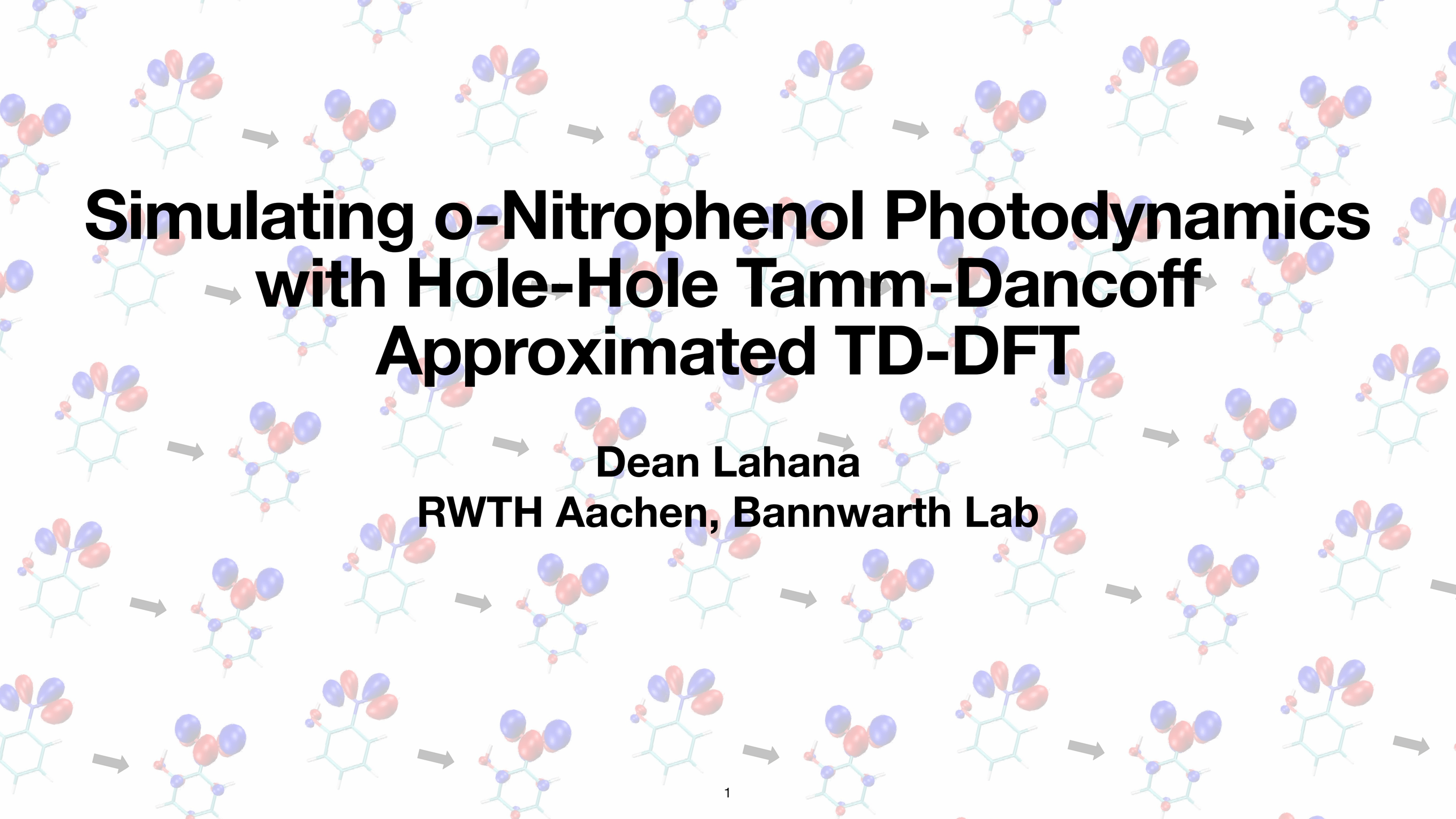
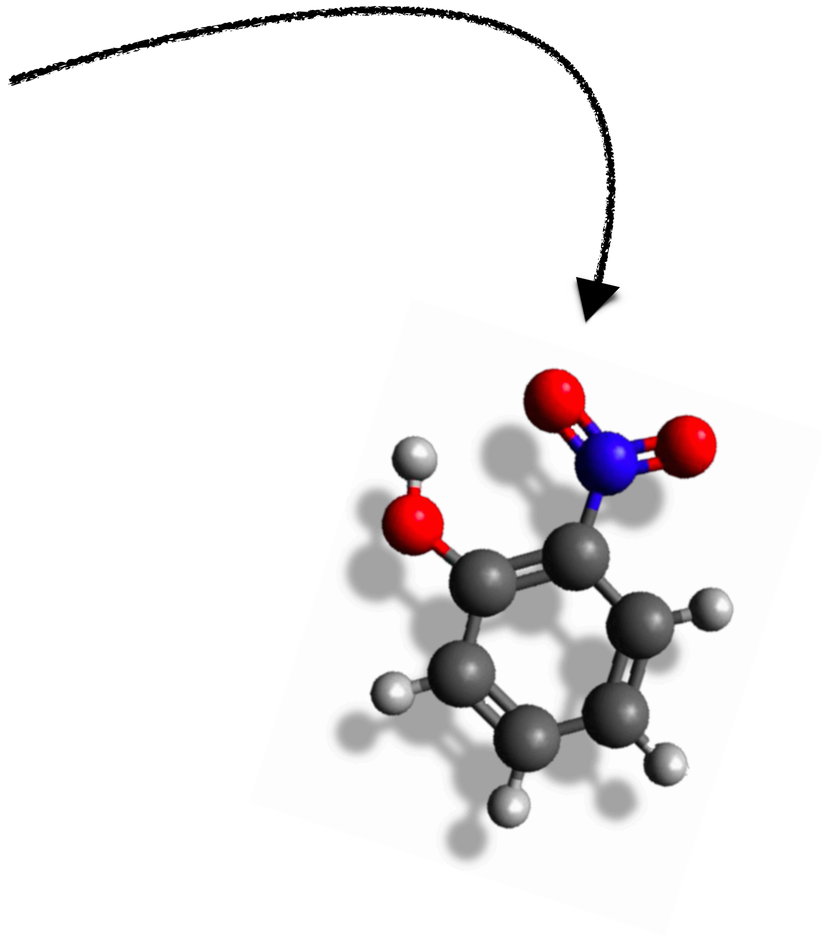


Simulating o-Nitrophenol Photodynamics with Hole-Hole Tamm-Dancoff Approximated TD-DFT

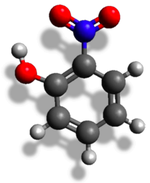
Dean Lahana
RWTH Aachen, Bannwarth Lab

The story within the story

- A small molecule that’s been the subject of many investigations
- Results have been repeatable, but paradoxical
- The resolution was sitting under our noses



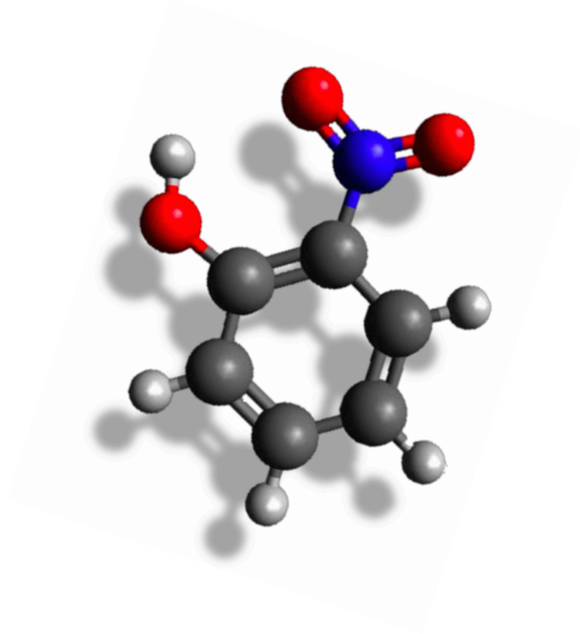
o-nitrophenol



- o-nitrophenol (oNP) got a lot of attention for ~30 years
  - Combustion product/industrial intermediate that was implicated in the production of daytime smog

$$oNP \xrightarrow{\lambda} C_6H_4O + HONO$$

$$HONO \xrightarrow{\lambda} NO\cdot + HO\cdot$$



- Many different theoretical and experimental techniques were applied in order to understand oNP photochemistry

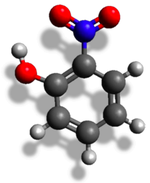
Landau-Zener **Ion-TOF** **TRPES**

UED **TA** **CASSCF** **TD-DFT**

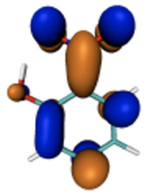
ADC **EOM-CC**

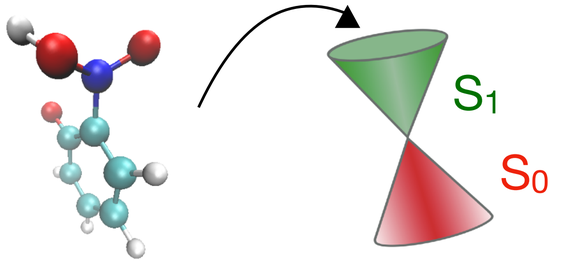
CASPT2 **FSSH** **AIMS** **FOMO-CASCI**

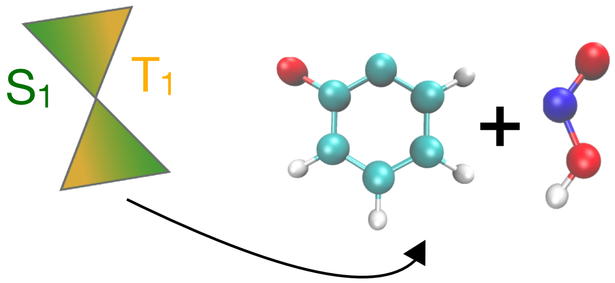
Problem solved?



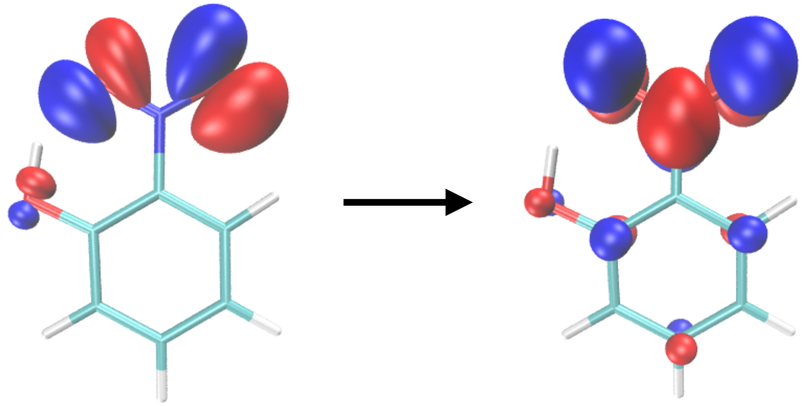
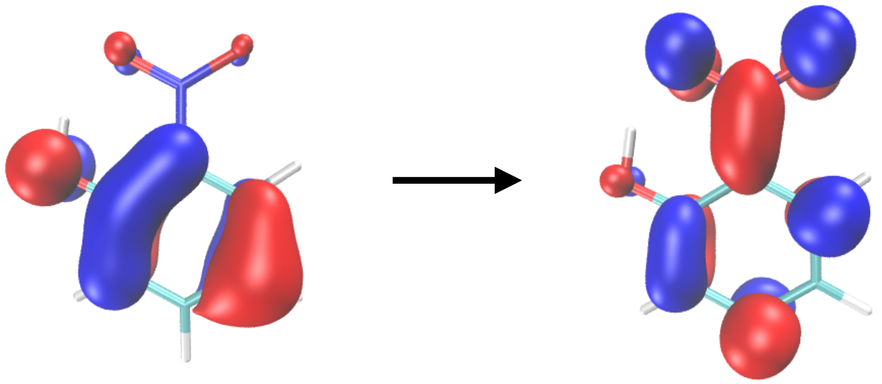
- A consensus was mostly a
  - S_1 is a bright state with $\pi\pi^*$
  - Excitation to S_1 is follow ular proton transfer to form a p)
  - Ground state recovery is d MECI within ~500 fs
  - Complicated dynamics (ion) occur on triplet manifold
- How to reconcile ultrafast internal conversion with eventual intersystem crossing?



