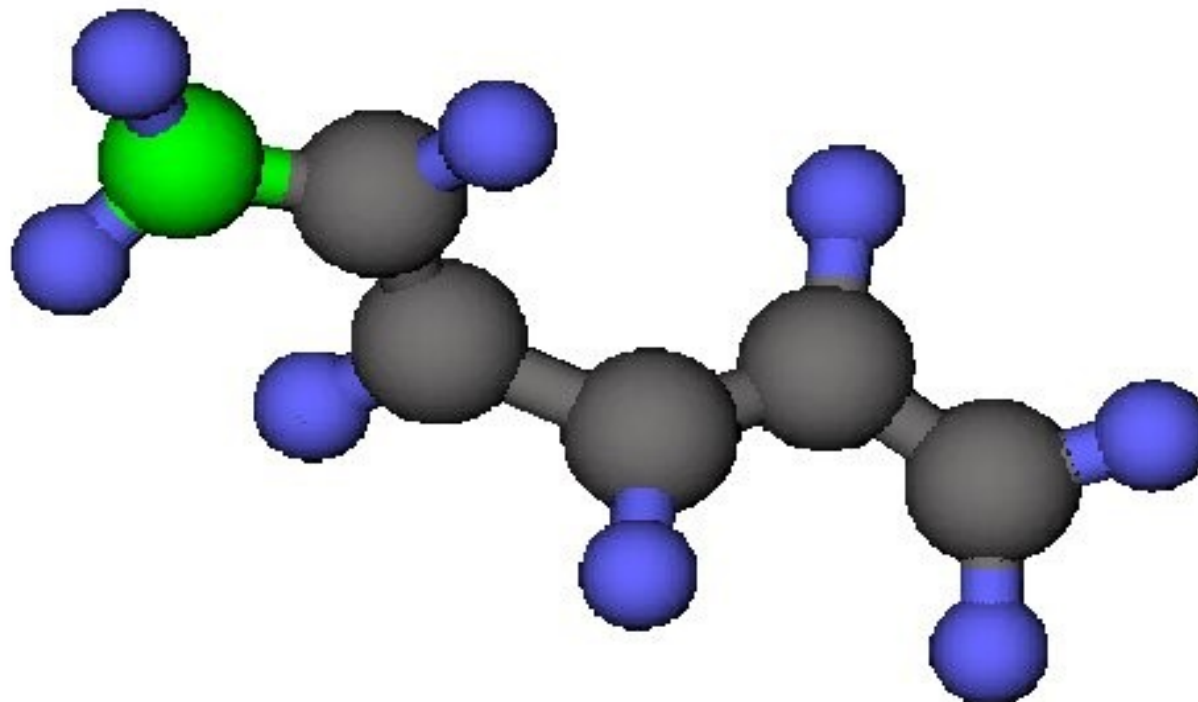


# Photodynamics of the Pentadieniminium-Cation



# Photodynamics of PDI+ (PSB3)

- Why do we want to compute this?
- theoretical background
- results obtained
- a few conclusions

# Reasons for the present work

- all-trans-PDI+ is a model for bacteriorhodopsine
- logical consecutive step after shorter imines
- trying to push the frontier
- because we can!

# theoretical background

- molecular mechanics doesn't deal with  
excitation
- QM treatment necessary
- Newton mechanics on QM-PES
- nonadiabatic coupling

# computational considerations

- using Tully's fewest switches algorithm
- Newtonian equations on PES
- comparing methods
- comparing basis sets

# methods and basis sets

- MRCIS
- SA-CASSCF
- Pople-sets: 3-21g\* and 6-31g\*
- TDDFT and CC2 for comparison (both SV(P))

# methods and basis sets

- evaluating vertical excitation
- evaluating calculation time
- evaluating qualitative results

# vertical excitations

Level	basis	$\Delta E$ (vert.exc.)/eV
SA-2-MCSCF(6,6)	3-21g*	4,38
SA-2-MCSCF(6,6)	6-31g*	4,46
MRCIS(4,5)[MCSD(6,6)]	3-21g*	4,18
TDDFT	SV(P)	4,20
RICC2	SV(P)	4,09

L iterature: 4.2eV for R I C C 2 (aug-cc-pV D Z )

# calculation time

- SA-2-MCSCF(6,6)-6-31g\*: ~ 2d 14h/traj.
- SA-2-MCSCF(6,6)-3-21g\*: ~ 7-8h/traj.
- MRCIS(4,5)[MCSCD(6,6)]-3-21g\*: ~ 13h/traj.

