First-principles Simulations of Transient Absorption Spectrum

Arshad Mehmood and Benjamin G. Levine
Institute for Advanced Computational Science and Department of Chemistry
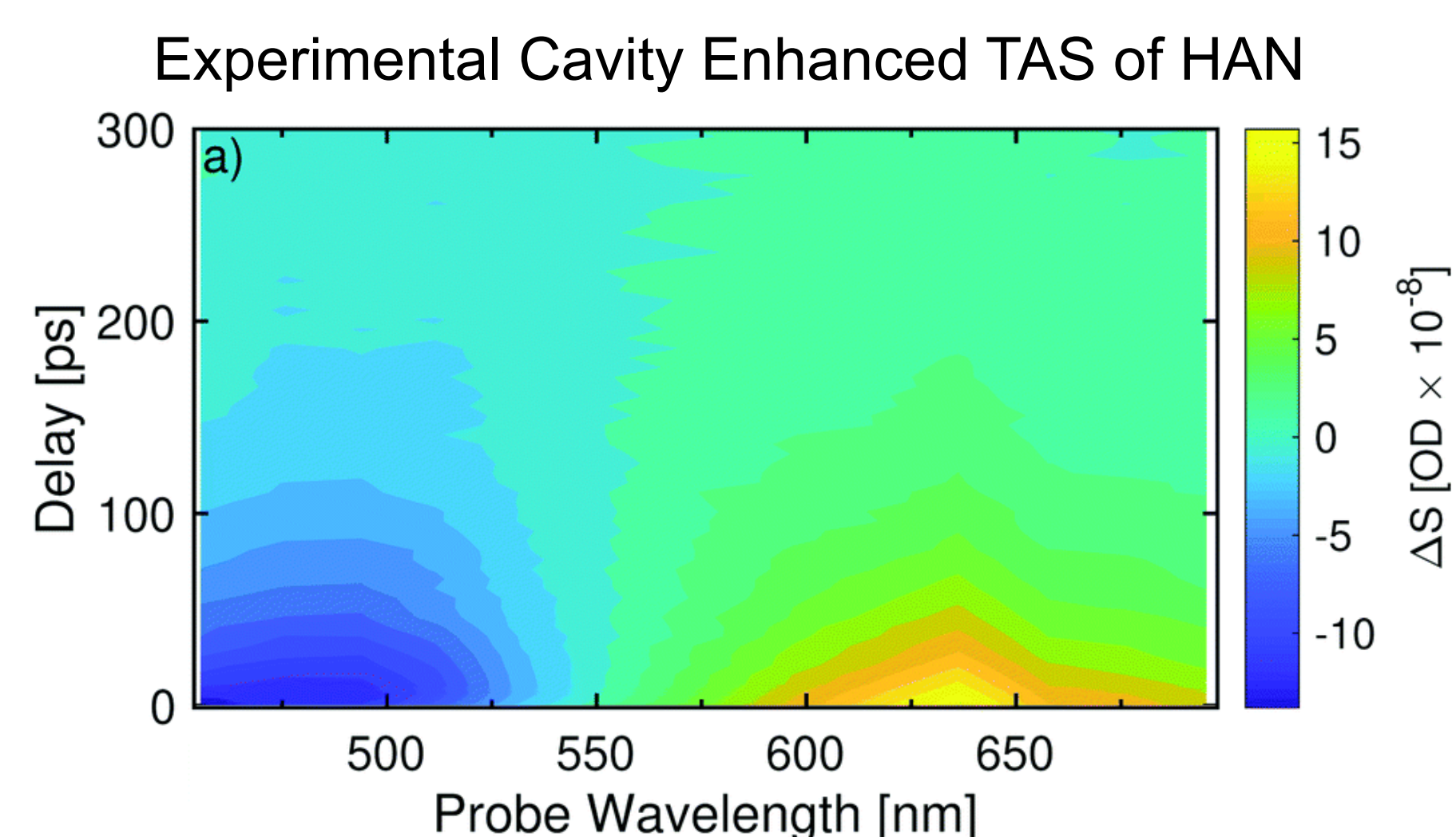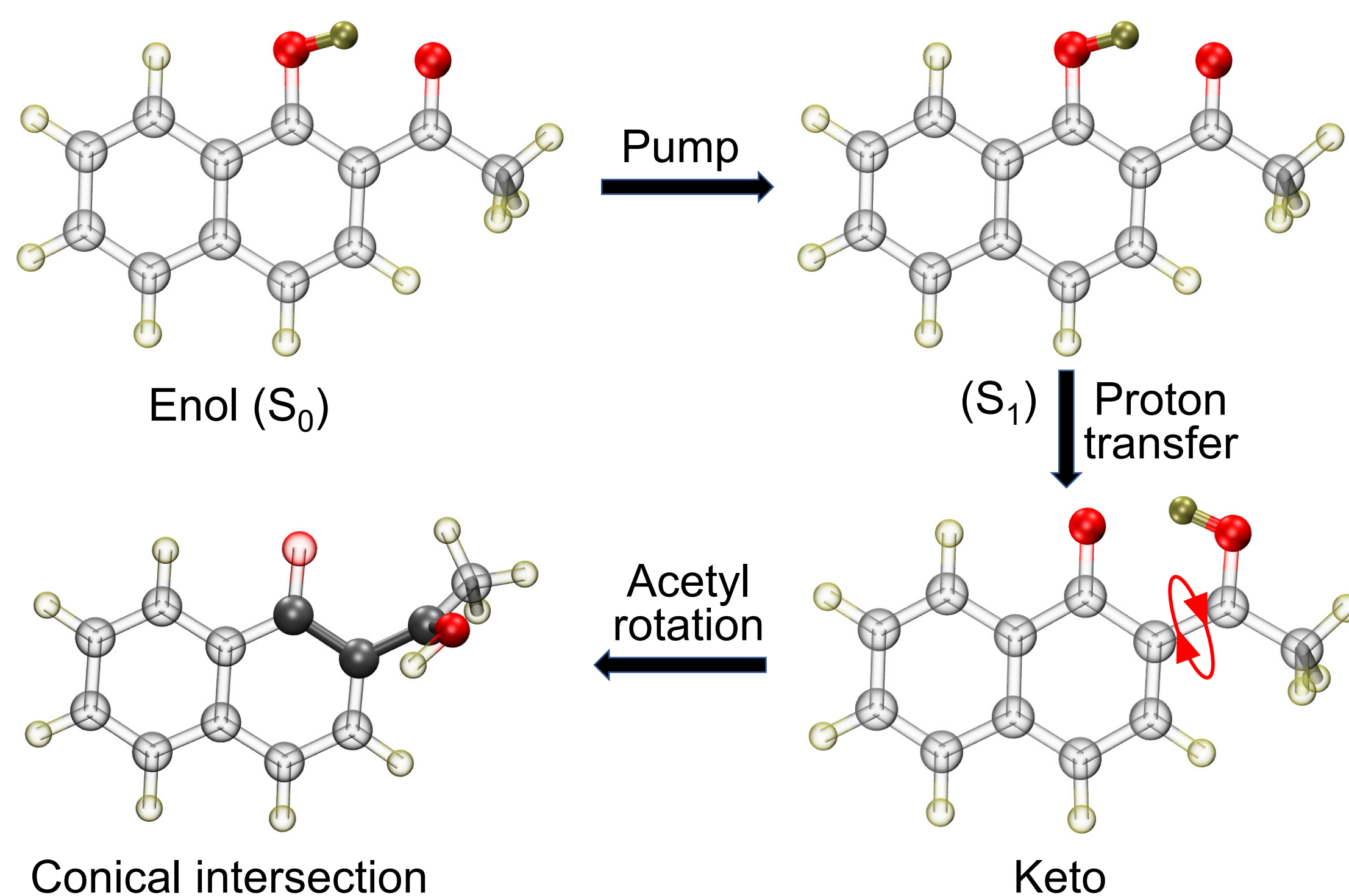### Stony Brook University, New York

Why to Simulate TAS?

