



The University of Edinburgh



***Ab initio* surface-hopping simulations of CS₂ photodissociation**

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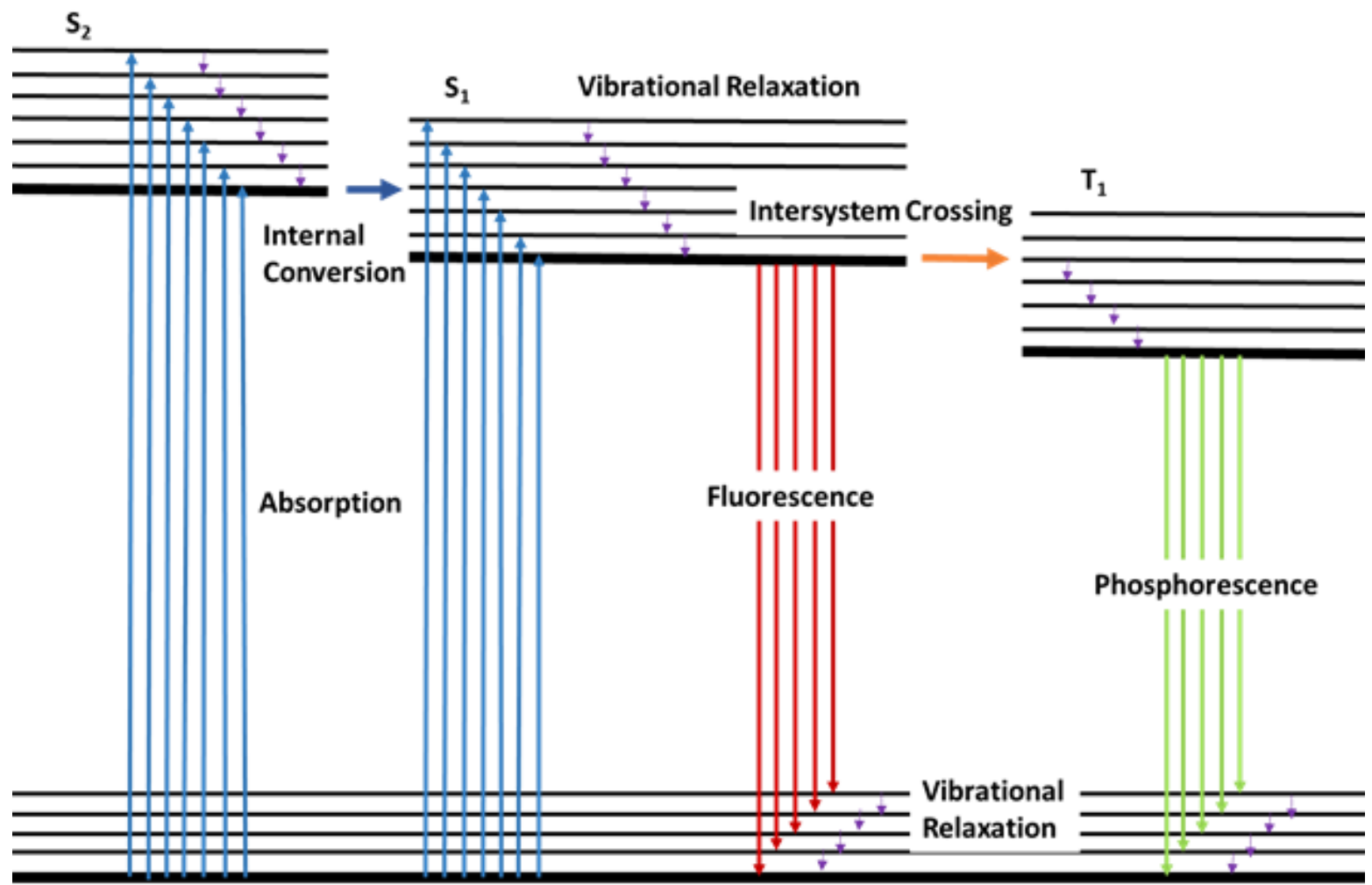
15/5/18



Excited state dynamics

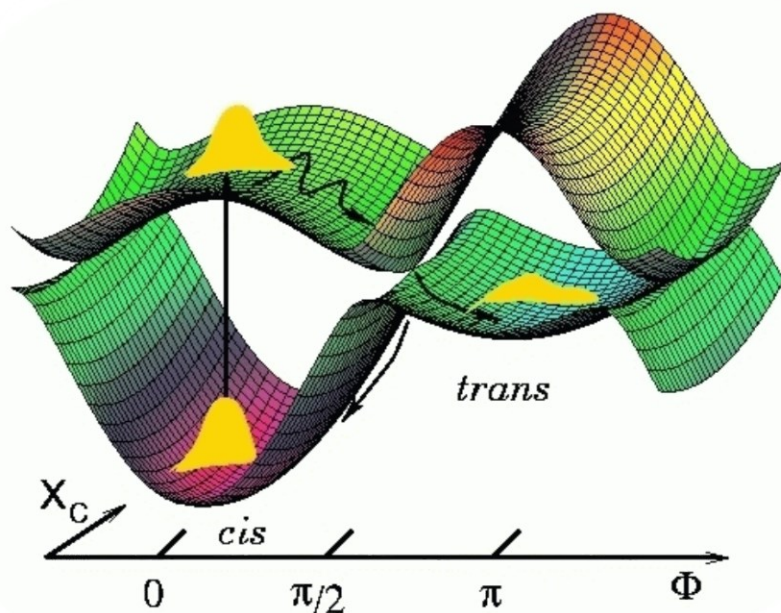
- Photochemistry
 - Photosynthesis, bioluminescence
 - DNA damage avoidance
- Photovoltaics/OLEDs
 - *Spin-orbit coupling*
- Atmospheric chemistry



