Modeling of Relaxation and Decoherence Processes at the Interfaces of Ligated and Core/Shell Quantum Dots

Svetlana Kilina

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

We have used time-domain non-adiabatic dynamics based on density functional theory and Tully's fewest surface hopping techniques to determine conditions that govern the mechanisms of exciton relaxation in photoexcited semiconductor quantum dots (QDs). We specifically focus on the role of a soft layer of organic lignds or/and a shell of a different semiconductor covering the QD surface (core/shell QDs) have on the light driven processes in these systems. 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. 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 QDs capped with ligands are much longer than that in bare QDs. 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 hybridized between ligands and the QD, and therefore, ligands increase the electron-phonon coupling in the case of inelastic processes. To investigate to what extend the passivation of lead chalcogenide QDs with wider band gap materials like cadmium chalcogenides affect their photophysical properties, we have modeled QDs composed of $Pb_{16}X_{16}$ (X = S, Se, Te) inner core with $Cd_{52}Y_{52}$ (Y = S, Se, Te) outer shells. We found that relaxation rates generally lower for heavier shells. Our calculations also reveal slower relaxation rates in PbSe/CdY structures, compared to PbS/CdY QDs, which is rationalized by well-pronounced subgaps in PbSe/CdX density of states. Overall, our calculations provide insights into the surface chemistry of QDs and offering guidance for controlling the optical response of nanostructures by means of core/shell and QD-ligand engineering.