Simulating Time-Dependent Spectroscopic Observables in Molecular Systems

Light absorption triggers coupled electronic and nuclear motion in molecules on ultrafast timescales. Advances in spectroscopy and diffraction experiments now allow these processes to be observed directly, while excited-state dynamics simulations provide a powerful framework for their interpretation.

This presentation will discuss key challenges in nonadiabatic dynamics simulations, including the description of systems with many electronic states, complex environments, and processes spanning from femtoseconds to hundreds of picoseconds. Building predictive simulations from first principles requires both accurate electronic-structure models and efficient methods for treating the large number of nuclear degrees of freedom involved.

I will present our work on the simulation of UV-Vis excited-state dynamics in organic molecules. In particular, I will compare the photodynamics of tetraphenylpyrazine (TPP) and tetraphenylpyrrole (TePP), two closely related molecules that display very different emission behavior. Using surface-hopping simulations, together with simulated time-resolved fluorescence and ultrafast electron diffraction signals, we identify the distinct excited-state relaxation pathways that govern their photophysics. The simulations are directly connected to experimental observables and provide insight into how these mechanisms evolve from the gas phase to condensed environments.