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

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Motivation

- Transient absorption (TA) spectroscopy excels in ultrafast dynamics studies, owing to its superb temporal resolution and broad applicability.
- The interpretation of the TA spectrum (TAS) is inherently indirect, primarily attributable to the energy-time uncertainty principle.
- TAS projects numerous active degrees of freedom onto a lower-dimensional observable, leading to substantial information loss.
- The spectral "***blobs***" observed in TA experiment are less informative regarding the underlying dynamics of competing photochemical channels.
- The pressing necessity for a theoretical method that precisely simulates the TA experiment by calculating both ultrafast excited state dynamics and relevant observables is underscored.

• Objectives

- We aim to synergize 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 the dynamics and TAS of photoactive molecules.
- We aim to comprehensively assign the components of the experimental cavity-enhanced CE-TAS and offer a dynamic depiction of TAS development.

GPU-accelerated TD-CASCI

- The CI wavefunction is a linear combination of configuration state functions:

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

- TD-CASCI models the electronic dynamics over a period of time:

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

- It recasts the time dependent Schrödinger equation in symplectic form, splitting expansion coefficients into their real and imaginary parts:

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

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

- Multiplication of $\vec{H}(t)\vec{p}(t)$ and $\vec{H}(t)\vec{q}(t)$ is carried out at each integration time step by using efficient GPU-accelerated implementations in `TeraChem` program.
- Electric field excitation are included by using the electric dipole approximation:

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

Here $\hat{\boldsymbol{\mu}}$ is dipole operator, $E(t)$ is the external field polarized in direction $\vec{d}$.

- Given a δ-function pulse, the Fourier transform of the time correlation function yields the components of TAS :

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

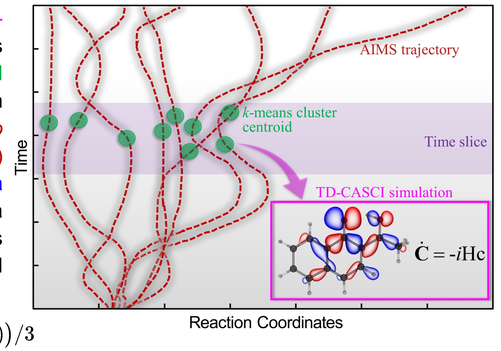
where ε is a time immediately after the end of the pulse.

• Salient Features

- It gives the TAS without the need to calculate all higher excited states, making it an excellent approach when numerous excited states are of interest.
- It allows a large complete active space configuration expansions.
- The direct configuration interaction (CI) approach obviates the necessity to explicitly build, store, and diagonalize of the Hamiltonian matrix.
- The efficient GPU-accelerated implementation allows cost-effective simulation of TAS through thousands of individual TD-CASCI calculations.

Computational Approach

We performed 100 fs TD-CASCI electronic dynamics on each selected conformation derived from the time-slices of *Ab-initio* Multiple Spawning (AIMS) NAMD trajectories on **Nvidia A-100 GPU**. A δ-kick with a field strength of 10^{24} W/m^2 is polarized along the *x*, *y*, and *z* axes of the molecular axis.

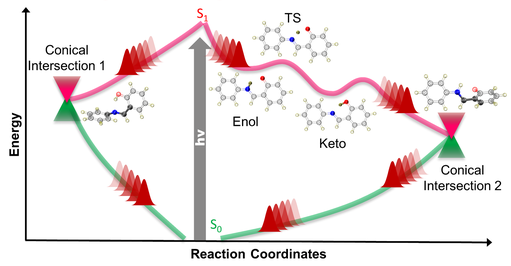


$$R_{\mathrm{magic}}(E) = \big(R_{\parallel}(E) + R_{\perp}(E)\big)/3$$

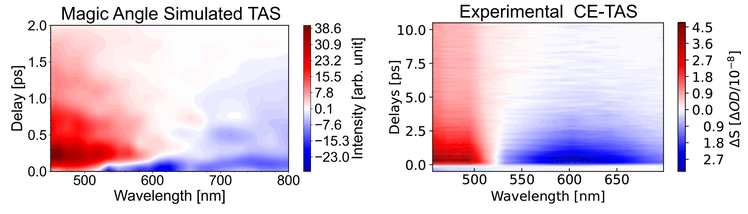
$$R_{\parallel}(E) = 0.2R_x^2(E) + 0.2R_y^2(E) + 0.6R_z^2(E) \qquad R_{\perp}(E) = 0.4R_x^2(E) + 0.4R_y^2(E) + 0.2R_z^2(E)$$

