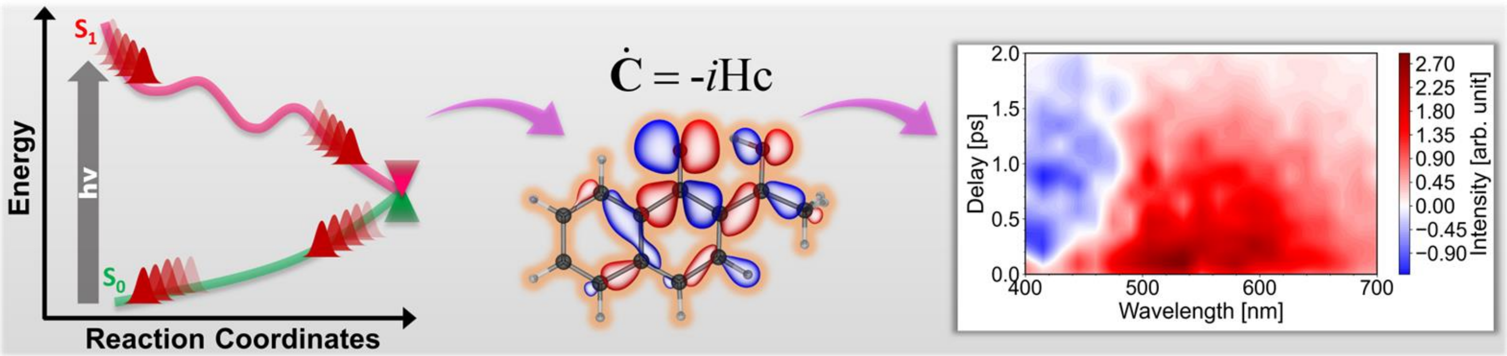
Simulations of Ultrafast Spectroscopy Observables Using the GPU-accelerated Time-dependent Complete Active Space Configuration Interaction Method



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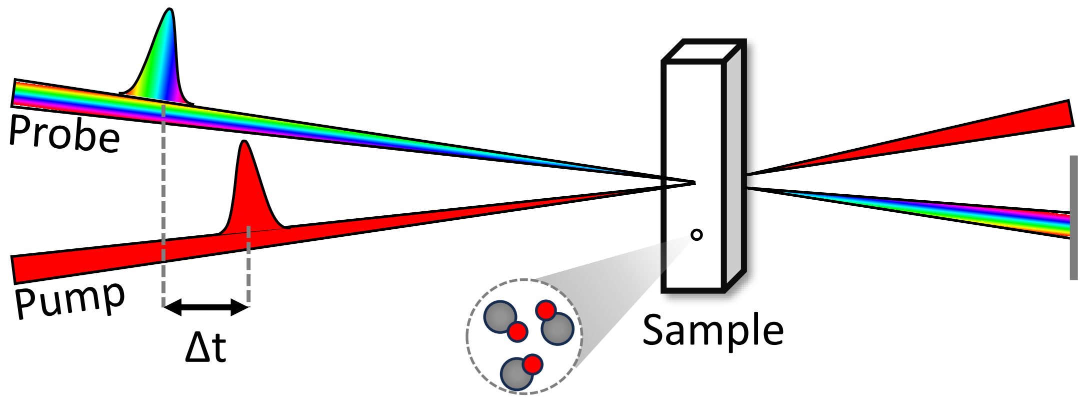
Transient Absorption Spectroscopy (TAS)



Characteristics

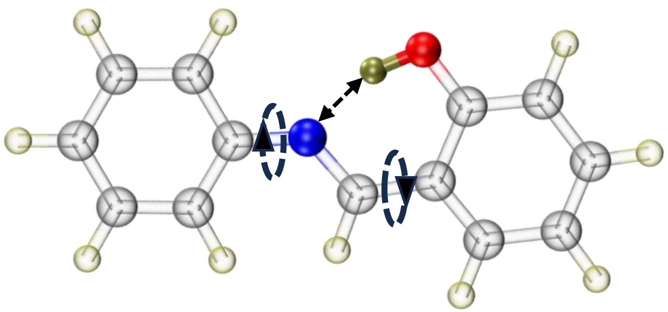
- **Time Resolution**: TAS offers extremely high time resolution allows to monitor ultrafast processes in femtoseconds scale
- **Versatility:** This technique is versatile and can be applied to a wide range of systems
- **Sensitivity:** highly sensitive to changes in electronic and structural properties of molecules or materials

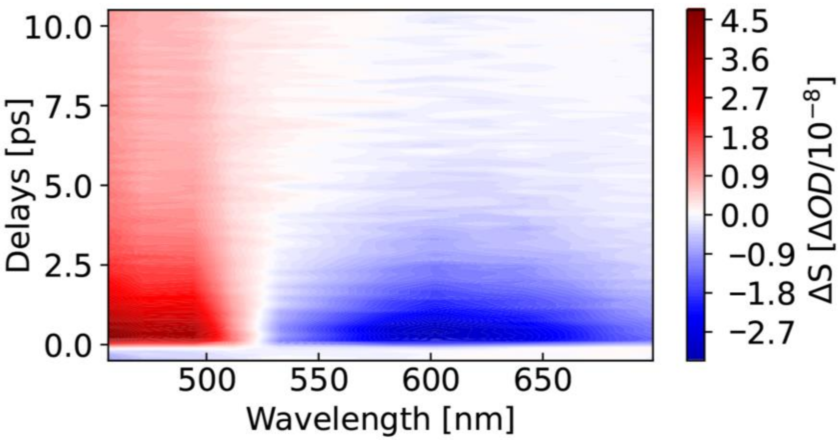
Berera, R., van Grondelle, R. & Kennis, J.T.M., *Photosynth Res* **2009**, *101*, 105-118.

Limitations of TAS – The Motivation

The interpretation of the TA spectrum (TAS) is inherently indirect:

- Lower-dimensional Observables





- Overlap of positive (excited state absorbance) and negative (stimulated emission and ground state bleach) signals

Ultrafast theory has become an essential partner to experiment and is a standard requirement to correctly assign the ultrafast signals.

Silfies, M. C.; Mehmood, A.; Kowzan, G.; Hohenstein, E. G.; Levine, B. G.; Allison, T. K. *J. Chem. Phys.* **2023**, *159,* 104304.
Silfies, M. C.; Kowzan, G.; Lewis, N.; Allison, T. K., *Phys. Chem. Chem. Phys.*, **2021**, *23*, 9743-9752.

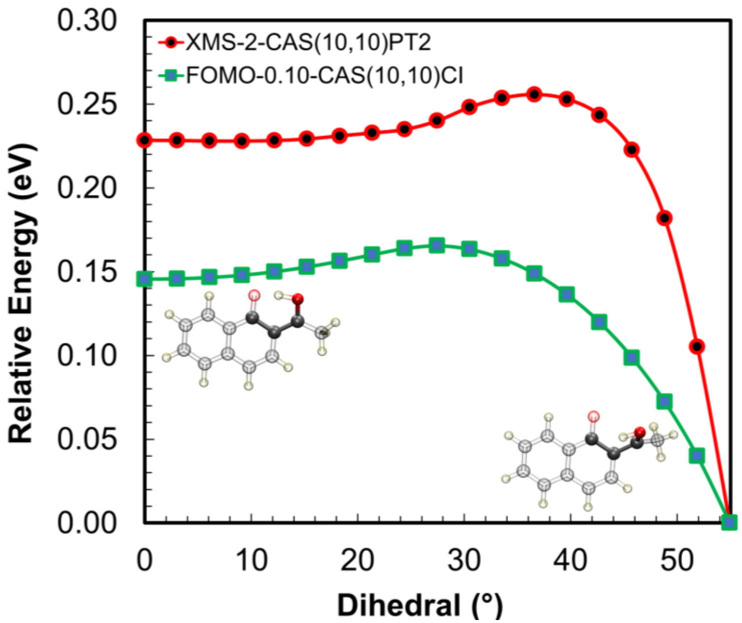
Why to Simulate Ultrafast Signals…?

