

## Hole intraband relaxation in strongly confined quantum dots: Revisiting the “phonon bottleneck” problem

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We study hole intraband relaxation in strongly confined CdSe quantum dots. We observe a dramatic reduction in the hole energy-loss rate in the final stage of hole relaxation at the bottom of the valence band. This reduction occurs because of a significantly increased inter-level spacing near the band edge, and, in particular, because of a large energy gap separating the lowest (“emitting”) hole states from a dense quasi-continuum of higher lying states. A slowed population buildup of the lowest hole state indicates that the “phonon bottleneck,” which is bypassed in the conduction band due to Auger-type electron-hole interactions, still plays a significant role in hole relaxation.

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Nanoscale semiconductor particles, known also as semiconductor quantum dots (QDs), exhibit atomlike electronic spectra consisting of well-separated energy states.<sup>1,2</sup> The existence of discrete electronic energies implies reduced efficiencies for electron-phonon interactions because of the reduced availability of pairs of electronic states that satisfy energy conservation. This effect was anticipated to significantly slow carrier intraband relaxation due to a “phonon bottleneck.”<sup>3,4</sup>

In II–VI QDs, the energy separation between electron states is much greater than that between hole states; therefore, the “phonon bottleneck” was expected to affect electron intraband dynamics more strongly compared to hole intraband dynamics. Recently, electron dynamics were extensively studied using ultrafast transient absorption (TA) techniques applied to highly monodisperse colloidal CdSe QDs.<sup>5–7</sup> Extremely fast sub-picosecond (sub-ps) electron intraband relaxation measured in these studies indicated the existence of mechanisms that bypass the “phonon bottleneck.” Furthermore, observed correlations between the strength of the electron-hole (e-h) coupling and the rate of electron relaxation<sup>6,7</sup> provided strong evidence that electron energy losses in small-size QDs are dominated by Auger-type energy transfer from electrons to holes, a mechanism originally proposed by Efros *et al.*<sup>8</sup> The reverse process, energy transfer from hole to electron, is not efficient due to small inter-level separations in the valence band. Because of this “unidirectional” nature of the energy transfer, energy dissipation from a photoexcited e-h system in QDs should ultimately rely on hole interactions with lattice/molecular vibrations in the dot or outside of it in the matrix/solvent system.

In bulk II–VI materials, hole energy losses are dominated by interactions with longitudinal optical (LO) phonons.<sup>9</sup> In QDs, the efficiency of these interactions is predicted to be strongly modified due to the discrete structure of energy states, making it more difficult to satisfy energy conservation, and due to changes in the strength of carrier-phonon coupling. For example, carrier polar coupling to LO phonons (the Fröhlich mechanism) should be strongly reduced compared to bulk systems,<sup>10,11</sup> while coupling via deformation potential is predicted to be enhanced by a factor that is pro-

portional to  $R^{-2}$  ( $R$  is the dot radius).<sup>12</sup> Despite the preliminary theoretical work on hole-phonon interactions in QDs, a coherent description of hole relaxation behavior in 3D strongly confined systems does not currently exist, even at a qualitative level.

Experimental studies of hole intraband dynamics are complicated due to difficulties in detecting valence-band populations. Most carrier relaxation studies in QDs have been performed using femtosecond (fs) TA experiments.<sup>5,6</sup> In strongly confined QDs, TA bleaching signals (absorption changes  $\Delta\alpha < 0$ ), normally used as “markers” of populated states, are dominated by filling of *electron* quantized levels.<sup>13</sup> Holes are only weakly pronounced in TA spectra because of a high spectral density of valence band states resulting in a significant spread of hole populations over multiple levels. In order to study hole intraband relaxation, we monitor fs dynamics of “hot” photoluminescence (PL) in addition to monitoring TA. In contrast to state-filling-induced TA signals that are proportional to the sum of the electron and hole occupation numbers, PL is proportional to the product of these numbers. Therefore, electron and hole dynamics can be decoupled by performing both PL and TA measurements.

In this work, we study CdSe QDs prepared by organometallic synthesis.<sup>14</sup> To evaluate the effect of interface states and the surrounding matrix/solvent on carrier intraband dynamics we prepared samples in two different solvents (hexane and toluene) and with two different types of surface passivations—trioctylphosphine oxide (TOPO)-capped CdSe QDs and TOPO-capped CdSe/ZnS core/shell QDs.

