Ultrafast intraband relaxation in colloidal quantum dots

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Abstract— **We independently determine the subpicosecond cooling rates for holes and electrons in CdSe quantum dots using time-resolved luminescence and time-resolved TeraHertz spectroscopy. The rate of hole cooling, following photoexcitation of the quantum dots, depends critically on the electron excess energy. This constitutes a direct proof of electron-to-hole energy transfer, the hypothesis behind the Auger cooling mechanism proposed in quantum dots, which is found to occur on a 1 ± 0.15 ps time scale**.

I. Introduction And Background

Semiconductor Quantum Dots (QDs) exhibiting strong quantum confinement of electrons provide a rare opportunity to study the fundamental properties of electronic excitations in a size regime between the atomic and bulk limits. Electron confinement gives rise to discrete energy levels (with [$1S_e$; $1P_e$; …] electron and [$1S_{3/2}$; $1P_{3/2}$; …] hole states)[1], rather than the continuum of states present in bulk semiconductors.

The principal electronic absorption and emission of semiconductor QDs lies in the visible to near-infrared spectral range and they have important applications in biology and electro-optical devices. Such electro-optic devices rely on the conversion of light into excited electrons and holes (excitons) and vice versa. Knowledge of the processes immediately following photoexcitation is therefore essential for these applications, in addition to the fundamental interest in exciton and charge dynamics in QDs. As such, there has been much interest recently in exciton cooling in these materials[2,3,4].

Cooling of 'hot' charges occurs both in bulk and QD semiconductors, when absorption of a photon generates charges with energies in excess of the band edge. While in bulk materials cooling occurs readily through sequential one-phonon emission, the electron energy level spacing in QDs (typically hundreds of meV) is large compared to typical longitudinal optical phonon frequencies (~25 meV), and electron cooling via coupling to phonons is expected to be slow. Accordingly, it has been proposed that cooling in QDs is hindered by a so-called ''phonon bottleneck''.

In the prototypical case of CdSe QDs, the radiative lifetime of the lowest exciton $1S_{3/2}$ $1S_e$ cold state has been studied extensively by time-resolved luminescence measurements[5]. However, when the *hot* $1P_{3/2}$ → $1Pe$ exciton is generated through optical excitation, this state is not observed in the emission spectrum[1,5]. This means that nonradiative processes, i.e., electron cooling ($1P_e$ → $1S_e$) and hole cooling ($1P_{3/2}$ → $1S_{3/2}$), compete effectively with radiative decay of the hot exciton. Thus, fast electron and/or hole cooling processes must occur, in contradiction with the predicted phonon bottleneck. To explain the apparent fast cooling, an Auger-like mechanism has been proposed[2,3,4,6], in which efficient transfer of energy from electrons to holes occurs followed by relatively fast hole relaxation through the more closely spaced valence levels. Other explanations for rapid electron cooling include fast multiphonon relaxation[7] and polaron effects[8].

Most experimental studies to date have concentrated on the dynamics of the electron cooling through optical transient absorption measurements[2,6]. However, transitions in the optical regime correspond to *interband* transitions and are per definition determined by the dynamics of both electrons and holes. $1P_e$ to $1S_e$ *electron* relaxation has been studied with transient techniques using infrared pulses. In particular, Refs. 3 and 9 demonstrate that electron relaxation is slowed on modification of the QD surface, an effect explained by surface state induced hole trapping. While such a link between the relaxation of electrons and holes is strong evidence of an Auger cooling mechanism, a definitive proof of electron-to-hole energy transfer requires independent determination of electron and hole relaxation dynamics, to demonstrate that the two are connected. However, the lower energy hole transitions (which lie in the far-infrared[10] are much more difficult to access with sufficient time resolution, and there have been only few reports in literature on the dynamics of hole intraband transitions in CdSe QDs[4,11]. A direct and independent determination of electron and hole cooling rates, which is required to unequivocally verify the Auger process and determine its cross section (i.e., to quantify the electron-hole interaction), has therefore remained elusive.

