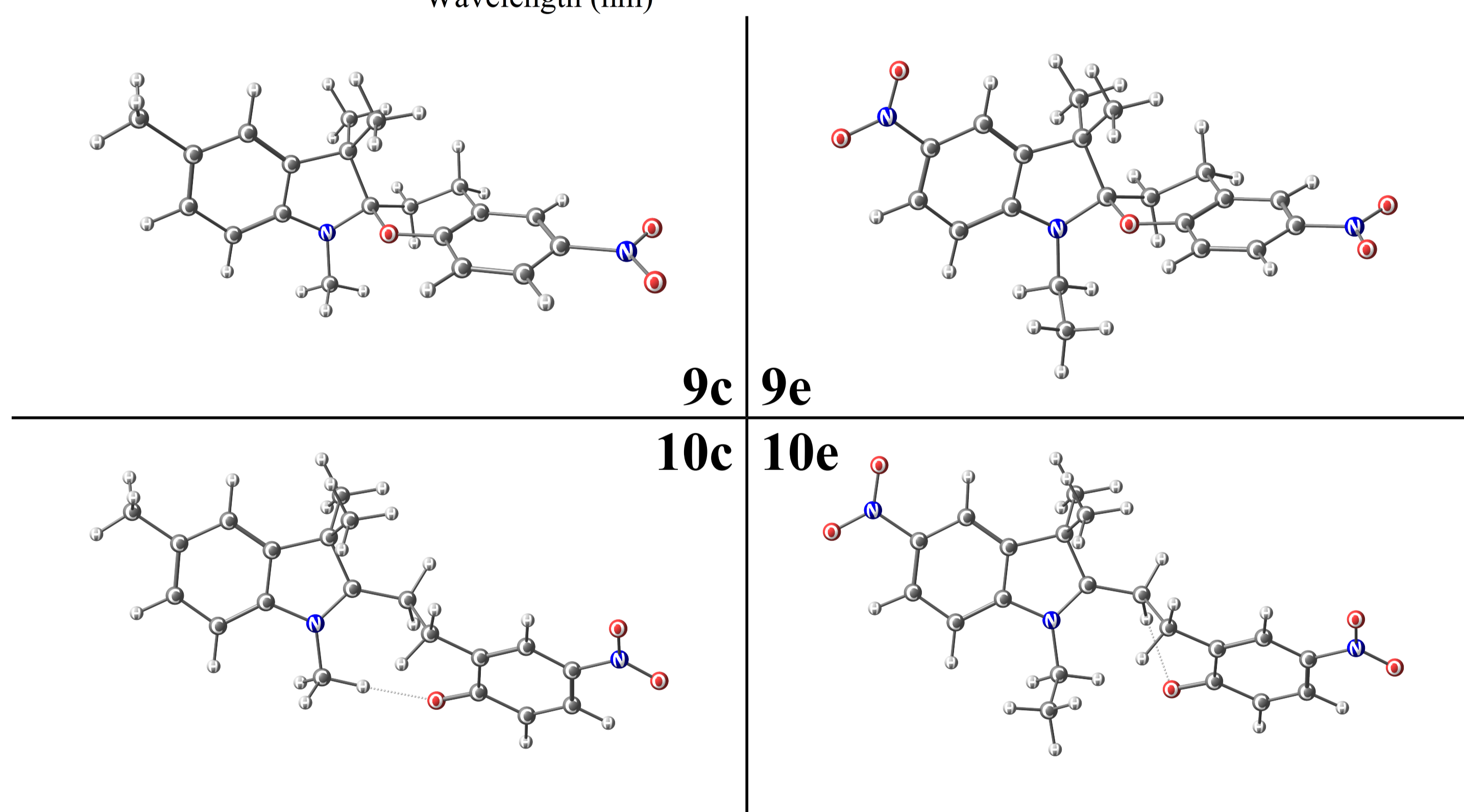
Single barrier case



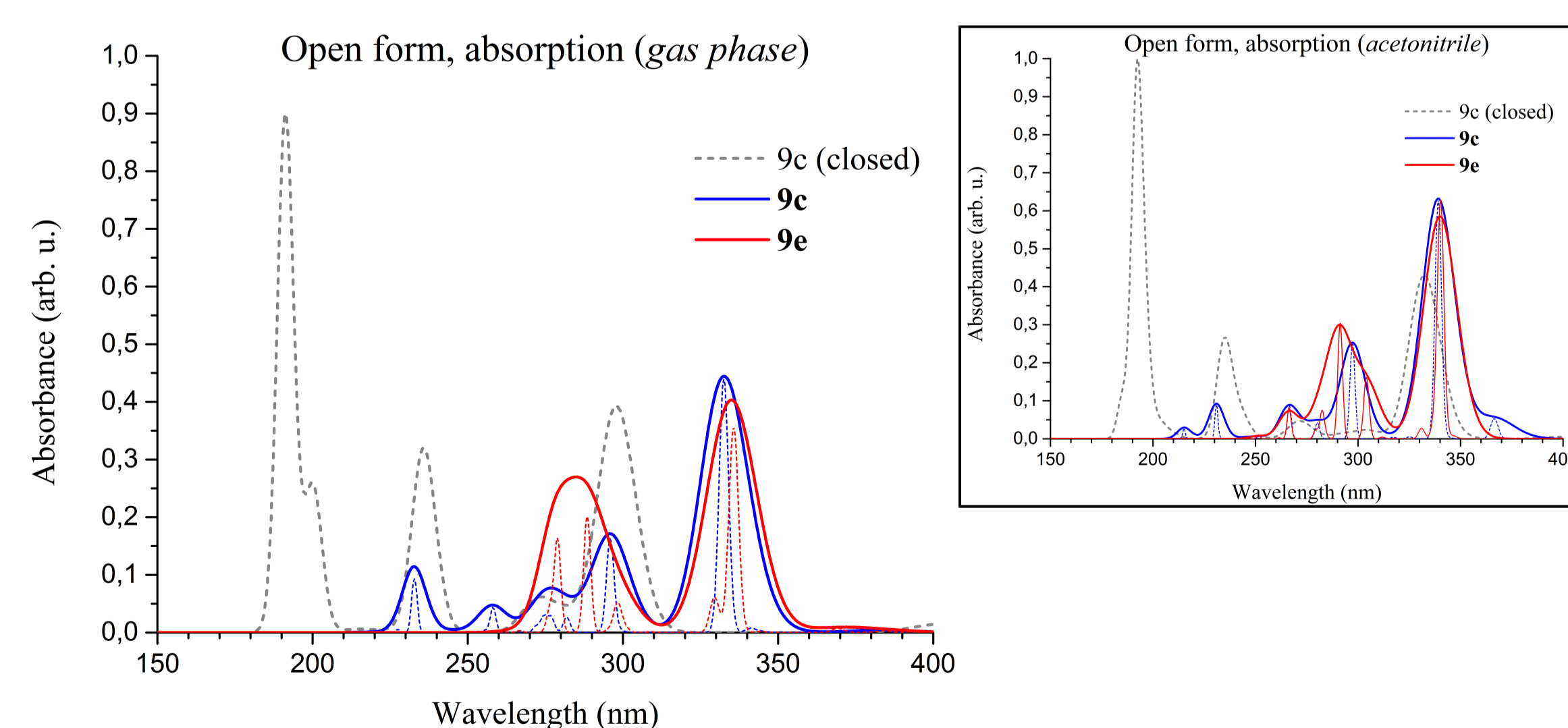
× Very broad (ill-defined) barrier