For TA measurements, samples were pumped at 3.1 eV by frequency-doubled 100-fs pulses from an amplified Ti:sapphire laser. The transmission of the photoexcited spot was probed over the range 1.2–3 eV with variably delayed broadband pulses of a fs white-light continuum. Time-resolved PL measurements were performed using fs PL up-conversion.<sup>15</sup> In this method, sub-ps time resolution is achieved by frequency-mixing emission from the sample with an intense fs gating pulse in a nonlinear  $\beta$ -barium borate crystal. To exclude effects of many-particle interactions on carrier dynamics, the relaxation data were taken at low pump intensities corresponding to  $N_{eh} < 1$ , where  $N_{eh}$  is the average num-

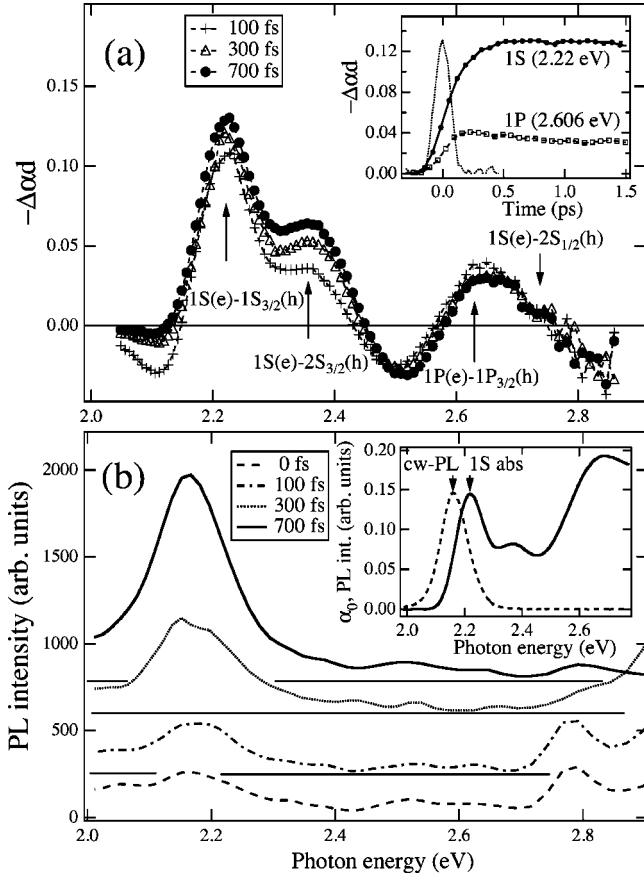


FIG. 1. (a) Time-resolved spectra of pump-induced absorption changes ( $\Delta\alpha$ ) for TOPO-capped CdSe QDs ( $R=1.8$  nm) in hexane solution detected at 100, 300, and 700 fs after excitation ( $d$  is the sample thickness). Inset: TA dynamics at the position of the 1S and 1P transitions (symbols) along with a pump-pulse autocorrelation (dotted line). (b) Time-resolved PL spectra of the same sample detected at 0, 100, 300, and 700 fs after excitation (spectra arbitrarily offset for clarity). Inset: Linear absorption and cw-PL spectra of the QD sample.

ber of e-h pairs excited per QD;  $N_{\text{eh}}$  was calculated as described in Ref. 13. All results shown below were taken at room temperature.

In Fig. 1, we compare early time (0–700 fs after photoexcitation) TA (a) and PL (b) spectra of CdSe QDs with a mean radius of 1.8 nm. Due to high sample monodispersity, TA spectra exhibit several well resolved bleaching features that mark the positions of QD optical transitions involving the ground (1S) and the first excited (1P) electron states. The transitions in Fig. 1(a) are assigned according to previously reported PL excitation data<sup>16</sup> and deconvolved linear absorption spectra.<sup>13</sup> The hole states involved in these transitions are  $1S_{3/2}$  (2.219 eV; the 1S transition),  $2S_{3/2}$  (2.356 eV),  $1P_{3/2}$  (2.627 eV; the 1P transition), and  $2S_{1/2}$  (2.744 eV) (for notation of electron and hole states in spherical QDs see Ref. 17).