In this paper, we determine the hole cooling dynamics in well-defined CdSe QD ensembles using terahertz time-domain spectroscopy (THz-TDS)[12,13]. The THz frequency range is sufficiently low that the response is dominated by hole transitions[13], and we observe subpicosecond hole cooling. Using this technique combined with femtosecond time-resolved photoluminescence[14], we directly observe electron-to-hole energy transfer, confirming earlier reports on the Auger-like mechanism of intraband relaxation.

II. Results

Low-defect QD samples with small size dispersion (~5%) and high luminescence quantum yields (50%–90%) are prepared by a modified version[5] of the high-temperature organometallic synthesis, with QD size varying from a mean diameter D ~ 1.7 nm to D > 10 nm. Quantum confinement is expected to be negligible for D > 10 nm. In order to study intraband relaxation dynamics, we excite QDs of various sizes with 400 nm (3.1 eV) photons. For this fixed excitation energy,

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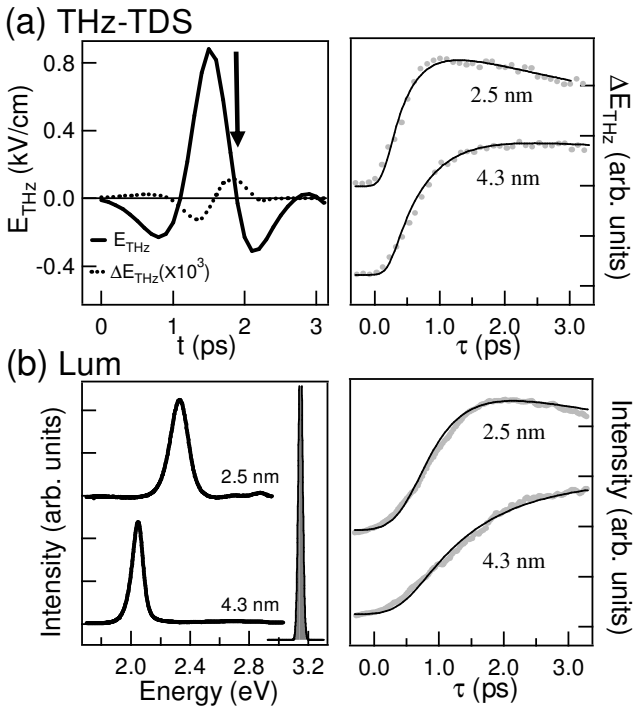

FIG. 1. (a) LEFT: The transmitted THz pulses, $E_{THz}(t, \tau)$ and the exciton-induced modulation thereof, $\Delta E_{THz}(t, \tau)$. RIGHT: The modulation is measured at the point marked with an arrow in the left panel (t=1.9 ps), as a function of τ, giving rise to the transient hole population of the $1S_{3/2}$ level. (b) LEFT: Luminescence spectra. Also shown is the excitation pulse (shaded). RIGHT: We measure the increase in intensity at the peak of the luminescence spectra (grey lines) as a function of delay, τ. The dynamics in both (a) and (b) are adequately described by exponential rise times determined by the carrier cooling rates (black lines in the right hand panels).

excitation of the $1P_h1P_e$ (hot) electron transition is only allowed for QDs with D > 3.3nm. In QDs with D < 3.3nm, the electron is always excited to the $1S_e$ state so no intraband electron relaxation should be observed. We monitor intraband relaxation dynamics by THz-TDS and femtosecond time-resolved photoluminescence.

As can be seen in the right panels of Fig. 1(a) and 1(b), the rise time of both the THz-TDS and the luminescence signal is clearly faster for the 2.5nm QDs, as compared to the rise time in 4.3nm QDs. This is expected, as the carrier excess energy is much larger for the larger particles, which have a smaller band gap. The cooling dynamics in both (a) and (b) are adequately described by exponential rise times (black lines in the right hand panels). The rise times were determined for all particle sizes under investigation and the extracted rise times are plotted as a function of QD diameter D in Fig. 2 (open circles for luminescence measurements, closed circles for THz-TDS results).