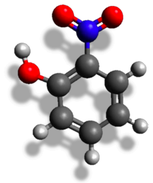




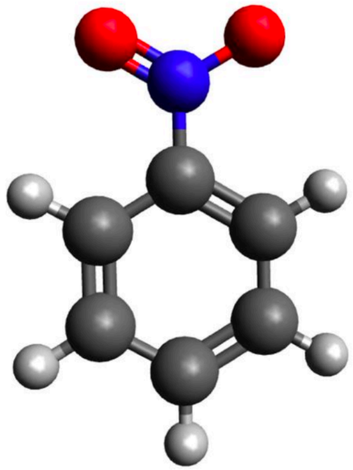
Excited states of oNP

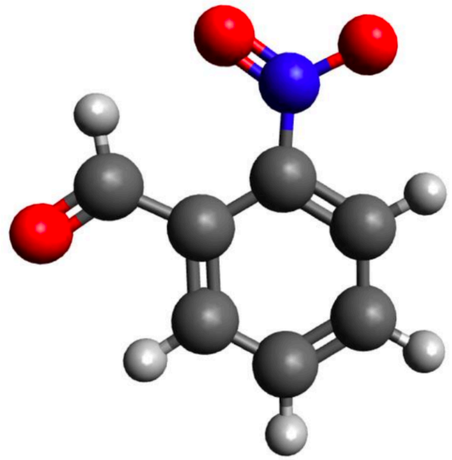
	S_1	S_2
EOM-CCSD Reference		
Dynamics		

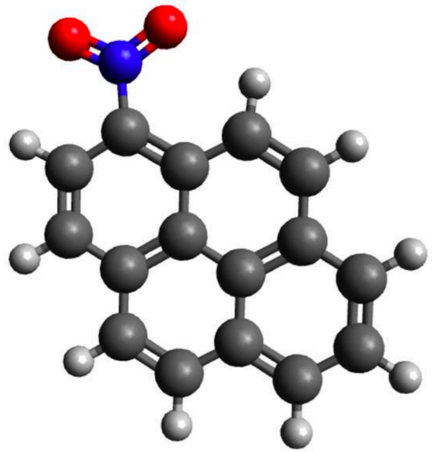
How did we miss that?



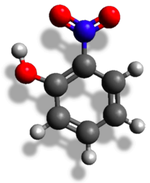
- Sort of understandable
  - Dark $n \rightarrow \pi^*$ state is energetically degenerate with bright $\pi \rightarrow \pi^*$ state in FC region (no absorption signature)
  - There is some consensus about oNP photodynamics in the literature
- But also not totally understandable
  - Everything that looks anything like o-nitrophenol has a low-lying $n \rightarrow \pi^*$ state

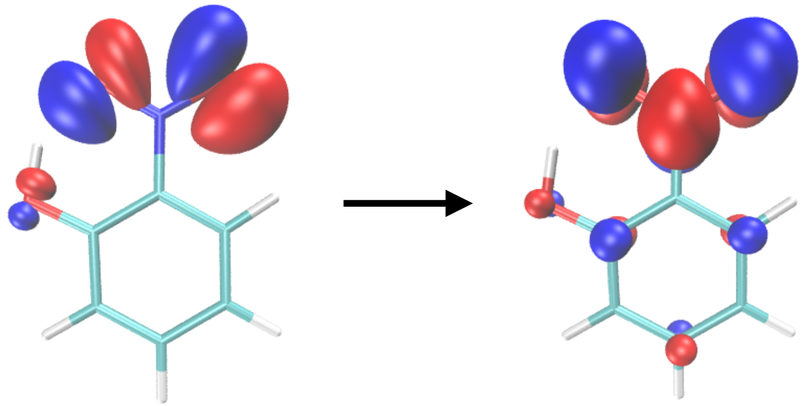
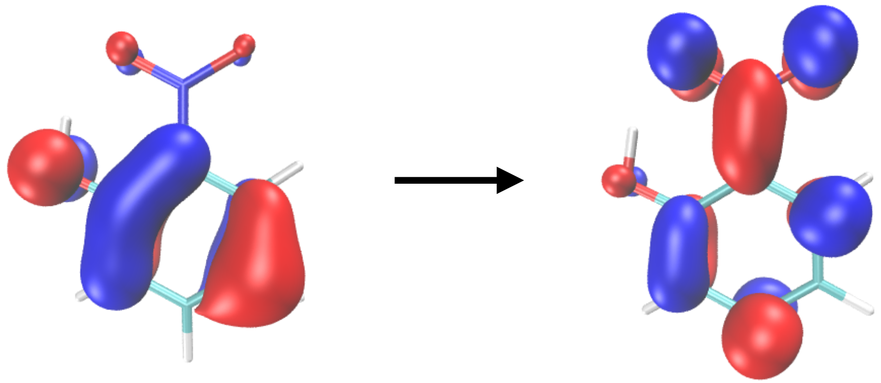




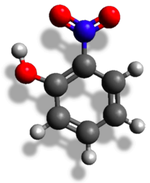


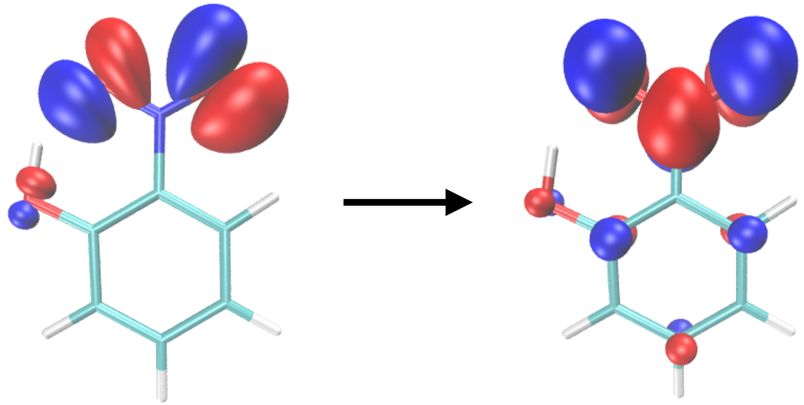
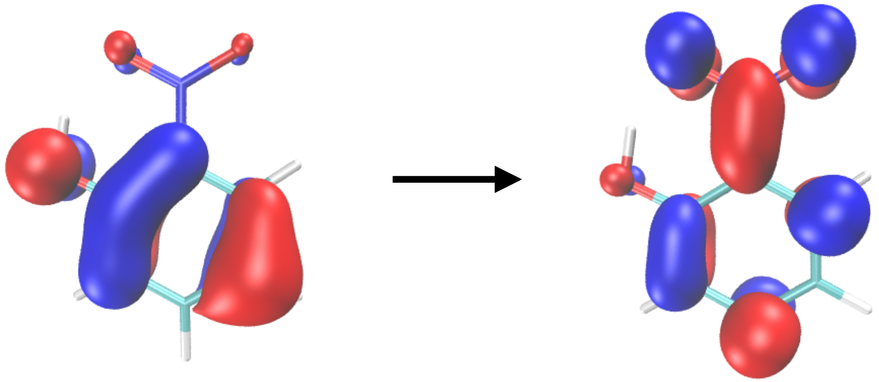
Electronic structure candidates for dynamics



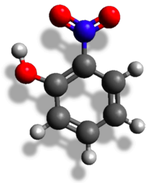
	S_1	S_2
EOM-CCSD Reference		
EOM-CCSD? Dynamics	• Good description of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ states ✅ • Expensive ❌ • No S_0/S_1 conical intersections* ❌ *Methods like SC-CCSD now exist and have gradients and NACVs implemented	

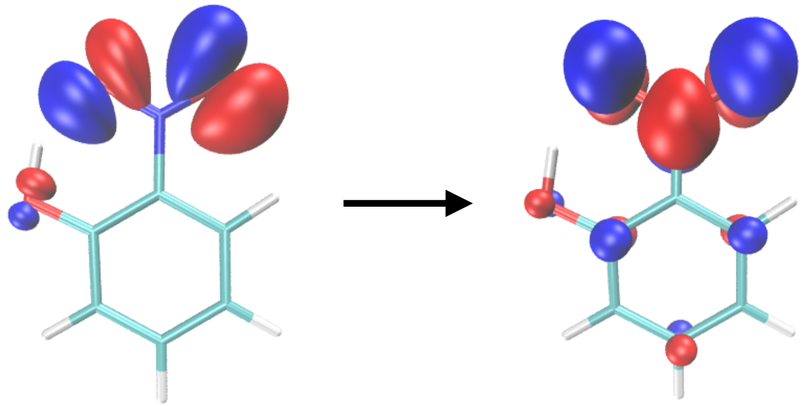
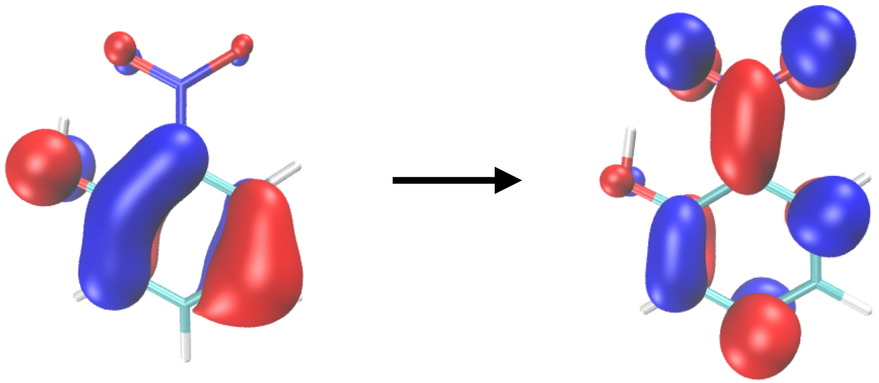
Electronic structure candidates for dynamics



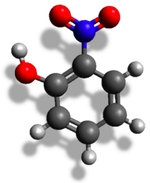
	S_1	S_2
EOM-CCSD Reference		
TD-DFT? Dynamics	• Good description of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ states ✅ • Cheap ✅ • No S_0/S_1 conical intersections ❌	

