Computational Insights into the Photodynamics of 2-Hydroxyazobenzene

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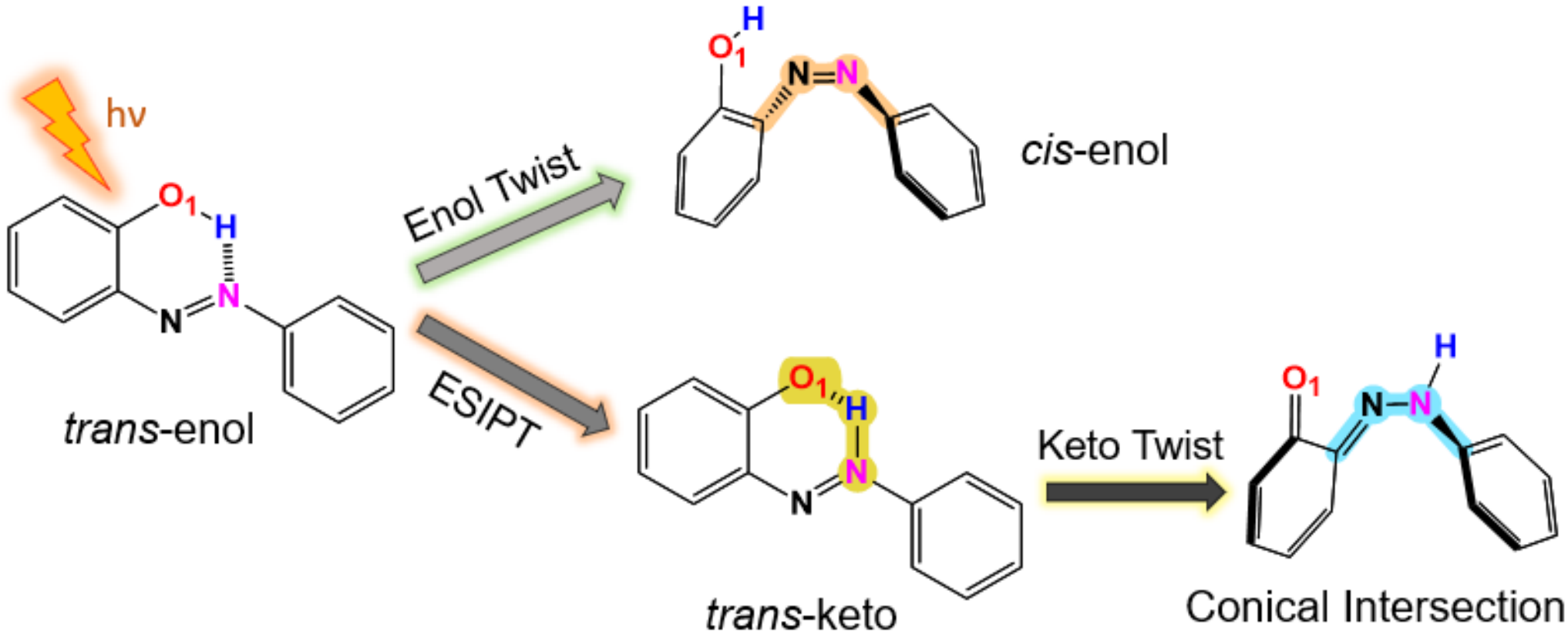
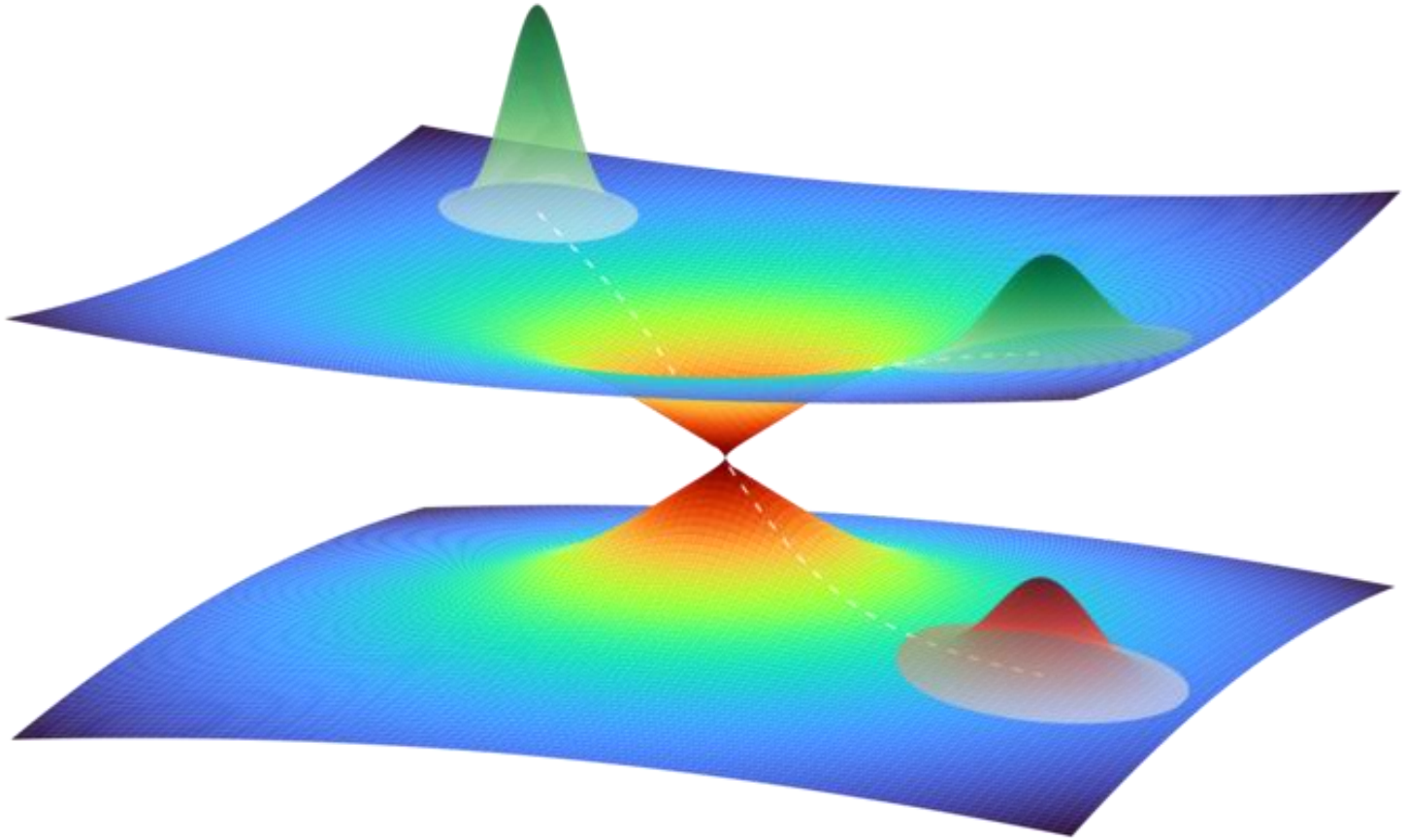
2-Hydroxyazobenzene Undergoes Competing Photoisomerization and Excited State Intramolecular Proton Transfer (ESIPT)



