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Title: FEMTOSECOND CHIRP-FREE STUDIES OF ENERGY RELAXATION IN SEMICONDUCTOR QUANTUM DOTS: SEARCH FOR A PHONON BOTTLENECK

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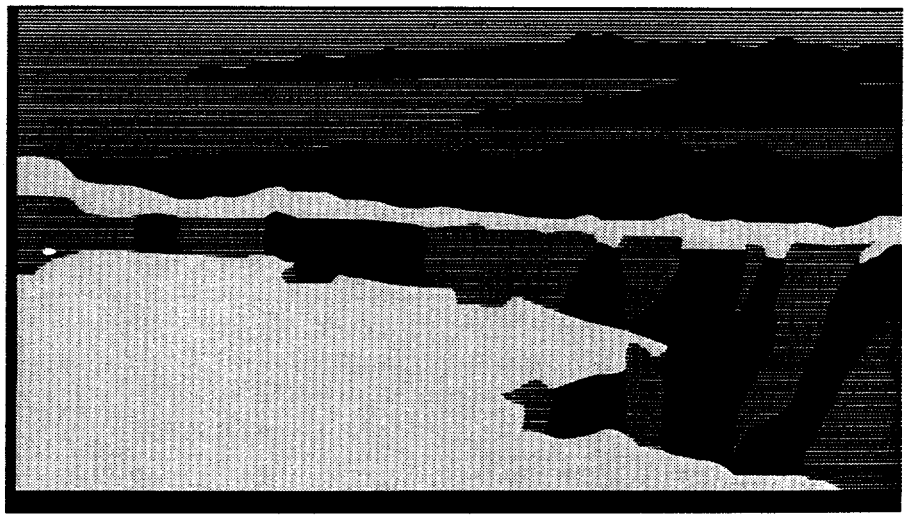

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ABSTRACT

Contrary to the predictions of phonon bottleneck theories, we observe very fast subpicosecond energy relaxation in strongly confined semiconductor nanocrystals with electron level spacing as large as 20 LO phonon energies.

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Femtosecond chirp-free studies of energy relaxation in semiconductor quantum dots: Search for a phonon bottleneck

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Semiconductor nanocrystals (NCs), or semiconductor quantum dots, exhibit a number of novel physical properties not observable in bulk materials [1]. Three-dimensional (3D) carrier confinement results in a discrete atomic-like energy spectrum with a level spacing which can greatly exceed typical phonon energies. If the electronic energy relaxation occurs primarily by coupling to phonons, then carrier relaxation in strongly confined systems can only occur via multi-phonon processes. This should significantly inhibit carrier relaxation, an effect commonly referred to as a phonon bottleneck [2, 3]. However, it has been suggested recently [3] that the Coulomb electron-hole interaction, which is strongly enhanced in systems with 3D confinement, can provide additional relaxation channels which result in the removal of the phonon bottleneck. In this paper we report femtosecond (fs) studies of the electron intraband relaxation in CdSe quantum dots of different sizes, with the energy spacing between the two lowest electron levels varying from about 2 to 20 longitudinal optical (LO) phonon energies. Contrary to the predictions of phonon-bottleneck theories, we observe subpicosecond electron relaxation, with a rate which is enhanced in NCs of smaller radius. These observations can be explained by an Auger-like relaxation mechanism resulting in efficient energy transfer from the electron to the hole, with a subsequent fast hole relaxation through its dense spectrum of states.

To probe carrier relaxation dynamics we monitor carrier-induced absorption changes using a fs pump-probe experiment in two different configurations. In the first configuration, we apply the novel technique of high-sensitivity, chirp-free detection of transient absorption (TA) spectra [4] which provides information on nonequilibrium carrier energy distributions. Alternatively, we monitor single-wavelength TA time transients to study the population (depopulation) dynamics of selected electron states in NCs. The samples under investigation are CdSe NCs prepared either as colloids, or grown in a glass matrix ,with an average radius R ranging from 2.3 to 5.6 nm.

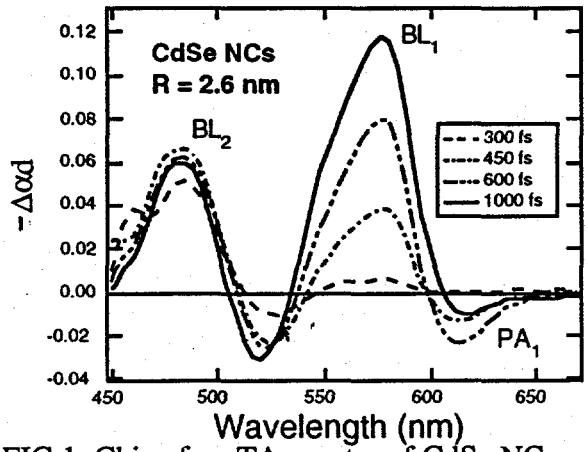

FIG.1. Chirp-free TA spectra of CdSe NCs taken at different delay times between pump and probe pulses.