There is a clear slowing down of the luminescence rise time for D>3.3 nm. These results can be understood by considering the energy of the $1P_{3/2}1P_e$ transition[1] (the lowest energy, optically allowed transition for which hot electrons are photo-generated). For the fixed excitation energy used in the experiments, excitation of the $1P_{3/2}1P_e$ and higher energy (hot) electron transitions are only allowed for QDs with D>3.3 nm. This means that for D<3.3 nm the electron is always excited into the $1S_e$ cold state, and hole cooling is solely responsible for the luminescence dynamics. For D>3.3 nm, the luminescence signal rise is slowed, owing to the finite electron relaxation time from the $1P_e$ to the $1S_e$ state. A very similar slowing of dynamics has also been observed in the $1S_{3/2}1S_e$ absorption bleach for D>3.3 nm (see fig. 7(b) in ref. 6), but was interpreted as change in electron cooling, rather than the onset.

Though such fast dynamics indicate that a phonon-bottleneck clearly does not limit the cooling, luminescence and optical transient absorption measurements do not offer direct proof of Auger assisted cooling. This requires observation of electron-to-hole energy transfer, which we infer from the THz-TDS measurements. The relaxation times found from THz-TDS describe the rate at which the lowest energy hole state is occupied, limited by the slowest step in the overall relaxation process. For QDs with D<3.3 nm, the THz rise times follows the luminescence rise times very closely (~0.3 ps, see Fig. 2), suggesting that both are determined by hole cooling. For D>3.3 nm there is a clear slowing of the luminescence rise (to ~1.2 ps), indicating that electron cooling determines the delayed luminescence in larger particles. Remarkably, it is evident from the THz-TDS rise times that the hole cooling rate also slows down for D>3.3 nm, despite the fact that the hole itself has less excess energy when the electron is excited to the $1P_e$ rather than the $1S_e$ state, as was calculated using the transitions from ref. 1.

The very fast intraband relaxation in CdSe QDs suggests that a mechanism is available in which the phonon bottleneck is bypassed. The observation of delayed hole cooling upon higher electronic excitation reveals that this mechanism entails energy transfer from electrons to holes (the holes are re-excited upon electron cooling, resulting in an apparent slowing down of hole cooling), and constitutes the first direct confirmation of electron-to-hole energy transfer and the Auger cooling mechanism. The observed ~1 ps electron-hole coupling time is in good agreement with theoretical predictions that range from 500 fs[15] to 2 ps[16]. An additional small increase (~0.25 ps) in the luminescence rise time for D= 4.5 to 5 nm , similar to that observed with transient absorption measurements in ref. 6, may be attributed to either electron cooling from higher lying excited states down to the $1P_e$ state or slowing of the $1P_e \rightarrow 1S_e$ transition. As there must be a match to the energy separation between hole states involved in the Auger process (in order to conserve energy), one may expect the energy separation between $1P_e$ and $1S_e$ states (which varies with diameter[17]) to strongly affect Auger rates. However, when phonon interactions are included in the calculations in both refs. 15 and 16 the effects of energy level matching are smeared out, leading to electron-hole coupling times only weakly dependent on QD diameter, and accounting for our modest size dependence of the luminescence rise time for D>3.3 nm.

To establish that the step in the hole cooling around D=3.3 nm can be quantitatively accounted for by electron-to-hole energy transfer, we have modeled the system with a five-level calculation. Hot electron and hole states are represented by one level each (probabilities of occupation N_{elec}^{hot} and N_{hole}^{hot}