The pump photon energy used in the present experiments is close to the energy of the  $1S(e)-3S_{3/2}(h)$  transition ( $\sim 3.2$  eV). Therefore, for a significant number of dots in the sample, electrons are generated directly in the lowest 1S state. At low excitation densities ( $N_{\text{eh}} < 1$ ), the 1S absorption

bleaching is proportional to the population of the 1S electron state.<sup>18</sup> The 1S buildup dynamics [solid line in inset to Fig. 1(a)] indicate that almost 80% of the 1S bleaching signal (1S population) develops within the duration of the pump pulse. Additionally, the 1P-transition dynamics [dashed line in inset to Fig. 1(a)] do not show significant changes in the 1P state populations at times  $>100$  fs, also confirming that populations of electron states almost completely establish on the time scale of the pump pulse duration. The large nonzero 1P TA signal that remains almost unchanged on the time scale shown in the inset to Fig. 1(a) is due to the Stark shift of the 1P transitions induced by local fields associated with carriers in the lowest 1S electron and hole states, rather than to filling of the 1P state.<sup>13</sup>

Since electrons are primarily generated in the lowest conduction-band state, most of the photogenerated holes carry a large excess energy ( $\sim 0.9$  eV for the 1.8-nm sample). “Hot” hole dynamics are well pronounced in time-resolved PL spectra [Fig. 1(b)]. In contrast to TA that shows only weak changes at times  $>100$  fs, the PL spectra evolve dramatically on the same time scale, indicating a gradual relaxation of holes from high-energy states (manifested, e.g., as a “hot” PL peak at  $\sim 2.8$  eV) to the lowest “emitting” state giving rise to the band-edge PL band. The cw-PL band (2.18 eV) is red shifted with respect to the 1S absorption [inset to Fig. 1(b)], which is due to the fact that these bands originate from two different fine-structure hole states (groups of hole states) formed due to the splitting of the lowest  $1S_{3/2}$  hole level induced by e-h exchange interactions, the crystal field in a hexagonal lattice, and QD shape anisotropy.<sup>19</sup> The intense 1S absorption peak is due to a strong optical transition coupling high-energy fine-structure “absorbing” hole states to the lowest 1S electron level; whereas, the band-edge PL is due to a weaker transition involving the lower energy manifold of hole “emitting” states.

A descent of holes through the ladder of the valence band states is easily seen from “hot” PL time transients recorded at different spectral energies that show a progressive increase in the delay ( $t_d$ ) of the PL maximum with reducing the detection energy ( $E$ ) [Figs. 2(a) and 2(b)]. The derivative,  $dE/dt_d$ , provides a measure of the hole energy-loss rate. For 1.8-nm dots, the energy relaxation rate is nearly constant ( $1.5$  eV  $\text{ps}^{-1}$ ) between 2.3 eV and 3.1 eV, but reduces dramatically (down to  $\sim 0.26$  eV  $\text{ps}^{-1}$ ) below the 1S absorption peak, i.e., at the stage of final hole relaxation from the “absorbing” to the “emitting” state. Two stages in hole relaxation are also observed for dots with radii 1.2 and 3 nm [Fig. 2(b)]. The spectral onset of the “slow” relaxation region is size dependent, closely following the position of the 1S absorption peak. The “fast” and “slow” relaxation rates were in the range  $1.3$ – $1.8$  eV  $\text{ps}^{-1}$  and  $0.19$ – $0.3$  eV  $\text{ps}^{-1}$ , respectively [Fig. 3(a)]. These rates were not dependent on either the QD surface passivation (TOPO or ZnS) or the type of the solvent (hexane or toluene).

