PRL **98,** 177403 (2007) PHYSICAL REVIEW LETTERS week ending 27 APRIL 2007

Breaking the Phonon Bottleneck for Holes in Semiconductor Quantum Dots

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(Received 15 December 2006; published 27 April 2007)

Size dependent hole dynamics are measured in colloidal CdSe quantum dots for a specific state-to-state excitonic transition. These experiments show that the hole energy loss rate increases for smaller quantum dots, contradicting known relaxation mechanisms for holes. These experiments reveal a new mechanism for hole relaxation in colloidal quantum dots which circumvents the expected phonon bottleneck for holes. The data are consistent with a nonadiabatic surface channel as the dominant pathway for hole relaxation in colloidal semiconductor quantum dots.

DOI: 10.1103/PhysRevLett.98.177403 PACS numbers: 78.67.Hc, 73.21.La, 78.47.+p

Semiconductor quantum dots have a unique electronic structure which is between the limits of atomic and bulk size scales [1]. Spatial confinement of the electrons and holes can result in size dependent electronic structure of the particle [2,3]. Quantum size effects can furthermore control dynamical processes in these materials [4,5]. Probing carrier relaxation dynamics in semiconductor quantum dots is important both for understanding the fundamental physics of nanoscale materials as well as for their incorporation into optoelectronic devices [4,6].

In order to understand how the size of a quantum dot might control the relaxation pathways for excitons, spectroscopic experiments have been performed on colloidal semiconductor quantum dots as a function of particle size [4,6]. As the level spacing increases for smaller particles, it was anticipated that electron relaxation would be slower due to the necessity of multiphonon processes [4,6–9]. Subsequently, confinement enhanced Auger mechanisms were proposed for electrons which would overcome the ‘‘phonon bottleneck’’ [4,6,10,11]. Following early experiments in doped glasses [12], a series of experiments were performed on high quality colloidal CdSe samples by Klimov and co-workers [4,13–15]. These experiments monitored relaxation of the optically excited exciton, confirming the presence of a confinement enhanced femtosecond Auger relaxation channel, thereby breaking the phonon bottleneck for electrons [10,11]. In order to focus more directly on the isolated electron relaxation dynamics, experiments were done by Guyot-Sionnest *et al.* [16,17] and Klimov *et al.* [14] which monitored electron relaxation in which the primary Auger channel was removed by decoupling of the hole. These experiments showed the importance of the surface on electron dynamics in colloidal quantum dots. A unified picture for exciton dynamics now includes at least two new mechanism for electron relaxation in colloidal quantum dots.

In contrast to electrons, the phonon bottleneck was expected for holes due to the absence of the femtosecond Auger channel [4,13,17]. Whereas electrons may relax on an ultrafast time scale by unidirectional coupling to holes, the holes should ultimately determine the final stages of exciton relaxation. Prior work used time resolved photoluminescence (PL) in conjunction with pump-probe methods providing an indirect measure of hole dynamics, suggesting the presence of a phonon bottleneck for holes [13]. The PL experiments do not follow transitions between specific states, making it difficult to measure dynamics with sufficient precision to quantitatively establish size dependence for specific states. Recent time resolved THz experiments have suggested that the arrival time of the hole to its band edge state is both fast (350 fs) and independent of particle size, provided the electron is initially in its cold 1*S* state [18]. Though the THz experiments show hole relaxation to a well-specified final state, they do not probe state-to-state transition dynamics. In order to measure the hole relaxation rates with sufficient precision and specificity to establish size dependent hole relaxation mechanisms, specificity in the initial and final excitonic states is required.

Because of the complex electronic structure of semiconductor quantum dots [3,19], state selectivity with femtosecond resolution is essential towards a quantitative measure of relaxation dynamics in quantum confined semiconductors. We recently reported that the initial excitonic state in semiconductor quantum dots has a dramatic influence upon the subsequent femtosecond carrier relaxation dynamics [20]. Prior femtosecond pump/probe experiments employed excitation at 3.1 eV [4,13–15], precluding initial state specificity for each size of particle [3,18]. Initial state specificity enables measurement of state-to-state dynamics, allowing quantitative evaluation of the relaxation processes.

In this Letter, we report on the size dependence of hole relaxation times with excitonic state-to-state specificity. By focusing specifically on state-to-state transitions, one can establish the size dependent transition rate by holding the initial and final states constant for each size of quantum dot. These experiments show that hole relaxation times are independent of particle size in direct contradiction to the expected phonon bottleneck. Furthermore, the hole energy loss rate increases for smaller particles. These measurements show unexpected hole relaxation dynamics which suggest a new mechanism which dominates hole dynamics in colloidal quantum dots.