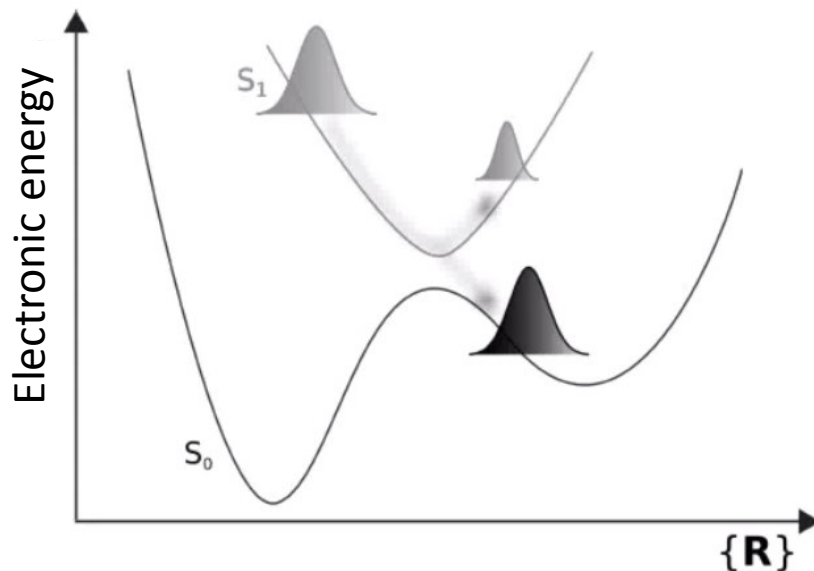




Nonadiabatic dynamics – challenge for theoreticians...



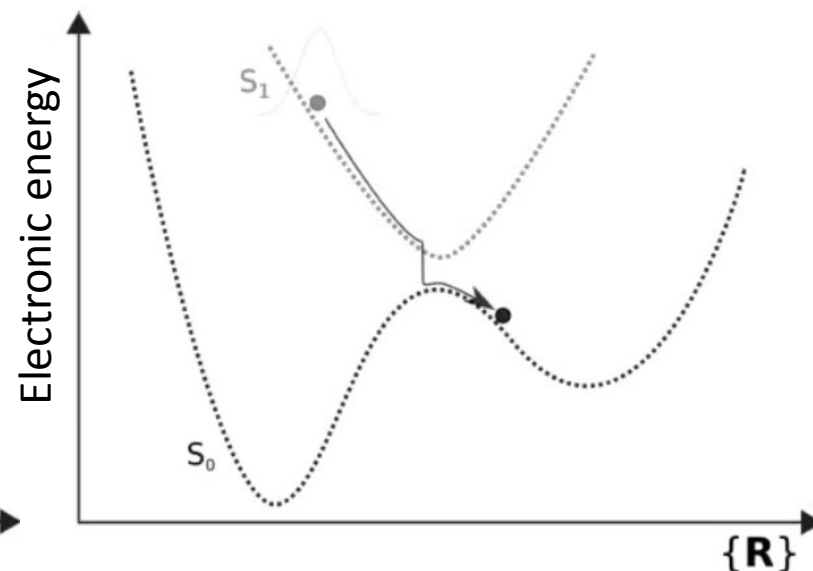
- Breakdown of BOA
- Must treat:
 - Electronic structure
 - Nuclear dynamics
 - *Nonadiabatic effects*
- *Internal conversion (IC)*
- *Intersystem crossing (ISC)*



Nuclear wavepacket approaches

- Fully quantum
- Pre-calculated potentials
- Limited DoF
- *e.g. MCTDH*

Phys. Rep. **324**, 1 (2000)



Classical trajectory approaches

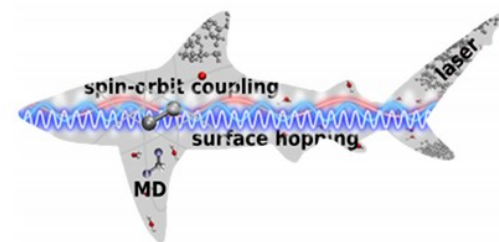
- Mixed quantum/classical
- “On-the-fly” potentials
- Fully-dimensional
- *e.g. Surface-hopping*

J. Chem. Phys. **93**, 1061 (1990)



Trajectory surface hopping

- Quantum electrons, classical nuclei
 - “On-the-fly” potentials
 - Newtonian nuclear dynamics
- SHARC - accounts for nonadiabatic (IC) and spin-orbit coupling (ISC)
- Trajectories “hop” probabilistically



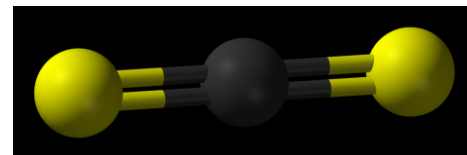
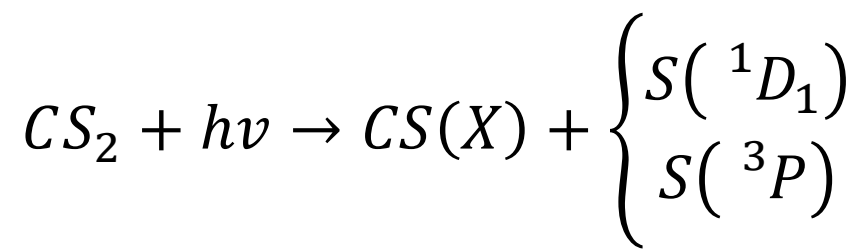
SHARC dynamics code



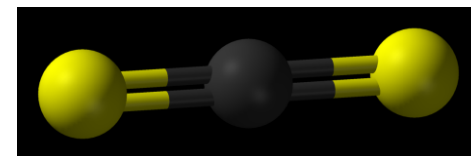
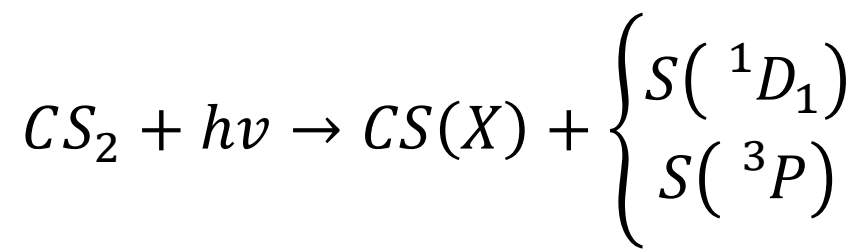
Int. J. Quantum Chem., **115**, 125-1231 (2015).

