Molecular modeling of the dynamics and structure of molecular aggregates in liquid solution and their spectroscopic signature

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In this talk, I will present three examples of our ongoing attempts towards developing a theoretical and computational framework for modeling the dynamics and structure molecular aggregates in liquid solution and its spectroscopic signature

In the first example, I will discuss our attempts to model the recently observed signatures of coherence transfer in the 2DIR spectra of dimanganese decacarbonyl in liquid cyclohexane. To this end, we describe the system in terms of a vibrational excitonic Hamiltonian and the dynamics in terms of a quantum master equation that can account for population relaxation, dephasing, coherence-to-coherence transfer and coherence-to-population transfer. A unique feature of our approach is that, in principle, it does not rely on any adjustable fitting parameters. More specifically, the anharmonic vibrational Hamiltonian is derived from ab-initio electronic structure theory and the system-bath coupling is expressed explicitly in terms of liquid degrees of freedom whose dynamics can be obtained via molecular dynamics simulations.

In the second example, I will discuss our attempts to model the unique spectroscopic signature of nonequilibrium dynamics in the case of hydrogen-bonded methanol oligomers in methanol/carbon-tetrachloride liquid mixtures. To this end, we employed a mixed-quantum classical approach where the hydroxyl stretch of one of the methanol molecules is treated quantum mechanically, while the remaining degrees of freedom are treated classically. The ability of different force fields to reproduce the experimental absorption, emission and pump-probe infrared spectra of the hydroxyl stretch was examined as well as the insights it gives regarding hydrogen-bonding structure, dynamics and photochemistry. I will also show how nonlinear mapping relations between the hydroxyl transition frequency and bond length and the electric field along the hydroxyl bond axis can be used in order to reduce the computational cost of the mixed quantum-classical treatment to that of a purely classical molecular dynamics simulation.

In the third example, I will discuss our attempts to understand the photochemistry of electronically photoexcited silsesquioxanes octa-functionalized by organic dyes. I will present evidence from DFT calculations that employ range-separated hybrid functionals and from continuum and mixed quantum-classical solvation models for the emergence of dark states involving charge transfer between dyes. I will argue that these charge transfer states are responsible for the unusually large Stokes shift between the electronic absorption and emission spectra of these systems in comparison to the individual dyes, and that these systems can be thought of as dye aggregates held together by the otherwise inert silsesquioxane cage.