# choice of method

- MRCIS(4,5)[MCSCF(6,6)] - 3-21g\*
- SA-2-MCSCF(6,6) (6-31g\* and 3-21g\*)  
for comparison
- TDDFT and RI-CC2 (SV(P)) for completeness

# results

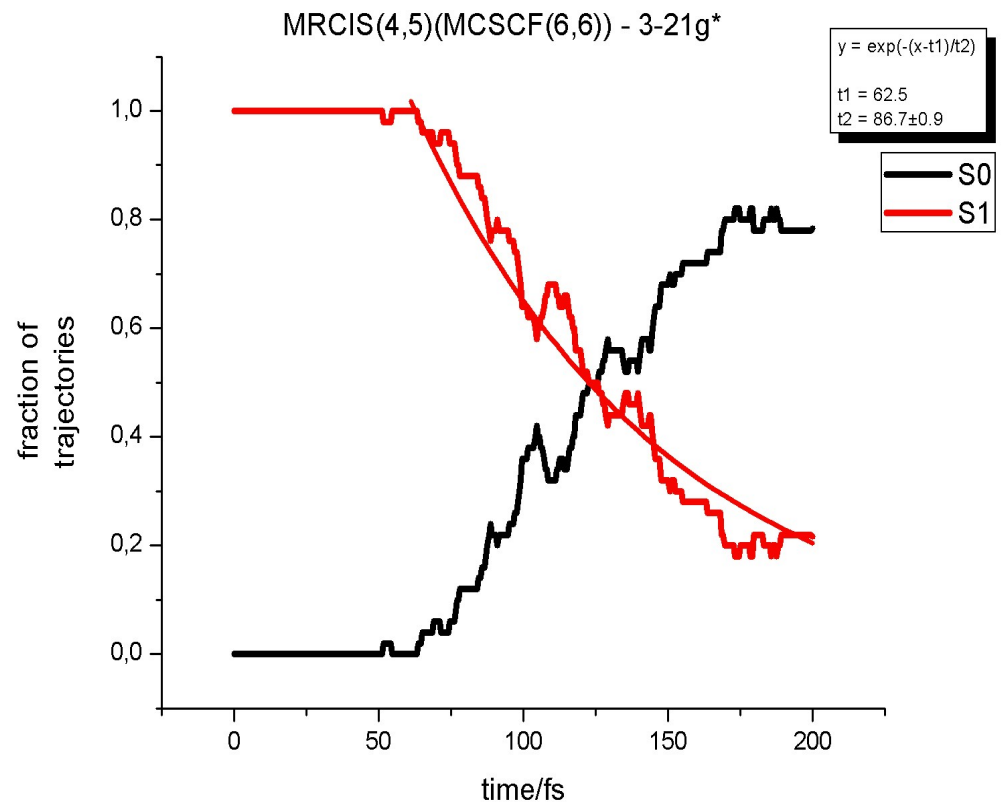
- conical intersection reached mainly by central torsion
- C=N - stretch second main mode for CI ?
- bond lengths (double-single) change regularly upon excitation
- ~50fs delay before torsion begins