- The AIMD provides $|\Psi_{\mathrm{approx}}(t)\rangle$ that can be used to assign ultrafast experiment

- Common procedure involve comparing experimental and AIMD time constants

- Due to the exponential relation, error in rates are amplified due to a small error in the barrier height

- **Direct comparison of experimental and simulated observables provide a more accurate solution.**

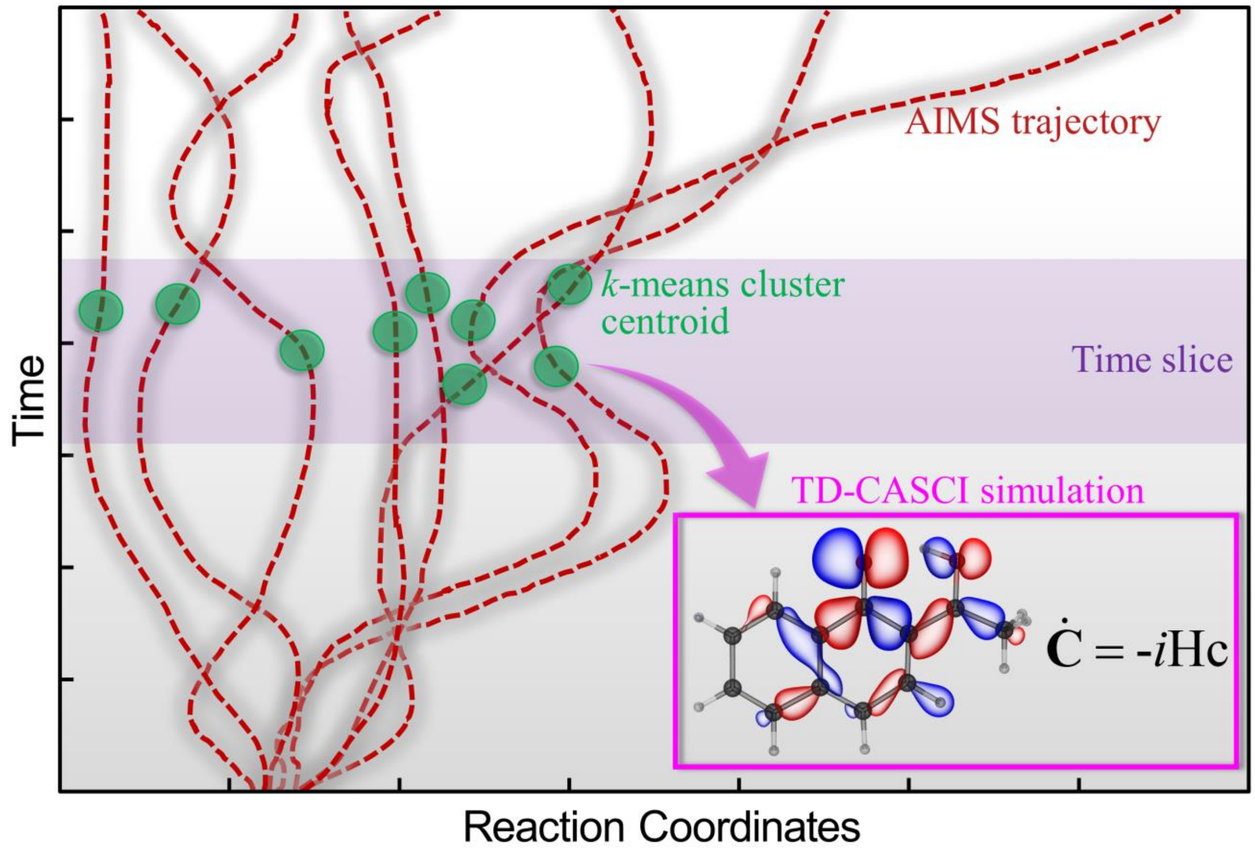


- **Our Approach**

We combined non-adiabatic molecular dynamics (NAMD) simulations (a pump) with our GPU-accelerated Time-dependent Complete Active Space Configuration Interaction (TD-CASCI) method (a probe) for simulating both the ultrafast dynamics and TAS.

Silfies, M. C.; Mehmood, A.; Kowzan, G.; Hohenstein, E. G.; Levine, B. G.; Allison, T. K. *J. Chem. Phys.* **2023**, *159,* 104304.
Silfies, M. C.; Kowzan, G.; Lewis, N.; Allison, T. K., *Phys. Chem. Chem. Phys.*, **2021**, *23*, 9743-9752.

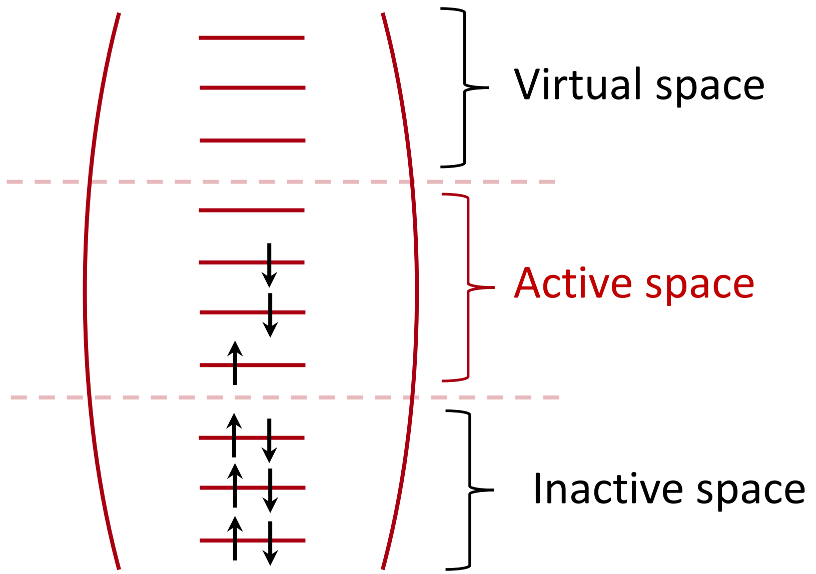
Simulation Protocol



- TD-CASCI electronic dynamics are run on each selected conformation derived from the time-slices of NAMD trajectories
- A *δ*-kick with a field polarized along the *x*, *y*, and *z* axes of the molecular axis.

Time-dependent CASCI (TD-CASCI): The Probe

- Linear variational method for solving the Schrödinger equation using a wave function that is a linear combination of configuration state functions:



$$\Psi^{\mathrm{CI}} = C_{\mathrm{HF}}\Phi_{\mathrm{HF}} + \sum_{i,a} C_i^a \Phi_i^a + \sum_{i,j,a,b} C_{i,j}^{a,b}\Phi_{i,j}^{a,b} + \sum_{i,j,k,a,b,c} C_{i,j,k}^{a,b,c}\Phi_{i,j,k}^{a,b,c} + \cdots = \sum_K C_K \Phi_K$$

$$i\frac{\partial \vec{C}(t)}{\partial t} = \vec{H}(t)\vec{C}(t)$$

$$\vec{C}(t) = \vec{q}(t) + i\vec{p}(t)$$

$$\frac{\partial \vec{p}(t)}{\partial t} = -\vec{H}(t)\vec{q}(t) \qquad \frac{\partial \vec{q}(t)}{\partial t} = \vec{H}(t)\vec{p}(t)$$

Peng, W.-T.; Fales, B. S.; Levine, B. G., *J. Chem. Theory Comput*. **2018**, *14*, 4129-4138.