Applications

• Photochemistry of Salicylideneaniline

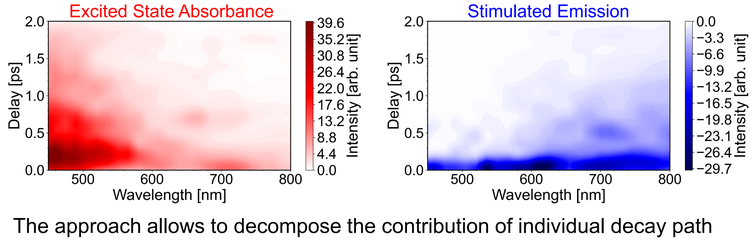


- 2ps AIMS simulations with 360 initial conditions at ωPBEh-CAS(2,2)CI/6-31G**.
- $\frac{2032\mathrm{fs}}{24.2\mathrm{fs}}\mathrm{Slices} \times \frac{80\ \mathrm{Geoms}}{\mathrm{Slice}} \times \frac{3\ \vec{d}}{\mathrm{Geom}} \times \frac{100\mathrm{fs}}{\vec{d}} = \mathbf{2.0ns\ TDCAS(8,8)CI\ dynamics}$

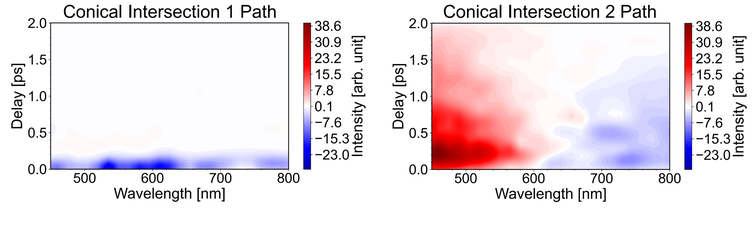


Red = Excited State Absorbance (ESA) Blue = Stimulated Emission (SE)

- Our approach allows to visualize the individual components of TAS.

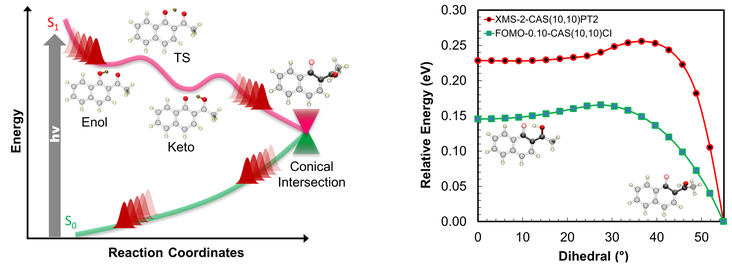


- The approach allows to decompose the contribution of individual decay path

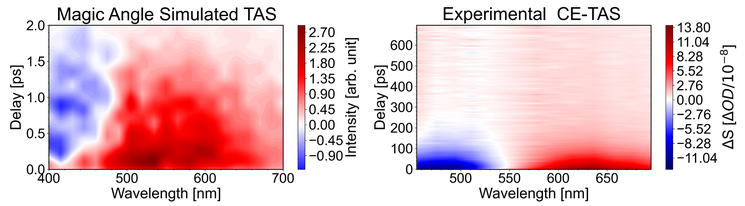


• Photochemistry of 1′-Hydroxy-2′-acetonaphthone (HAN)

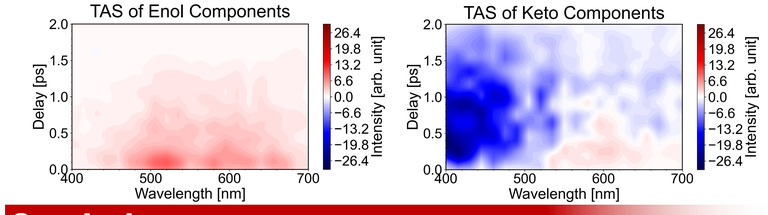
- The electronic structure method used in NAMD simulations of HAN underestimate the rotational barrier which controls the excited state lifetime of by just **1.2 kcal/mol** relative to the barrier estimated from experiment.
- We expand the scope of our method even though the S_1 lifetime from NAMD is 42 times smaller than that derived from experimental global analysis.



- 2ps AIMS simulations with 42 initial conditions at FOMO-CAS(10,10)CI/6-31G**.
- $\frac{2032\mathrm{fs}}{12.1\mathrm{fs}}\mathrm{Slices} \times \frac{80\ \mathrm{Geoms}}{\mathrm{Slice}} \times \frac{3\ \vec{d}}{\mathrm{Geom}} \times \frac{100\mathrm{fs}}{\vec{d}} = \mathbf{4.0ns\ TDCAS(10,10)CI\ dynamics}$



- The time of proton transfer (542 fs) and S_1 lifetime (1686 fs) are significantly distinct in AIMS which allows the assignment of the components of CE-TAS.



Conclusions

- Utilizing GPU-accelerated TD-CASCI, the NAMD trajectories are post-processed to simulate and identify the components of experimental CE-TAS.
- The protocol facilitates the dissection of a simulated TAS into its contributions to distinct photochemical decay channels, observing their temporal evolution.
- Utilizing efficient algorithms and implementations, numerous excited states can be simulated with minimal computational overhead, leveraging thousands of conformations from time-resolved NAMD trajectories.

Acknowledgments

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