The spectroscopic measurements were made in the pump/probe configuration, the details of which were previously described [20]. The instrument response function (IRF) was improved from prior work [20], to 60–70 fs over all wavelength combinations. Transients were collected simultaneously for two pump wavelengths to improve precision [20]. Samples of colloidal CdSe quantum dots passivated with either organic ligands (octadecylamine and trioctylphosphine oxide) or a two monolayer ZnS shell were prepared using published procedures [21]. CdSe quantum dots were dispersed in toluene and circulated through a 1 mm path length quartz flow cell at 295 K. The pump fluence was set to maintain the same exciton occupancy, $\langle N \rangle = 0.5$.

Exciton selective pump/probe data are shown in Fig. 1 which focuses on state-to-state hole dynamics from $2S_{3/2} \rightarrow 1S_{3/2}$. The pump pulses are tuned to excite into the $|1S_e\text{-}1S_{3/2}>$ or the $|1S_e\text{-}2S_{3/2}>$ excitonic states. The probe pulses are subresonant to the band edge exciton, thereby probing an induced absorption due to biexcitonic interactions [4,12,15,20,22]. The key observation is that pumping into the band edge state produces a small bleach, while pumping into an exciton consisting of a hot hole ($2S_{3/2}$) and a cold electron ($1S$) produces an instantaneous induced absorption which decays to match the signal from band edge excitation [20]. The initial exciton has the electron in its $1S$ state for both pumping conditions. Hence the difference between these transients reflects relaxation of the hole from the $2S_{3/2}$ to the $1S_{3/2}$ state. Here, subtraction is essential since the $1S$ bleaching signal decays on multiple picosecond time scales due to trapping [20]. The relaxation times for the holes are 248 fs + / − 10 fs for all sizes of quantum dots measured, Figs. 1 and 2. The uncertainties represent standard deviations of fits to at least 15–20 transients.

These numbers are qualitatively consistent with recent THz time domain experiments which measured hole relaxation times of 300–600 fs [18]. Earlier experiments used femtosecond photoluminescence in conjunction with pump/probe methods to extract hole dynamics [13]. Those experiments showed multiple cooling times for the hole as it relaxed down its manifold of states. In both

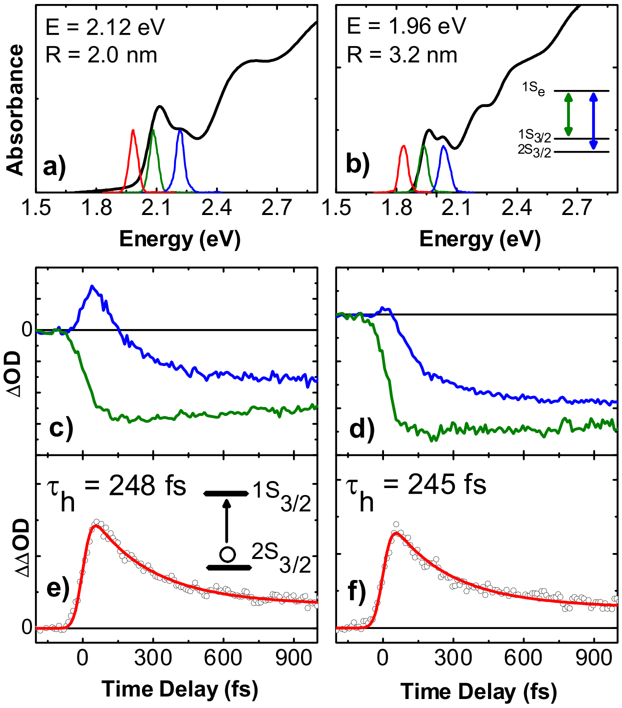

FIG. 1 (color online). Absorption spectra and laser spectra for two sizes of CdSe quantum dots, (a) and (b). The subresonant spectra corresponds to the probe pulses, while the two resonant spectra correspond to the pump pulses. Femtosecond pump/probe transients for two sizes of CdSe quantum dots, (c) and (d). The colors reflect the laser spectra used for exciton selectivity. Panels (e) and (f) show the ΔΔOD transient which is the subtraction of the ΔOD transients. The points are data and the solid line is the fit. The ΔΔOD transient directly monitors the hole population as described in the text.