- Transient absorption spectroscopy (TAS) is a promising technique to measure the dynamics of ultrafast processes such as excited-state intramolecular proton transfer, due to its excellent time resolution and applicability to a diverse class of systems.
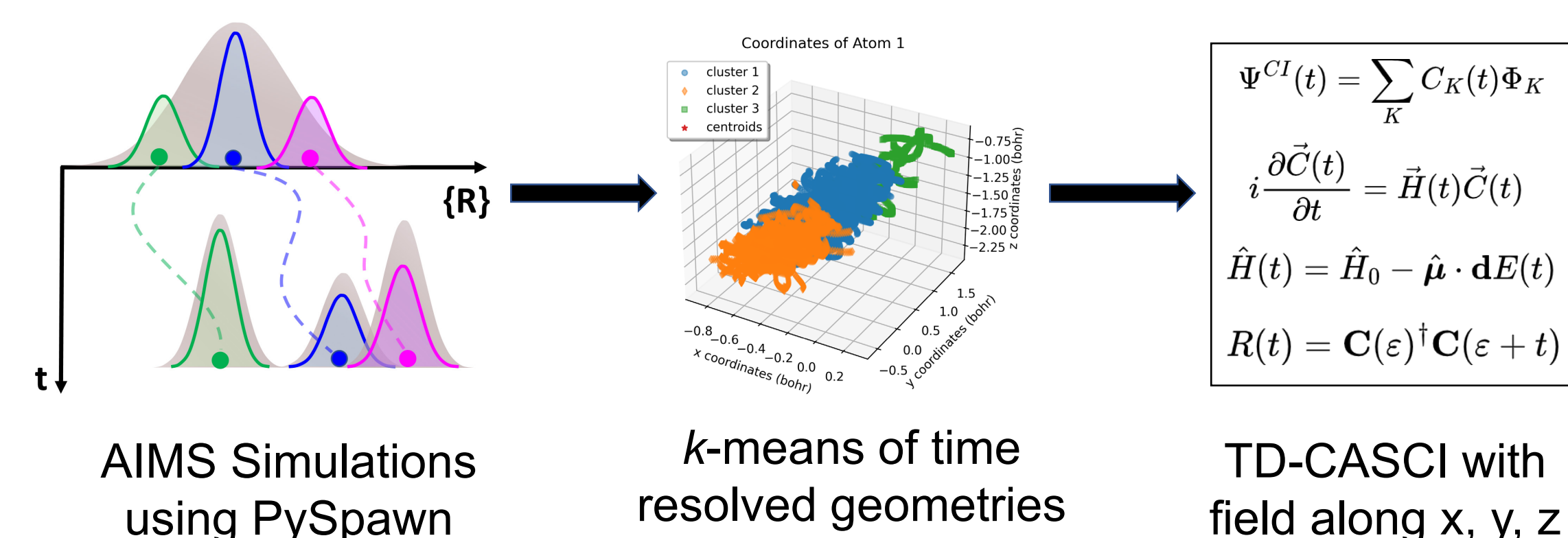
1'-Hydroxy-2'-acetonaphthone (HAN)

Enol (S_0)   Pump   (S_1)   Proton transfer

Conical intersection   Acetyl rotation   Keto

Experimental Cavity Enhanced TAS of HAN

Blue = Stimulated Emission   Yellow = Excited State Absorbance

- The spectral "**blobs**" observed in TAS experiment are less informative regarding the underlying dynamics due to the involvement of large numbers of active degrees of freedom.

Our Approach: AIMS + TD-CASCI

- We used FOMO(0.10)-CAS(10,10)-CI/6-31G** *ab initio* multiple Spawning (AIMS) non-adiabatic dynamics simulations in combination with GPU-accelerated time-dependent complete active space configuration interaction (TD-CASCI) method to simulate the excited state dynamics and gas-phase TAS of HAN.