Time-dependent CASCI (TD-CASCI): The Probe

- Electric field excitation are included by using the electric dipole approximation:

$$\hat{H}(t) = \hat{H}_0 - \hat{\boldsymbol{\mu}} \cdot \overrightarrow{dE}(t)$$

$$R(t) = \vec{C}(\varepsilon)^{\dagger}\vec{C}(\varepsilon + t)$$

- Pump-probe orientations:

$$R_{\text{magic}}(E) = \left(R_{\|}(E) + R_{\perp}(E)\right)/3$$

$$R_{\|}(E) = 0.2R_{\mathrm{x}}^2(E) + 0.2R_{\mathrm{y}}^2(E) + 0.6R_{\mathrm{z}}^2(E)$$

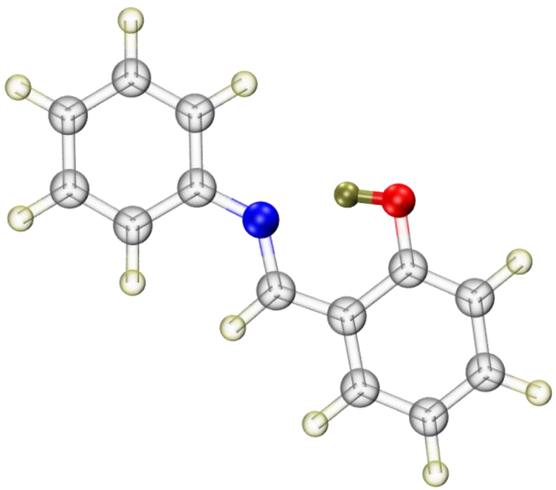
$$R_{\perp}(E) = 0.4R_{\mathrm{x}}^2(E) + 0.4R_{\mathrm{y}}^2(E) + 0.2R_{\mathrm{z}}^2(E)$$

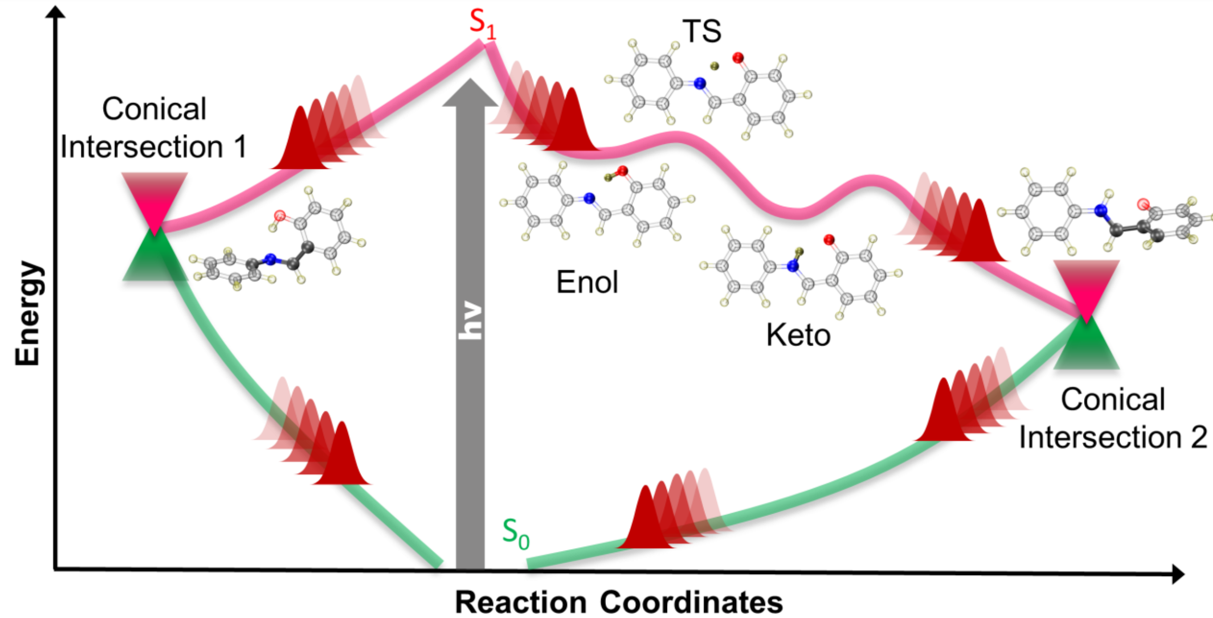
Salient Features

- It gives the TAS without the need to calculate all higher excited states
- It allows a large complete active space configuration expansions
- No need to explicitly build, store, and diagonalize of the Hamiltonian matrix
- The GPU-accelerated implementation allows cost-effective simulation of TAS.

Peng, W.-T.; Fales, B. S.; Levine, B. G., *J. Chem. Theory Comput*. **2018**, *14*, 4129-4138.

Salicylideneaniline (SA)





Non-adiabatic Dynamics Simulations (the pump):

- 2ps AIMS simulations with 360 initial conditions at ωPBEh-CAS(2,2)CI/6-31G**

TD-CASCI Simulations (the probe):

- 84 time slices (each slice 24.2 fs) of 2ps NAMD trajectories
- 80 representative geometries from each slice on S_1 electronic state
- 100 fs TD-CASCI electronic dynamics by applying field along *x, y, z* axis

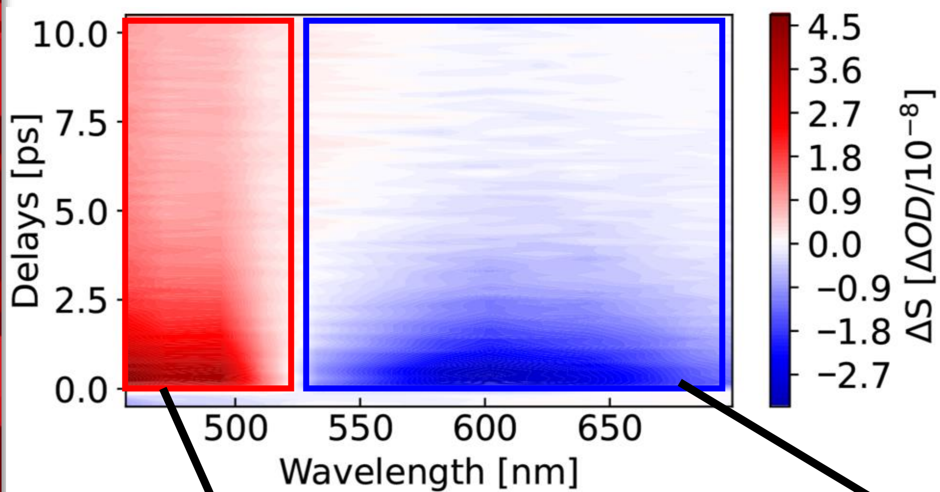
Silfies, M. C.; Mehmood, A.; Kowzan, G.; Hohenstein, E. G.; Levine, B. G.; Allison, T. K. *J. Chem. Phys*. **2023**, *159*, 104304.
Pijeau, S.; Foster, D.; Hohenstein, E. G. *J. Phys. Chem. A* **2018**, 122 (25), 5555-5562.

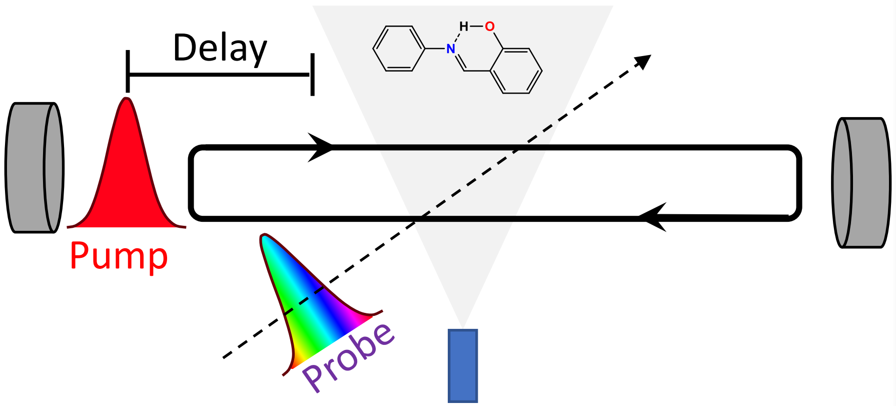
SA Experimental Cavity-Enhanced TAS (CE-TAS)

- Gas phase TAS provides an opportunity to compare with theory as complexity of model is reduced significantly.