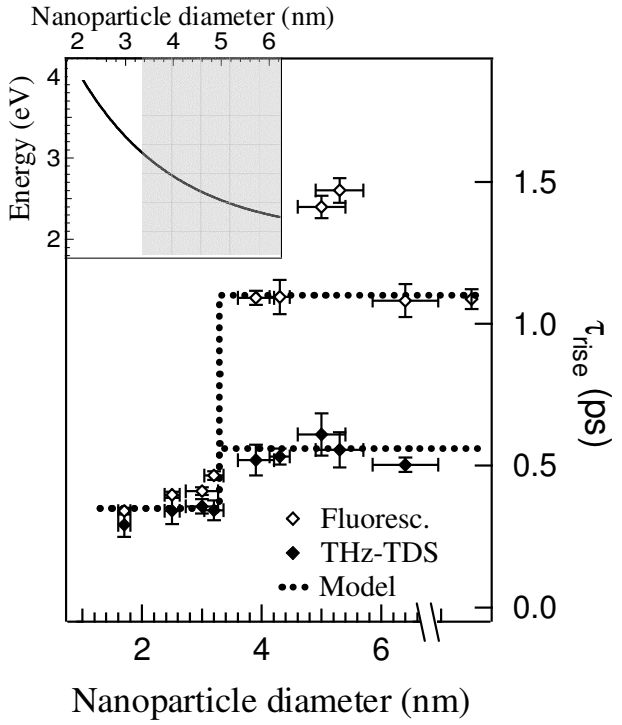

FIG. 2. Cooling times (describing the return to the cold electron and hole states) obtained from exponential fits to the THz-TDS and luminescence measurements as a function of mean particle diameter (horizontal error bars indicate size distributions). Dashed lines are the result of the model described in the text. Inset: Line indicates the energy of the $1P_{3/2}1P_e$ excitation (the lowest energy transition allowing hot electron generation) calculated from ref. [1]. The grey region indicates particle diameters for which (given the excitation energy) **hot** electrons are photo-generated, marking a clear step in the luminescence and THz rise times

respectively), as are the cold states (described by N_{elec}^{cold} and N_{hole}^{cold}). The transitions between these levels are described by the hole cooling rate rates $(1/\tau_h)^{-1}$ and the electron-hole coupling rate $(1/\tau_{e\text{-}h})^{-1}$. For D<3.3 nm, only cold electrons are produced upon photo-excitation, along with hot holes. Relaxation of hot holes leads to population of the cold state holes, from which the trapping rate $(1/\tau_{decay})^{-1}$ is included for generality[13]. For D>3.3 nm, hot electrons are also produced, and electron relaxation is accompanied by the generation of hot holes (i.e. the Auger cooling mechanism). The set of equations that are solved reads:

$$\frac{\partial N_{elec}^{hot}}{\partial t} = -\frac{1}{\tau_{e-h}} N_{elec}^{hot} \begin{cases} +0, \mathrm{D} < 3.3 \text{ nm} \\ +\delta(t), \mathrm{D} > 3.3 \text{ nm} \end{cases},$$

$$\frac{\partial N_{elec}^{cold}}{\partial t} = \frac{1}{\tau_{e-h}} N_{elec}^{hot} \begin{cases} +\delta(t), \mathrm{D} < 3.3 \text{ nm} \\ +0, \mathrm{D} > 3.3 \text{ nm} \end{cases},$$

$$\frac{\partial N_{hole}^{hot}}{\partial t} = -\frac{1}{\tau_h} N_{hole}^{hot} + \frac{1}{\tau_{e-h}} N_{elec}^{hot} + \delta(t)$$

$$\frac{\partial N_{hole}^{cold}}{\partial t} = \frac{1}{\tau_h} N_{hole}^{hot} - \frac{1}{\tau_{e-h}} N_{elec}^{hot} - \frac{1}{\tau_{decay}} N_{hole}^{cold},$$

where δ(t) denotes photoexcitation at time t=0.

Numerical solution to this model including details of the independently determined pulse shapes used in the experiments, fully reproduces all observed transients for D< 4.5 nm (the diameter at which states higher than $1P_e$ are excited, and more levels need to be included for an accurate description) with τ_h=330±50 fs and $\tau_{e\text{-}h}$=1±0.15 ps. The latter is in good agreement with both theoretical estimates of the electron-hole coupling time[15,16] and with the $1P_e \rightarrow 1S_e$ electron relaxation experimentally determined by infrared pump-probe spectroscopy[2,3]. The derived exponential times are shown as dashed lines in Fig. 2. Clearly, the increase in hole cooling time for D>3.3 nm can be fully accounted for by electron-to-hole energy transfer.

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