J. Chem. Theory Comput., **7**, 1253-1258 (2011).

CS₂ photodissociation

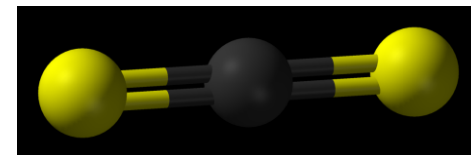
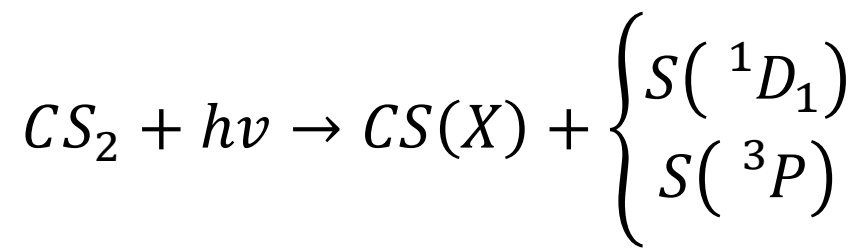


CS₂ photodissociation

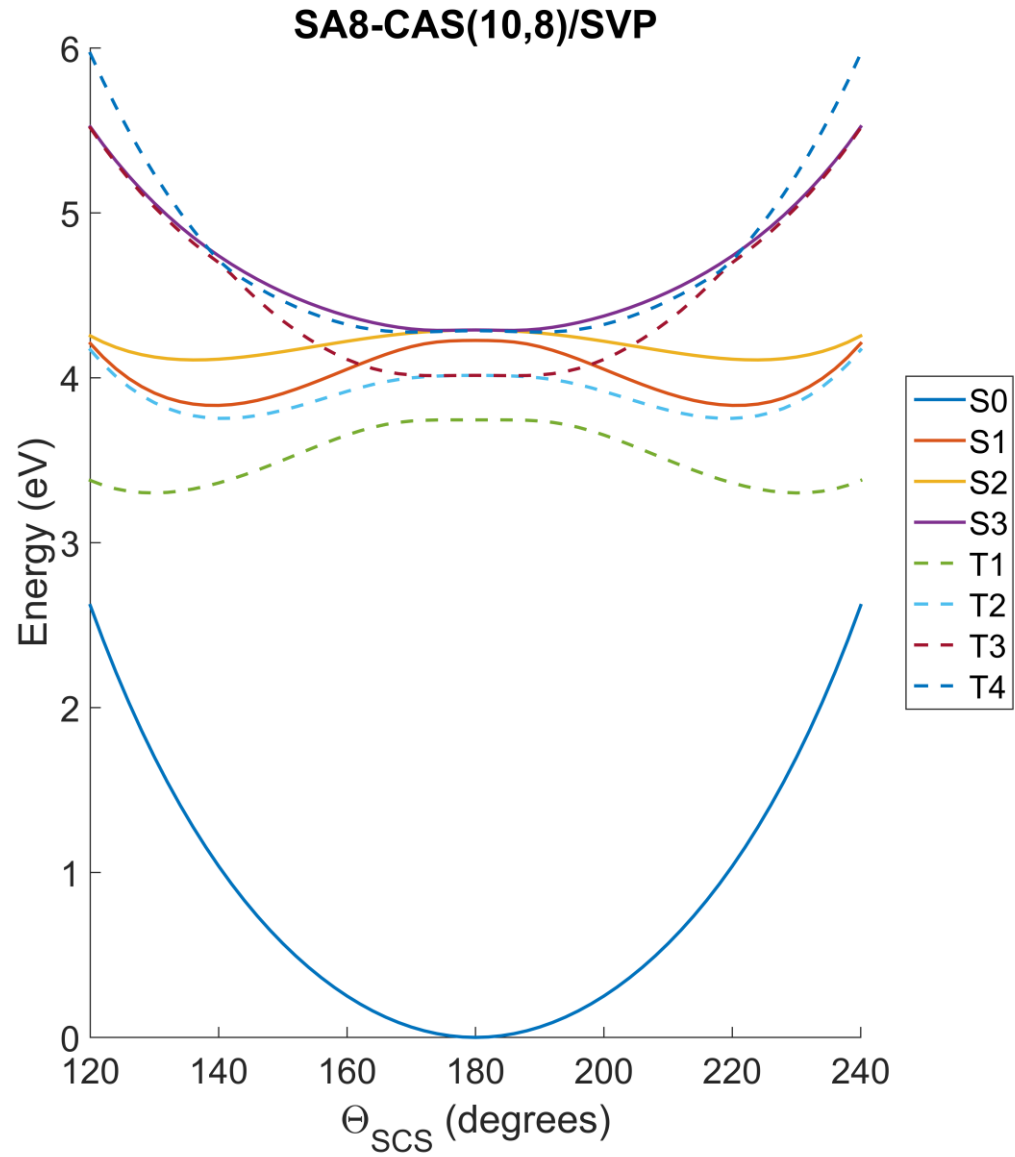


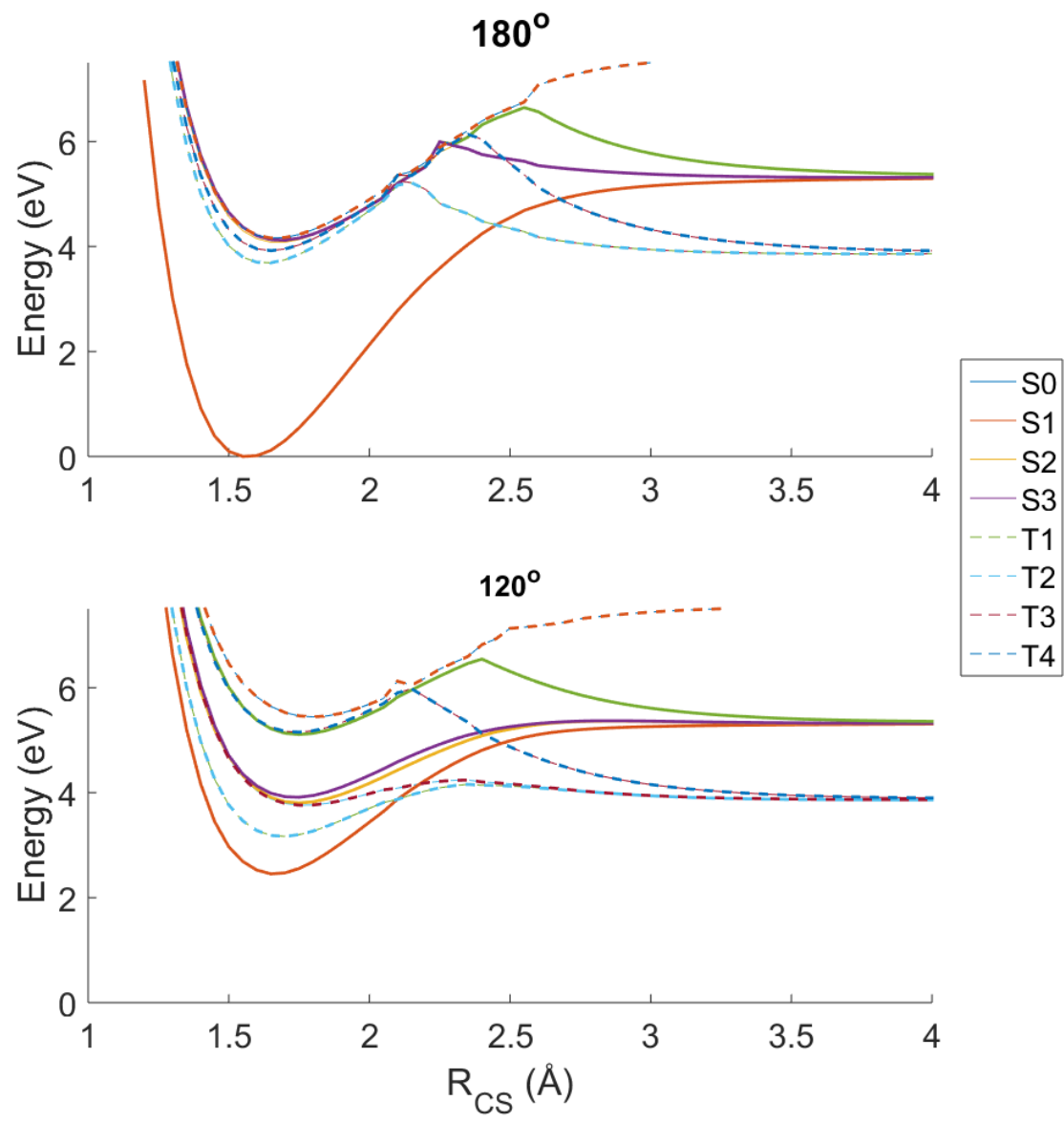
- **Large spin-orbit (SO) coupling**

CS₂ photodissociation



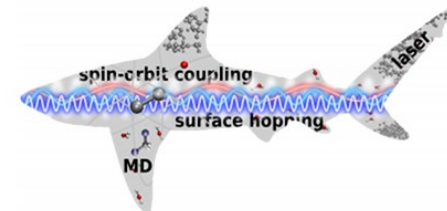
- Large spin-orbit (SO) coupling
- **Simple reaction \neq simple dynamics!**
 - Competing dissociation channels involving multiple electronic states







SHARC setup



Simulation details

CASSCF active space

(10,8)