What do the potential energy surfaces look like?

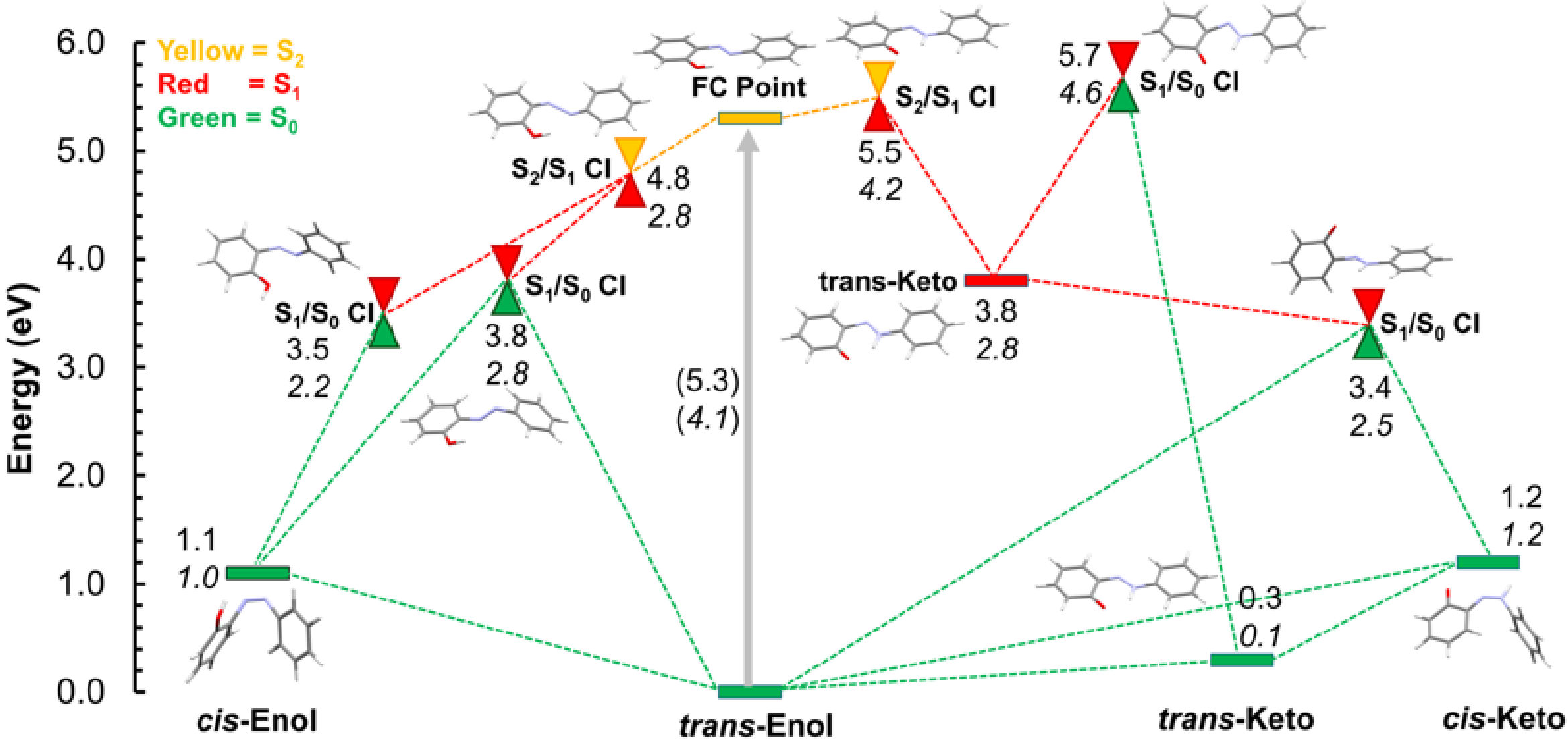


T. Zoufal. *Nature*, 2021.