Our previous studies of electron intraband dynamics in CdSe QDs indicated large rates of electron relaxation ( $0.4$ – $4$  eV  $\text{ps}^{-1}$ ) that strongly increased with decreasing the dot radius [Fig. 3(a), open circles].<sup>5,13</sup> Very fast electron relaxation with rates exceeding those for bulk materials, as

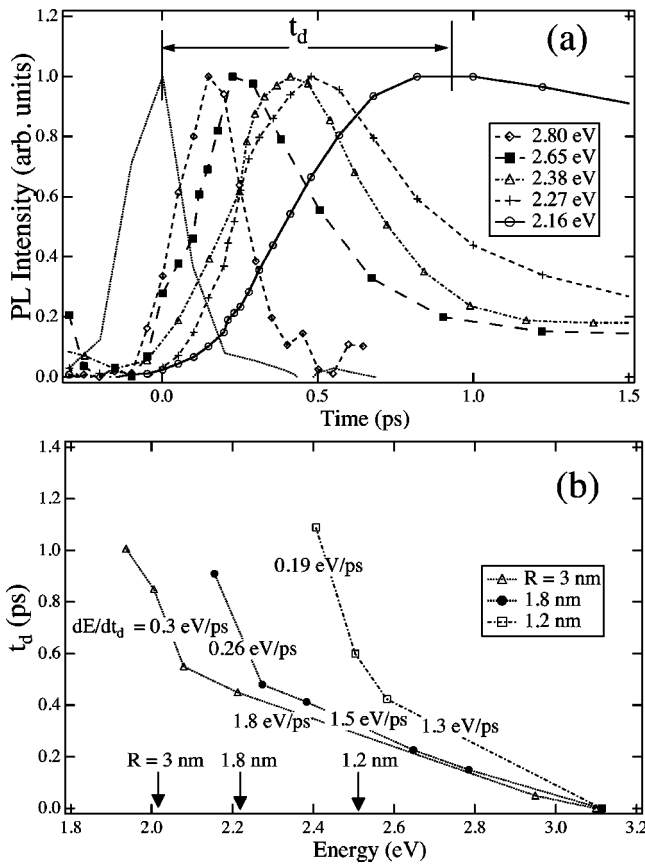


FIG. 2. (a) Dynamics of “hot” PL detected at different spectral energies (symbols) along with a pump pulse autocorrelation (dotted line) (the same sample as in Fig. 1). (b) The time delay of the “hot” PL maximum with respect to a pump pulse plotted as a function of the detection energy for CdSe QDs of three different radii: 1.2 nm (ZnS cap), 1.8 nm (TOPO cap), and 3 nm (TOPO cap). The data shown are for hexane solutions; similar dependences are observed for toluene solutions. The energy-loss rates ( $dE/dt_d$ ) derived from the plotted data at “fast” and “slow” stages of hole relaxation are indicated in the figure. The spectral onset of “slow” relaxation is compared with the position of the 1S absorption resonance (marked by arrows).

well as a confinement-induced enhancement in the relaxation process, provided a clear indication of a *nonphonon* mechanism for electron energy losses that was assigned to Auger-type e-h energy transfer.<sup>5,7</sup>

In contrast to electron relaxation that becomes faster for dots of smaller sizes, hole relaxation shows an opposite trend. Hole energy-loss rates decrease with decreasing the dot size [Fig. 3(a), solid circles and solid squares], indicating a mechanism that is different from the Auger-type process responsible for electron intraband relaxation. One possible energy relaxation mechanism in QDs involves coupling to defects as suggested in Ref. 20. For this mechanism, the rate of energy relaxation should strongly depend on the number of QD surface defects. In the case of chemically synthesized dots, the number of these defects can be controlled via surface-modification schemes.<sup>21</sup> For example, it is well established that overcoating CdSe dots with an epitaxial layer of ZnS greatly reduces the number of surface traps and leads