Basis set

SVP

Coupling approach

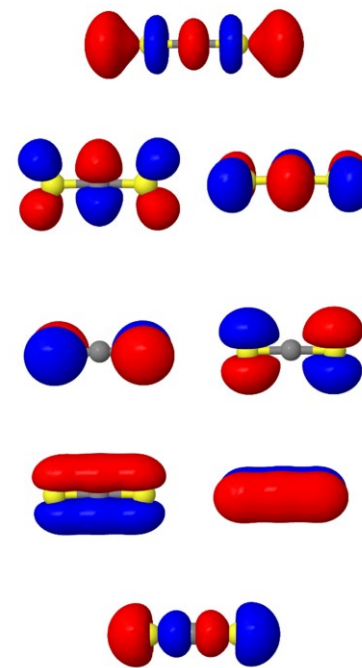
Overlaps

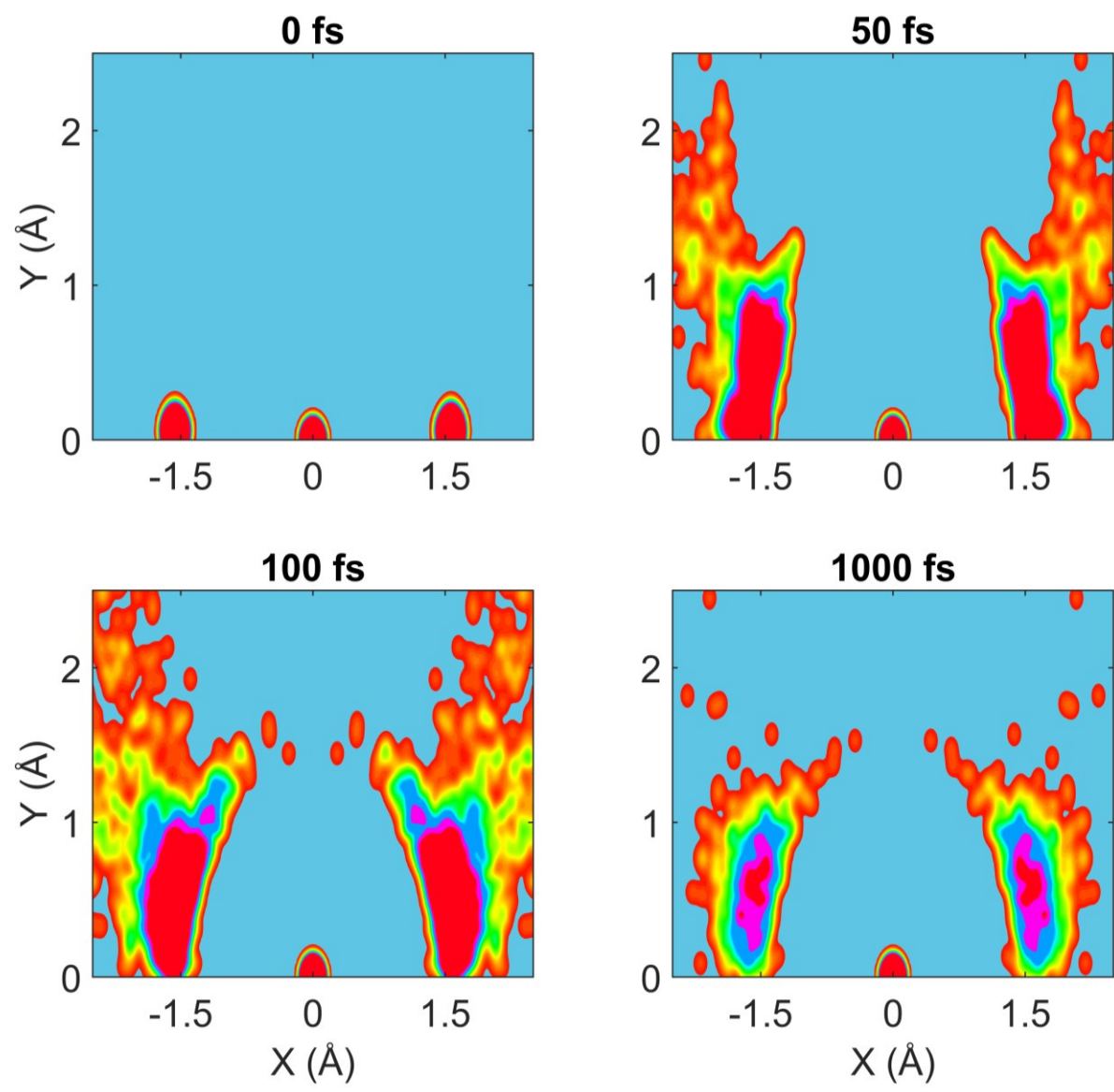