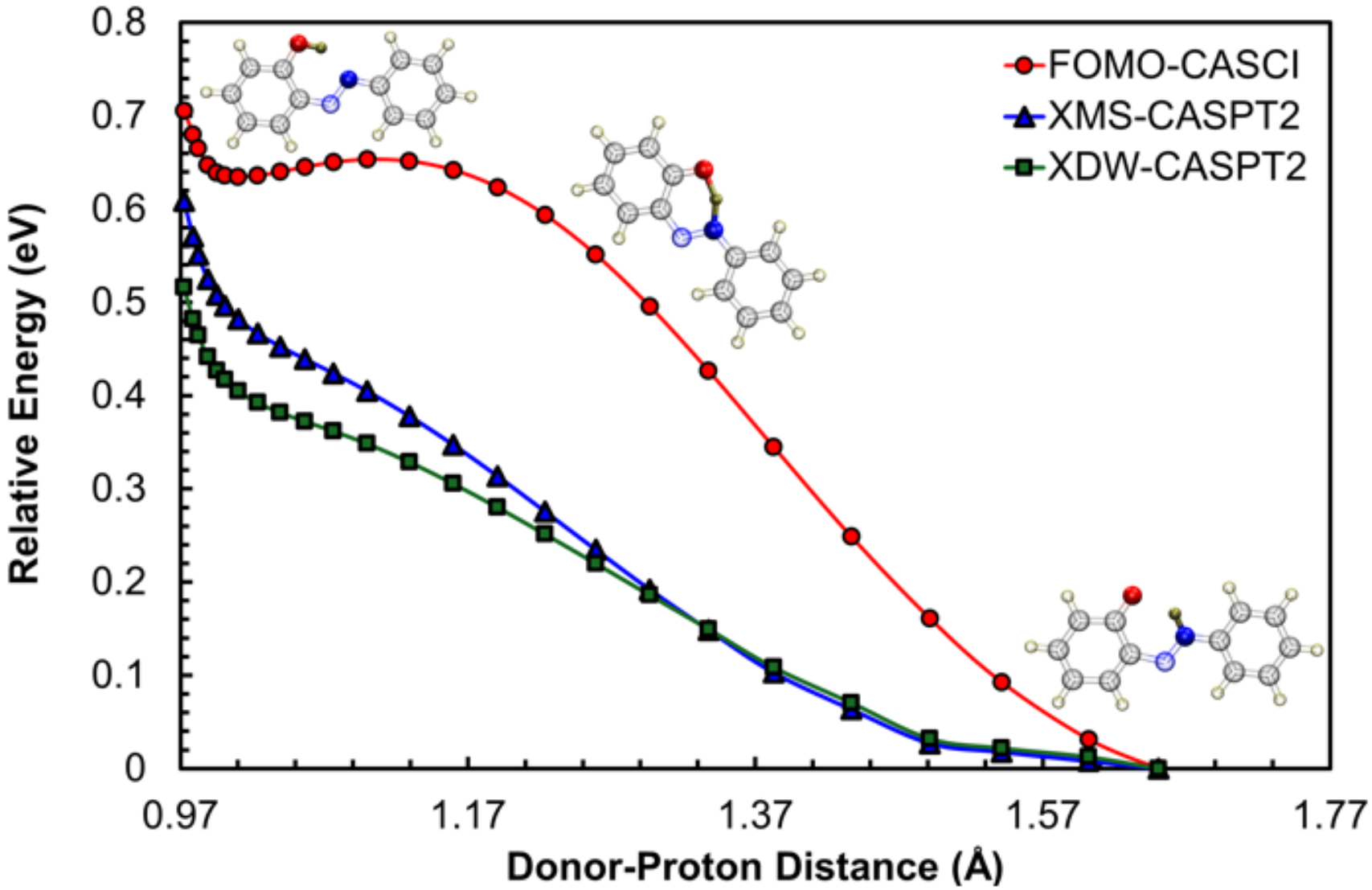
Mapping out the potential energy surfaces with static calculations