- The simulations consisted of 42 initial trajectory basis functions on the S_1 state sampled from a S_0 harmonic Wigner distribution.

$$\Psi^{CI}(t) = \sum_K C_K(t)\Phi_K$$
$$i\frac{\partial \vec{C}(t)}{\partial t} = \vec{H}(t)\vec{C}(t)$$
$$\hat{H}(t) = \hat{H}_0 - \hat{\mu}\cdot \mathbf{d}E(t)$$
$$R(t) = \mathbf{C}(\varepsilon)^\dagger \mathbf{C}(\varepsilon + t)$$

AIMS Simulations using PySpawn   k-means of time resolved geometries   TD-CASCI with field along x, y, z

- For TAS, the electronic spectrum of the time-separated conformations are computed using a δ-kick with field strength of 10^{24} W/m^2 polarized separately along the *x*, *y* and *z* directions.

Why TD-CASCI?

- TD-CASCI does not require the convergence of all higher excited states in the CAS. It gives the excited state absorbance spectrum without calculating the higher excited states.
- It allows a large complete active space configuration expansions.
- Highly efficient GPU-accelerated implementation make it possible to run thousands of individual TD-CASCI simulations needed to simulate the TAS in a reasonable time with a reasonable cost.
- Our implementations uses direct configuration interaction approach that eliminates the need to explicitly build, store, or diagonalize the Hamiltonian matrix.
- Excellent method when many excited states are of interest