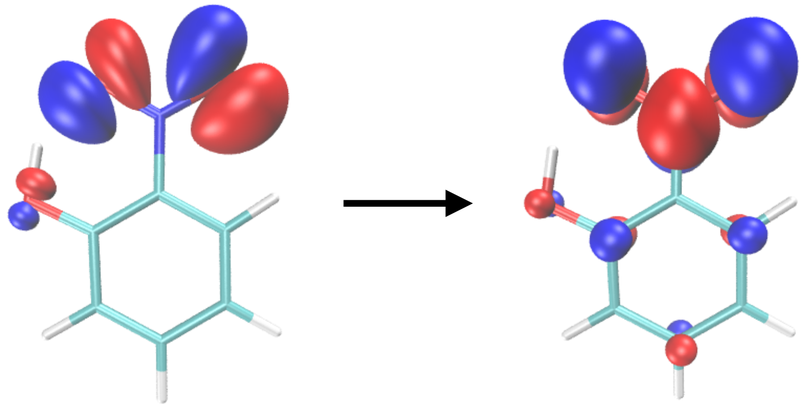
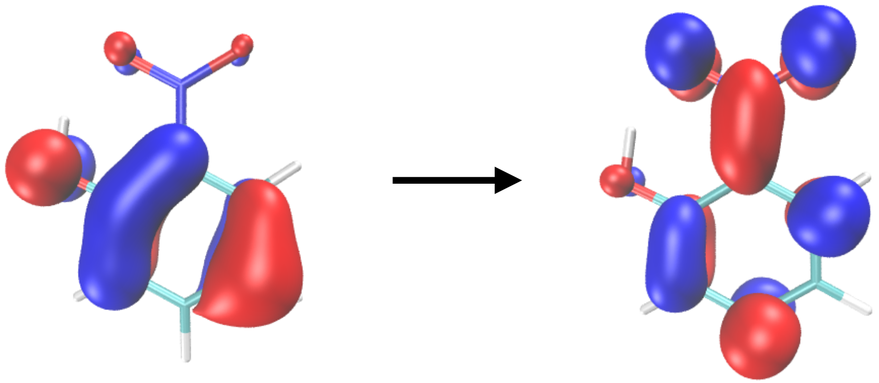
Electronic structure candidates for dynamics



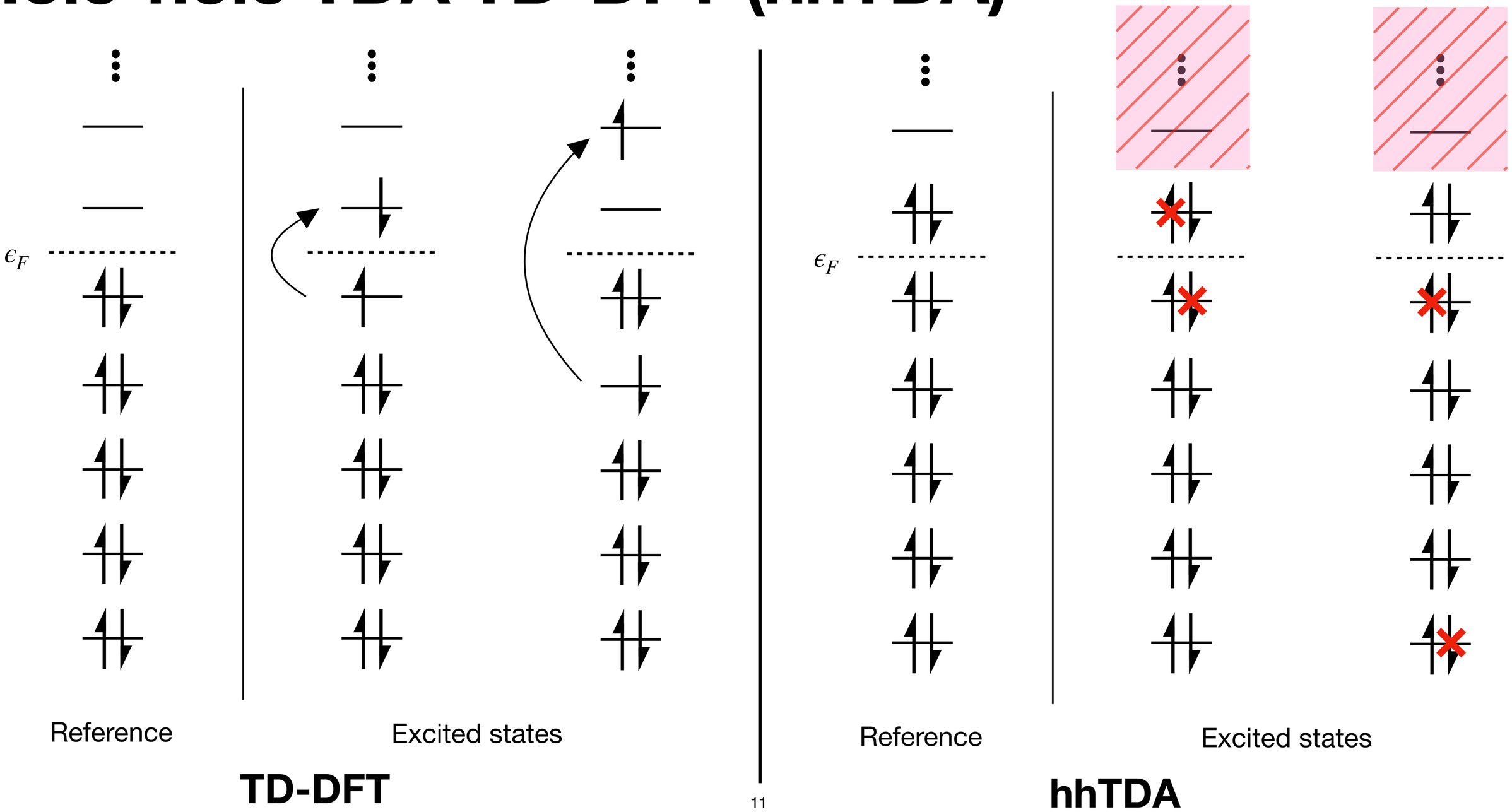
	S_1	S_2
EOM-CCSD Reference		
CAS? Dynamics	• Cheap(-ish) ✅ • S_0/S_1 conical intersections ✅ • Poor description of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ states ❌	

Electronic structure candidates for dynamics

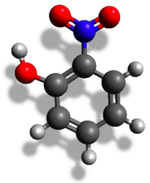


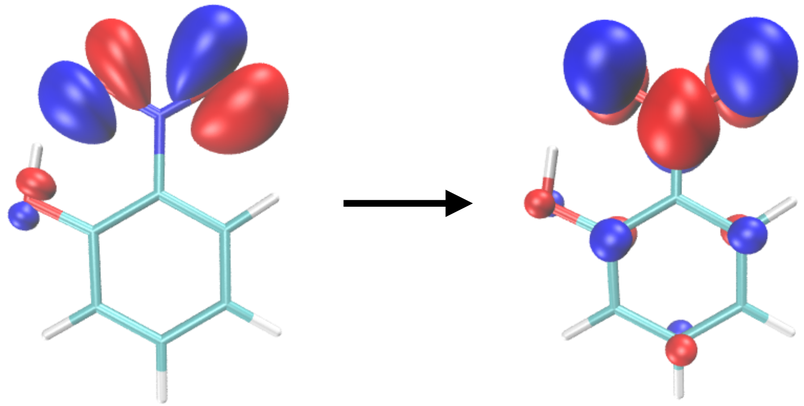
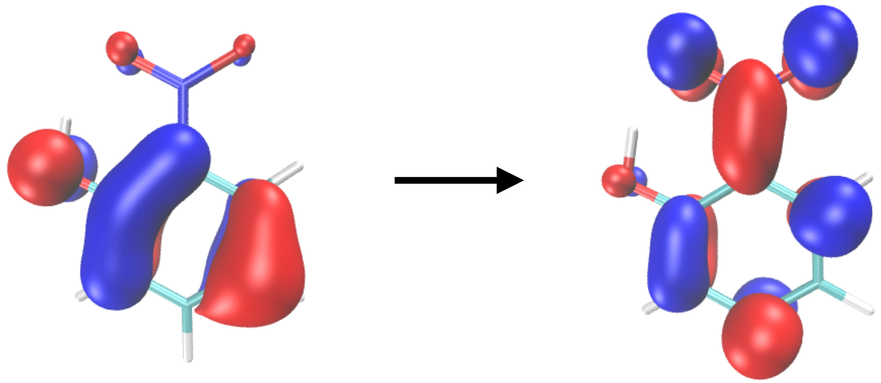
	S_1	S_2
EOM-CCSD Reference		
CASPT2? Dynamics	• S_0/S_1 conical intersections ✅ • Decent description of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ states ✅ • Expensive ❌	

Hole-hole TDA TD-DFT (hhTDA)

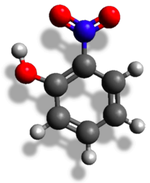


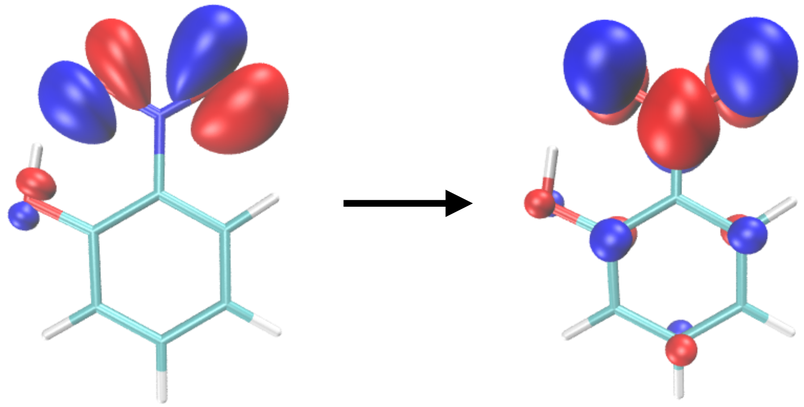
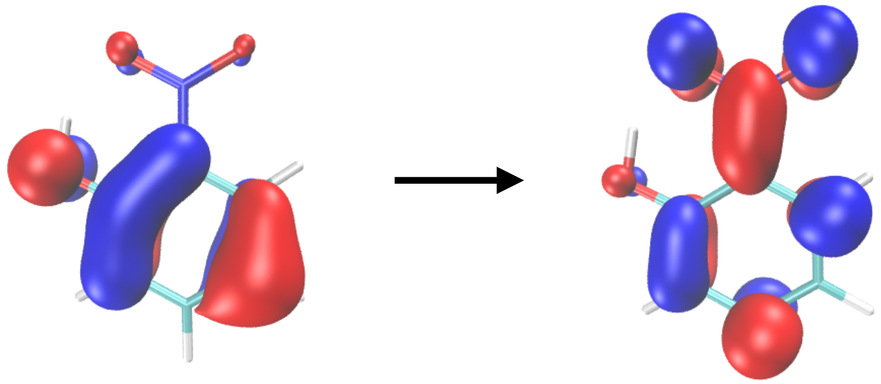
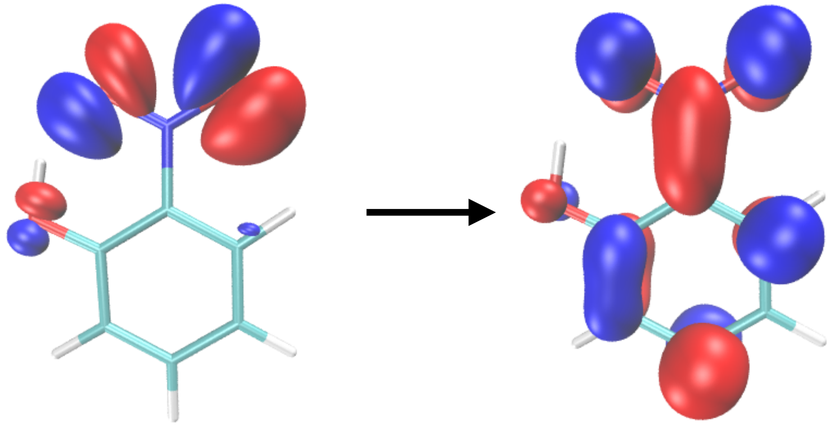
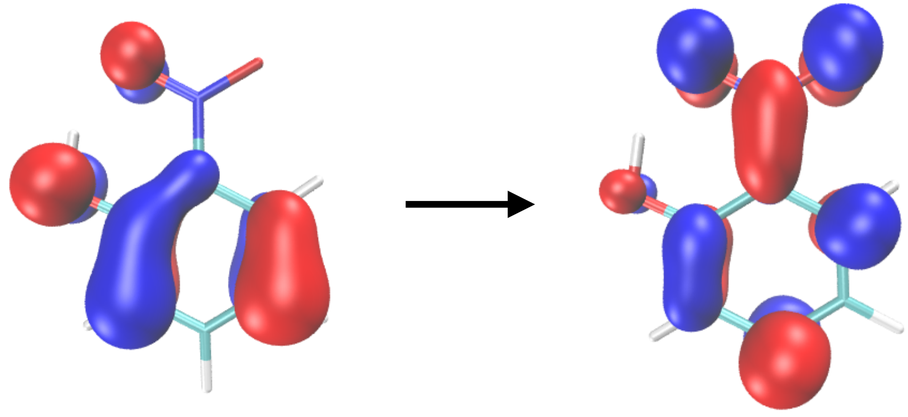
Electronic structure candidates for dynamics