FOMO(0.15)-CAS(10,7)CI

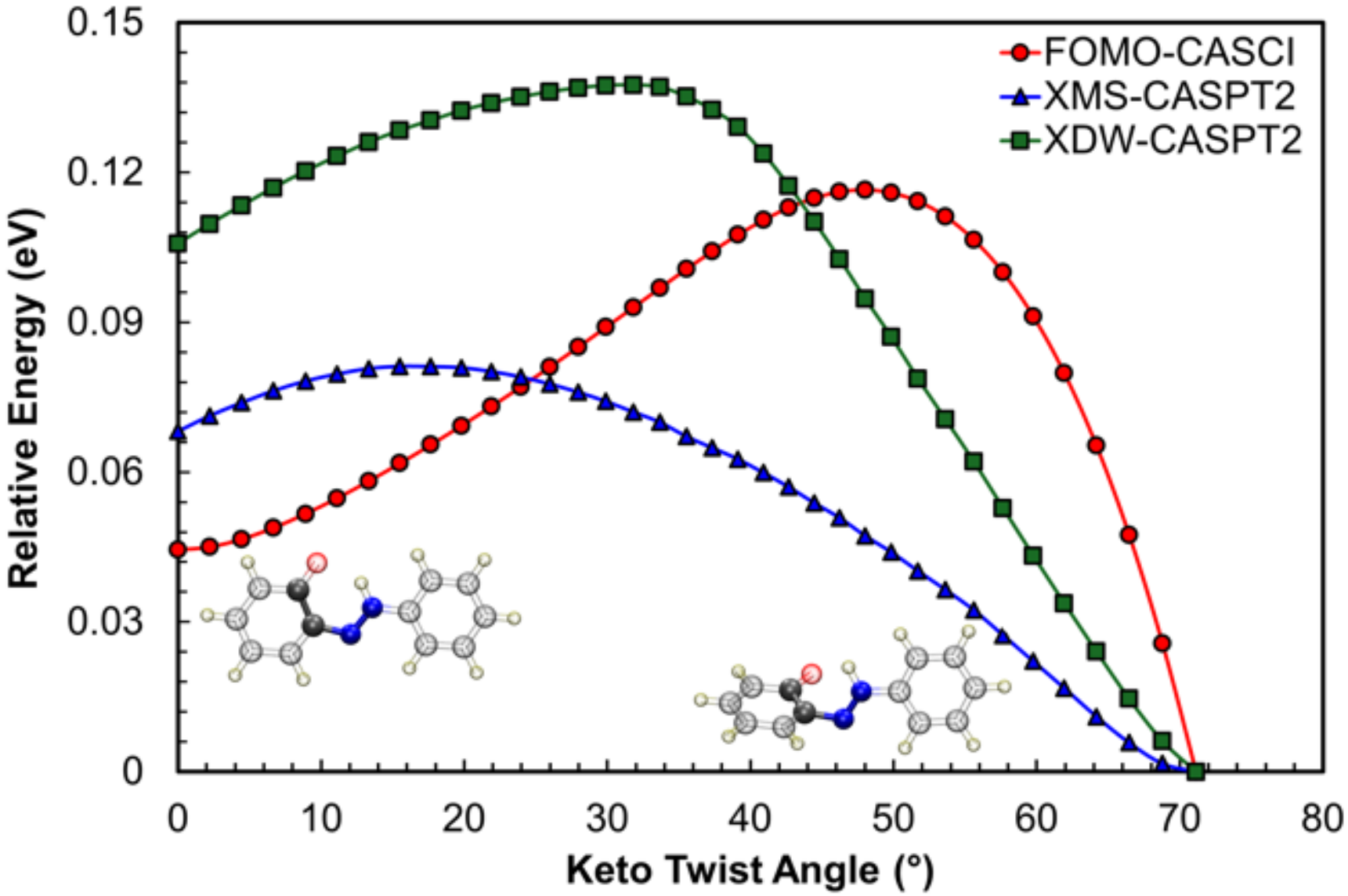
XMS-CAS(10,7)PT2



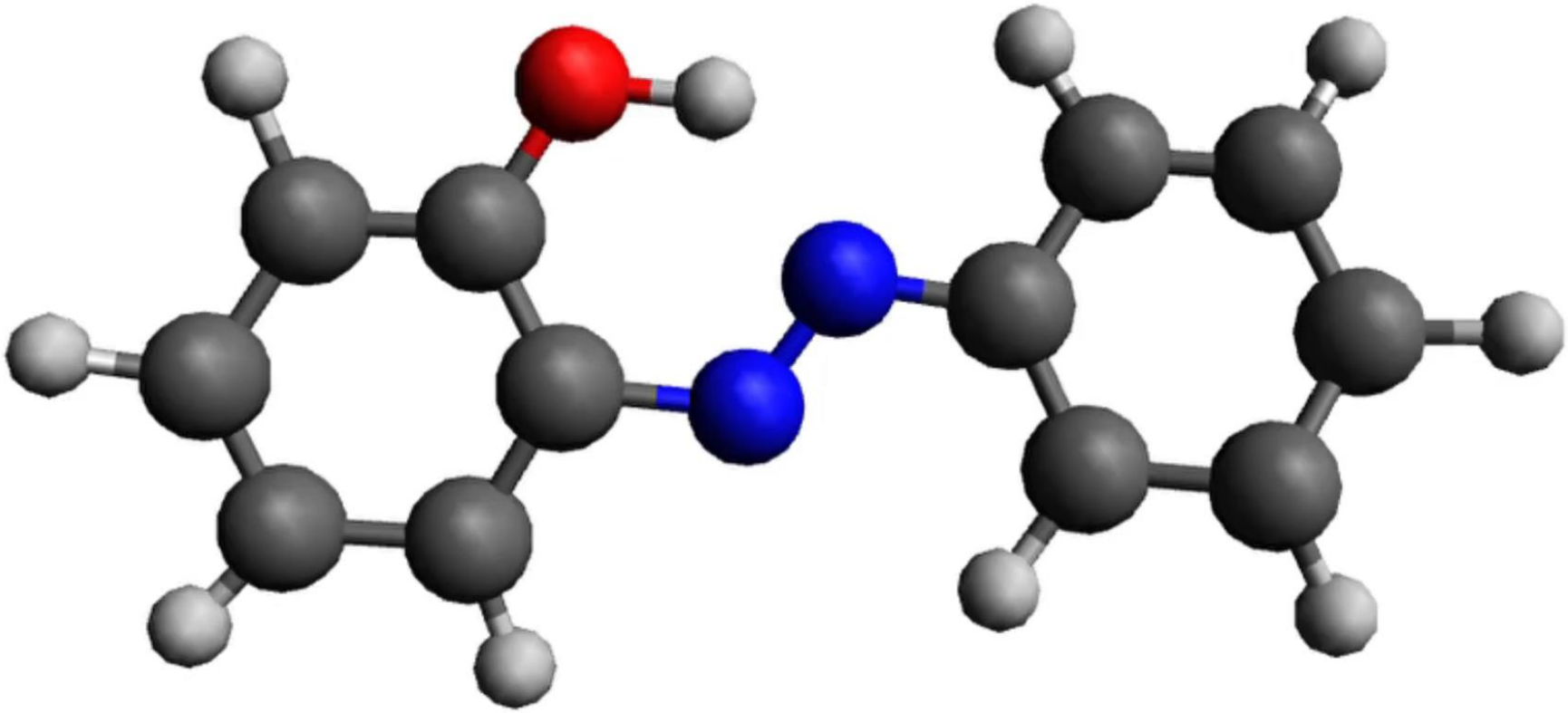
Linearly Interpolated Internal Coordinate (LIIC) Path for Proton Transfer on S_1 State