As a representative example, we describe how the population dynamics of the ground (1S) and the first excited (1P) electron states can be determined from TA data recorded for colloidal NCs with an average radius of 2.6 nm. In this case, the 1P-1S electron energy separation is equal to 410 meV, or about 16 LO phonon energies. Under excitation with 3.1 eV photons, the TA spectra of these NCs (Fig. 1) are dominated by two bleaching bands at 576 nm (BL_1) and 484 nm (BL_2). The BL_1 feature marks the position of the lowest optical transition coupling the 1S electron to the $1S_{3/2}$ hole state, whereas the band BL_2 is due to combined contributions from the $1S(e)-2S_{1/2}(h)$ and the $1P(e)-1P_{3/2}(h)$ transitions. The nonlinear optical response of NCs is mainly due to two effects: state filling-induced bleaching of the optical transitions and the Coulomb two-pair interaction (biexciton effect) resulting in a the shift of the transitions [5]. The state-filling contribution to the TA signal is dominated by the electron population due to the degeneracy of the valence band and the much larger effective mass for the hole [6]. The temporal evolution of the biexciton-related portion of the BL_1 bleaching can be derived from the analysis of the photoinduced absorption feature PA_1 located below the BL_1 band [5]. After subtracting this contribution from the BL_1 signal, we get dynamics related entirely to population changes of the 1S electron state, which are shown by open squares in Fig. 2. In addition to the contribution from the 1P(e)

states, the BL_2 signal has a contribution from the bleaching of the 1S(e)–$2S_{1/2}$(h) transition. The latter can be subtracted using the derived temporal evolution of the 1S-state population. As expected, the resulting 1P-state population dynamics (solid circles in Fig. 2) are complementary to those of the 1S state (open squares in Fig. 2); both are characterized by the same time constant of ~350 fs. Given the 1P-1S energy spacing, this implies a value for the electron energy-loss rate of ~1.2 meV/fs. This is more than twice the electron energy relaxation rate for the unscreened polar scattering in bulk CdSe with a quasi-continuous energy spectrum, and exceeds by several orders of magnitude the relaxation rate due to multi-phonon emission expected in strongly confined systems with a large energy-level separation [2]. Thus, phonon relaxation mechanisms cannot explain the high electron energy-loss rates measured experimentally. As suggested in Ref. 3, one of the effects of spatial confinement is an enhancement of the Coulomb electron-hole interaction, which can lead to the opening of new relaxation channels. In particular, this interaction can result in the efficient energy transfer of the electron excess energy to the hole, with a subsequent fast hole energy relaxation through its much denser spectrum of states. This process is analogous to nonradiative Auger recombination, which leads to efficient sub-picosecond carrier decay in II-VI NCs [6].

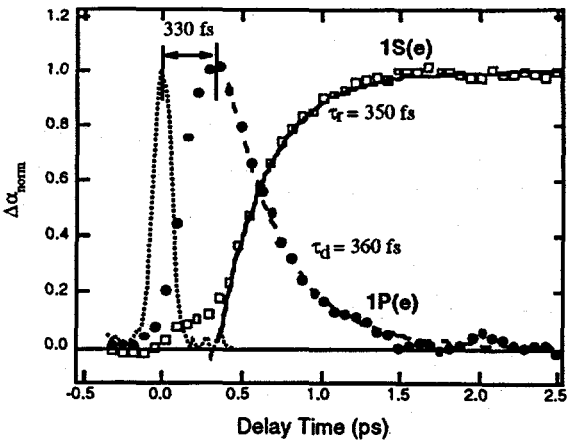

FIG. 2. 1S(e) and 1P(e) states population (depopulation) dynamics derived from the TA data, along with a pump-probe cross-correlation.

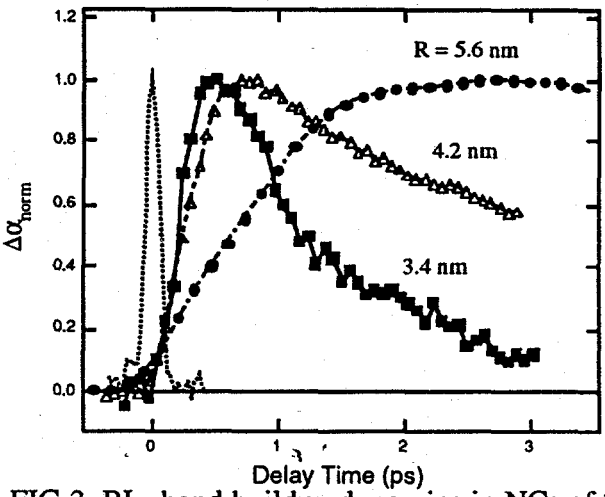

FIG.3. BL_1 band buildup dynamics in NCs of 3 different radii: R = 3.4, 4.2, and 5.6 nm.

Measurements of energy relaxation in NCs of different sizes in a glass matrix demonstrate that the relaxation rate decreases with increasing NC radius; the rise time of the 1S(e) population in NCs with R > 5 nm is greater than 1 ps (see Fig. 3, glass samples). This is consistent with Auger-type energy transfer enhanced by spatial confinement, and is in obvious contradiction with phonon-bottleneck theories which predict a faster relaxation for larger particles with more closely-spaced energy levels.

In addition to studies of intraband relaxation, we performed careful measurements of size-dependent electron trapping dynamics in NCs with differently treated surfaces. These results allow us to evaluate the role of the surface states in the trapping process. The electron trapping time varied by more than two orders of magnitude, being up to 1.5 ns in colloidal NCs with well passivated surfaces, while small-radius NCs in a glass matrix showed trapping times less than 10 ps.

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[1] A. P. Alivisatos, Science **271**, 933 (1996).
[2] T. Inoshita and H. Sakaki, Phys. Rev. B **46**, 7260 (1992).
[3] Al. L. Efros, V. A. Kharchenko, and M. Rosen, Solid State Commun. **93**, 281 (1995).
[4] V. Klimov and D. McBranch, Opt. Lett., submitted.
[5] V. Klimov, S. Hunsche, and H. Kurz, Phys. Rev. B **50**, 8110 (1994).
[6] V. Klimov and D. McBranch, Phys. Rev. B **55** (May, 1997).