# results - lifetime

- overall lifetime ( $t_1+t_2$ ): 149.2 fs
- delay ( $t_2$ ): 62.5 fs

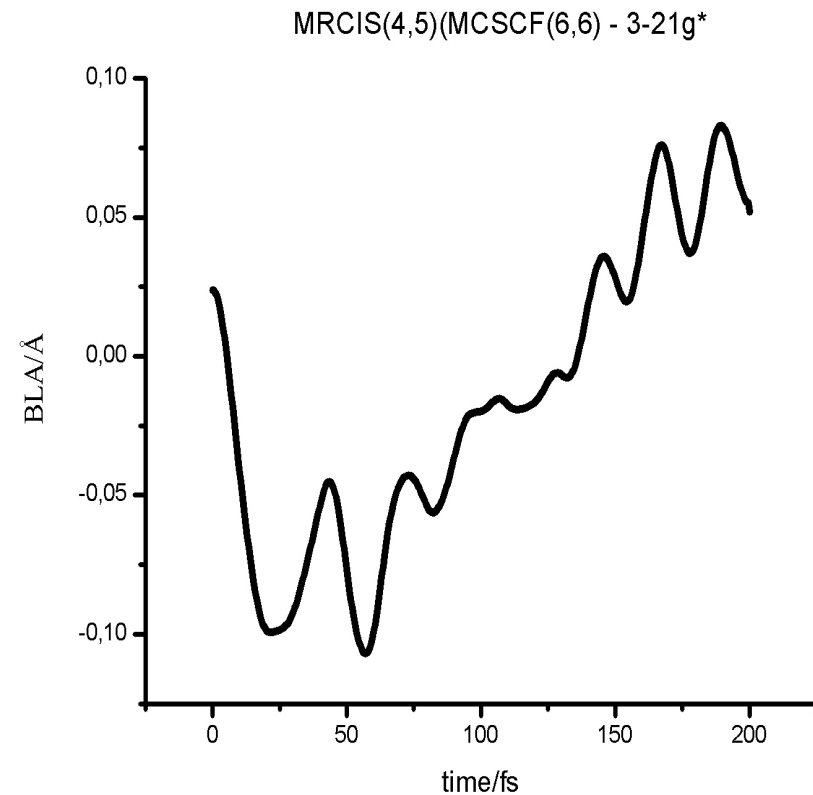
$$y = e^{-\frac{x-t_1}{t_2}}$$

- M C S C F (6-31g\*): 130.4 fs (47.5 fs)
- M C S C F (3-21g\*): 152.7 fs (32.5 fs)



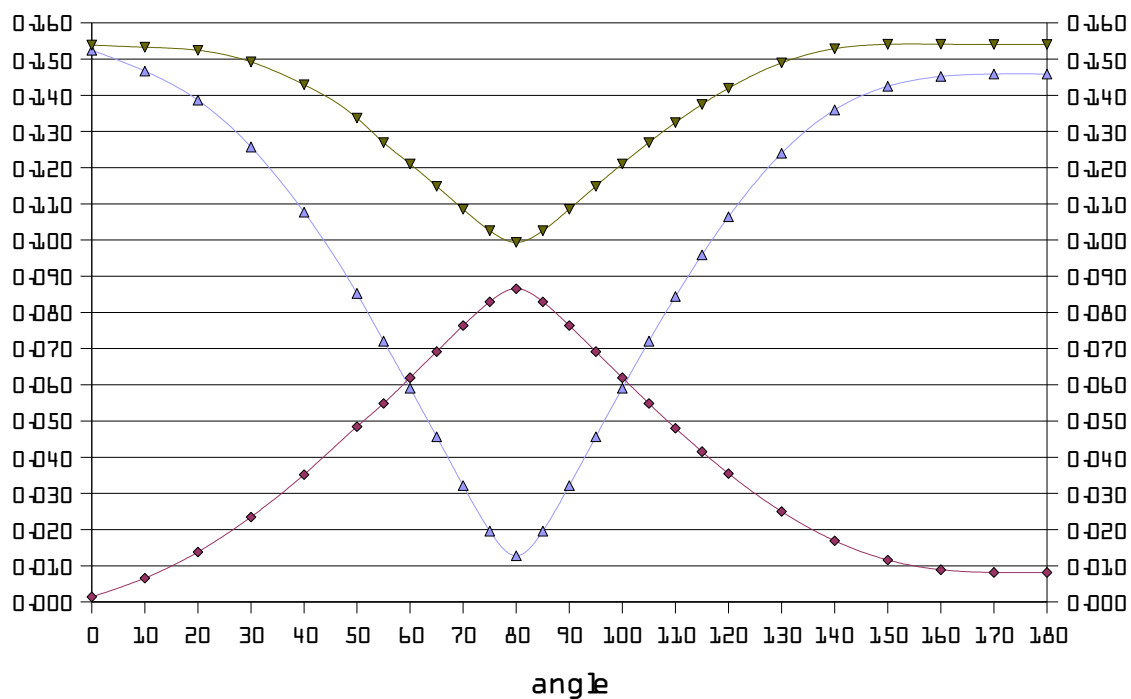
# results - BLA

- bond length average  
BLA=mean(single)-mean(double)
- changes right after excitation  
(no delay)
- possible connection to changes in orbitals