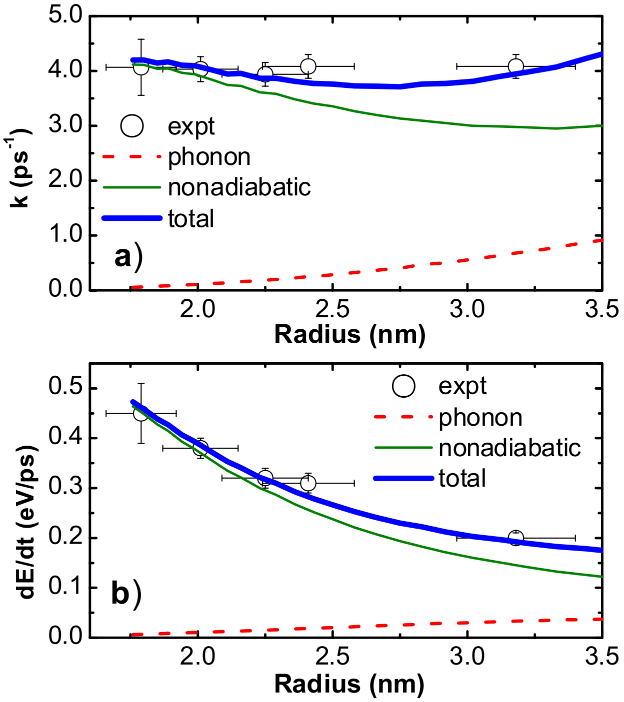

FIG. 2 (color online). The hole transition rate as a function of particle radius (a). The hole energy loss rate (dE/dt) as a function of particle radius (b). The experiment probes hole transitions from $2S_{3/2} \rightarrow 1S_{3/2}$ with the electron initially in the $1S_e$ state. The phonon channel is for emission of LO phonons via the Fröhlich interaction, while the nonadiabatic channel is for transitions induced by surface ligands. The total rate is the sum of the two channels.

experiments, there was insufficient time resolution and state specificity to measure the state-to-state hole dynamics with ~10 fs precision. This level of precision is needed to quantitatively measure hole transition rates, a requirement for evaluating the size dependent relaxation pathways in quantum dots.

These exciton selective experiments reveal the size dependent hole relaxation dynamics with state-to-state specificity, Fig. 2. The state-to-state hole transition rate is independent of size within the experimental uncertainties of +/ − 10 fs. The hole energy loss rate can be computed using the known energy gaps for the hole states [3]. These state-to-state measurements show that the hole energy loss rate increases for smaller particles, in direct contradiction with the expected behavior from phonon based theories for holes.

The dominant mechanism for electron relaxation in quantum dots is the Auger channel, in which energy is unidirectionally transferred from the electron to the hole [4,15]. In this manner, the electrons can overcome the phonon bottleneck. Decoupling of the holes, thereby removing the Auger channel, will result in picosecond electron dynamics [4,13,17]. The holes, however, have no ultrafast Auger channel since the energy spacings are smaller than for the electron [2,3]. Thus the phonon relaxation pathway, along with a phonon bottleneck, was expected for the holes. Figure 2. clearly shows a trend for the holes which is in opposition with expectations from a phonon based mechanism, overcoming the phonon bottleneck for holes. These experiments show size dependent hole dynamics which reveals the presence of a new mechanism which dominates hole relaxation in colloidal semiconductor quantum dots.

The state-to-state hole dynamics can be quantitatively treated by inclusion of nonadiabatic processes. The total rate for hole relaxation will be the sum of individual relaxation channels, e.g., $k_{\text{total}} = k_{\text{phonon}} + k_{\text{nonadiabatic}}$. The phonon based mechanism is via emission of LO phonons by the Fröhlich interaction [4,6–9]. The existence of additional channels can be evaluated by quantitatively measuring the size dependent state-to-state transition rates. Based upon the size and energy gap dependence of the transition rate, a nonadiabatic relaxation channel mediated by surface ligands can quantitatively reproduce the observed size independent transition rates for holes.

Nonadiabatic processes are well known in quantum molecular dynamics [23–27], and have recently been proposed as an electron relaxation channel in PbSe colloidal quantum dots [28]. The state-to-state nonadiabatic transition rate evaluated in a golden rule form will reflect the size dependence of the transition matrix element coupling the initial and final states,

$$k_{\text{fi}}(R) = \frac{2\pi}{\hbar}|M_{\text{fi}}(R)|^2\rho(E_f). \tag{1}$$

The transition rate was initially established for LO phonon based relaxation through the Fröhlich interaction [4,6–9] and subsequently for Auger relaxation for electrons [10,11]. The electron-nuclear portion of the matrix element for nonadiabatic transitions can be more explicitly recast using the Hellman-Feynman theorem [23],

$$\langle\psi_f|\frac{\partial}{\partial Q}|\psi_i\rangle = \langle\psi_f|\frac{\partial\hat{H}_i}{\partial Q}|\psi_i\rangle/(E_f - E_i). \tag{2}$$

The ψ's represent the adiabatic electronic states and Q represents a nuclear coordinate [23]. The energy denominator reflects the hole level spacing, which is $E(2S_{3/2})$-$E(1S_{3/2})$ for this state-to-state experiment. Assuming harmonic potentials, the Hellman-Feynman force will be proportional to the displacement of the adiabatic potential for the initial state along the relevant normal coordinate(s). Assignment of the relaxation mechanism can be obtained by considering the size dependence of the nonadiabatic transition matrix element.