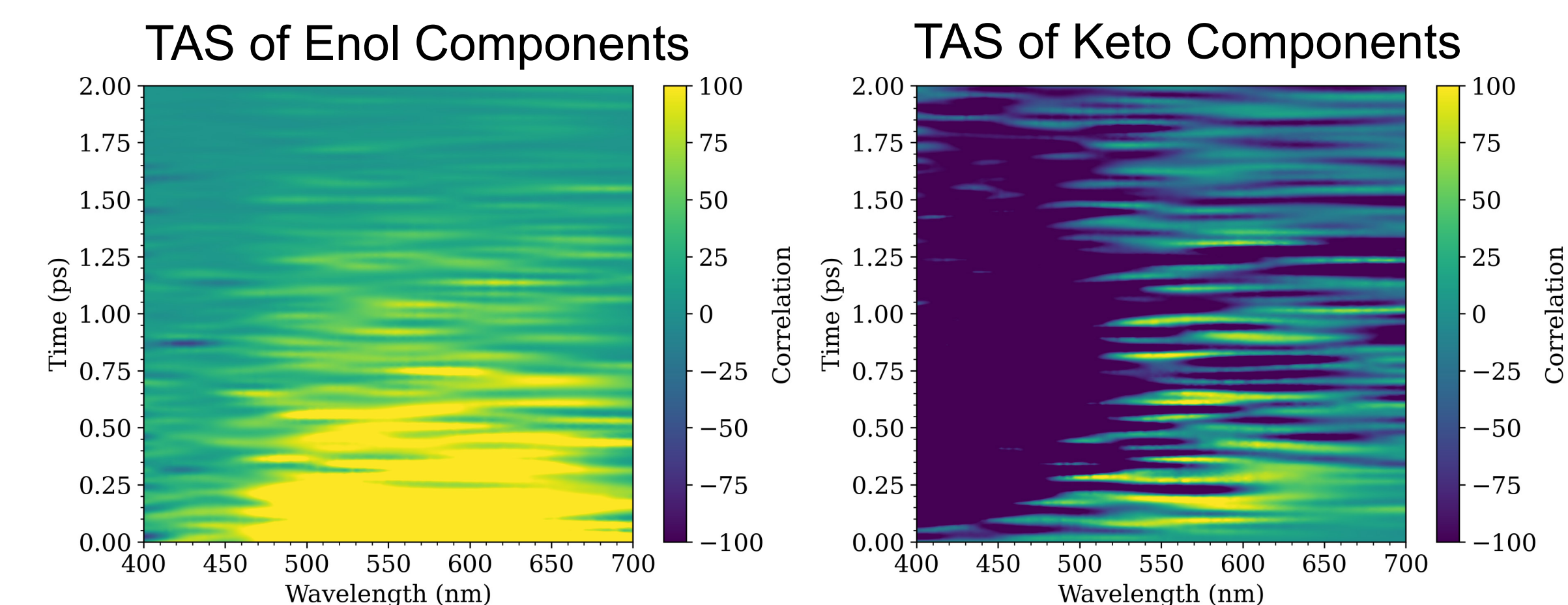## Simulated TAS of HAN

$$R_{magic} = \frac{R_x^2 + R_y^2 + R_z^2}{3}$$

Stimulated Emission shown in blue
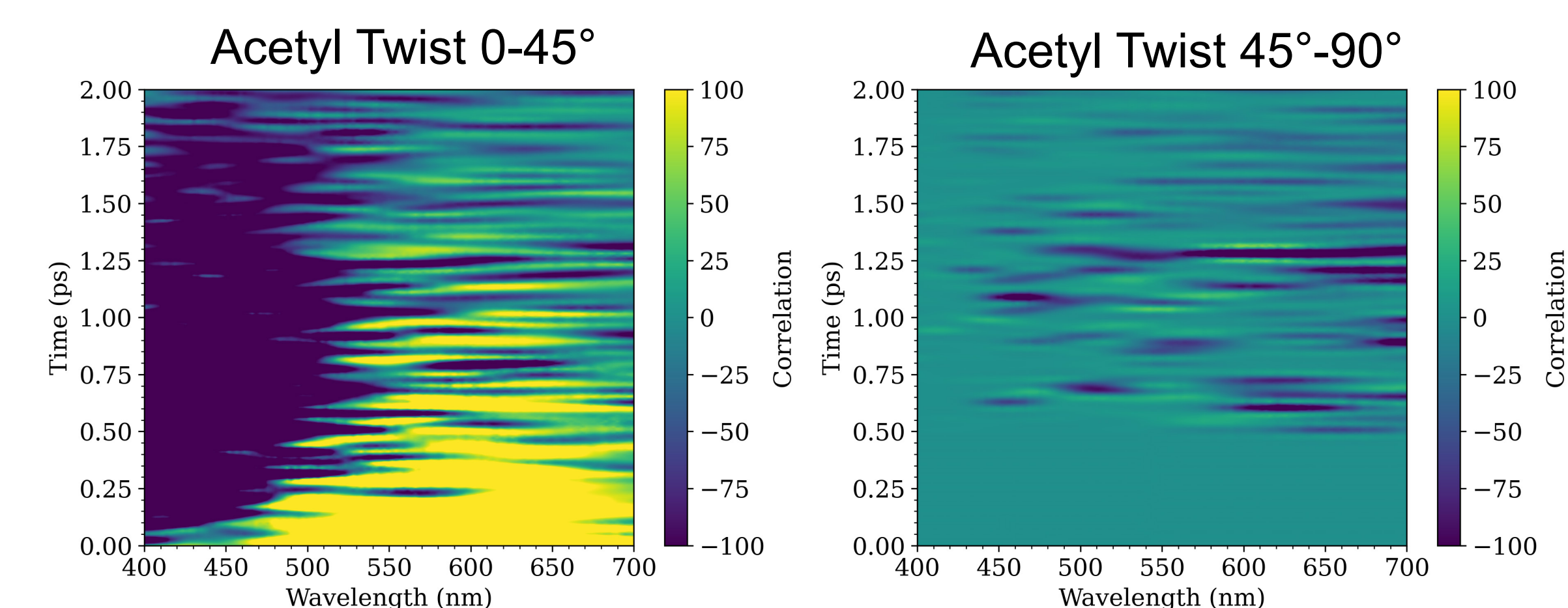
S_1 Absorbance shown in yellow
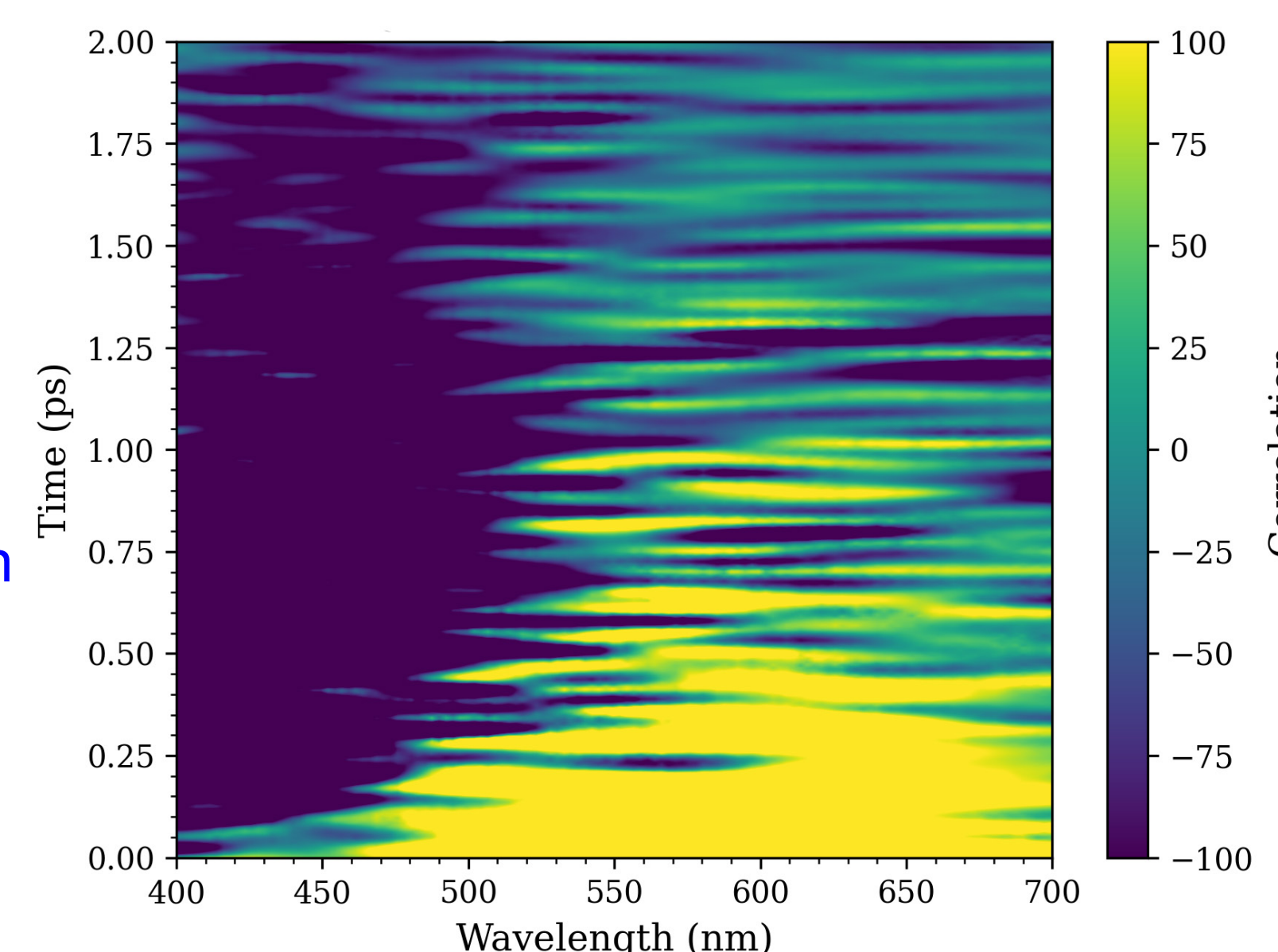
- HAN magic angle TAS simulated using **>20,000 individual TD-CASCI calculations involving 6720 conformations**


Assignment of the components of Experimental TAS

TAS of Enol Components   TAS of Keto Components

- The proton transfer red-shifts the stimulated emission

Acetyl Twist 0-45°   Acetyl Twist 45°-90°

- The methodology also provides a dynamic picture of TAS evaluation along a specific degree of freedom

