Photochemistry of 2-Hydroxyazobenzene: A Computational Study



Introduction

- In some molecules with both acidic and basic functional groups, the Excited State Intramolecular Proton Transfer (ESIPT) results in an excited state tautomer with a distinct electronic structure.
- ESIPT and photoisomerization are the fundamental processes used in laser dyes, fluorescence probes, light-emitting materials, and optical devices.
- Azobenzene compounds are the prototype molecules for photocontrolled materials due to their capability for ESIPT and photoisomerization.
- 2-hydroxyazobenzene (2HA) undergoes the competing ESIPT and cis-trans photoisomerization processes in the dark S_1 ($n \rightarrow \pi^*$) state upon photoexcitation to the bright $S_2 (\pi \rightarrow \pi^*)$ electronic state.



- While the dominant relaxation pathway of this molecule has been studied using multi-reference methods, there is a lack of research on its excited state molecular dynamics using ab initio methods which is the aim of my present research project.
- We perform static electronic structure calculations on singlet ground (S_0) and first two excited states (S_1 and S_2) employing multi-reference methods such as FOMO-CASCI and XMS-CASPT2, as well as wavefunction-based methods like EOM-CCSD to map out the potential energy surfaces.
- We also performed the non-adiabatic molecular dynamics simulations by using recently developed **TAB method** developed by the Levine Research Group.

Computational Details

- The static and TAB dynamics use FOMO-CASCI level of theory as implemented in the GPU accelerated TeraChem electronic structure program at the electronic temperature of 0.15 a.u.
- All CASPT2 and EOM-CCSD calculations were carried out using OpenMolcas and Psi4 programs, respectively. The multi-reference methods use an active space of 10 electrons in 7 orbitals, CAS(10,7) using cc-pVDZ basis sets.



- All relaxed scans use geometries optimized at the FOMO-CASCI level of theory.
- TAB dynamics use a step size of 10 a.u with initial positions and velocities sampled from a Wigner distribution of the S_0 harmonic vibrational wave function. The calculations were propagated till population decay to S_0 state.

Results

Results of Static Calculations

interactions and one major ESIPT followed by keto twisting path.



FOMO-CASCI energies are given in normal print while *italic* print represents XMS-CASPT2 energies. Numbers in brackets show vertical excitation energies.

- Both methods show that the *trans* \rightarrow *cis* photoisomerization of the keto tautomer is more feasible due to the low energy of the associated S_1/S_0 conical intersection.
- The *cis*-keto component is expected to be the major part of the ESIPT relaxation path, similar to how *cis*-Enol is the major product of the Enol twist path.
- The presence of multiple relaxation channels establishes the need for nonadiabatic molecular dynamics simulations to explore the contributions of all degrees of freedom in the photochemistry of 2HA.
- Since FOMO-CASCI is feasible for running dynamics simulations, it is important to characterize its limitations by comparing the estimated barriers of key steps with those from different flavors of CASPT2.



- barrier compared to CASPT2.
- will overestimate the S_1 lifetime of trajectories following the ESIPT path.

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• We found two energetically accessible pathways for relaxation down to the ground state: Enol twisting with two options involving two different S_0/S_1 conical

• The plot compares FOMO-CASCI energies along the O–H distance on the S_1 state with CASPT2 energies. FOMO-CASCI slightly overestimates the ESIPT

• The same is observed for the keto twist barrier, indicating that FOMO-CASCI



Results of Dynamics Simulations



- ground state via enol twist path.

Conclusions

Acknowledgment

References

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Reaction Coordinates

Out of 9 Initial conditions, 5 followed ESIPT path and remaining decayed to the

• Average time for S_1 state proton transfer is estimated to be 40 fs.

• Average lifetime of S_2 state is 5 fs, S_1 state is 322 fs for trajectories following proton transfer paths and 231 for those which undergo enol twisting path.

• FOMO-CASCI suggested that both photoisomerization and proton transfer are barrierless on the S_1 state and are not feasible on both S_2 and S_0 states.

TAB dynamic simulations supported these findings; with around half of the trajectories followed either the competing ESIPT or *cis-trans* isomerization paths.

• More detailed TAB dynamics with large number of initial conditions in future will help to provide a detailed picture of the photodynamics of 2HA.

• Seawulf and SDSC Expanse HPC clusters for computation facility (CHE140101). • This research was supported by the Data + Computing = Discovery! REU site, which is sponsored by the NSF under grant 1950052.

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