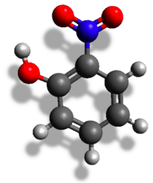
	S_1	S_2
EOM-CCSD Reference		
hhTDA? Dynamics	• S_0/S_1 conical intersections ✅ • Excellent description of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ states ✅ • Cheap ✅	

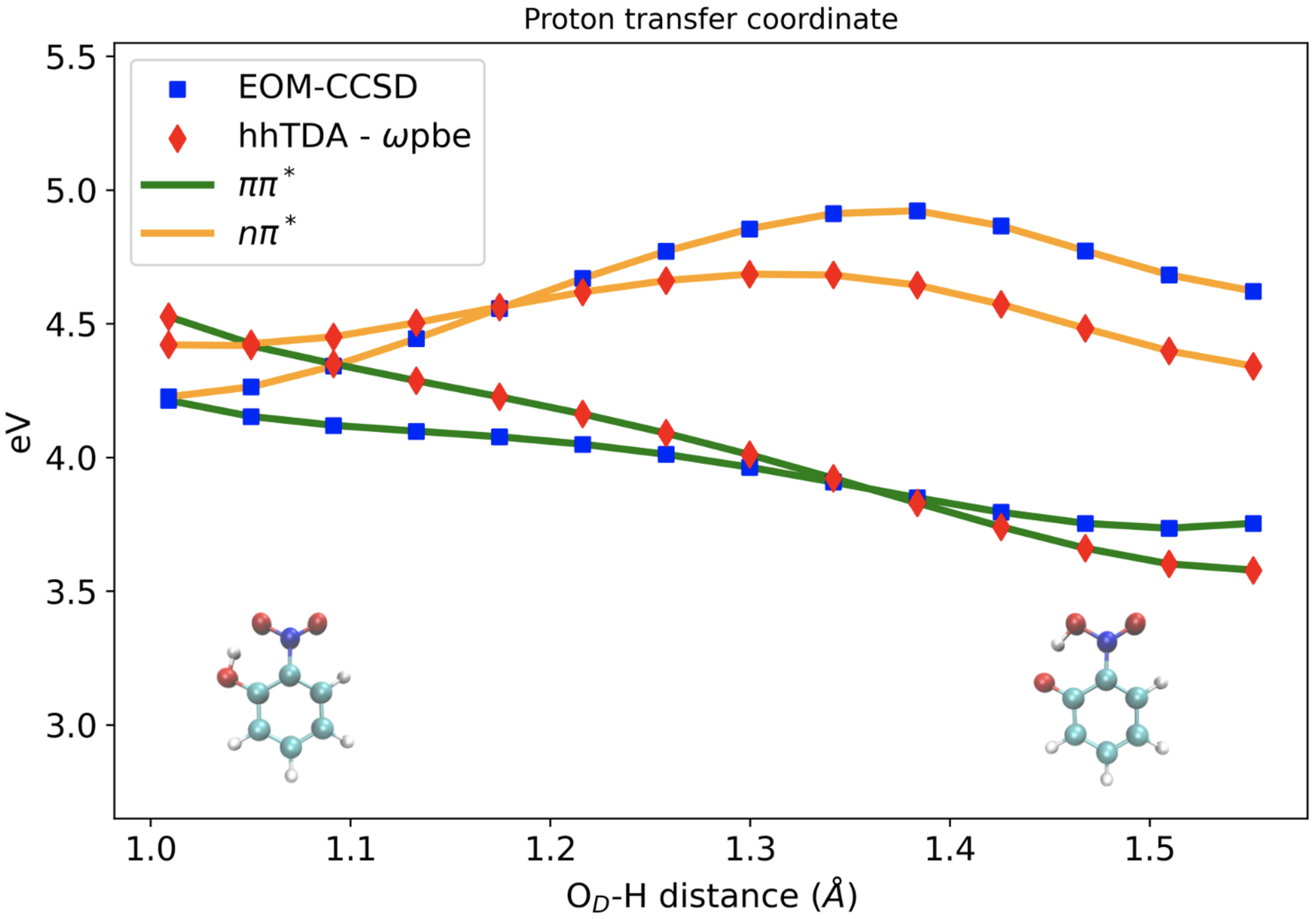
Electronic structure candidates for dynamics



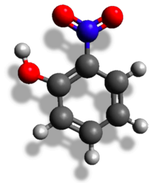
	S_1	S_2
EOM-CCSD Reference		
hhTDA Dynamics		

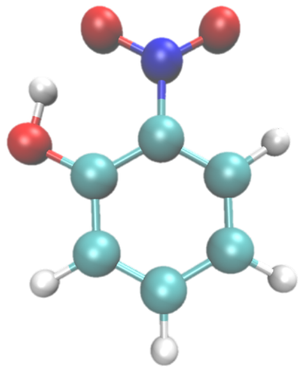
Excited-state intramolecular proton transfer