# results - central torsion

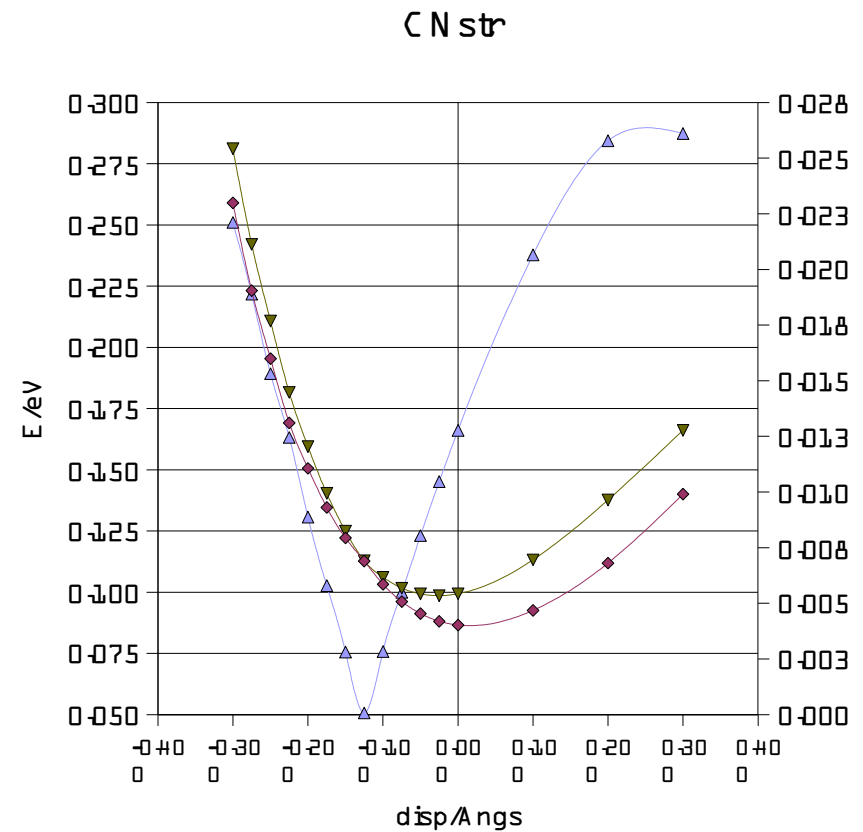
- CI not completely reached by central torsion
- minimum energy difference at  $\sim 80^\circ$
- MXS is at  $94^\circ$



potential energy curve for torsion around the central double bond of PSB3; ground state (red), excited state (yellow) and energy difference (blue); note that the CI is not completely reached by torsion alone; all values in eV