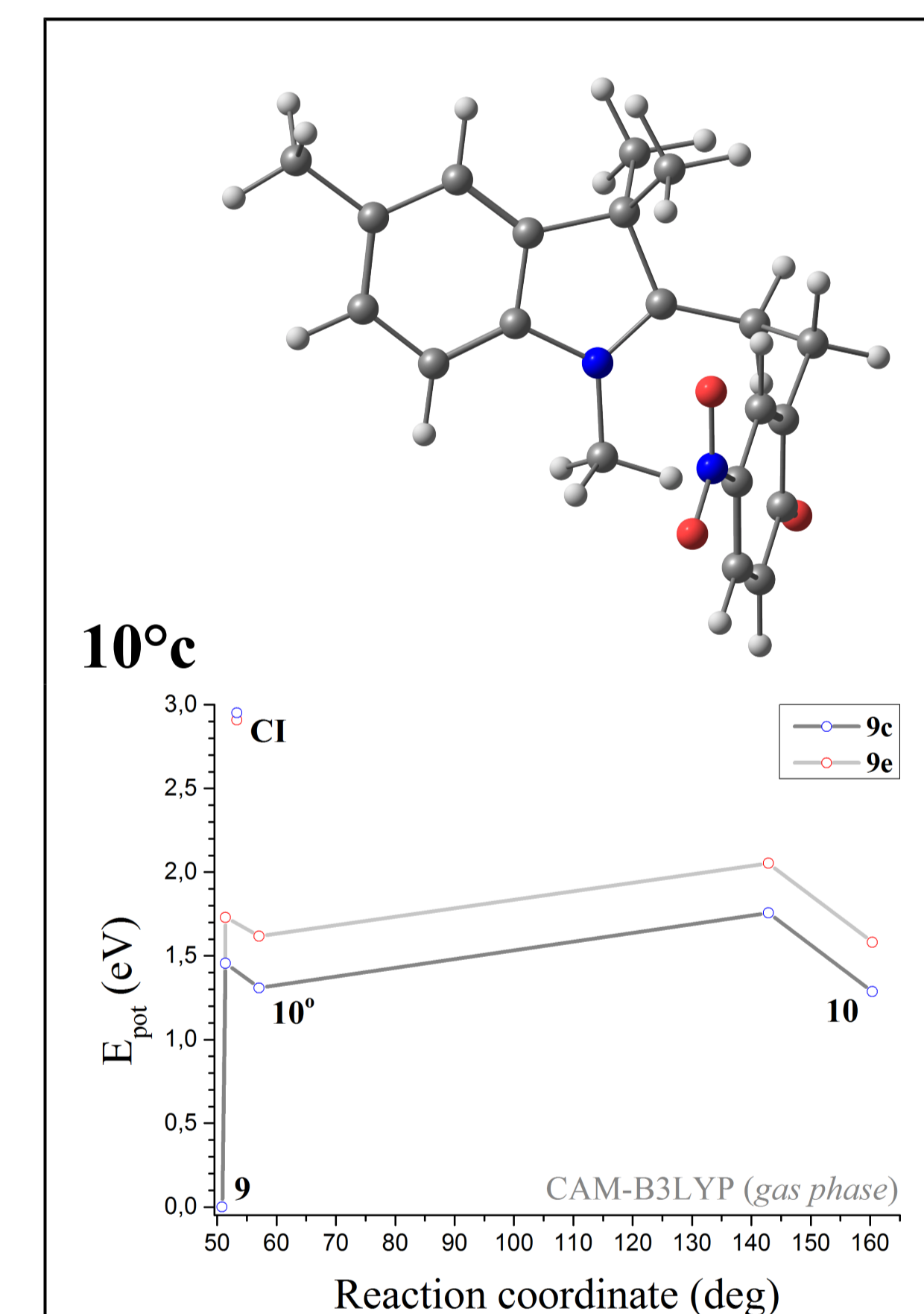
- × No notable differences in barrier height seen between 10c and 10e± compounds, regardless of energy estimation method
- × Structural deformation is complicated due to a flexibility of the CH₂-CH₂ bridge