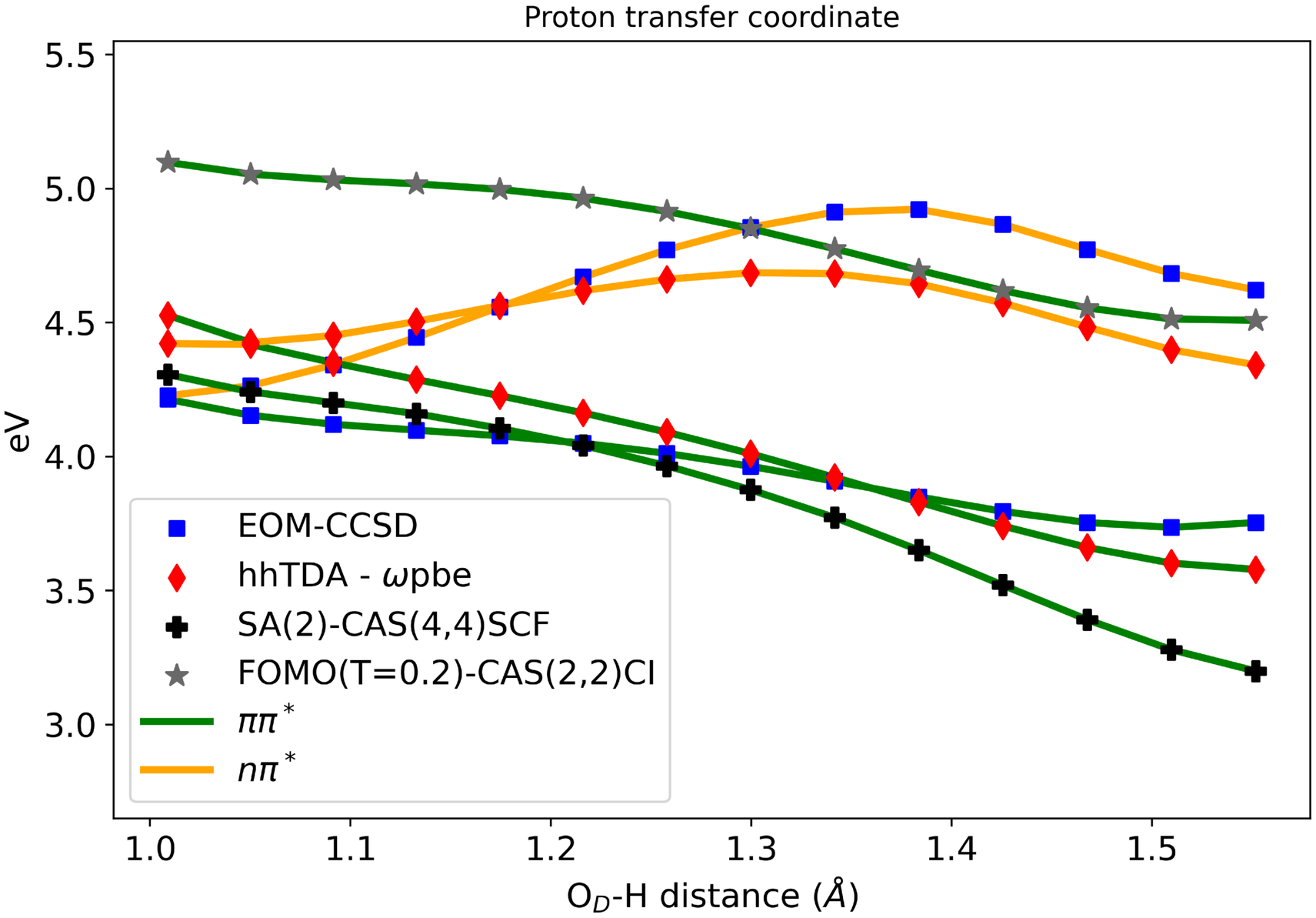


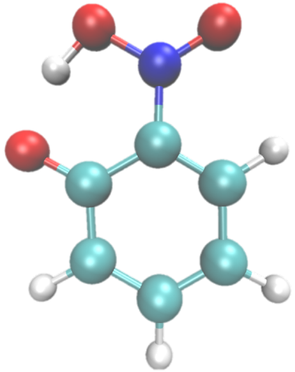


Excited-state intramolecular proton transfer

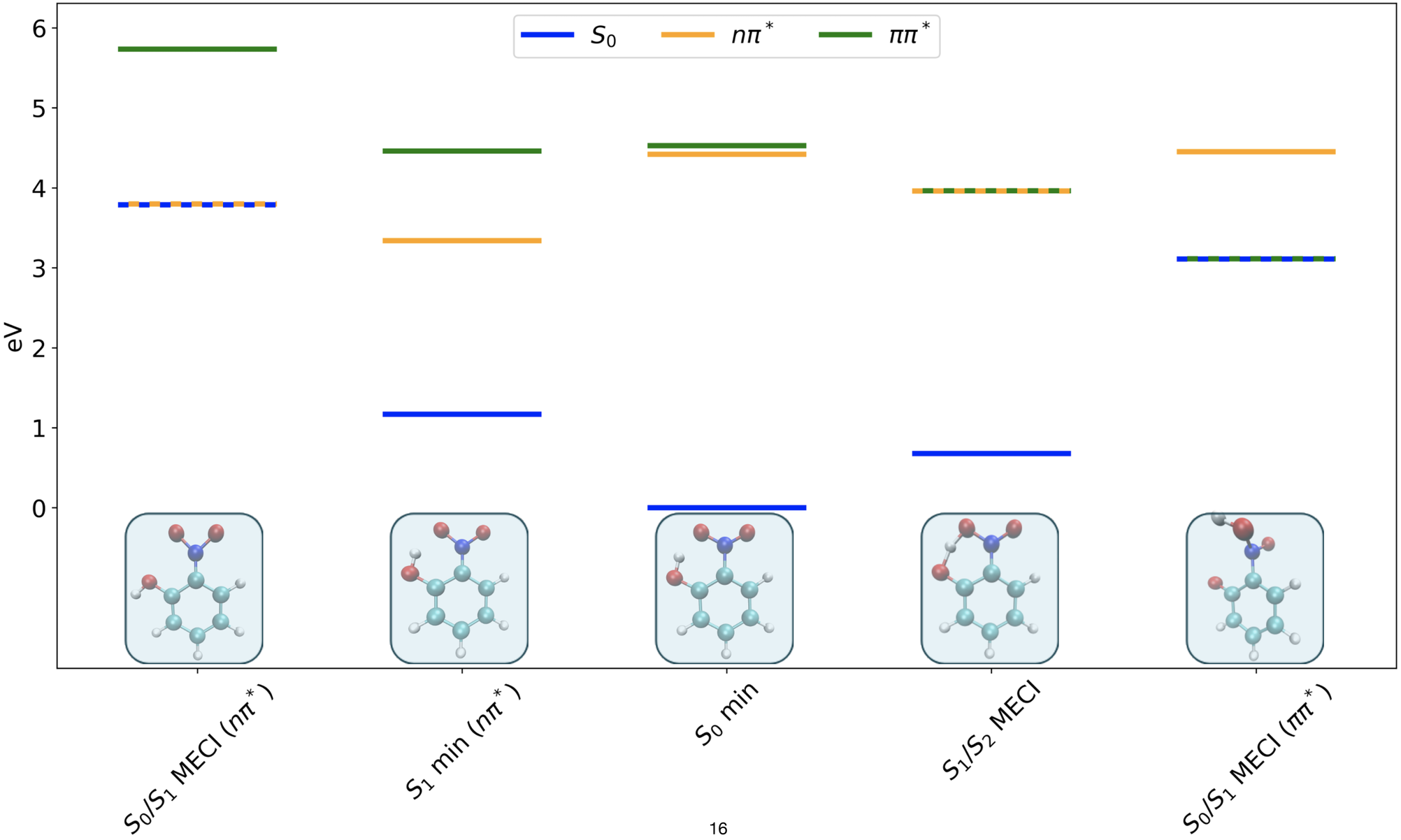




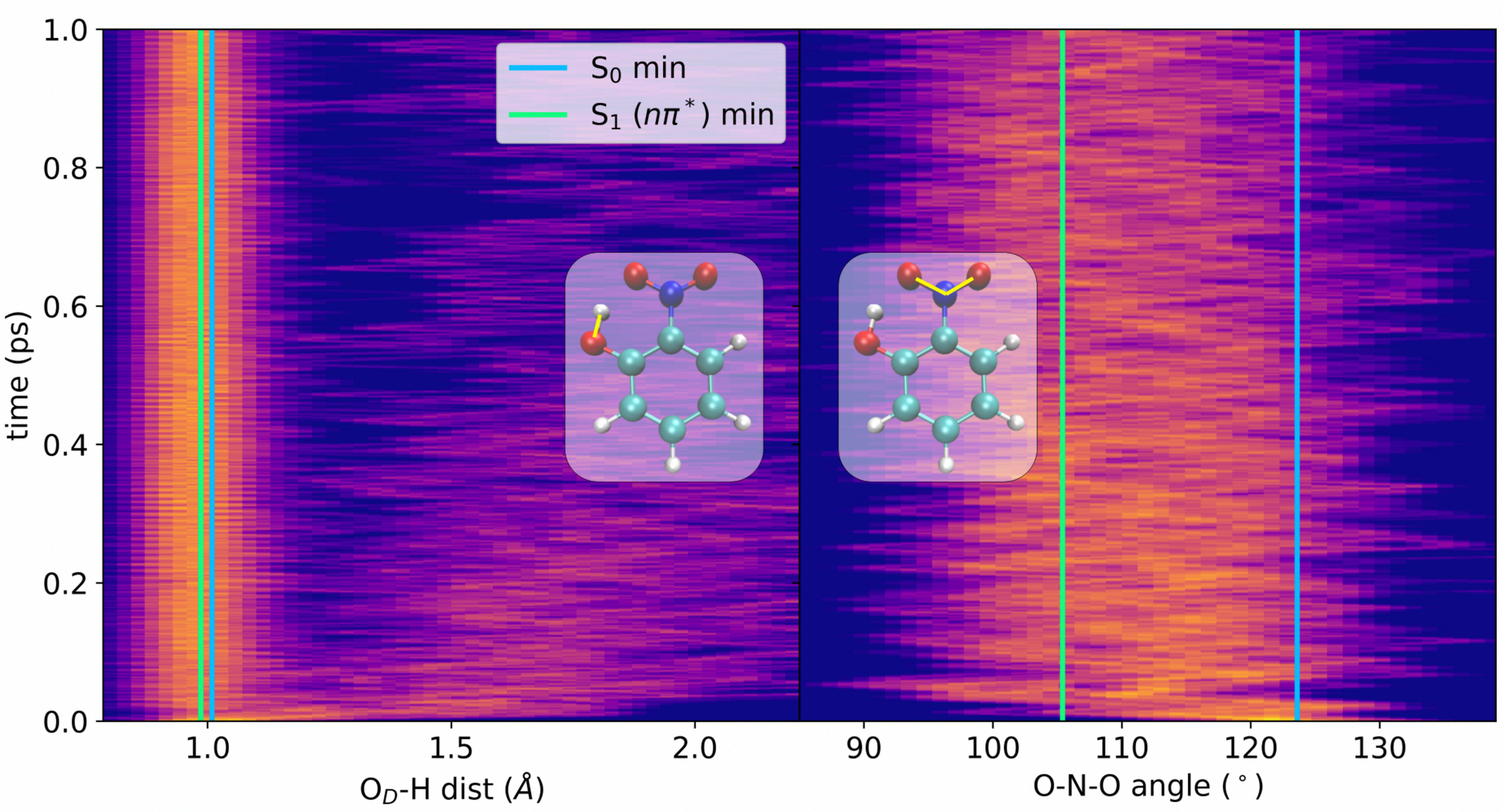




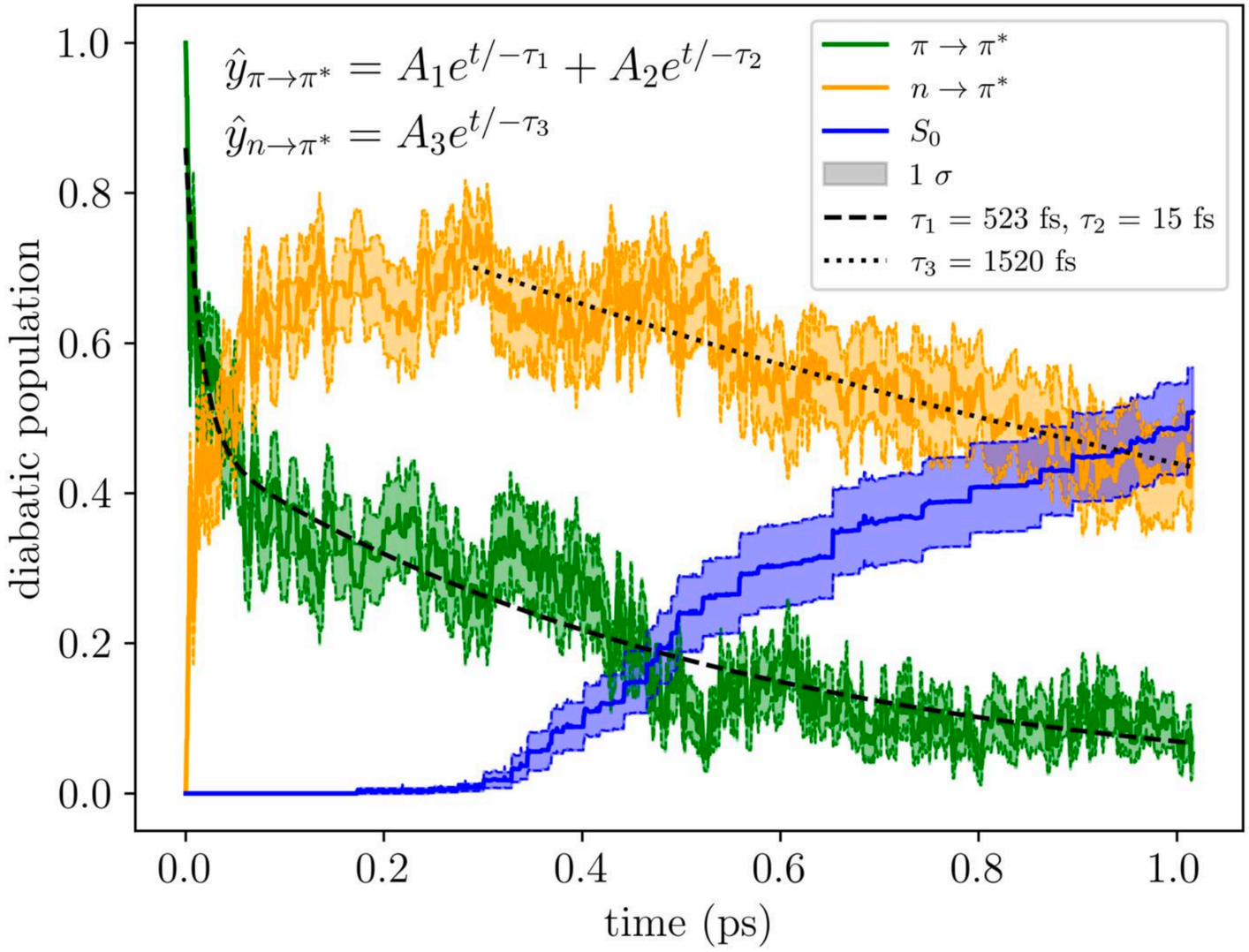
Critical geometries



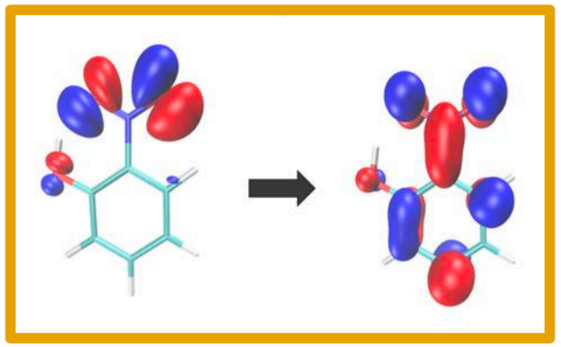
Geometric trends in dynamics



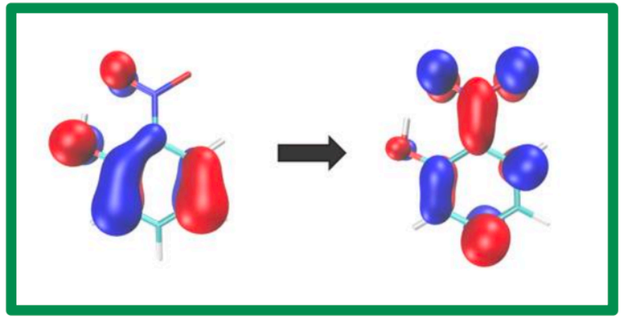
Population dynamics



$n \to \pi^*$

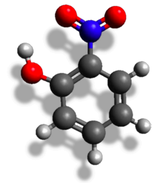


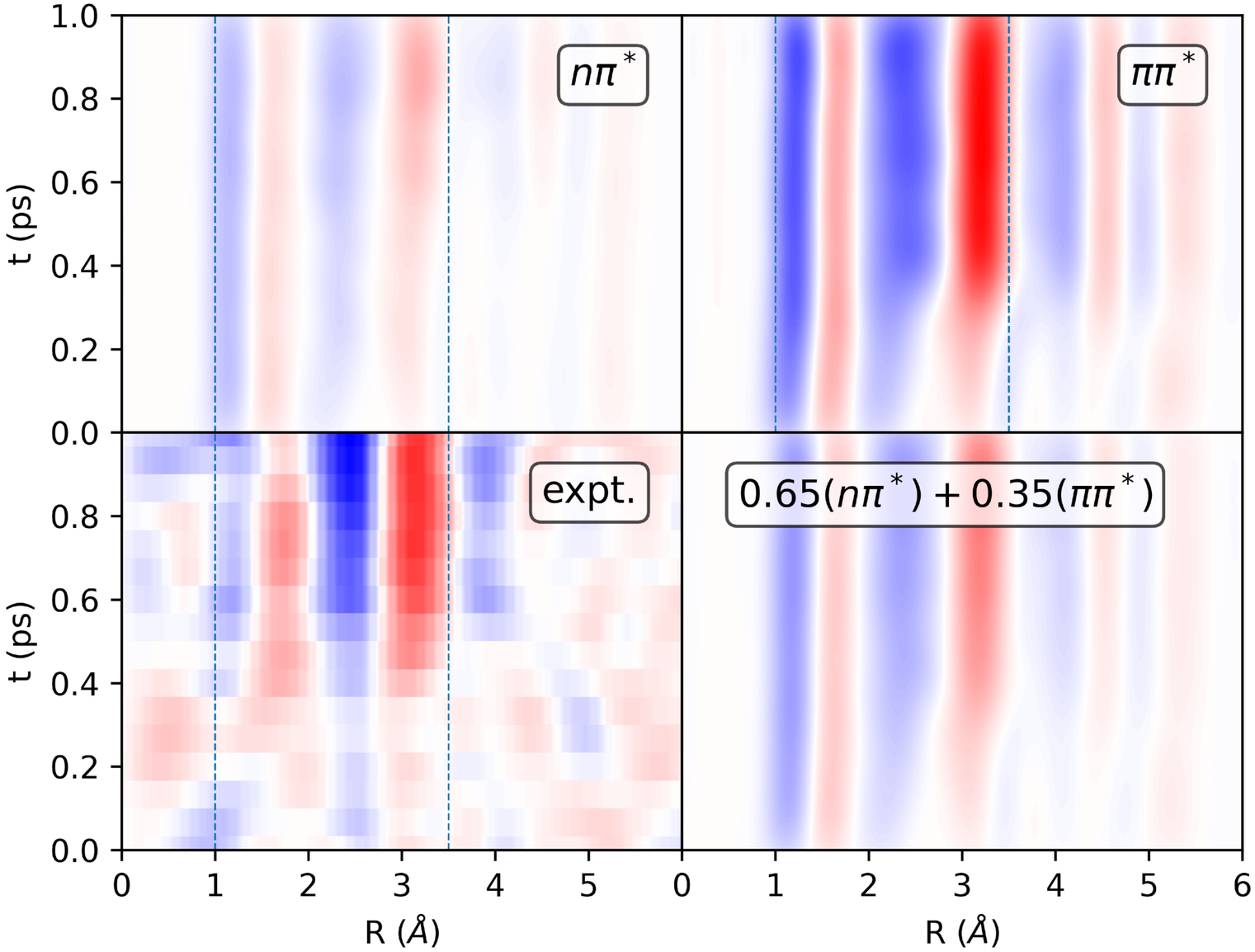
$\pi \to \pi^*$



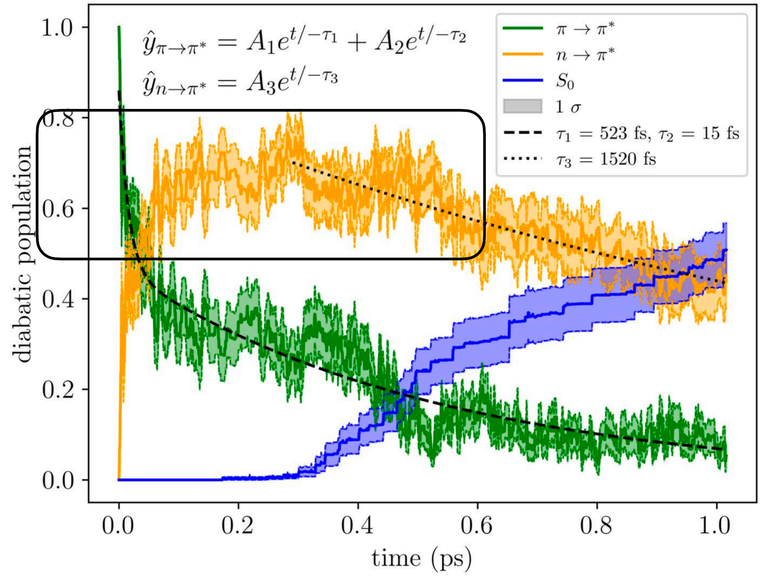
>60% undergoing $n \to \pi^*$ dynamics