M. Silfies

T. Allison





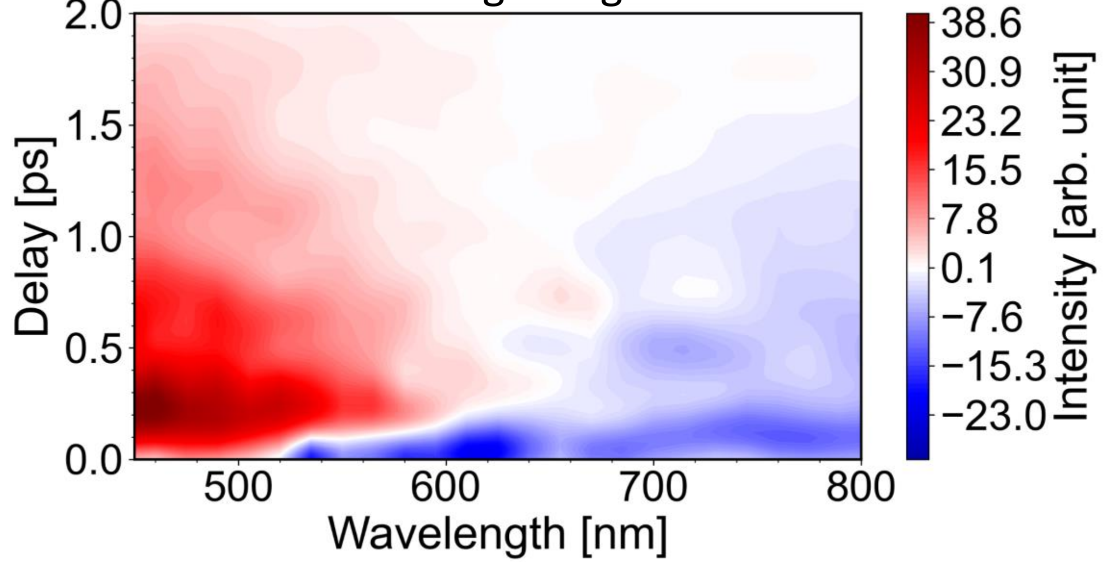
Excited State Absorbance

Stimulated Emission

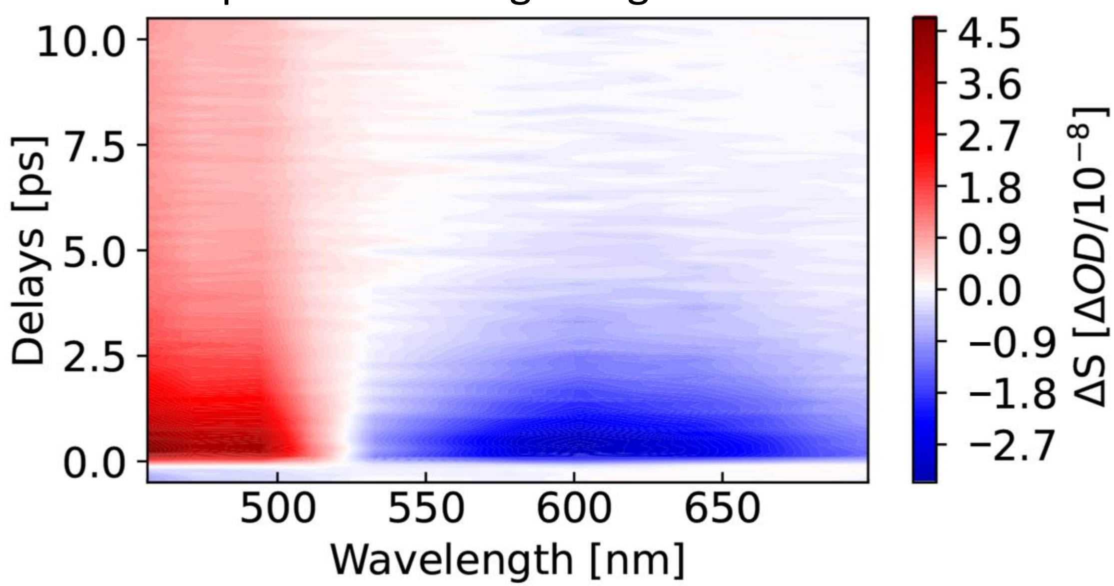
Silfies, M. C.; Mehmood, A.; Kowzan, G.; Hohenstein, E. G.; Levine, B. G.; Allison, T. K. *J. Chem. Phys.* **2023**, *159*, 104304.