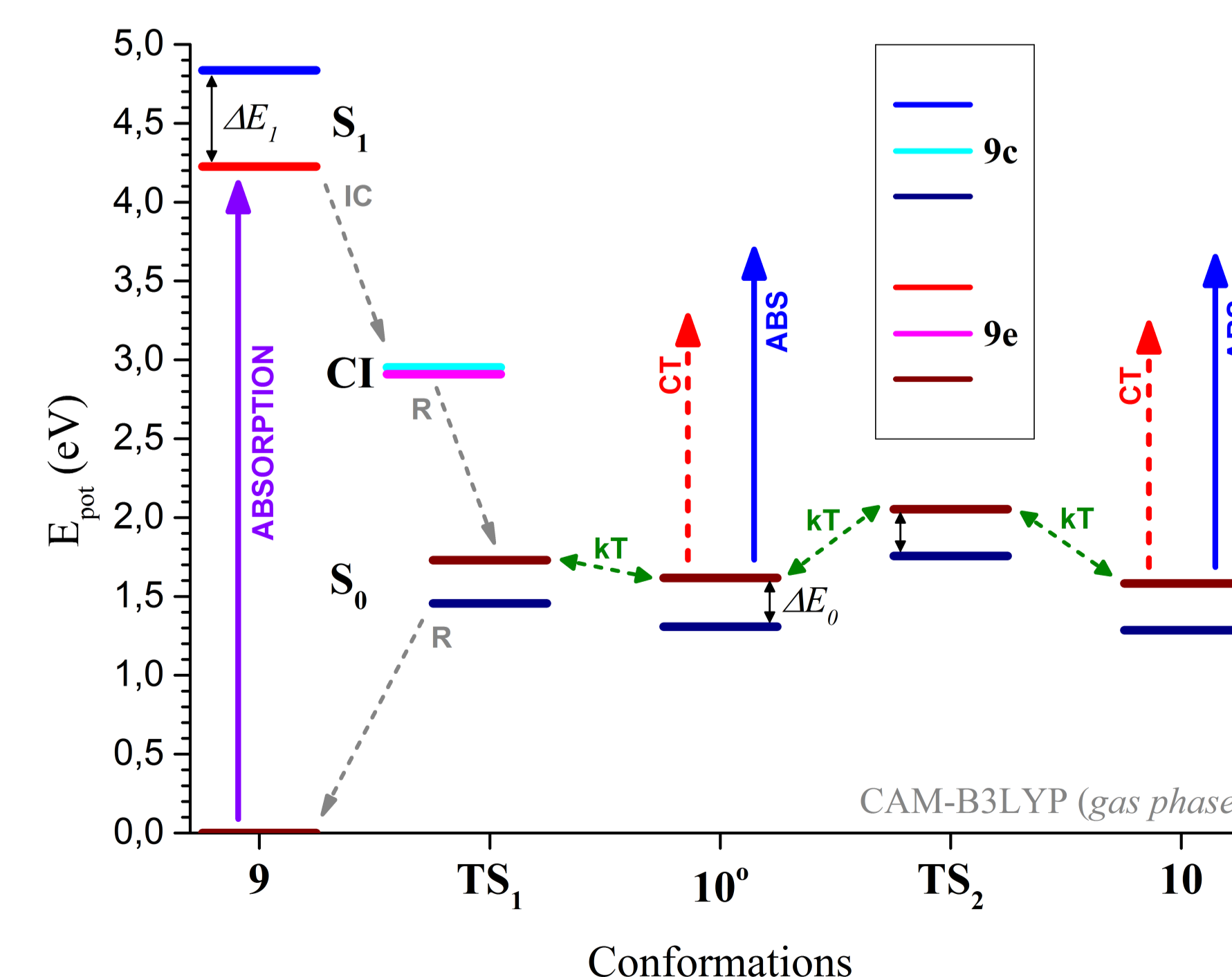
- ✓ Absorption of optimized open form(s) shows **no meaningful differences**
- ✓ Spectrum consists of **nitrochromene peak** and dark charge-separated states (not shown); all tested functionals reported the same qualitative picture
- ✓ Direct path^[5] (← left) and presence of intermediates (right →) were studied



Intermediate conformation



Proposed reaction scheme



Conclusions

- ✓ Presence of the NO₂ group yields a second chromophore in the molecular system
- ✓ Single change in *absorption* properties leads to the different *relaxation* profiles
- ✓ This phenomenon could be exploited while designing molecular devices

- ✓ Several local minima found in ground-state PES
- ✓ Respective barrier heights are very similar for 9c and 9e compounds (→ no differences in calculated spectrum)
- ✓ 9c has more potential energy both after excitation (ΔE_1) and at the CI (ΔE_0) (→ **faster relaxation**/ shorter trap escape time)

References

- [1] M. Dagilienė et al., *Tetrahedron* **69** (2013) 9309.
- [2] S. Toliautas et al., *Chem. Phys.* **404** (2012) 64.
- [3] *Gaussian 09*, Rev. **D.01**, Gaussian, Inc., Wallingford CT (2013).
- [4] M. W. Schmidt et al., *J. Comput. Chem.* **14** (1993) 1347.
- [5] S. Prager et al., *J. Phys. Chem. A* **118** (2014) 1339.