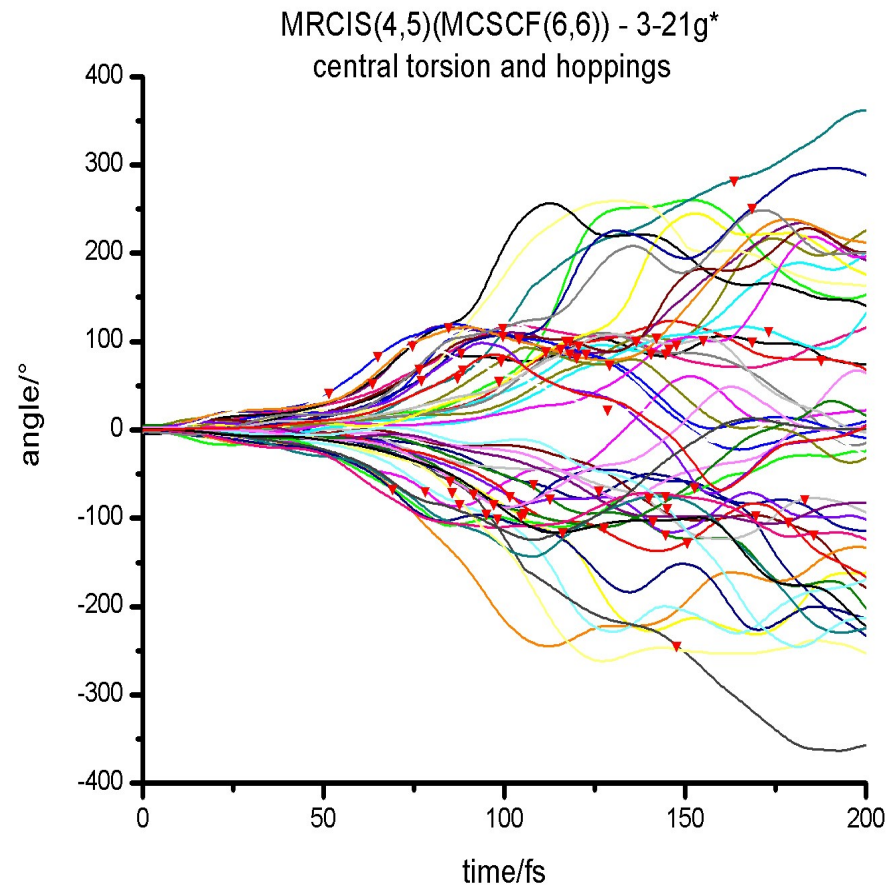
# results - central torsion

- additional C=N compression reaches Cl
- this is only one point of the seam



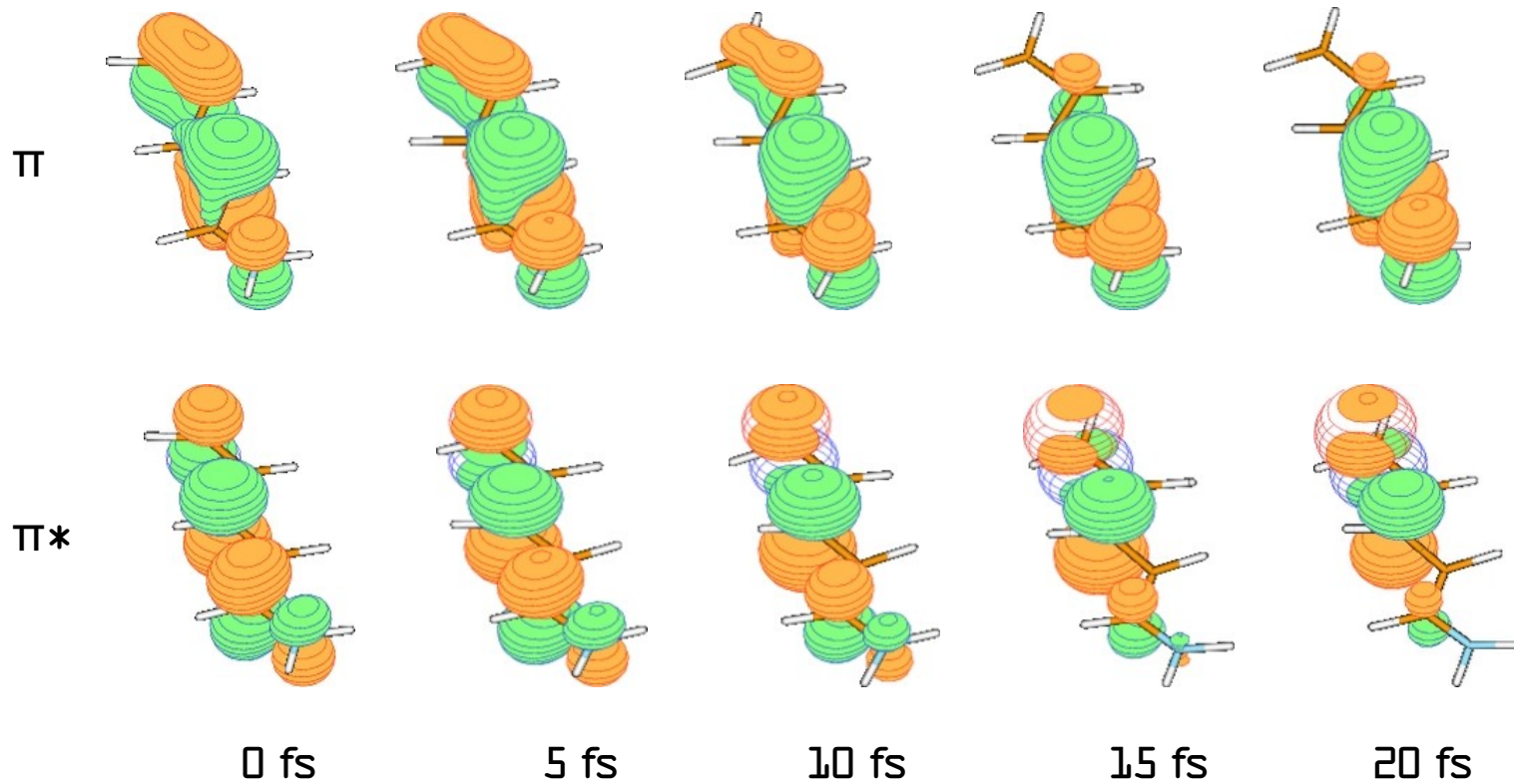
# results - central torsion

- mean torsional angle at hopping:  
 $90.4^\circ \pm 4.7^\circ$  ( $n=65; 95\%; s=18.98$ )
- initial delay clearly visible

