Revealing molecular photodynamics by trajectory surface hopping simulations

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Photodynamics of molecules are important for many application ranging from photo-switching for energy and data conversion and storage over photo-catalysis to photo-synthesis of new molecules.

Many non-adiabatic computer simulation methods exist for complementing experiments on UV-vis photodynamics. The most rigorous theoretical approach for such simulations is the framework of quantum dynamics, i.e., solution of the molecular time-dependent Schrödinger equation. While this leads to the numerically exact solutions, exponential scaling with the number of nuclear degrees of freedom (DoF) limits the applicability to 10-20 DoF. Alternatively, one may run semi-classical surface-hopping trajectories, which enables the treatment of the complete nuclear configurational space. Although not exact, we have found this technique to be very useful as an explorative tool, in conjunction with input from ultrafast pump-probe experiments, for unraveling molecular UV-vis photodynamics.

This talk will review our recent work using trajectory surface hopping simulations (in the program SHARC) for revealing the mechanisms, i.e., the decisive motions, of the non-adiabatic dynamics induced by photo-excitation of the electrons in the (isolated) molecules dihydroazulene [1], trimethylamine [2], pyrazine [3], azobenzene [4], and the solvated complex $Fe[(CN)_4(bpy)]^{2-}$ in water [5], including solvent reorganization dynamics.

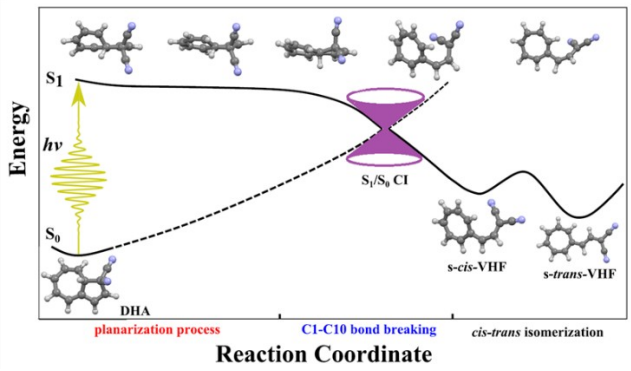

Figure 1: *Reaction path for dihydroazulene ring-opening from the FC region through the S1/S0 CI toward the cis-trans isomerization process, from [1].*

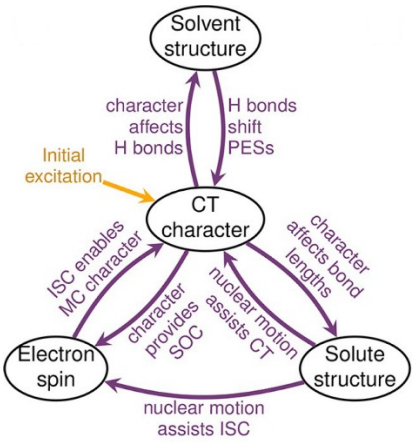

Figure 2: *Considered DOFs of $[Fe(CN)_4(bpy)]^{2-}$ in water with main processes and interactions, from [5].*

Index Terms: photo-excitation, molecular dynamics, surface hopping, mechanisms, gas phase, solution phase.

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