Simulated TAS of SA

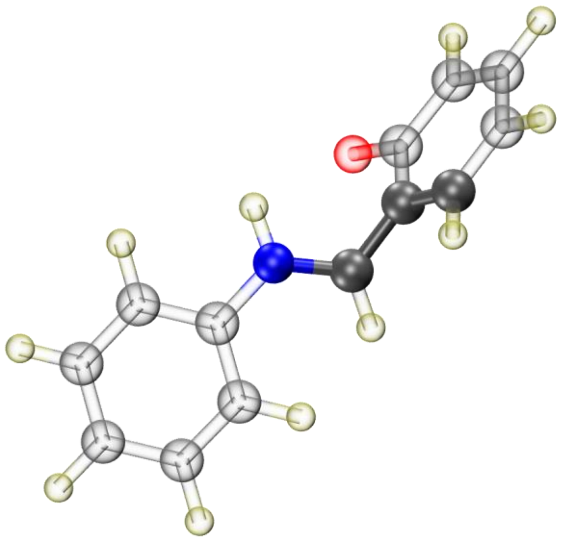
Simulated Magic Angle TAS

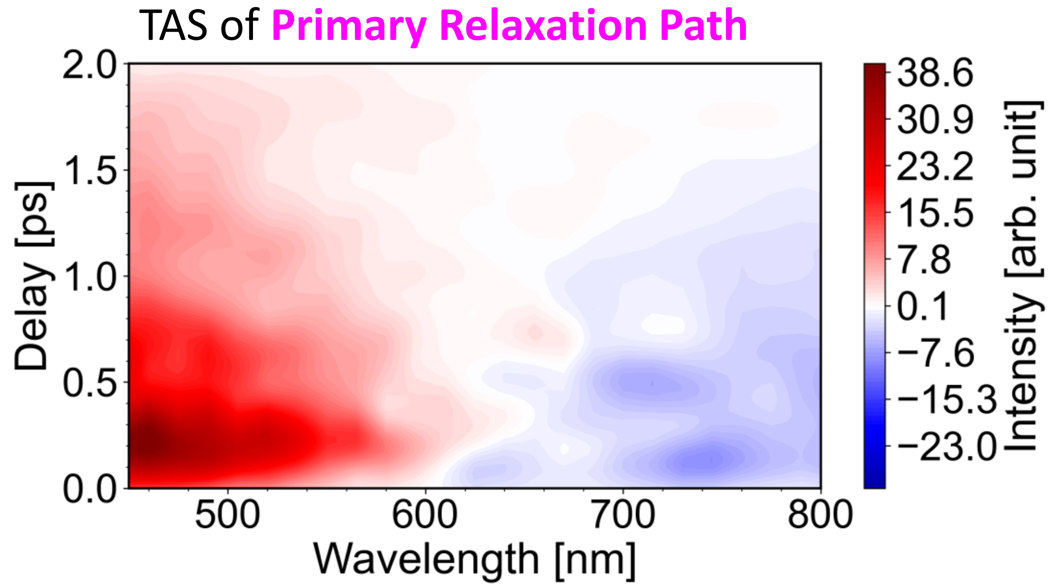


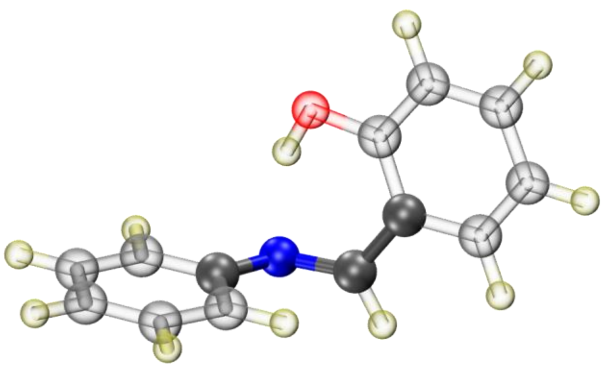
Experimental Magic Angle CE-TAS

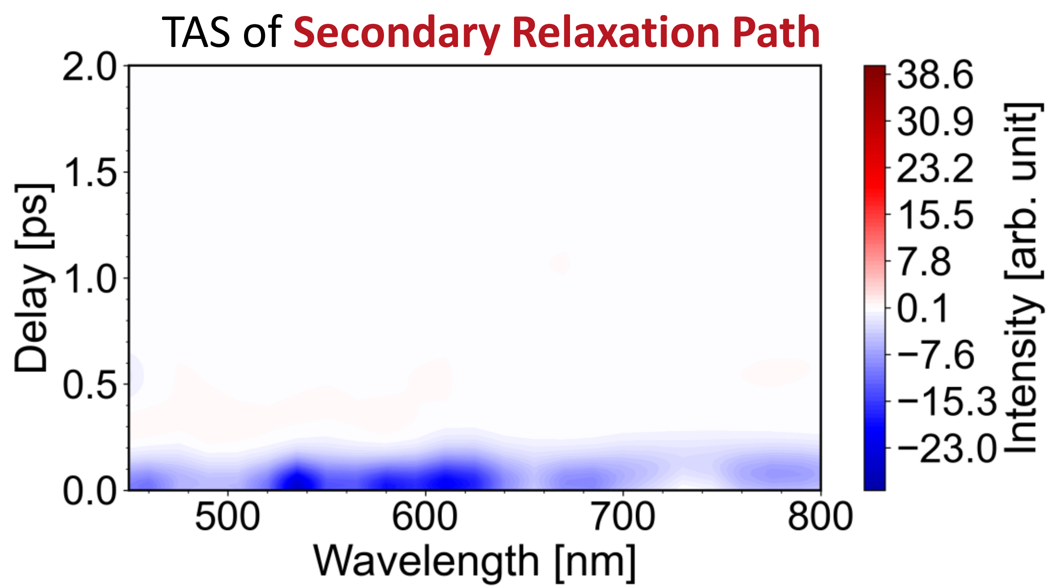


Simulation of TAS Along Different Relaxation Paths

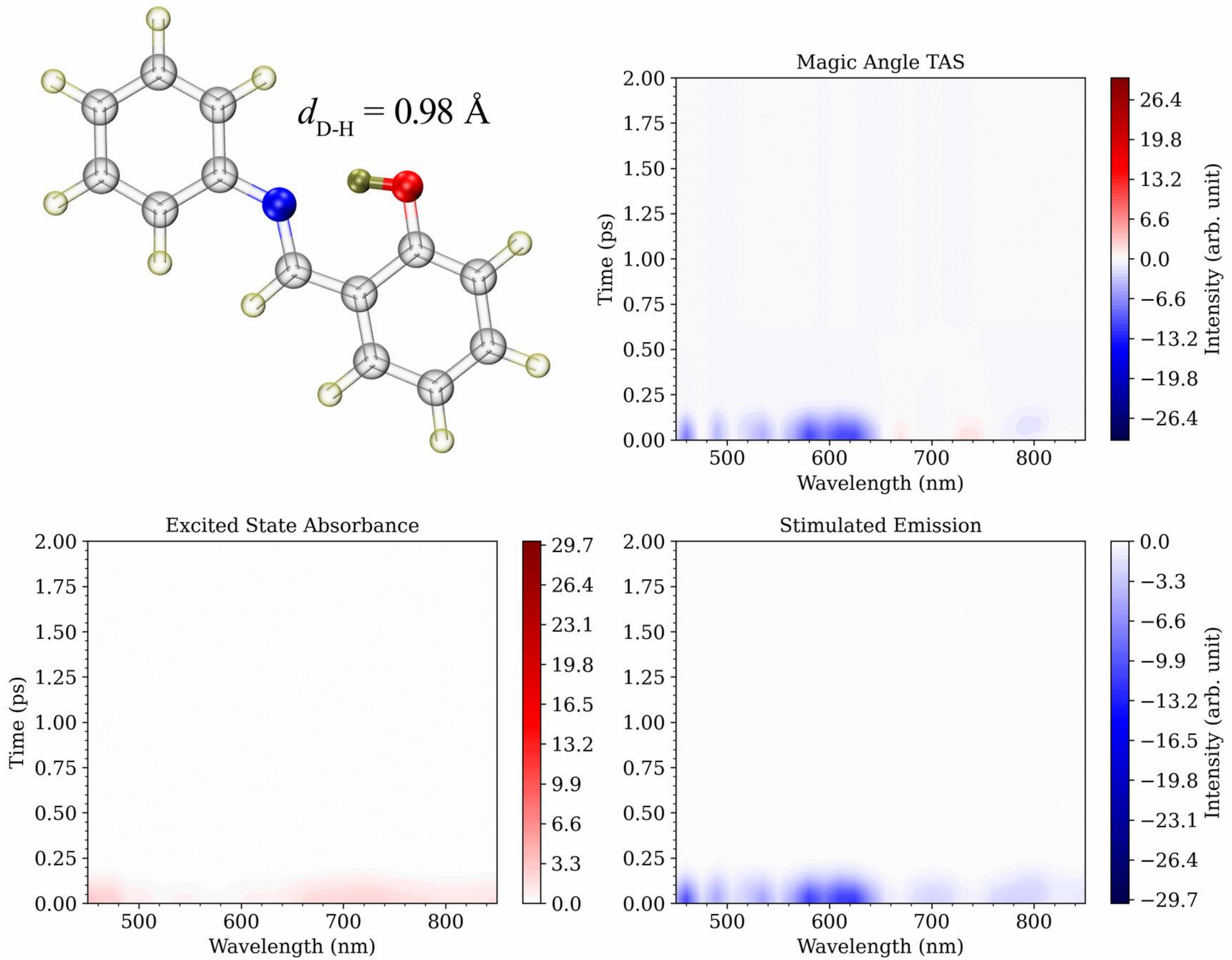




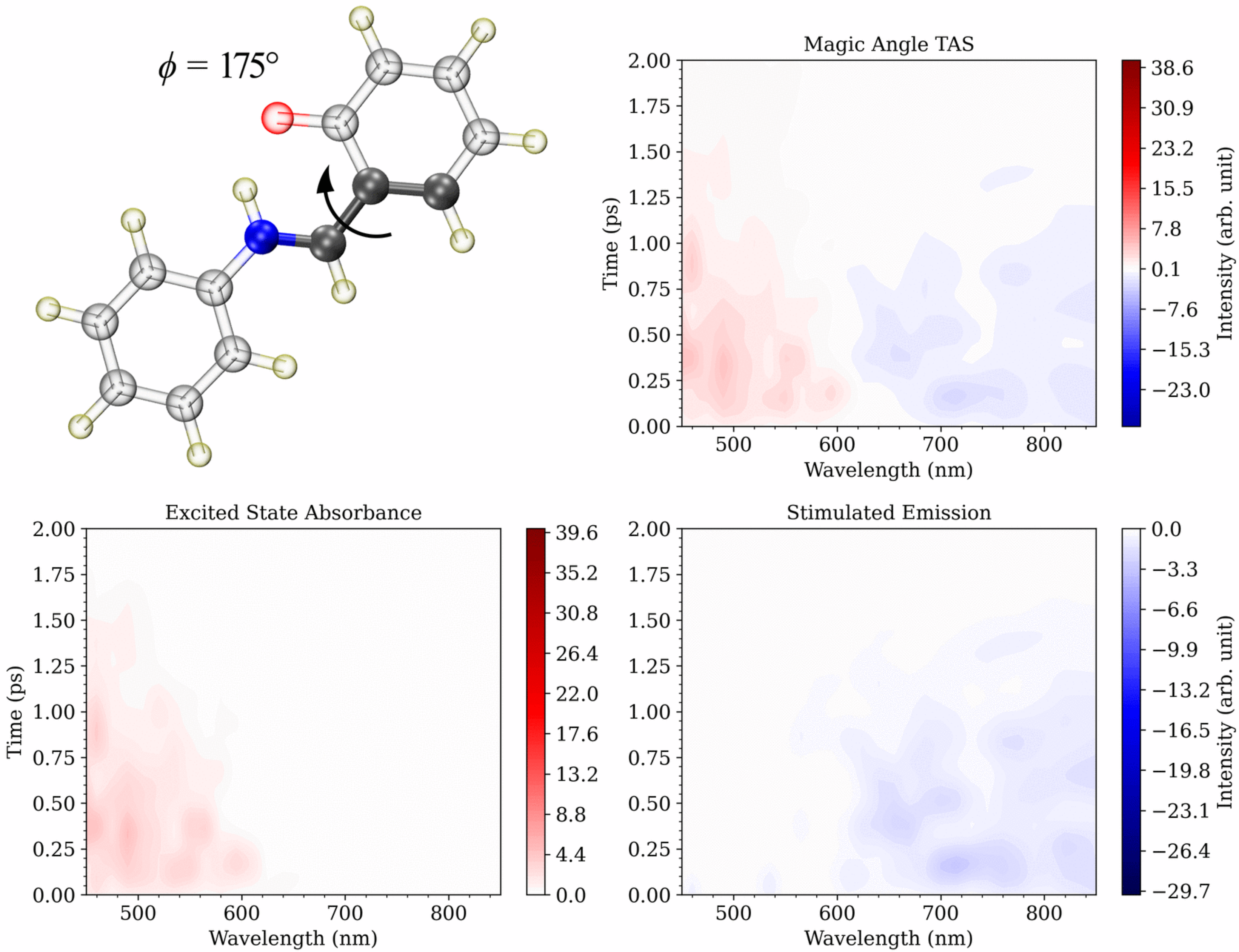




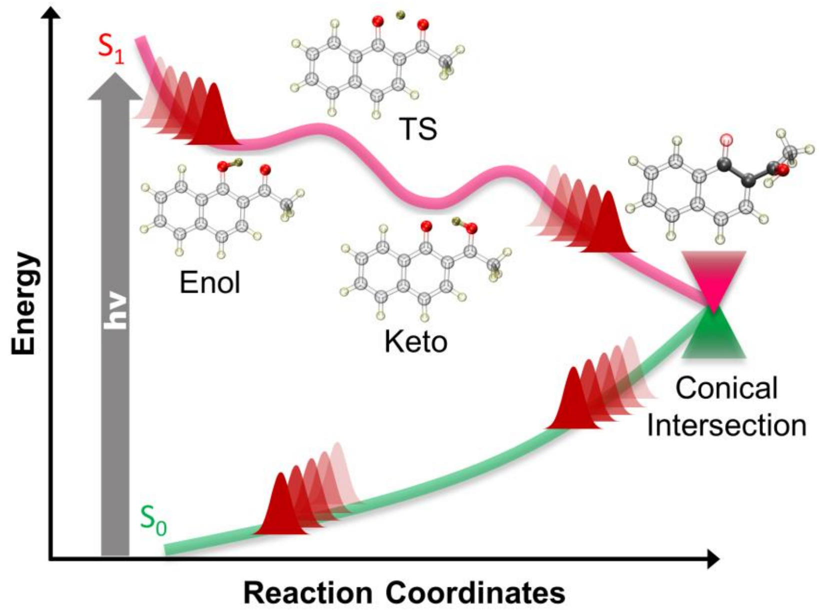
Dynamic Visualization of TAS Evolution on ESIPT Path

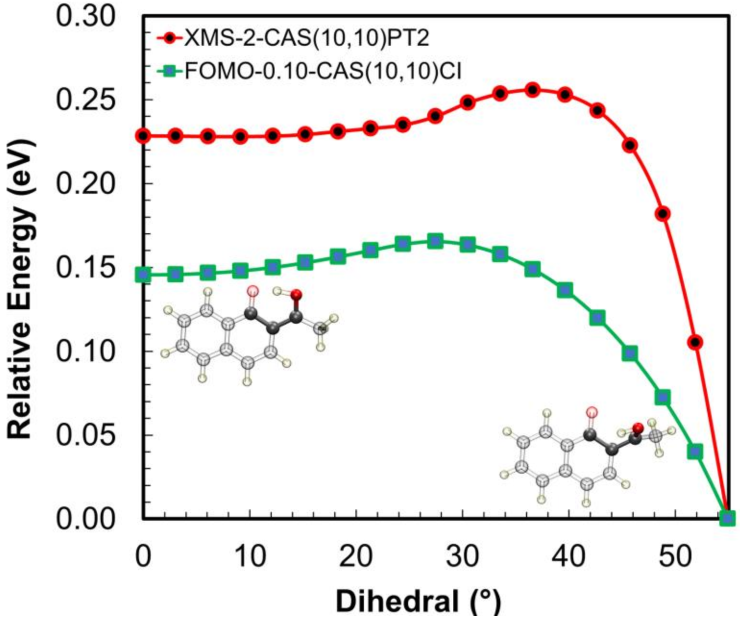


Dynamic Visualization of TAS Evolution on Twist Path



