Non-Adiabatic Exciton Relaxation in Quantum Dots: Effect of Surface Ligands.

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Quantum confinement can dramatically slow down electron-phonon relaxation in nanoclusters. Known as phonon-bottleneck, the effect remains elusive. Using a state-of-the-art time-domain first principle approach, we model the phonon mediated photoexcited dynamics in $Cd_{33}Se_{33}$ quantum dots (QDs). We have found that energy relaxation in QDs occurs under quantum Zeno conditions. Decoherence in the electronic subsystem, induced by elastic electronphonon scattering, should be significantly faster than inelastic scattering to favor the phonon-bottleneck. One of important non-radiative relaxation channels originates from the non-adiabatic (NA) coupling of electronic degrees of freedom to nuclear vibrations, which in QDs depend on the confinement effects and complicated surface chemistry. To elucidate the role of surface ligands in relaxation processes of nanocrystals, we have simulated the dynamics of the NA exciton relaxation in QDs passivated by either trimethylphosphine oxide or methylamine ligands. The large extent of hybridization between electronic states of QDs and ligand molecules is found to strongly facilitate exciton relaxation. Such states are coupled to both high frequency vibrations of the ligand atoms and low-frequency surface phonons, thus opening new relaxation channels allowing for ultrafast photoexcitation relaxation rates, which are typical for small molecules.