Comparing to UED

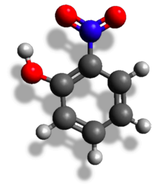


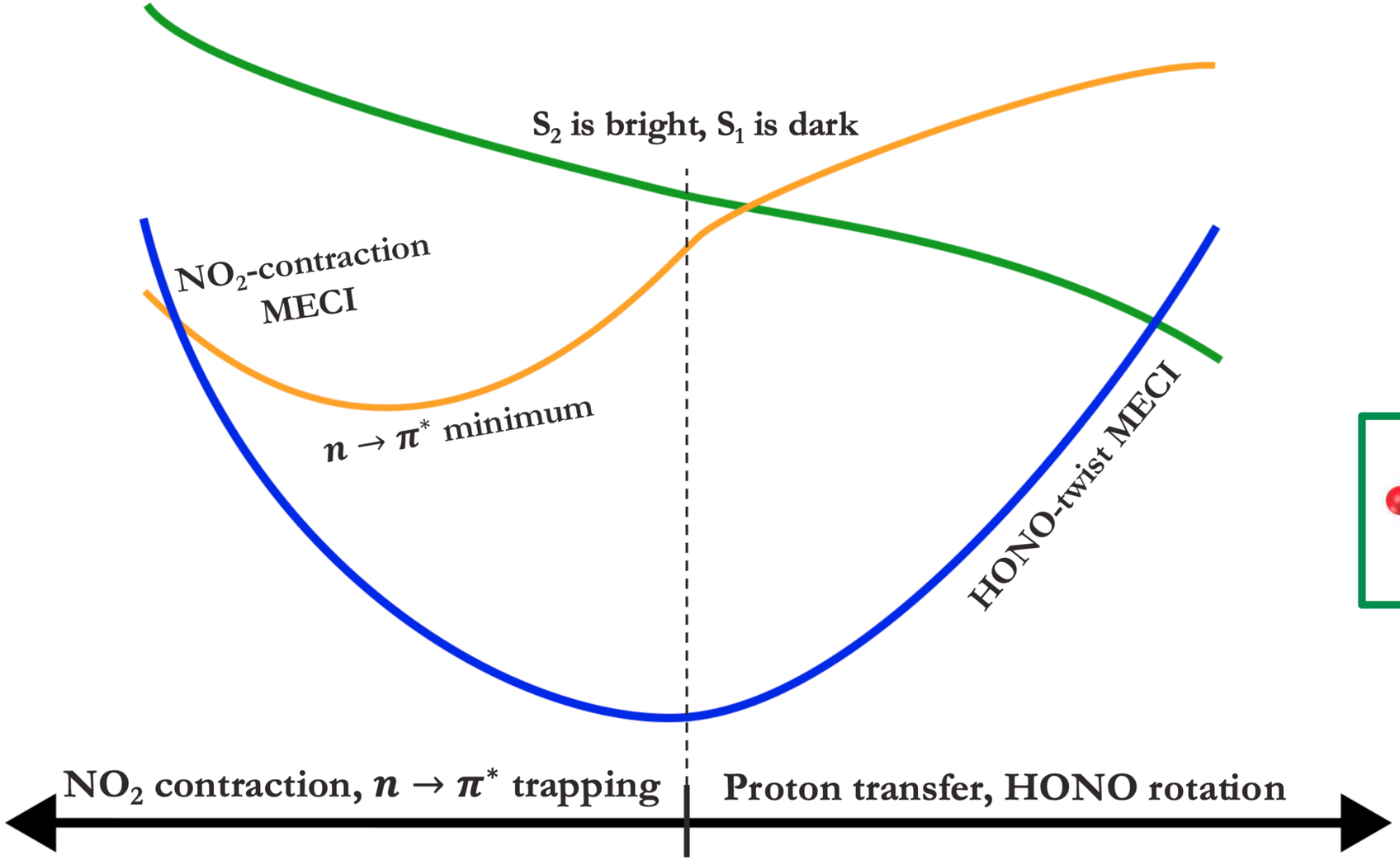


*state labels assigned by comparison to transition dipole moments at FC

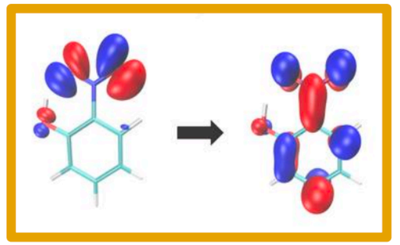


A new picture of oNP photodynamics

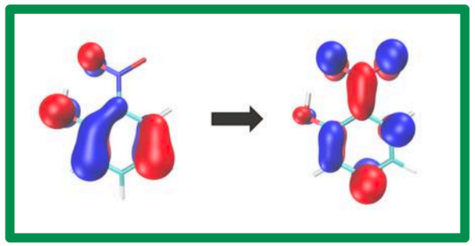




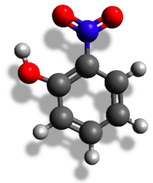
$n \rightarrow \pi^*$

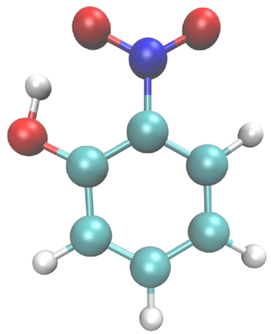


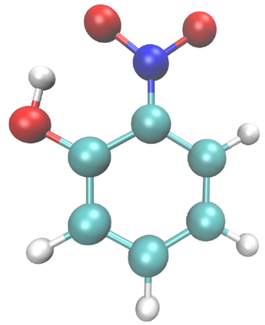
$\pi \rightarrow \pi^*$

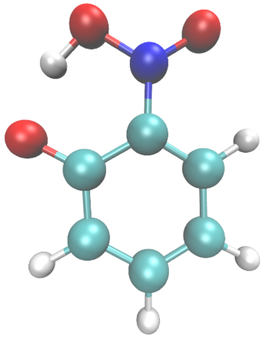


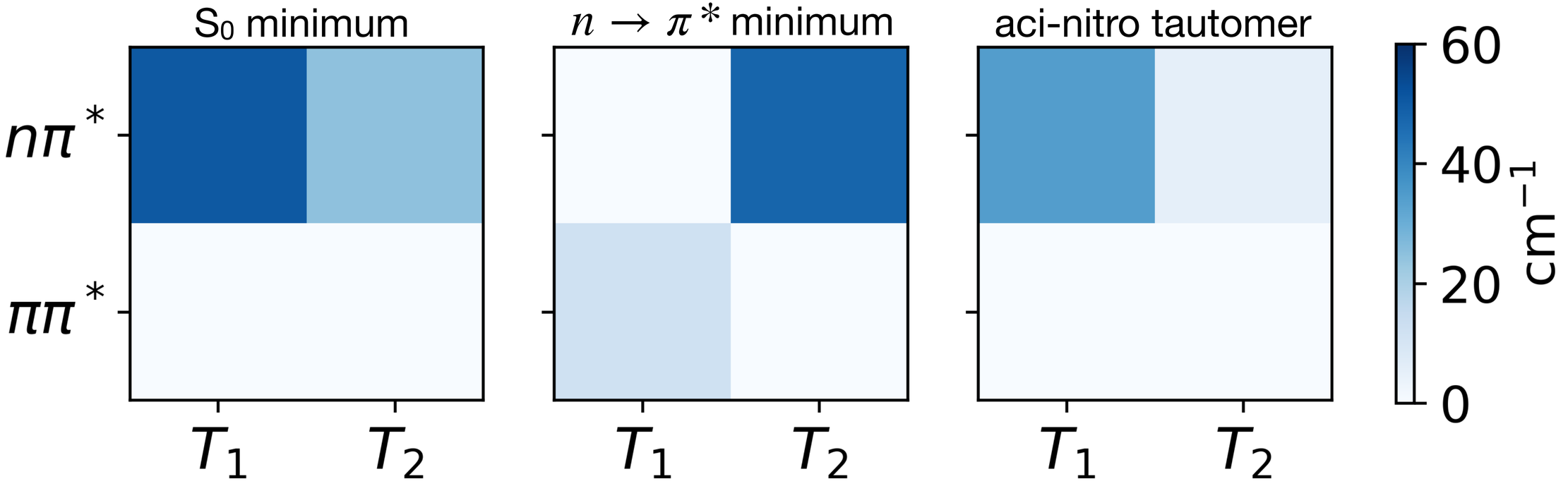
Intersystem crossing?