The matrix element scales with the Hellman-Feynman force and inversely with the energy gap. The size dependence of the energy spacing of hole levels will decrease the rate for smaller particles as the energy gap gets larger. This contradicts the experimental observation, Fig. 2. The size dependence of the exciton-phonon coupling, Δ (or Huang-Rhys parameter, S) is known from resonance Raman [29,30], photon echo [30], and pump/probe [31] experiments. This prior work shows that exciton-phonon coupling via LO phonons decreases for smaller particles for CdS [29], CdSe [30], and PbS [31]. Since the force is proportional to Δ, larger particles will have a larger Hellman-Feynman force. This also is opposite to experimental observations. Independent experimental data show that nonadiabatic transitions mediated by LO phonons cannot qualitatively reproduce the observed size dependent state-to-state hole transition rate.

Since nonadiabatic transitions can be induced by any coupled vibrational mode [24], the surface ligands should be included in a full treatment. The influence of surface ligands on electron relaxation dynamics (decoupled hole) was demonstrated by Guyot-Sionnest *et al.* [17]. The role of ligands on hole dynamics can be evaluated by setting Δ proportional to the overlap of the hole with the surface ligands. The wave function of the hole was modeled as a particle in a finite spherical potential. The fraction of the hole which exists outside the surface shows a size dependence which is nearly equal to that of the hole energy gap. These size dependences produce a matrix element, $M_{\text{fi}}(R)$ which is nearly size independent as reflected in the state-to-state transition rate, Fig. 2(a). A nonadiabatic surface channel, in conjunction with minor contribution from the phonon emission channel, quantitatively reproduces the observed size independent state-to-state transition rate for holes.

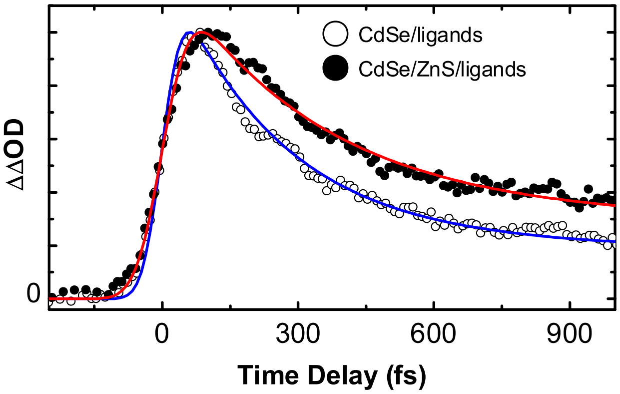

FIG. 3 (color online). Effect of surface passivation on hole relaxation dynamics. The hole relaxation times are 248 fs + / − 10 fs, independent of size, for ligand passivated surfaces. The hole relaxation time is 335 fs with two monolayers of ZnS shell. The ZnS shell provides a tunneling barrier between the quantum dot core and the surface ligands.

To further provide evidence of the role of surface ligands, experiments were performed with ZnS capped CdSe quantum dots. The ZnS shell will provide a tunneling barrier which will reduce the electronic coupling between the CdSe states and the ligands [32]. Passivation of CdSe with two monolayers of ZnS clearly increases the time scale for hole dynamics from 248 fs + / − 10 fs (all sizes) to 335 fs, Fig. 3. The size and surface dependent transition rates demonstrate the importance of the ligands, which dominate the final stages of hole dynamics.

In conclusion, the size dependence of hole transition rates in colloidal CdSe quantum dots was measured using a state-to-state approach. These experiments show evidence of size dependent dynamics which overcome the expected phonon bottleneck for holes. We show evidence for a new mechanism for ultrafast hole relaxation consistent with nonadiabatic electronic transitions induced by vibrations at the surface of the colloidal quantum dot. These experiments add to a unified picture of relaxation dynamics which can include Auger processes for electrons, nonadiabatic transitions, and phonon based relaxation. In the case of holes, surface based nonadiabatic channels are the dominant pathway for hole relaxation, which ultimately determines the final stages of exciton relaxation. This result opens doors for tuning the surface properties towards controlling hole relaxation dynamics.

Financial support from CFI, NSERC, FQRNT, and McGill University, is acknowledged. E. A. D. acknowledges financial support from NSERC.

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