

Coherent photoexcited dynamics and intermolecular conical intersections

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In this talk, I will overview some applications of semiempirical Non-adiabatic EXcited-state Molecular Dynamics (NEXMD) framework developed at several institutions and recently released to public. The NEXMD code is able to simulate tens of picoseconds photoinduced dynamics in large molecular systems with hundreds of atoms in size and dense manifold of interacting and crossing excited states. As an application, I will exemplify ultrafast coherent excitonic dynamics guided by *intermolecular* conical intersections (CoIns). Both simulations and time-resolved two-dimensional electronic spectroscopy track the coherent motion of a vibronic wave packet passing through CoIns within 40 fs, a process that governs the ultrafast energy transfer dynamics in molecular aggregates. Our results suggest that intermolecular CoIns may effectively steer energy pathways in functional nanostructures. In the second example, we use non-adiabatic excited state dynamical simulations to compute X-ray Raman signals, which are able to sensitively monitor the coherence evolution in a rigid synthetic heterodimer. The observed coherences have vibronic nature that survives multiple conical intersection passages for several hundred femtoseconds at room temperature. These spectroscopic signals are possible to measure at XFEL facilities, paving the way for detailed coherence measurements in functional organic materials. Observed relationships between spatial extent/properties of electronic wavefunctions and resulting electronic functionalities allow us to understand and potentially manipulate excited state dynamics and energy transfer pathways toward optoelectronic applications. Time-allowed, I will also briefly overview quantum-chemical simulations of chemically functionalized carbon nanotubes, which help to rationalize spectroscopic observation and fine tune synthetic strategies. Here an intentional introduction of quantum defects to the carbon nanotube surface leads to unique photoluminescence properties that may be useful for a wide range of optoelectronic, sensing, imaging and quantum communication applications.

Relevant references

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