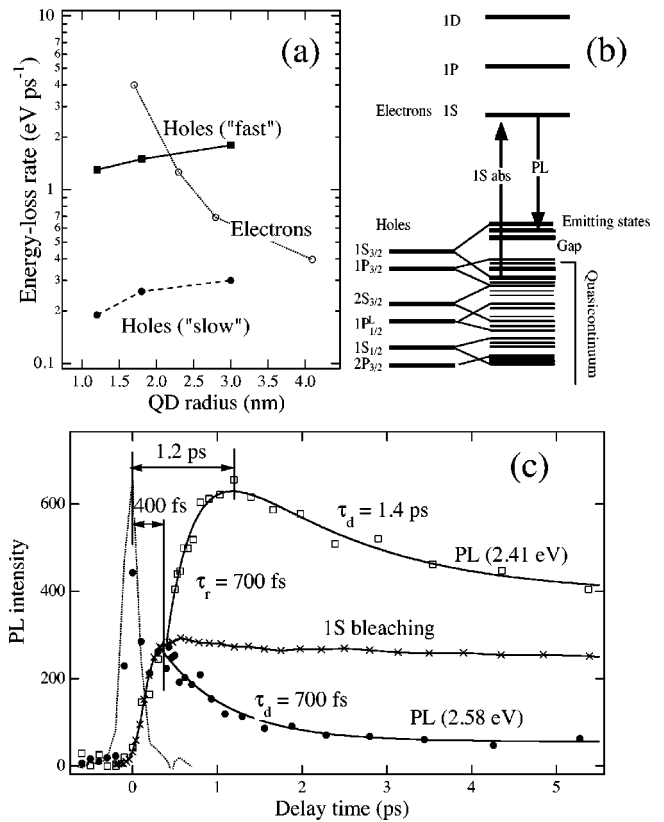


FIG. 3. (a) Energy-loss rates as a function of QD radius for “fast” (solid squares) and “slow” (solid circles) stages of hole relaxation, and for the IP to 1S electron relaxation (open circles; from Ref. 13). (b) Schematic illustration of the formation of the valence-band quasicontinuum separated by an energy gap from the lowest “emitting” hole states. Arrows show the transitions observed in optical spectra (1S absorption and band-edge PL). (c) Complementary PL dynamics detected at the positions of the “absorbing” (solid circles) and “emitting” (open squares) transitions for ZnS-capped 1.2-nm CdSe QDs (dotted line is a pump-pulse autocorrelation). The PL traces are compared to the 1S bleaching dynamics (crosses) detected using a TA experiment.

to a many-fold enhancement of the PL quantum yield. However, our time-resolved PL data do not indicate significant changes in hole dynamics following the overcoating procedure. A further indication that hole intraband relaxation is not sensitive to QD surface properties is that we do not observe modifications in PL dynamics as a result of changing a solvent (e.g., switching between hexane and toluene). These observations strongly suggest that hole relaxation is not due “extrinsic” mechanisms (e.g., coupling to surface defects or solvent molecules) but due to mechanisms that are “intrinsic” to QDs such as coupling to lattice vibrations (phonons).

The observed “fast” hole energy-relaxation rates ( $1.3\text{--}1.8$  eV ps<sup>-1</sup>) are close to those estimated for hole-LO phonon interactions in bulk CdSe ( $\sim 1.4$  eV ps<sup>-1</sup>).<sup>22</sup> The fact that phonon emission by “hot” holes is apparently not hindered by the discrete character of the energy levels implies that the valence band states form a very dense spectrum (*quasicontinuum*) at spectral energies above the 1S absorp-

tion peak. Large effective hole masses, the existence of three valence subbands strongly intermixed by quantum confinement,<sup>17</sup> and the fine-structure splitting of valence band states are all factors that can lead to a high density of hole states [the effect of splitting is qualitatively illustrated in Fig. 3(b) taking into account S- and P-type hole states; an even denser spectrum is expected if the states of other symmetries (D, F, etc.) are also taken into account]. The hole energy structures are further smeared out by broadening due to, e.g., dephasing induced by elastic carrier-phonon scattering.<sup>23</sup> Another factor that simplifies the process of meeting energy conservation requirements in QDs is the relaxation of momentum conservation which allows for a wider spread of  $k$ -vectors (i.e., phonon energies) in phonon-assisted processes.

