Coherent photoexcited dynamics and intermolecular conical intersections

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I will overview some applications of Non-adiabatic EXcited-state Molecular Dynamics (NEXMD) framework developed at several institutions and is released to public. The NEXMD code is able to simulate tens of picoseconds photoinduced dynamics in large molecular systems 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 dynamical simulations to compute X-ray Raman signals, which are able to monitor the coherence evolution. The observed coherences have vibronic nature that may 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.

Relevant references

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