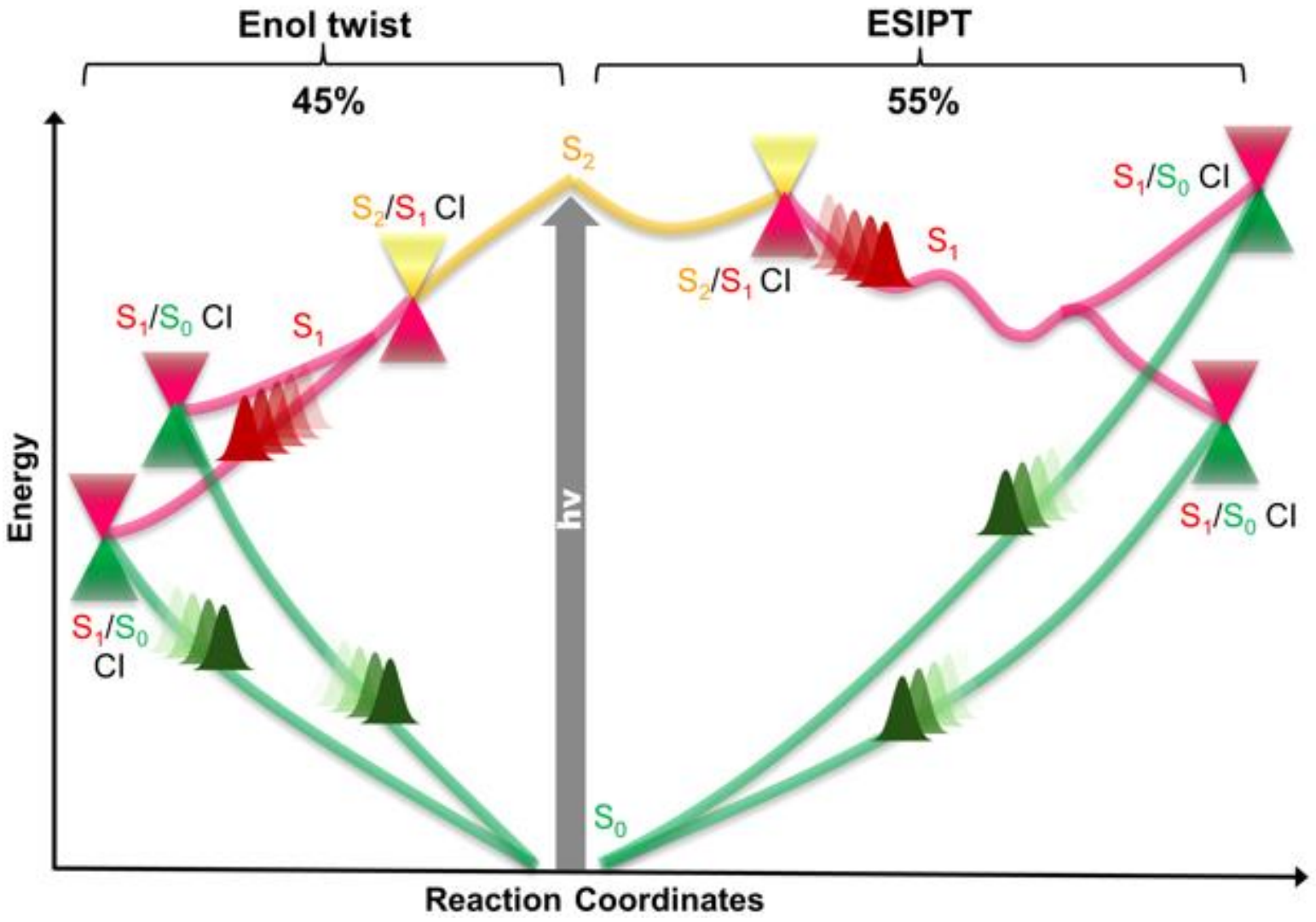
LIIC Path for Keto Twisting on S_1 State



Non-adiabatic *ab initio* molecular dynamics using TAB

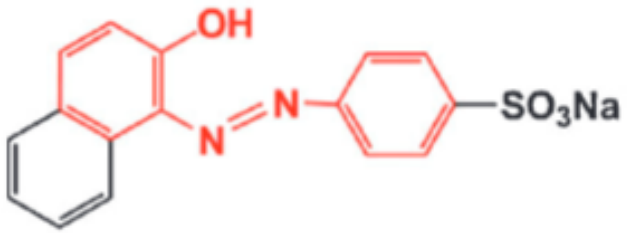


9 Simulations with different Initial Conditions



Average lifetime on S_2 was **5** fs

Average time to proton transfer was **40** fs



≈ **30** fs

A. Douhal, M. Sanz, L. Tormo, *Proc. Natl. Acad. Sci. USA* 2005.

Average time to S_0 was **322** fs for proton transfer paths and **231** fs for enol twisting paths

Acknowledgments

Seawulf and SDSC Expanse HPC clusters for computation facility (CHE140101)

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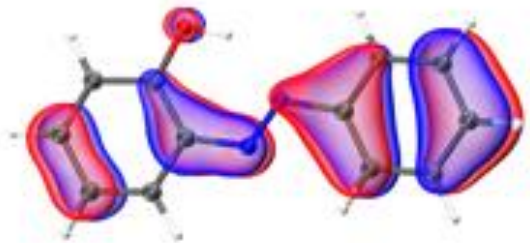
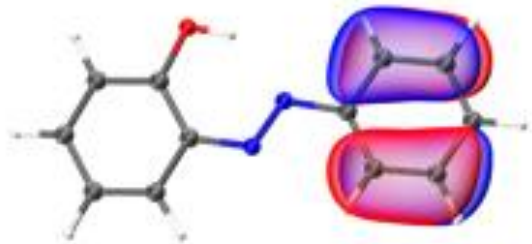
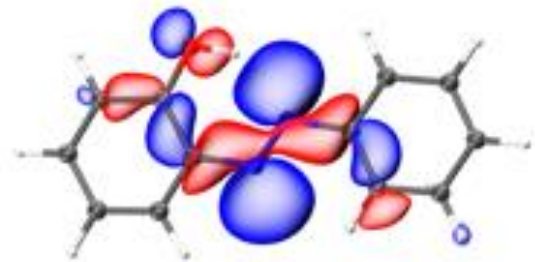
HOMO - 4