The reduction in the energy-loss rate in the final stage of hole relaxation [solid circles in Fig. 3(a)] can be explained by the fact that the hole spectrum becomes more sparse at the band-edge energies, i.e., at energies close to the 1S absorption resonance. In the case of large inter-level separations, two or more phonons are required to satisfy the energy conservation during hole relaxation, leading to a reduced relaxation rate (“phonon bottleneck”). The fact that the onset for reduced rates occurs at energies close to the 1S absorption resonance implies that the “absorbing” and “emitting” valence-band states are separated by a relatively wide energy gap formed due to a fine-structure splitting of the 1S<sub>3/2</sub> level.<sup>19</sup>

Within the effective-mass model,<sup>24</sup> the low-energy exciton manifold (manifold of “emitting” states) is formed from states with projections of the total angular momentum  $F = \pm 2$ ,  $\pm 1^L$ , and  $0^L$ , where a superscript is used to distinguish between two energy states that have the same momentum projection but belong to two different exciton manifolds ( $L$  is used for a low-energy manifold of “emitting” states, and  $U$  is used for a high-energy manifold of “absorbing” states). The lowest “emitting” state is a nominally optically forbidden (“dark”)  $F = \pm 2$  exciton that, however, can weakly couple to light via phonon-assisted processes. At temperatures above  $\sim 50$  K, carrier thermal re-excitation leads to a strong mixing of the “dark” exciton with an optically active  $F = \pm 1^L$  exciton that is only a few meV higher in energy. Therefore, at room temperature the PL maximum is approximately at the position of the  $F = \pm 1^L$  transition, whereas the lowest absorption maximum is at the position of the strong  $F = \pm 1^U$  transition. The splitting between these two transitions, observed experimentally as a nonresonant Stokes shift between the PL band and the 1S absorption peak, provides an approximate measure of the gap at the bottom of the valence band. For CdSe dots with radii between 3 and 1 nm, studied in this paper, the Stokes shift increases with decreasing the dot size from  $\sim 30$  to  $\sim 100$  meV [see spectra in the inset to Fig. 1(b) and detailed size-dependent data in Ref. 21]. This large shift indicates a wide energy gap at the bottom of the valence gap, implying that multi-phonon emission may be required at the final stage of hole relaxation between the “absorbing” and “emitting” states.

One may argue that superposition of fine-structure states originating from different “unperturbed” valence-band levels should close this gap. However, the strength of the e-h exchange (one of the factors contributing to splitting) decreases with decreasing wave function overlap. Therefore, the splitting resulting, e.g., from interactions of the first excited 1P<sub>3/2</sub> hole state with the electron 1S state should be smaller than the splitting of the S-symmetry ground hole state, leaving the gap at the bottom of the valence band at least partially open [see schematic illustration in Fig. 3(b)].

Slowed relaxation across the gap separating the “emitting” and “absorbing” hole states is well pronounced in very small-size QDs ( $R \approx 1$  nm) for which the fine-structure splitting is particularly large. In Fig. 3(c), we show the PL dynamics at the positions of the 1S absorption and the PL maximum recorded for 1.2-nm QDs. The 1S PL shows a rapid (700 fs) decay that is complementary to the growth of the emission at the center of the cw-PL band. This is consistent with a hole relaxing between two well defined levels. In the same plot, we show 1S bleaching dynamics recorded using a TA experiment. A nearly flat 1S bleaching signal at times  $> 500$  fs is indicative of an almost constant population of the 1S electron states, which further indicates that fast PL dynamics are due entirely to a hole relaxation process.

In addition to the effect of the energy gap, slowing in hole dynamics can also be expected in the case of relaxation involving the change in a spin state (spin-flip processes). However, this effect should not be strongly pronounced at room temperature for which carrier thermal energies are much greater than the splitting between the low-energy exciton states with different projections of angular momentum.

In conclusion, we apply time-resolved fs PL and TA experiments to study intraband hole relaxation in strongly confined CdSe quantum dots with sub-10-nm dimensions. We clearly observe two stages in hole relaxation: initial fast relaxation with rates consistent with those for the LO-phonon emission in bulk materials and a final stage of much slower (up to a factor of 10) relaxation at near-band-edge energies. The fact that the “phonon bottleneck” does not inhibit initial hole relaxation indicates that hole states form a dense continuumlike spectrum at energies above the 1S absorption peak. Reduction in the energy-loss rate in the second stage of hole relaxation can be explained by the existence of a relatively wide gap at the bottom of the valence band that can only be overcome via low-efficiency multi-phonon processes. These data indicate that the “phonon bottleneck” plays a significant role in hole relaxation, despite the fact that it is overridden by nonphonon mechanisms in the case of electron relaxation.

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