Theoretical insights into the surface chemistry and its effect on the excited state and its coherent properties in nanomaterials

Svetlana Kilina

Chemistry and Biochemistry Department, North Dakota State University,
Fargo, ND 58102, US

We have developed time-domain non-adiabatic dynamics based on density functional theory to determine conditions that govern the mechanisms of exciton relaxation in photoexcited semiconductor quantum dots (QDs) passivated by various ligands. Our approach treats phonons semi-classically, which allows us to explicitly incorporate quantum decoherence effects within the electronic subsystem. Both elastic and inelastic electron-phonon interactions play key roles in solar energy harvesting. Coherence of these processes is very important, because quantum transitions can occur only through buildup of coherence. Our simulations provide fundamental insights into the origin of the pure-dephasing process in the bare and passivated QDs. Thus, we have revealed the role of surface defects and decoherence in the ultrafast loss of photoexcitation to heat in QDs and established a connection between the slow energy relaxation — the phonon bottleneck — and Zeno effect. We also have found that elastic and inelastic scattering respond in the opposite manner to CdSe QD surface passivated by ligands. Phonon-induced pure-dephasing processes determined by elastic electron-phonon scattering in QD capped with ligands are much longer than that in bare QD. The difference is rationalized by the fact that ligands have no direct contributions to the electronic densities of the lower-energy states involved in the superpositions, while they indirectly reduce mobility and fluctuations of the surface atoms. In contrast, the higher-energy electronic states involved in the relaxation are delocalized over ligands and the QD, and therefore, ligands increase the electron-phonon coupling in the case of inelastic processes. We also investigate the effect of the QD-QD interaction on their optical properties. Our calculations suggest that a fast energy transfer between an excited QD to the nearest one provides an additional channel for occupation of long-leaving semi-dark and dark trap states in neighboring QDs forcing the emission to happen from higher-energy optically bright states. This pathway increases ‘on’ blinking time in aggregates of strongly interacting Si QDs, as experimentally observed. Overall, our calculations provide insights into the surface chemistry of QDs and offering guidance for controlling the optical response of nanostructures by means of OD-QD and QD-ligand engineering.