1-Hydroxy-2-acetonaphthone (HAN)





Non-adiabatic Dynamics Simulations (the pump):

- 2ps AIMS simulations with 45 initial conditions at FOMO-CAS(10,10)CI/6-31G**
- The proton transfer time (542 fs) and S1 lifetime (1686 fs) are significantly distinct in NAMD which allows the assignment of the components of CE-TAS

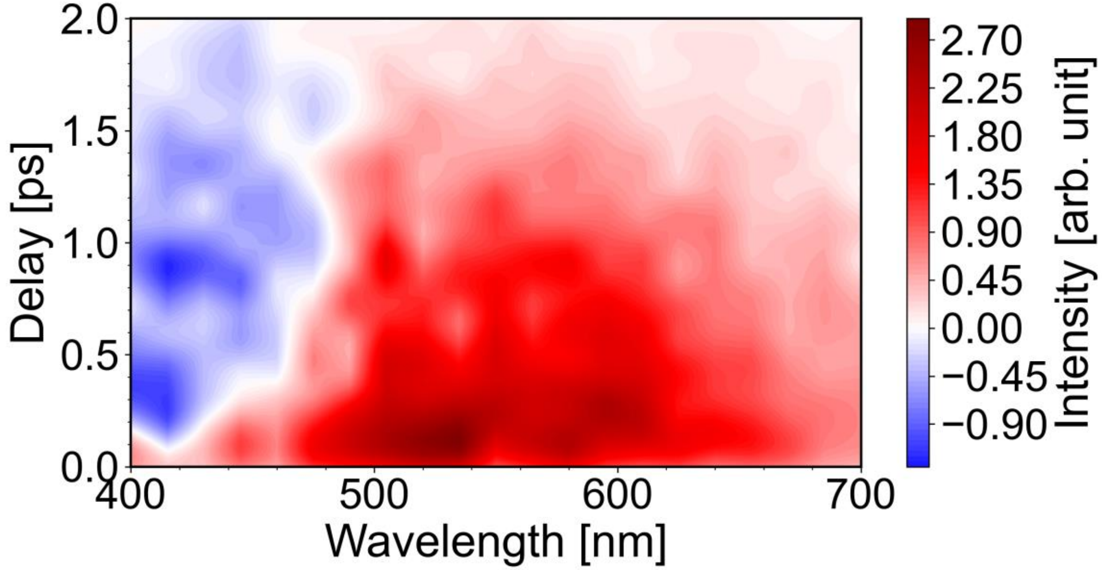
TD-CASCI Simulations (the probe):

- 164 time slices (each slice 12.1 fs) of 2ps NAMD trajectories
- 80 representative geometries from each slice on S_1 electronic state
- 100 fs TD-CASCI electronic dynamics by applying field along *x, y, z* axis