- The difference in the time axis of theory and experiment is due to lower rotation barrier predicted by FOMO-CASCI used in AIMS

Acetyl rotation relaxed scan   Population of acetyl rotation
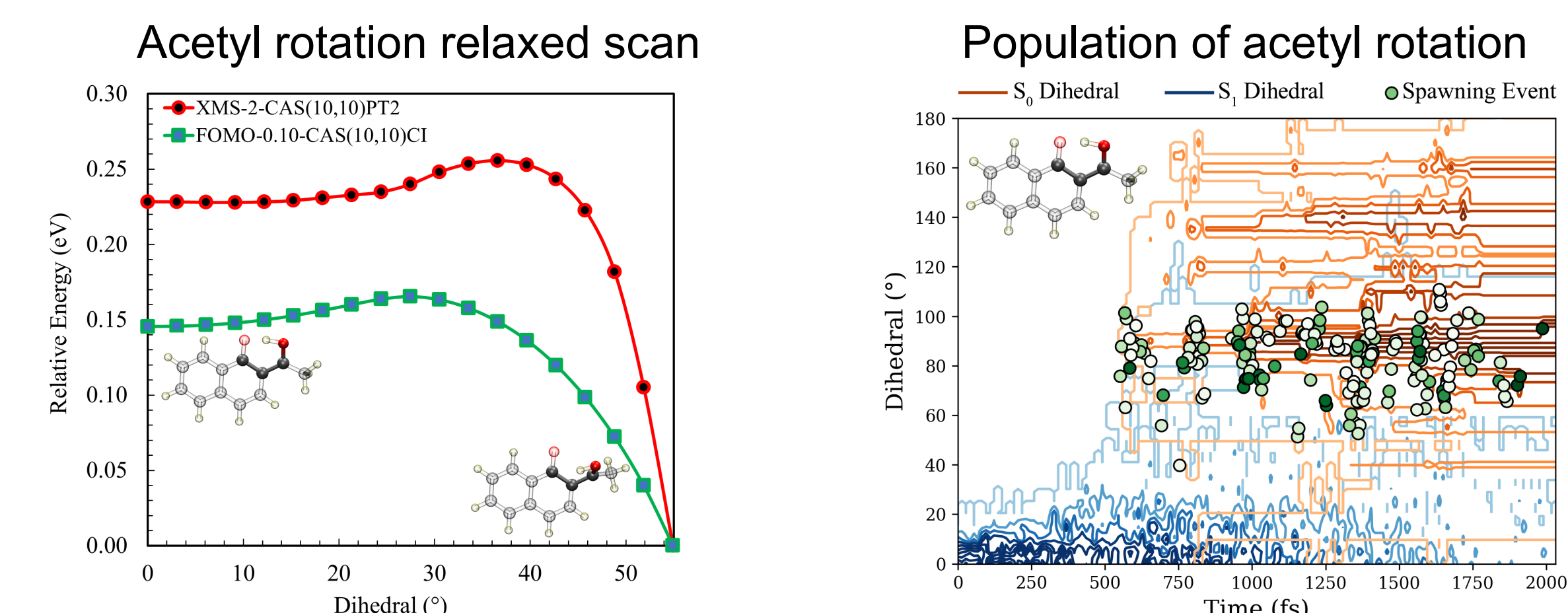
- Experimental barrier = 0.071 eV *vs* theory barrier = 0.020 eV.

Acknowledgment

References

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2. Peng, W.-T.; Fales, B. S.; Levine, B. G.. *J. Chem. Theory Comput.* **2018**, *14*, 4129-4138.
3. Fedorov, D. A.; Seritan, S.; Fales, B. S.; Martínez, T. J.; Levine, B. G. *J. Chem. Theory Comput.* **2020**, *16*, 5485-5498.
4. Silfies, M. C.; Kowzan, G.; Lewis, N.; Allison, T. K. *PCCP* **2021**, *23*, 9743-9752.