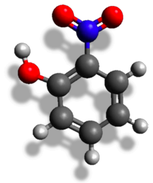








Conclusions

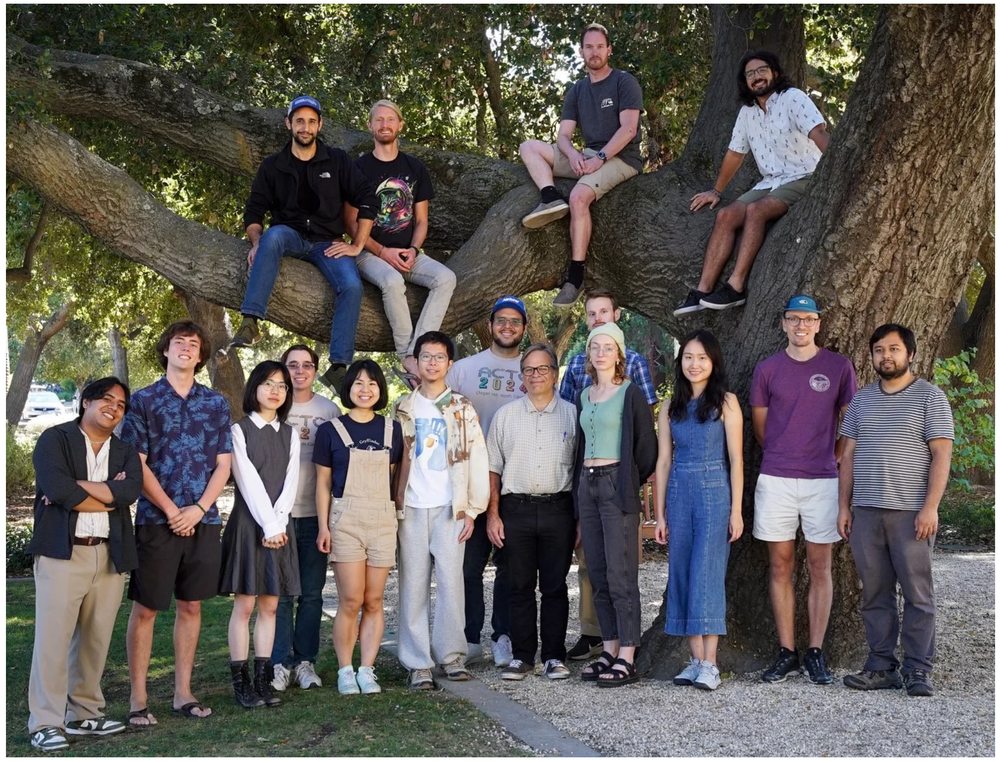


- hhTDA achieved EOM-CCSD-like accuracy but is fast enough for non-adiabatic dynamics simulations
- Low-lying $n \rightarrow \pi^*$ state exists in oNP and interacts with bright $\pi \rightarrow \pi^*$ state dynamics
- ISC to triplet manifold is enabled by $n \rightarrow \pi^*$ state trapping

Next steps

- Simulate TR-NEXAFS with hhTDA to show electronic signature of $n \rightarrow \pi^*$ dynamics
- Track ISC from $n \rightarrow \pi^*$ minimum via quasi-static rate theories and dynamics simulations including both singlet and triplet manifolds
- Throw hhTDA at other nitroaromatics

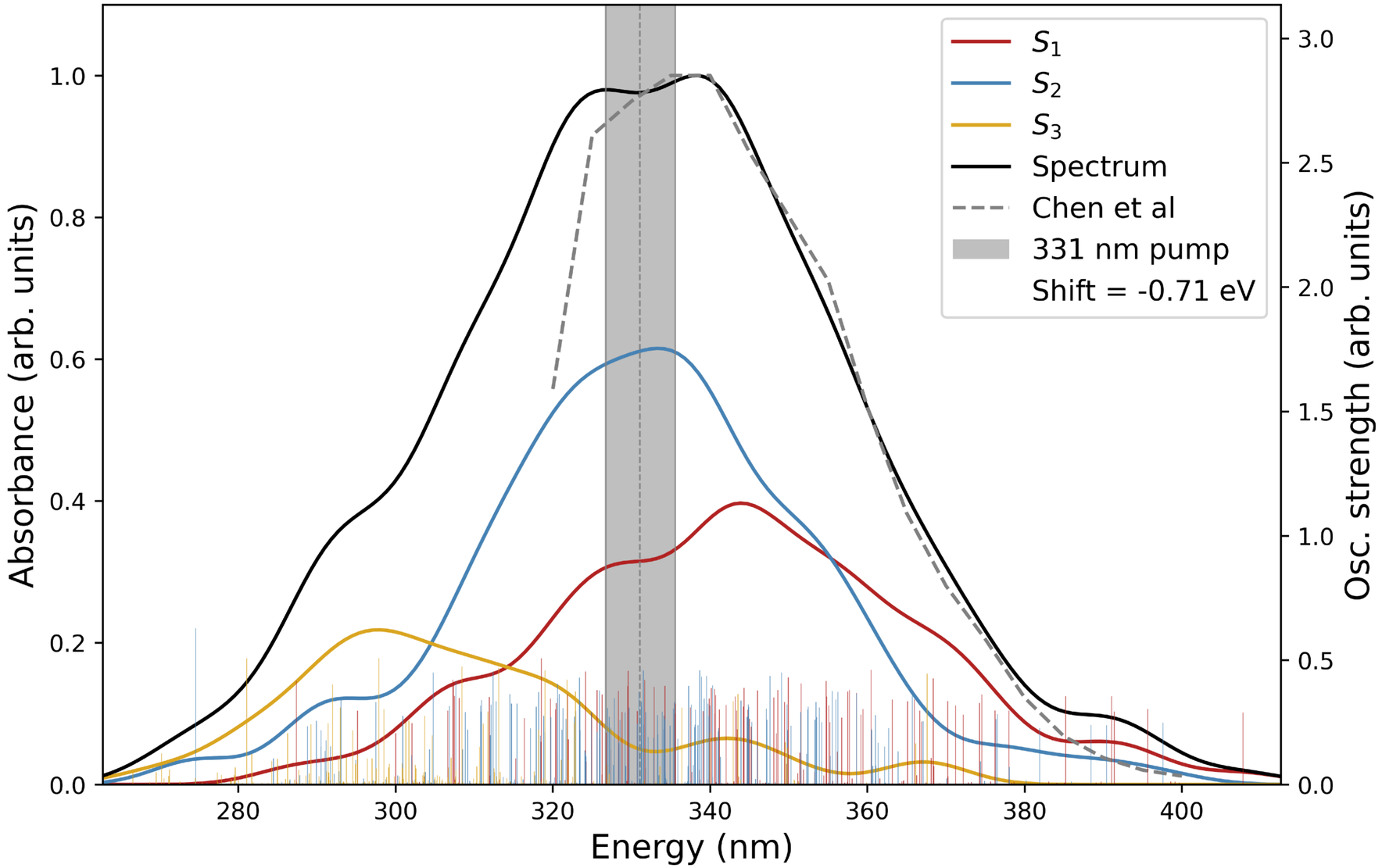
Thank you!



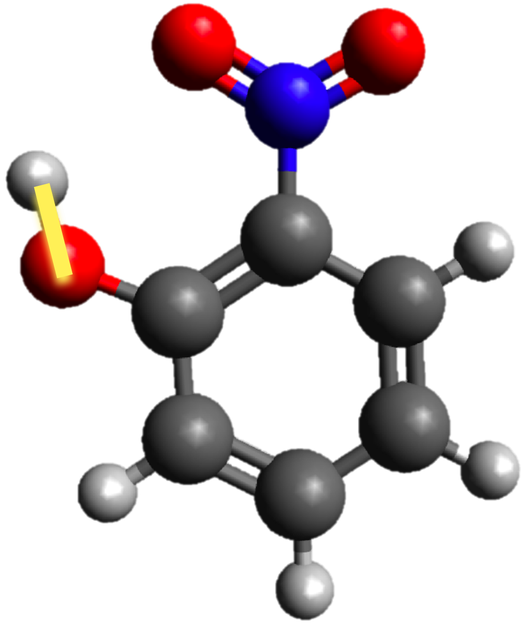
Todd Martinez Lab

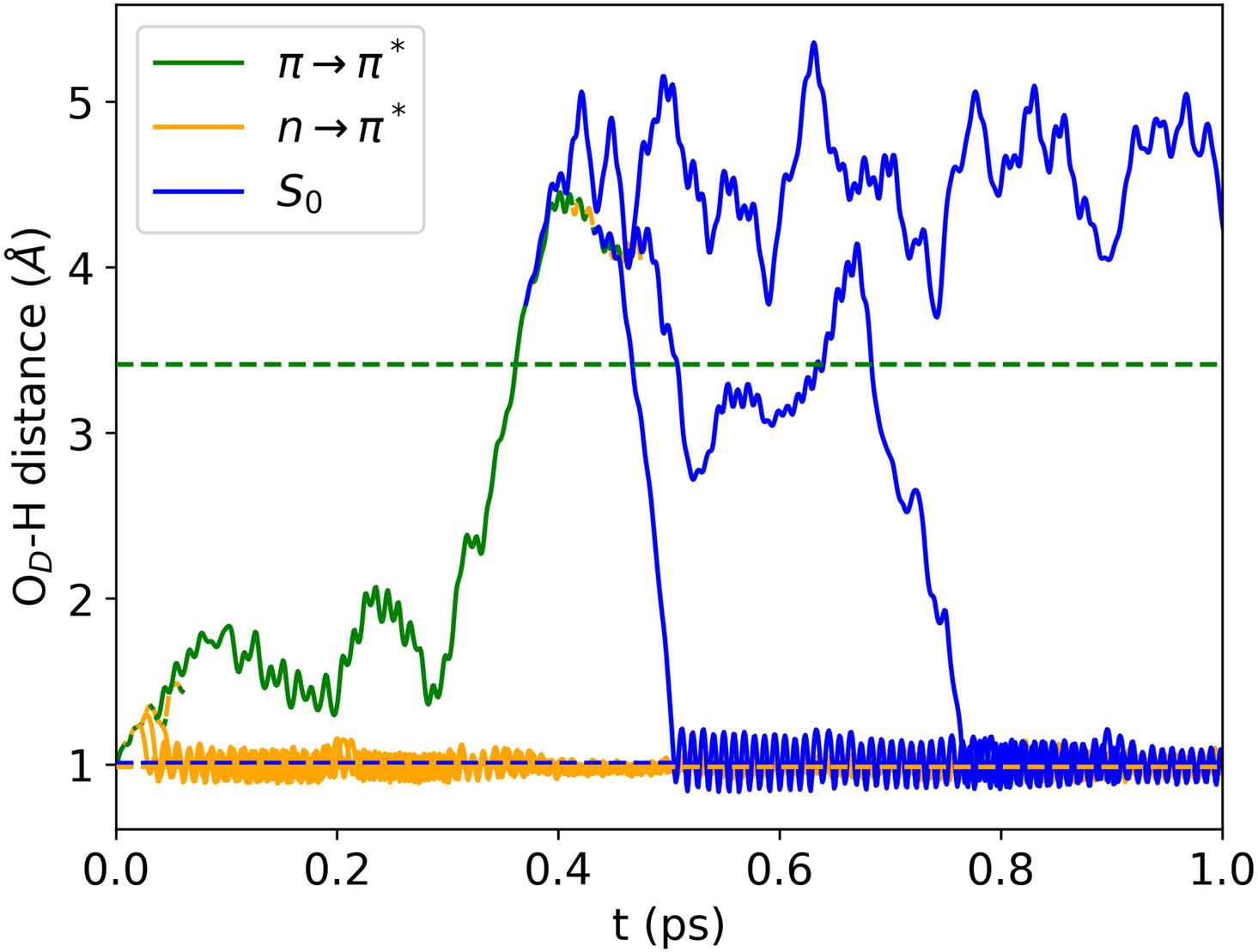
Christoph Bannwarth Lab
Advanced Research Opportunities Program