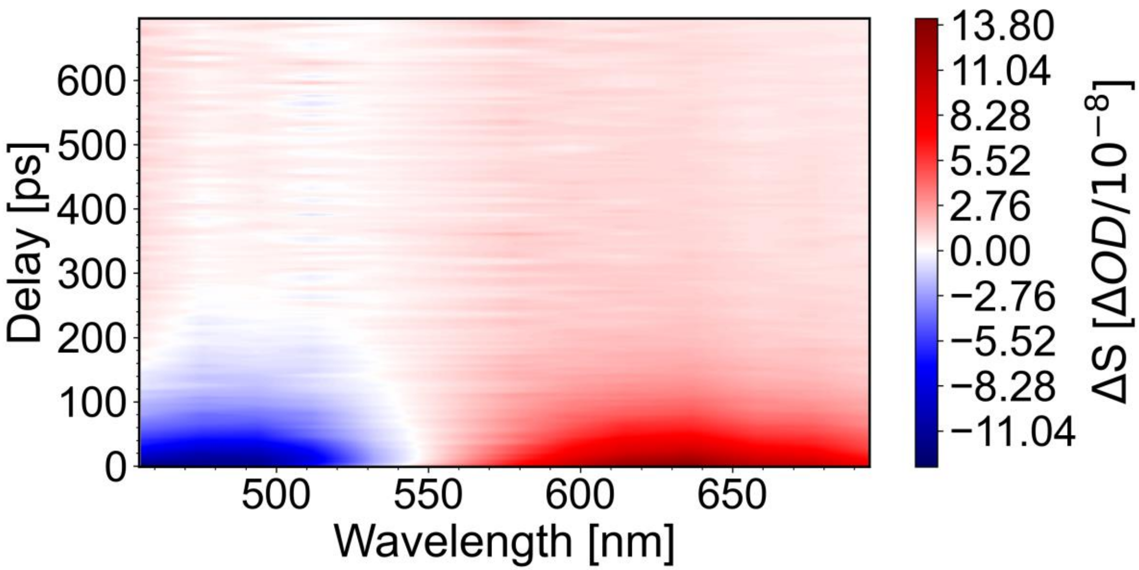
Mehmood, A.; Silfies, M. C.; Durden, S. A.; Allison, T. K. .; Levine, B. G. *J. Chem. Phys*. **submitted**.

