The Structure of Excited-State Transitions in Individual Nanocrystals Probed by Photoluminescence Excitation Spectroscopy

HAN HTOON, P.J. COX, V.I. KLIMOV, Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545 — We study the structure of excited-state transitions in CdSe nanocrystals (NCs) using our newly developed, single-NC, photoluminescence excitation (PLE) technique that mitigates the problem of blinking and spectral wandering of NC emission. The low-temperature (4K) PLE spectra of individual NCs show a few sharp band-edge peaks with 3 to 4 meV linewidths. The higher energy transitions, however, are not manifested as narrow peaks but they rather merge into a dense quasi-continuum. These spectroscopic observations can be rationalized based on results of intraband hole relaxation studies. Specifically, these studies indicate that the energy relaxation rate is very large (1 – 2 eV/ps) at high spectral energies, leading to significant lifetime broadening of optical transitions that merge into a structureless quasi-continuum. The relaxation rate sharply drops near the band-edge, which is consistent with our observations of the reduced density of states at low spectral energies. Overall, our studies indicate that, while the idealized description of NC excited-state transitions in terms of sharp atomic-like resonances may be applicable at near-band-edge spectral energies, this description is invalid at high spectral energies where optical transitions are significantly broadened because of ultrafast intraband relaxation.