primary mode, and S_{lm} is a function of both longitudinal and transverse acoustic phonon velocities (see [22] for more details related to this development).

The frequencies shown in Fig. 4 are approximately 0.28 THz (9.3 cm^{-1}) and 0.18 THz (6.0 cm^{-1}) for the QD and QR samples respectively. Using Eq. (4) and assuming the ellipsoidal mode, i.e. v_i = transverse acoustic phonon velocity, 2 nm as the QD radius and a calculated S_{lm} = 0.84 (from [22]), results in a frequency of 0.32 THz, which is close to the experimental value of 0.28 THz. The radial breathing mode frequency was calculated as 0.85 THz. Therefore, the ellipsoidal mode is dominant for the QD film sample. This result is not consistent with previous works on colloidal CdSe QDs of similar diameter [20,21]. The frequencies obtained from those works are roughly 0.6 THz (20.0 cm^{-1}) for 5.4 nm diameter QDs, which corresponds to the frequency of the calculated radial breathing mode. Furthermore, because the radial breathing mode is dominated by longitudinal acoustic phonons, colloidal QR samples with the same diameter as QD samples should have the same vibrational frequency [24]. This again is not consistent with our results. In our case, the QRs show much lower frequency compared to the result of the QDs of the same diameter. We attribute our result to the transverse phonon propagation in the axial direction of the QR, resulting in an overall lower frequency of lattice vibration. A closed form solution of the ellipsoidal breathing mode for QRs similar to Eq. (4) above for QRs does not exist in the literature (and deriving it is beyond the scope of this study). However, we can roughly estimate the QR as a QD by taking an effective radius of 3.5 nm which is the average of half its length and radius, v_i = transverse acoustic phonon velocity, and S_{lm} = 0.84 (from [22]). The calculated vibrational frequency of the ellipsoidal breathing mode is 0.19 THz (6.3 cm^{-1}) which matches well with the measured frequency of 0.18 THz.

While the above results show strong evidence for the ellipsoidal breathing mode for non-adiabatic relaxation, future TA studies are needed to further validate the above hypothesis. For example, by considering different diameters for the QD samples and different aspect ratios for the QR samples, the ellipsoidal mode phonon relaxation channel would be further validated for CdSe NC films.

4. Conclusion

We found that both morphology and sample preparation play a role in hot-exciton relaxation. For the QD film samples, the TA spectra was found to evolve in time consistent with the CISE theory, while for the QR film samples the TA spectra evolved in time consistent with the CISE only for probing energies greater than the B1 state. The deviation from the CISE picture for QR samples for probing energies below the B1 state is due to the reduction in the Coulomb interaction as a result of the relaxation in spatial confinement. The hot-exciton intraband relaxation was found to be approximately 400 fs longer for the QR sample than in the QD sample. This is thought to be due to a reduction in in the Auger – relaxation mechanism for the QR samples. Furthermore, when compared with other works focusing on colloidal NCs, e.g [5], the film samples measured here had longer hot-exciton intraband relaxation for both QRs and QDs. We have also shown the phonon relaxation channel is comprised of both transverse and longitudinal acoustic phonons for films, which is contrary to colloidal QDs and QRs showing only longitudinal acoustic phonons.

Acknowledgment

Support to this work by the National Science Foundation is gratefully acknowledged.

#175480 - $15.00 USD Received 4 Sep 2012; revised 31 Oct 2012; accepted 5 Nov 2012; published 12 Nov 2012