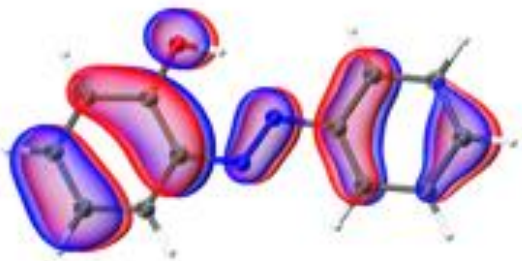
HOMO - 3



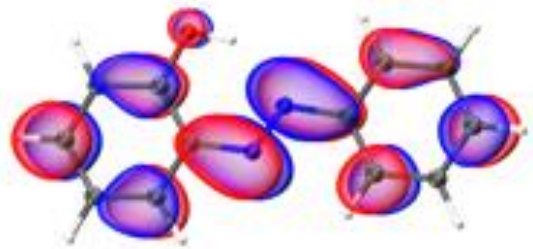
HOMO - 2



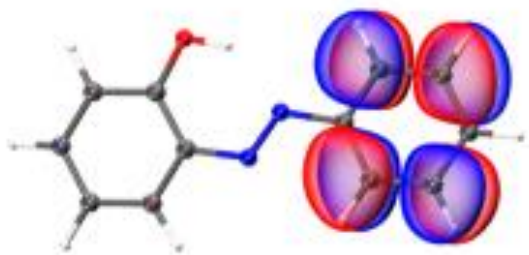
HOMO - 1



HOMO



LUMO



LUMO + 1

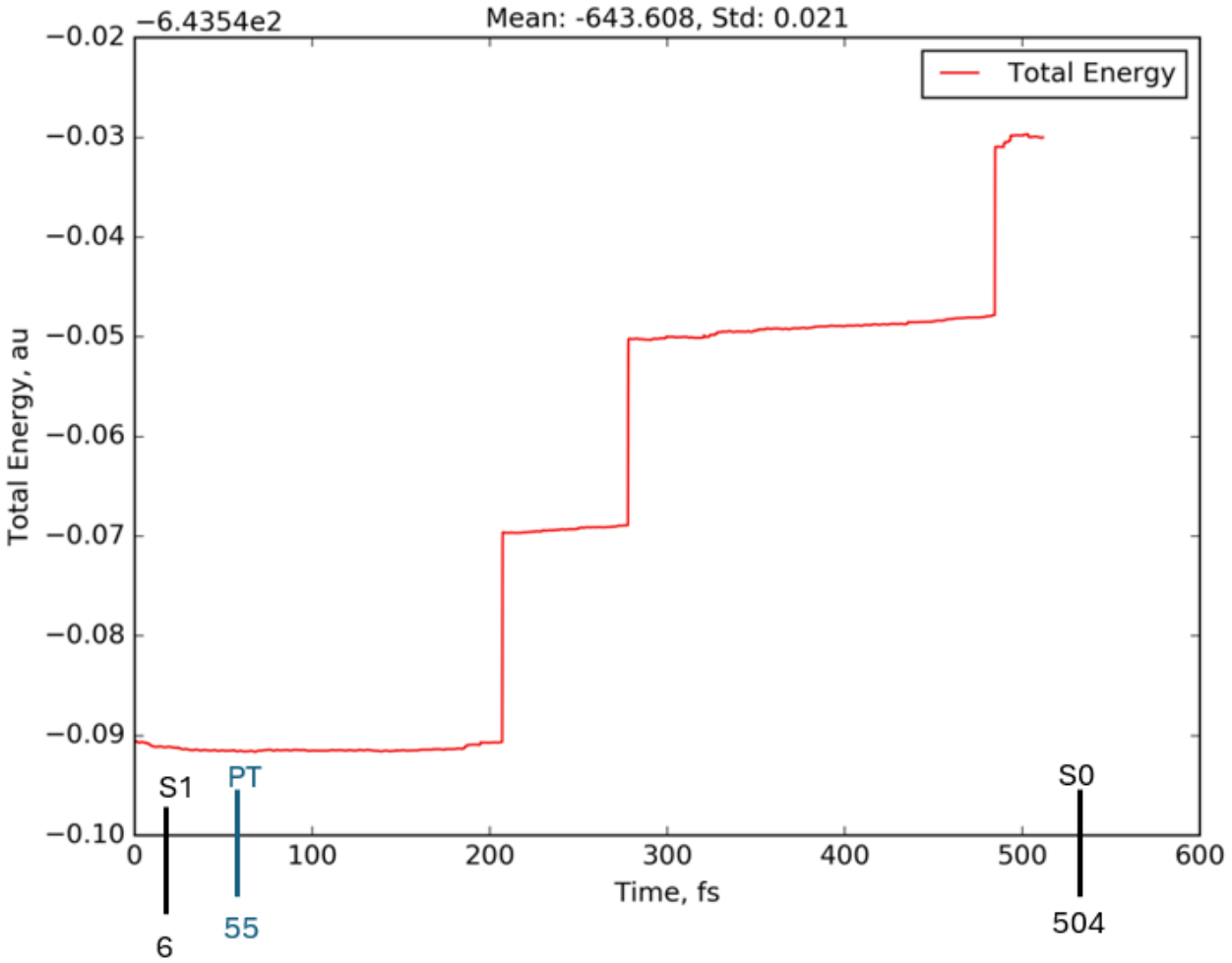
Ab initio molecular dynamics

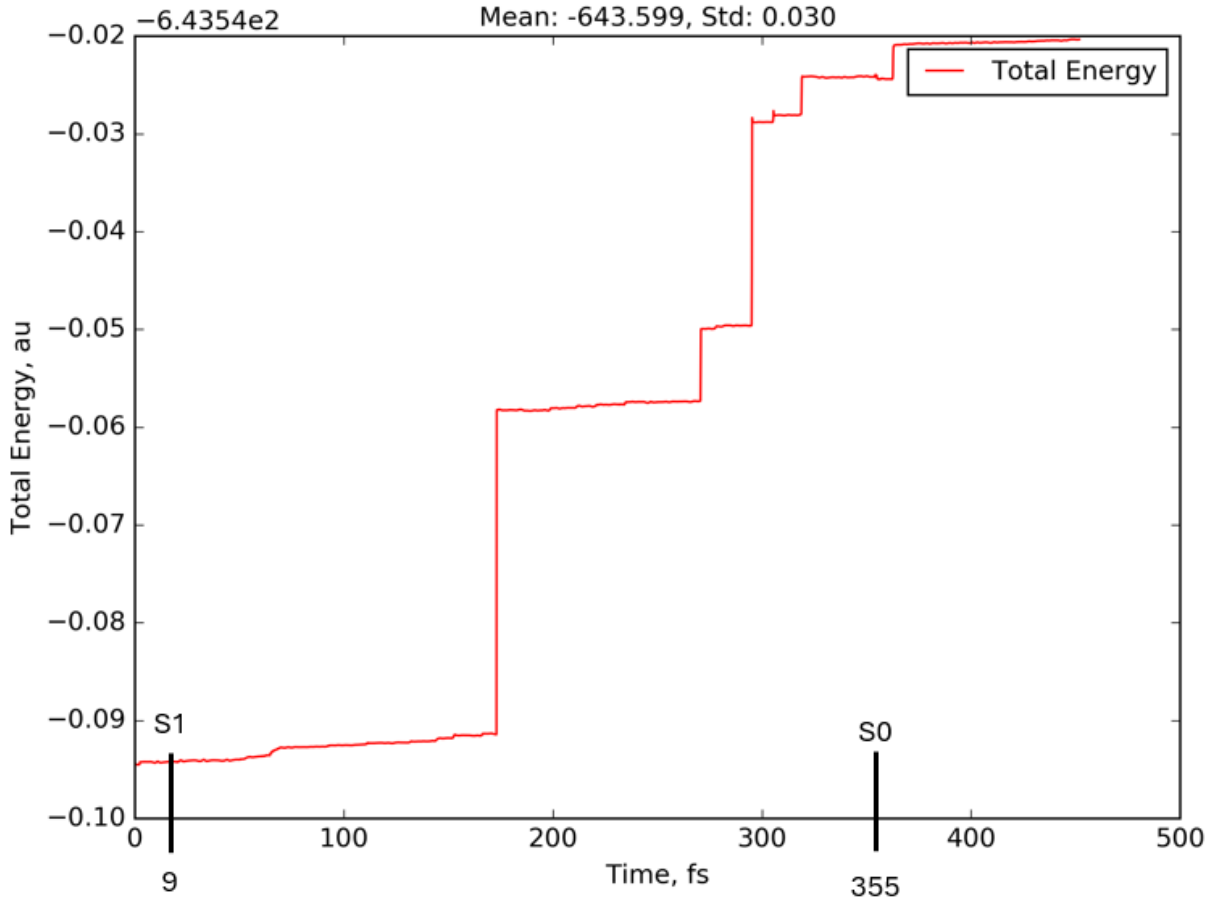
$|\psi(t)\rangle$ - Electronic wavefunction $\longrightarrow$ $i\frac{d}{dt}|\psi\rangle = \mathbf{H}(t)|\psi\rangle$

$\mathbf{R}(t)$ - Classical trajectory for nuclei $\longrightarrow$ $M_K\ddot{\mathbf{R}}_K = \mathbf{F}_K(\mathbf{R})$

$$\mathbf{F}_{MF}(t) = -\frac{d}{d\mathbf{R}}\frac{\langle\psi(t)|\mathbf{H}(t)|\psi(t)\rangle}{\langle\psi(t)|\psi(t)\rangle}$$

Problem: Energy is not conserved





Relaxed Scan for Enol Twisting