Simulated TAS of HAN

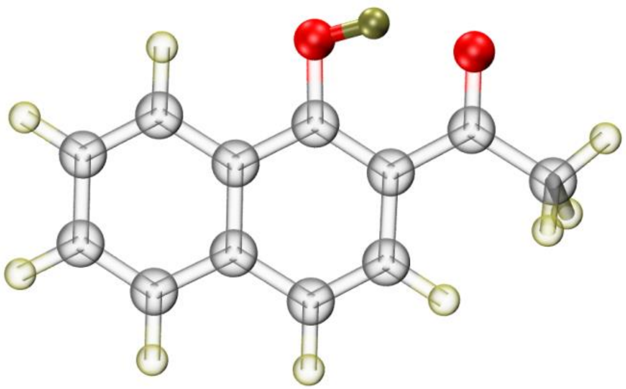
Simulated Magic Angle TAS

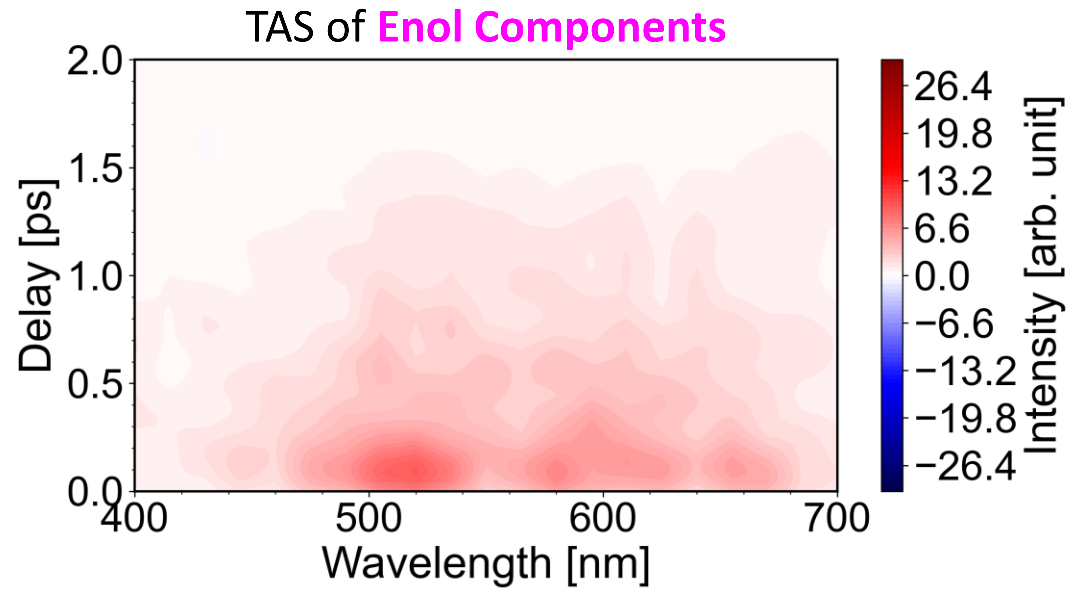


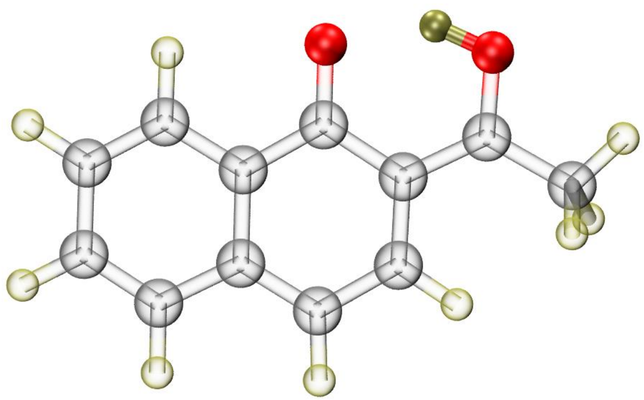
Experimental Magic Angle CE-TAS

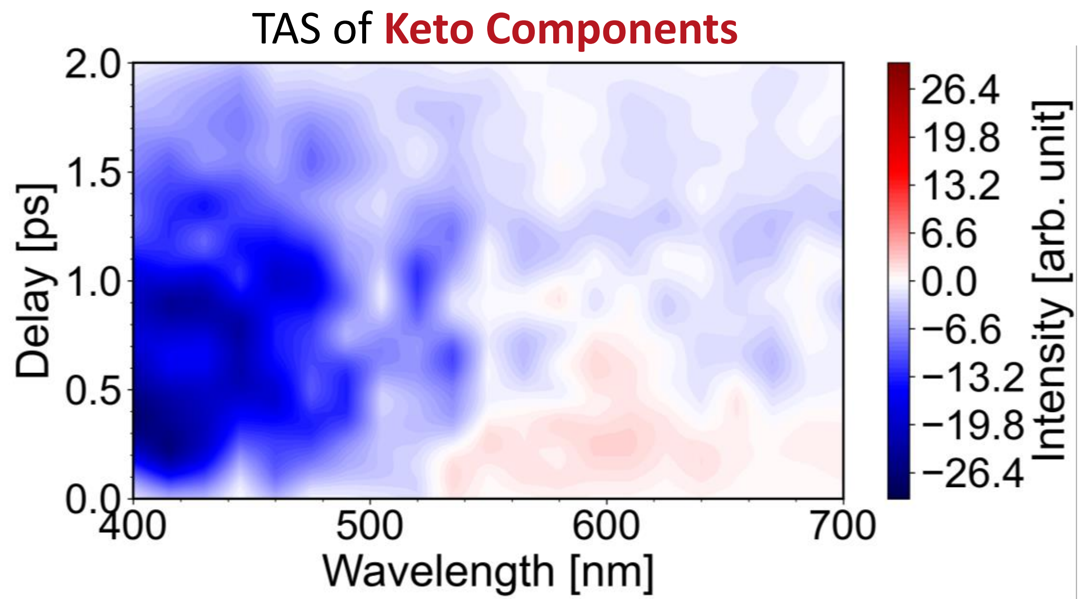


Simulation of TAS Along Different Relaxation Paths

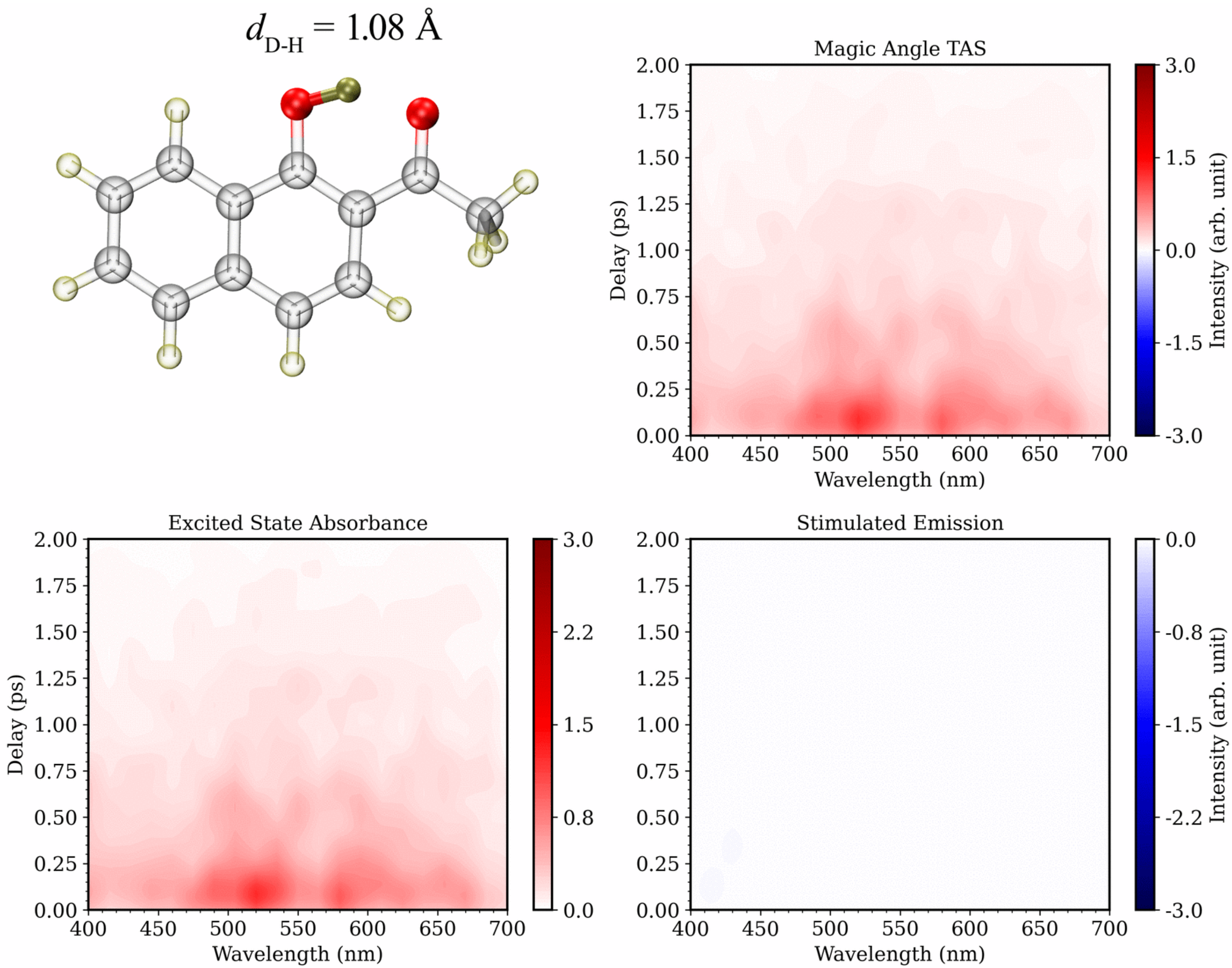




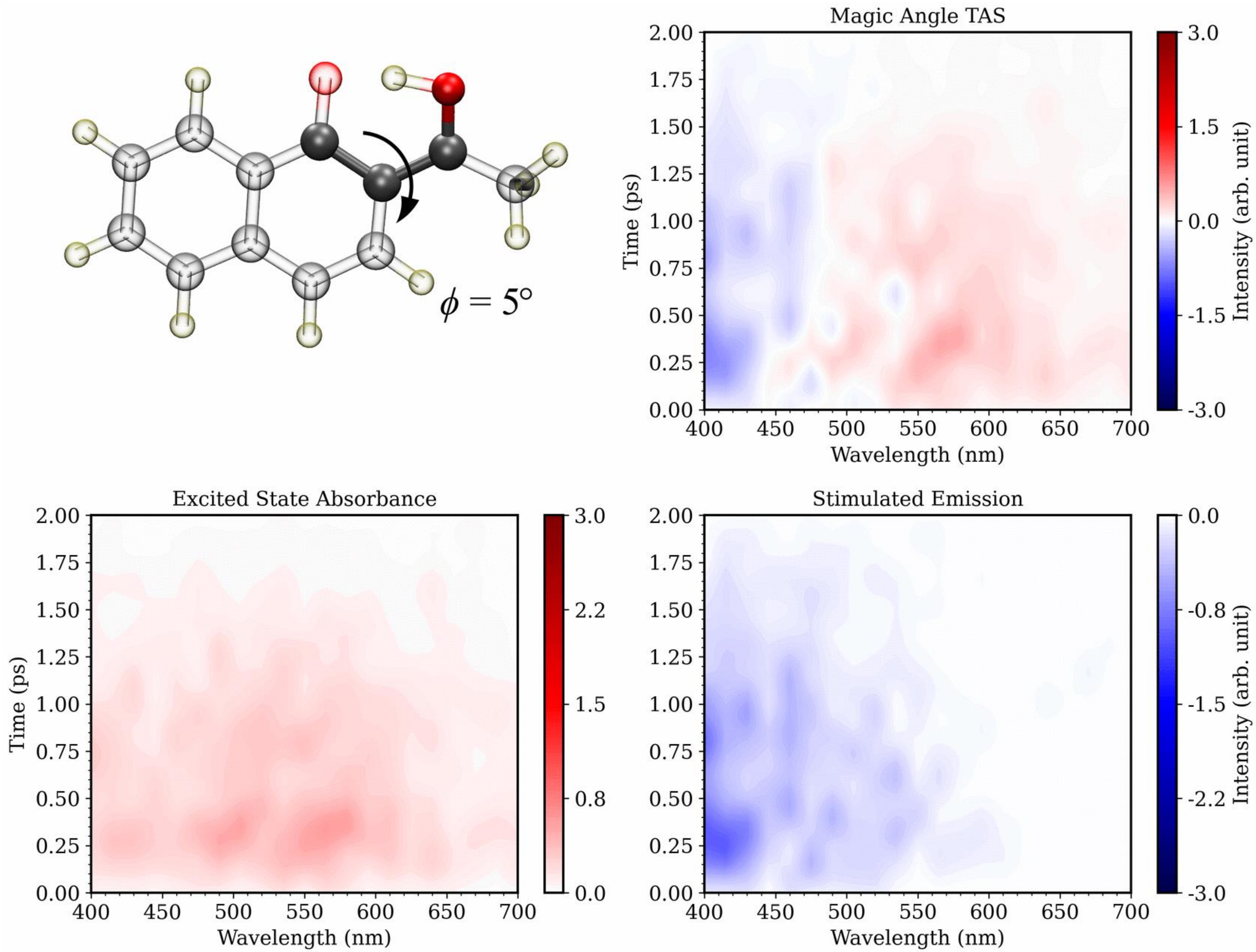




Dynamic Visualization of TAS on HAN ESIPT Path



Dynamic Visualization of TAS on HAN Twist Path



Conclusions

- The combination of non-adiabatic dynamic simulations such as AIMS, and TD-CASCI provides a power tool to simulate the TAS
- The simulated spectrum can be used to correctly assign the experimental TAS
- Splitting the simulated TAS signal into individual components can provide rich information about excited state chemistry of each competing photochemical path
- The methodology can be used to study the excited state chemical reactions including but not limited to ESIPT and photoisomerization etc.

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