Number of trajectories

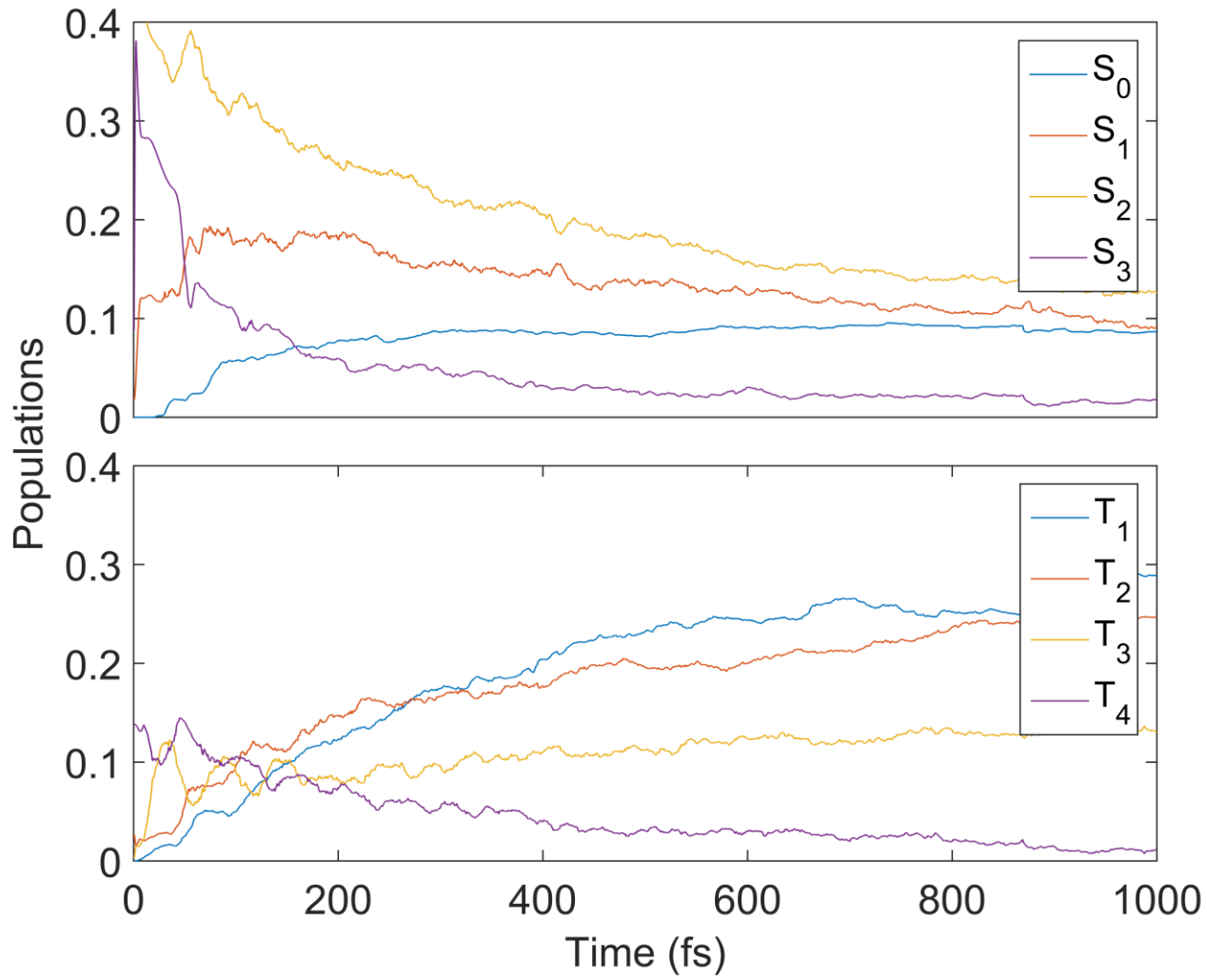
1024

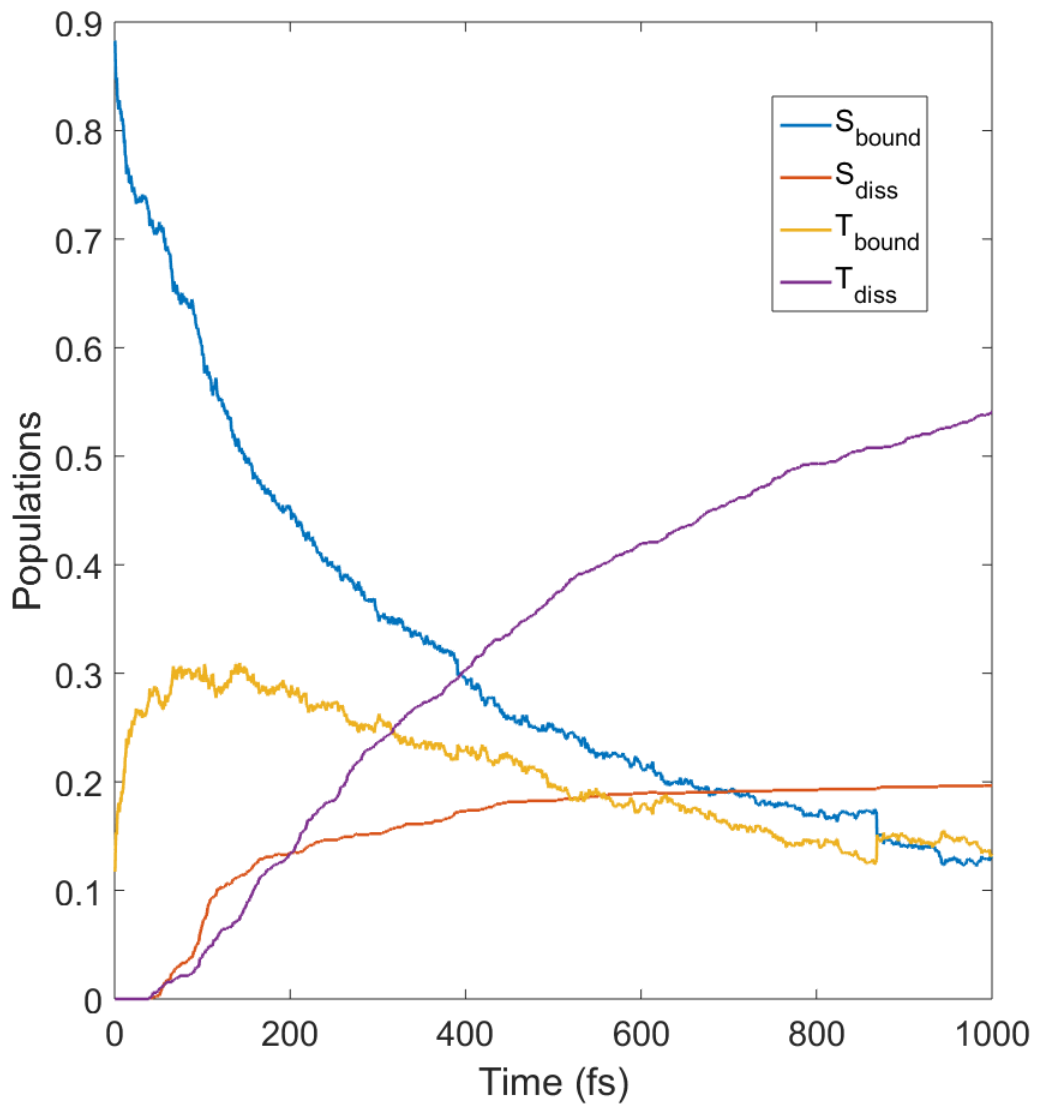
Time step / total time (fs)