Absorption spectrum and initial conditions

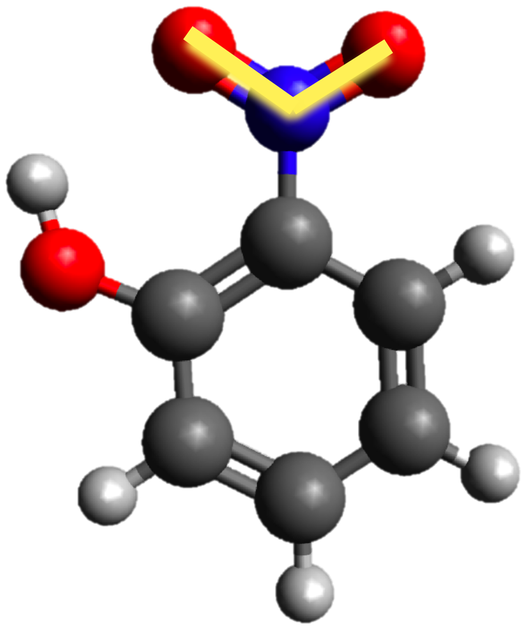


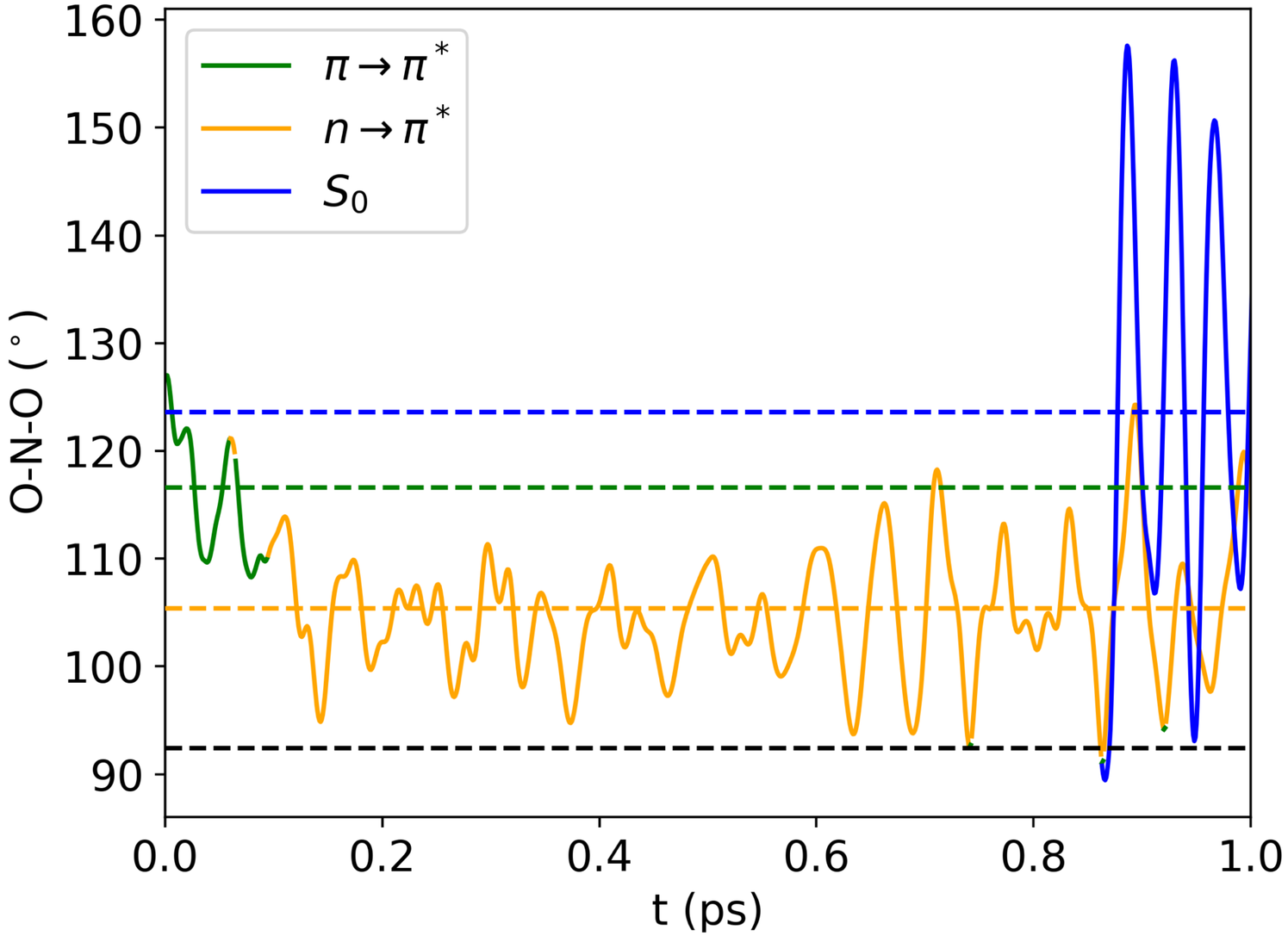
Representative trajectories



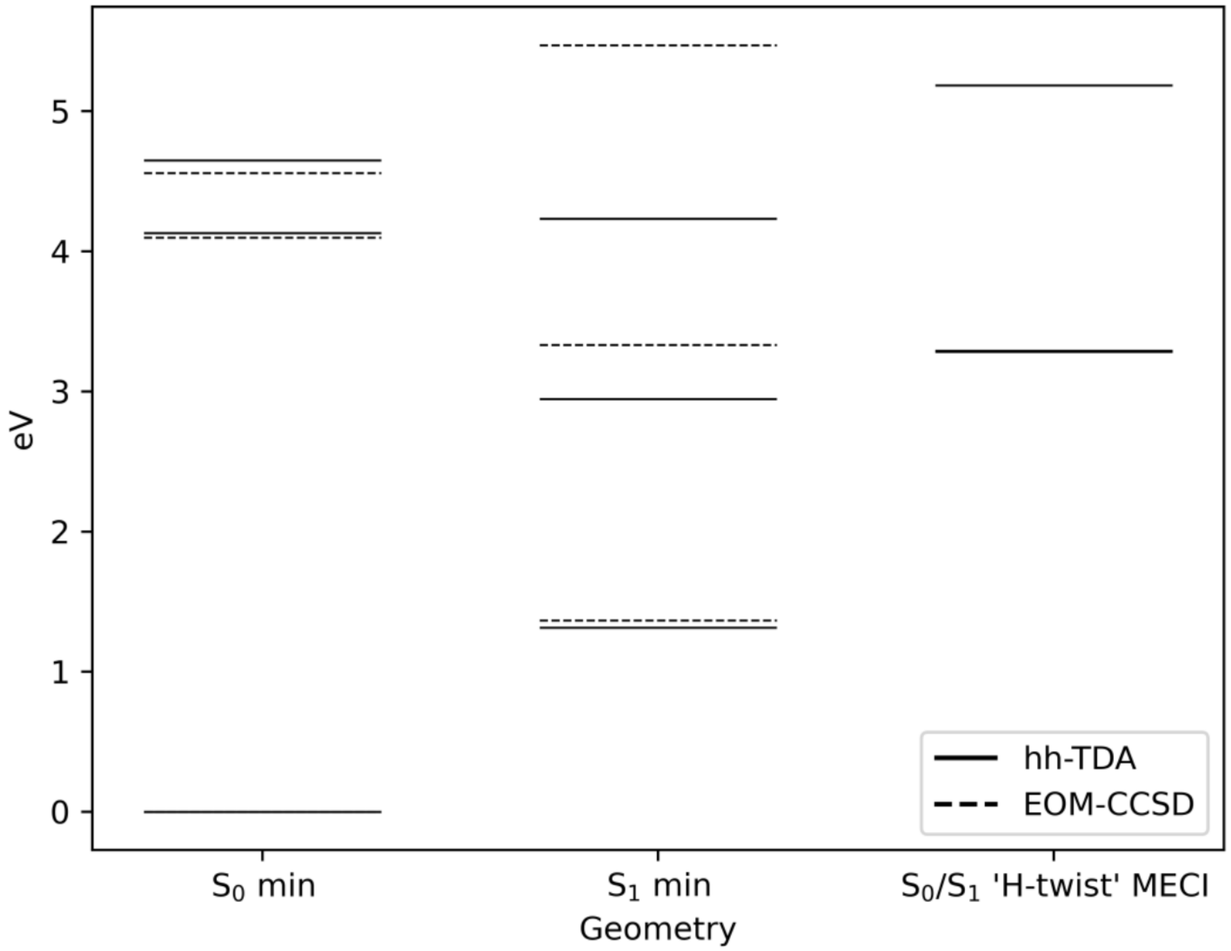


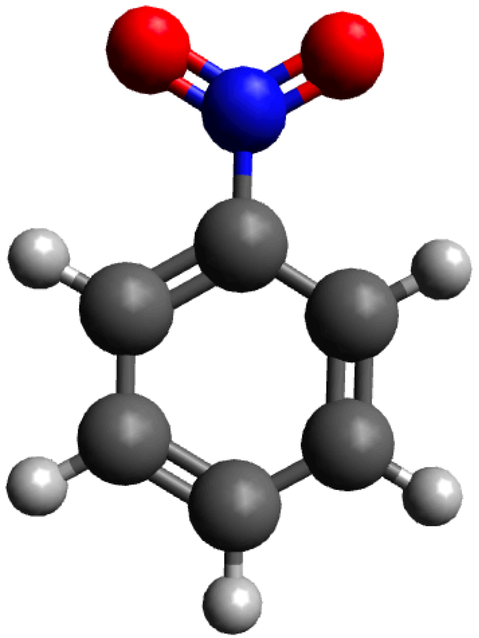
Representative trajectories





Nitrobenzene





Geometry	C-N (Å)	O-N-O (°)	C-C-N-O (°)
S_0 min	1.469	125.8	0.0
S_1 ($n\pi^*$) min	1.331	104.9	0.0
S_0/S_1 ($n\pi^*$) MECI	1.297	92.4	0.0