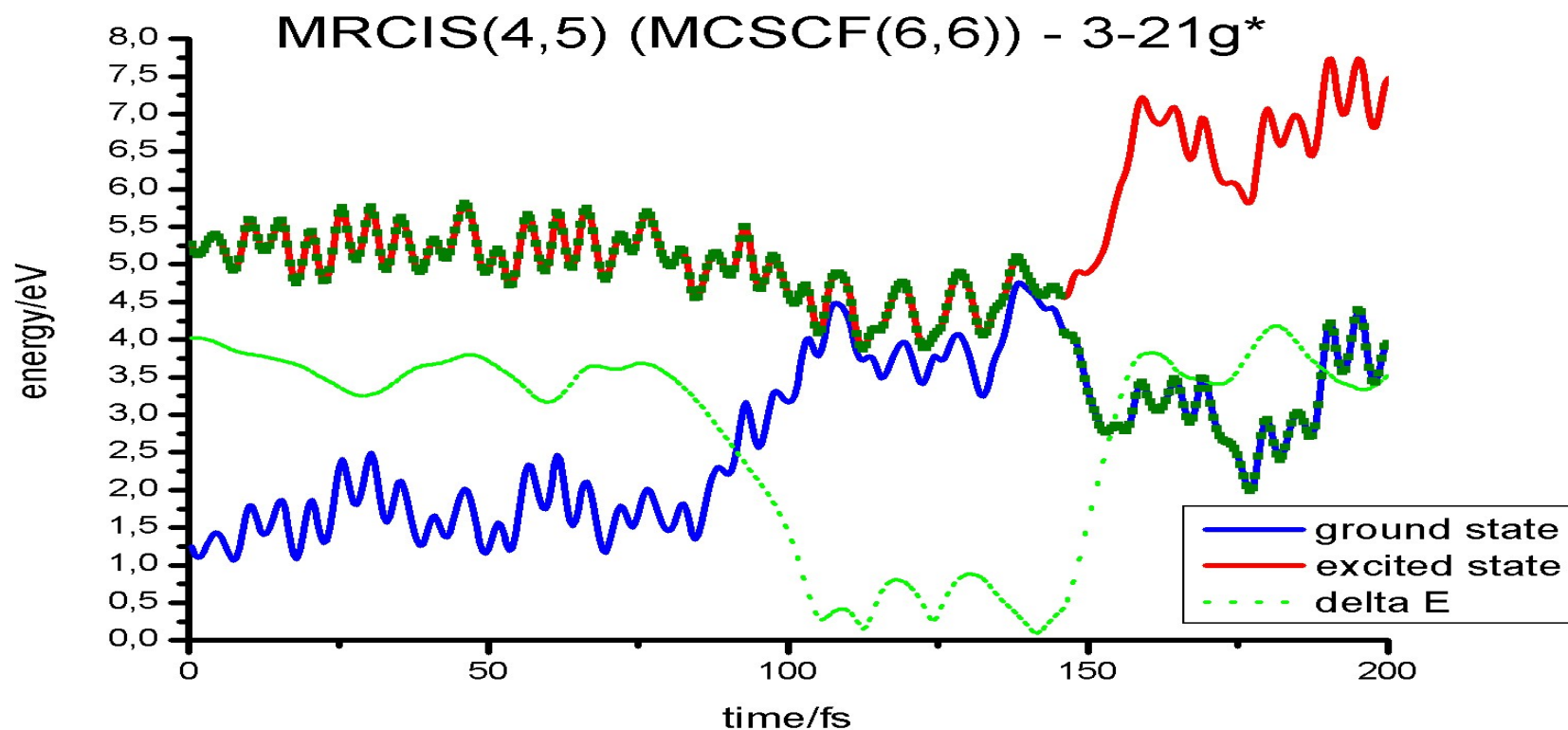


# results - orbitals

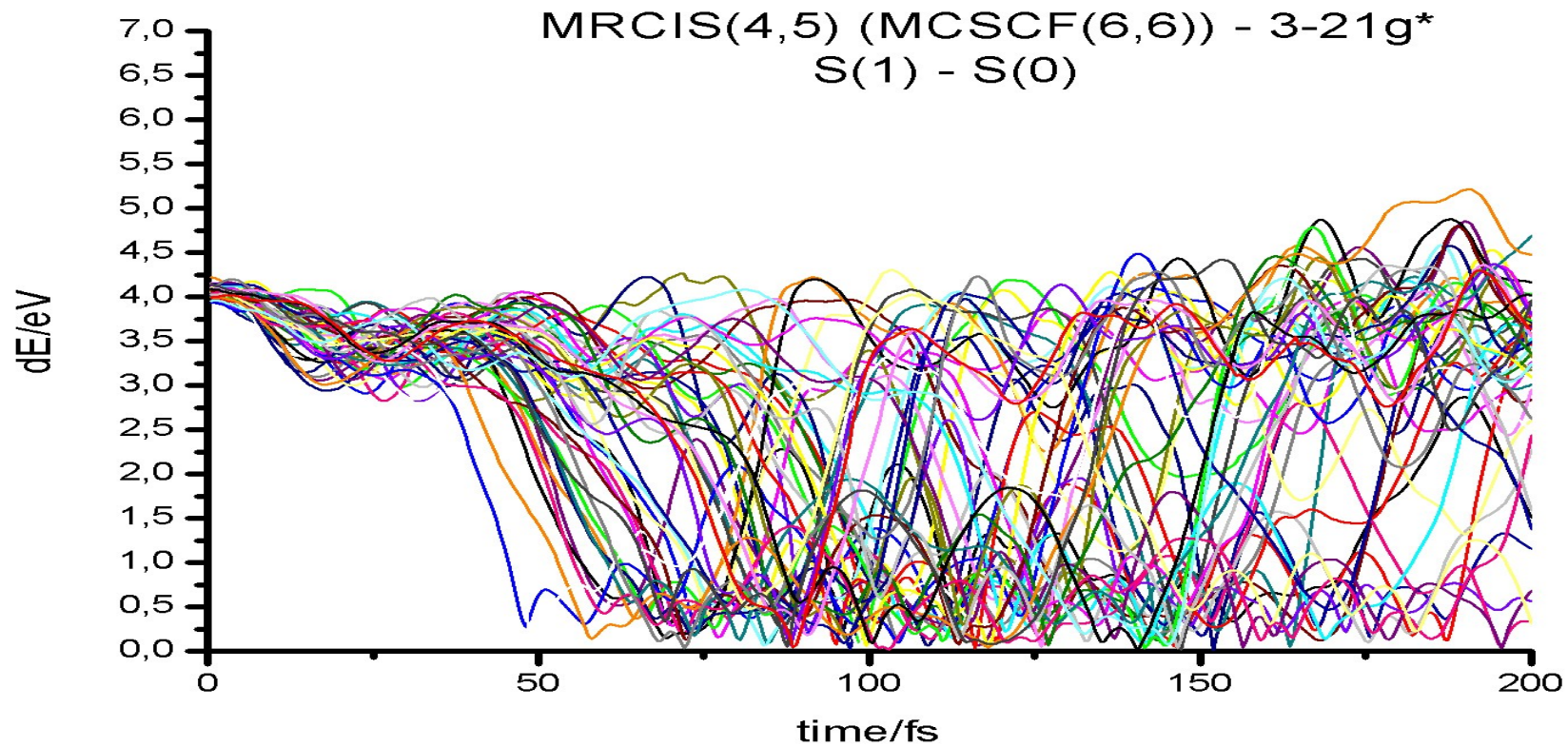
development of biradical structure ( $\pi$ - $\pi^*$ )



# results - energies



# results - energies



# conclusions

- descent to CI begins with evolution of biradical structure
- second step is a BLA-adjustment, possibly due to the above
- after  $\sim 50$ fs torsion around central double bond begins
- overall lifetime is  $\sim 150$ fs

Thank You for your attention!

Discussion/Questions