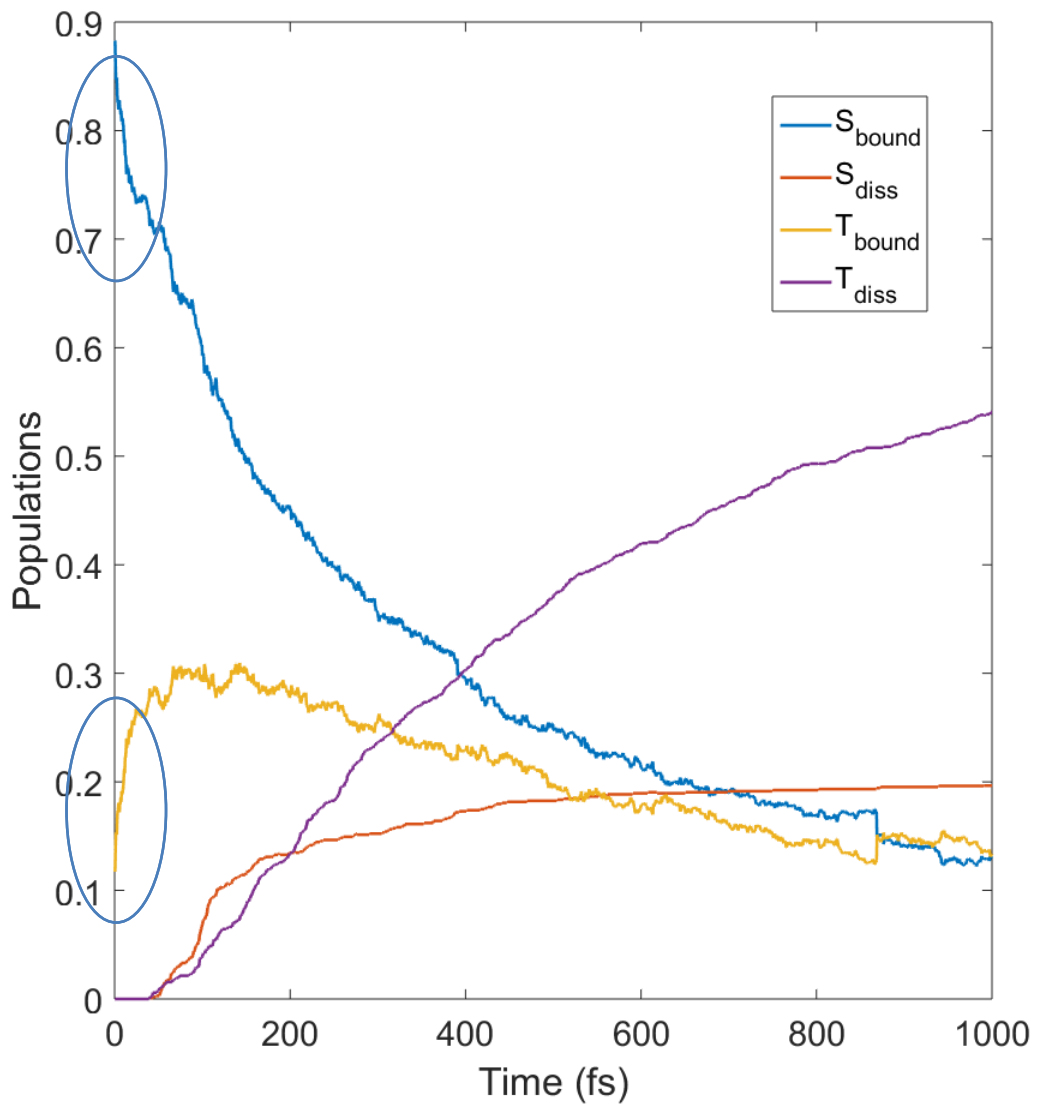
0.5 / 1000



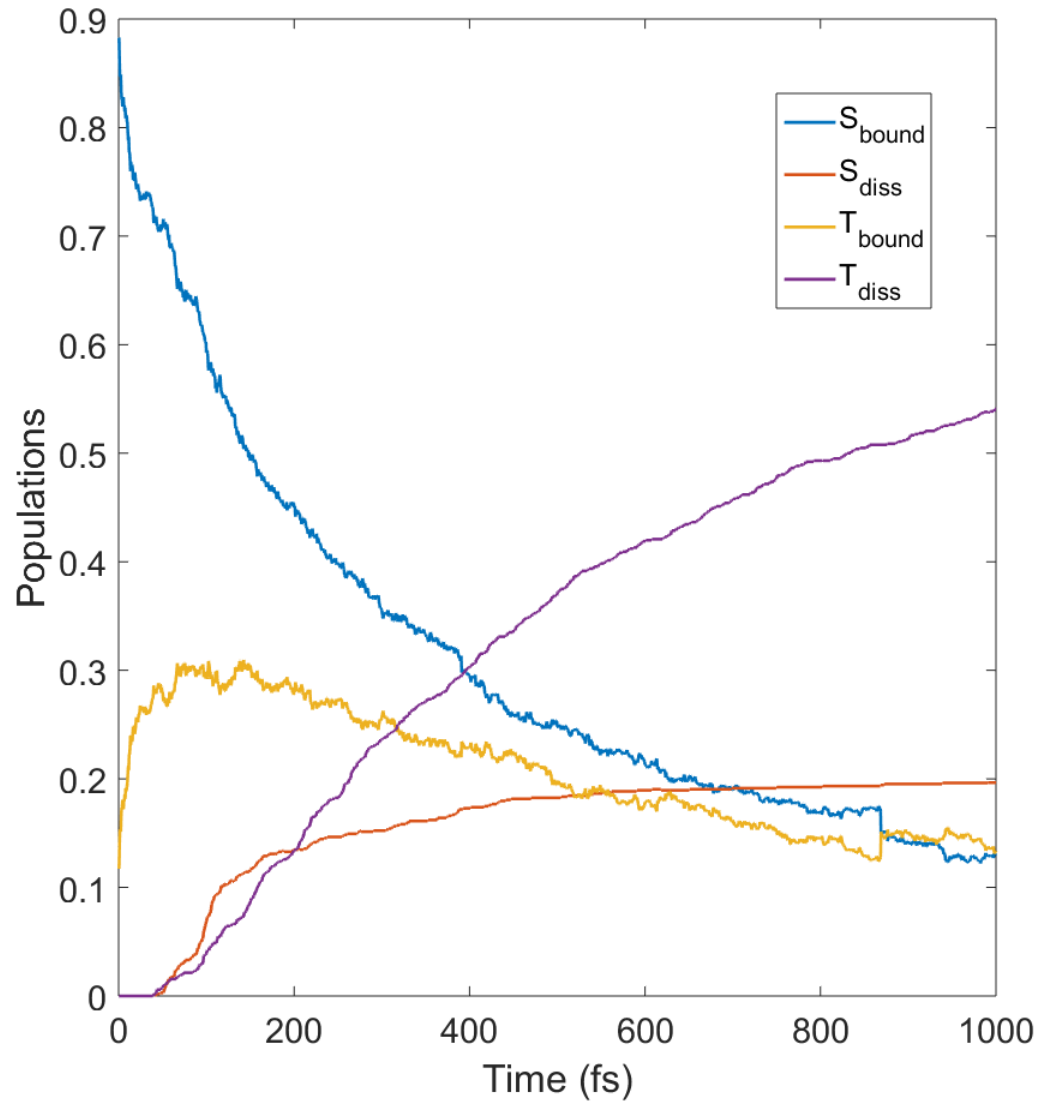




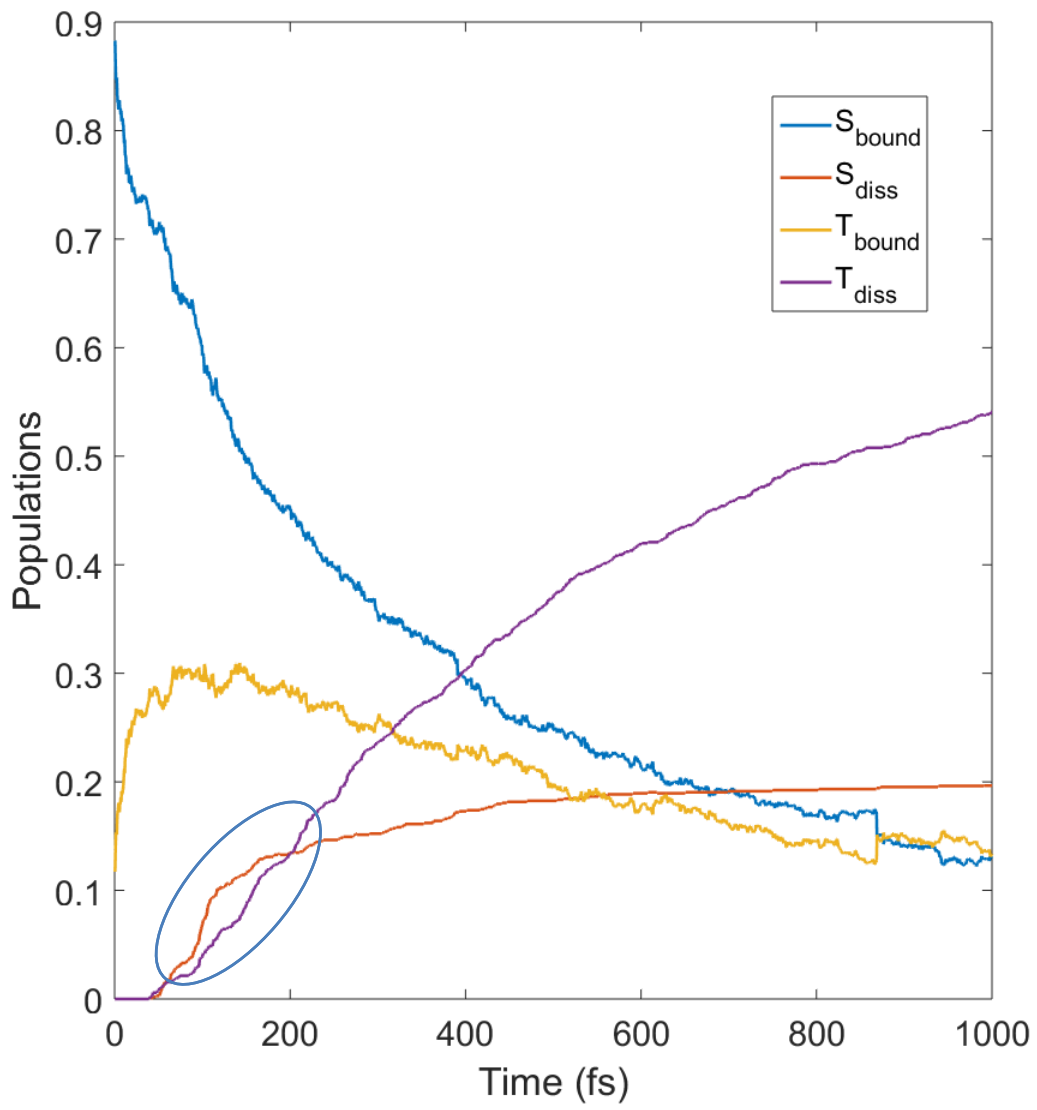




- Initial rapid redistribution



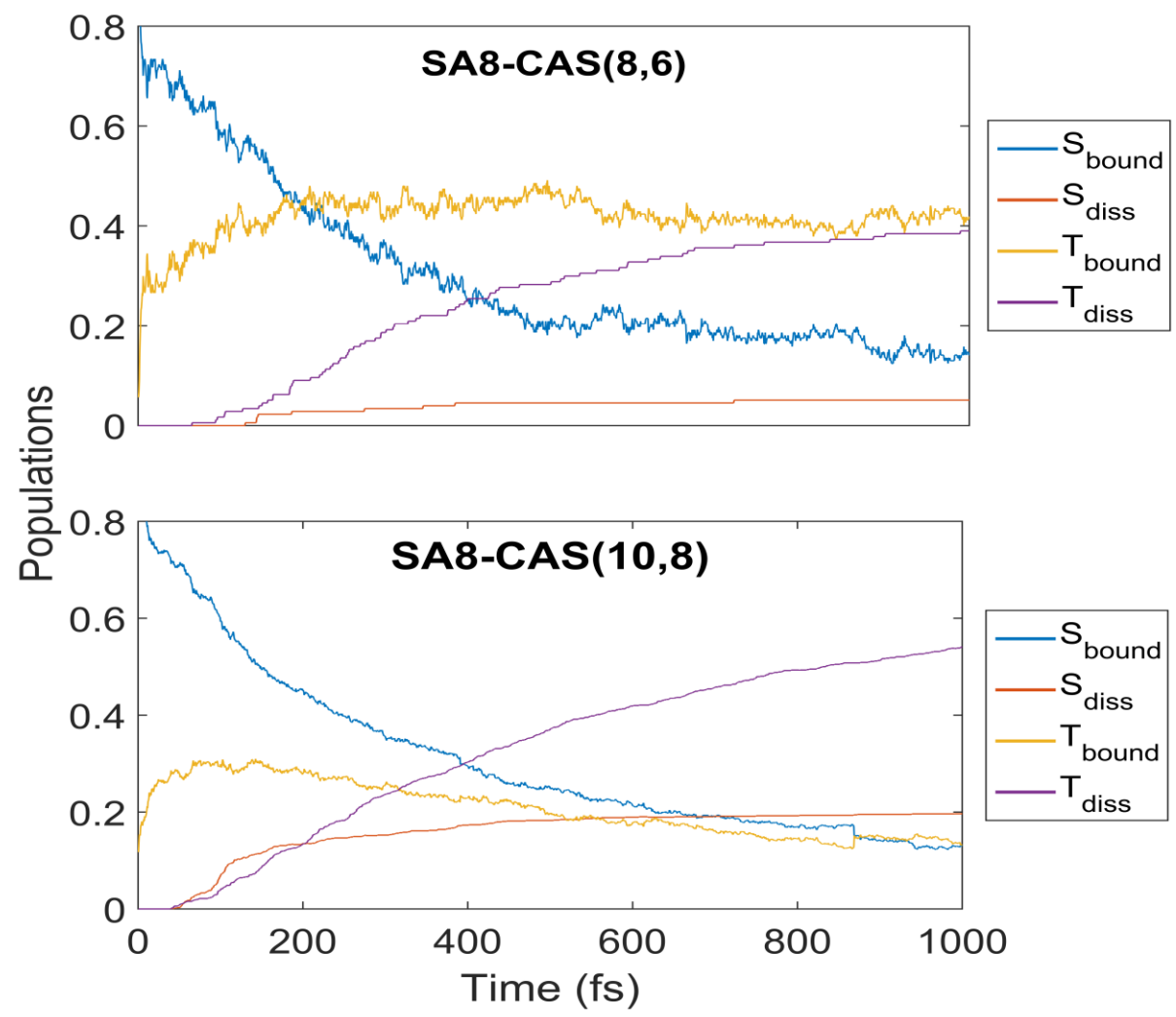
- Initial rapid redistribution
- Relaxation of bound curves



- Initial rapid redistribution
- Relaxation of bound curves
- Onset of dissociation



- *Ab initio* dependence...? Drop active space to (8,6).



Conclusions

- **IC & ISC considered sequential...**
... but not the case in some systems.



Conclusions

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... but not the case in some systems.



- **Simple system, complex dynamics!**

Conclusions

- IC & ISC considered sequential...
... but not the case in some systems.



- Simple system, complex dynamics!

- **Be wary of scrimping on computational expense!**



Acknowledgements



Kirrandar group (past and present)



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Thanks!

