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Observation of an Excitonic Quantum Coherence in CdSe Nanocrystals

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Abstract: Optical pump-probe spectroscopy with 6-fs pulses elucidates the $1S_e1S_{3/2}$ – $1S_e2S_{3/2}$ excitonic quantum coherence in CdSe nanocrystals. This coherence encodes hole migration over nanometer length scales and markedly alters the displacement amplitudes of coherent phonons.

OCIS codes: 320.7120 Ultrafast phenomena; 300.6530 Spectroscopy, ultrafast

1. Introduction

Among the multitude of artificial light harvesting systems, semiconductor quantum dots (QDs), stand out due to their desirable optical properties and relatively well-established synthetic procedures. While the excited-state dynamics and the coherent phonon phenomena of QDs have been actively investigated, it is only in recent years that excitonic quantum coherences have been studied in CdSe QDs. Two-dimensional electronic spectroscopy performed on zinc-blende CdSe QDs at ambient temperature reveals a coherent superposition of $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states, for which a dephasing time of 15 fs is found [1]. More recent 2DES measurements elucidate multi-level quantum coherences with dephasing times that extend to ~100 fs [2]. However, these studies did not address the excitonic decoherence mechanism, and the possibility of steering coherent phonon wave packet dynamics by the excitonic coherence remains unexplored.

Here, femtosecond optical pump-probe spectroscopy is employed to investigate coherent excitonic motion associated with the $1S_e1S_{3/2}$ – $1S_e2S_{3/2}$ excitonic superposition in wurtzite CdSe QDs [3]. In contrast with zinc blende CdSe QDs, it is noteworthy that excitonic coherences in the thermodynamically more stable wurtzite form of CdSe have so far eluded detection [4]. Spectral signatures of excitonic coherence are clearly discerned from our low-temperature optical pump-probe data, from which an ultrafast hole migration that is mediated by excitonic quantum coherence is reconstructed. Results from temperature-dependent measurements are suggestive of decoherence induced by exciton-acoustic phonon scattering, although the dominant contribution to decoherence is found to be temperature-independent. Finally, the presence of excitonic coherence is found to suppress exciton-LO-phonon coupling while the exciton-LA-phonon coupling is enhanced. These observations are supported by semiclassical *ab initio* molecular dynamics (AIMD) simulations.

2. Experiment

The optical pump-probe setup employs 6-fs pulses in the visible and pulse-to-pulse measurements of the differential transmission spectra. The typical excitation fluence is 0.4 mJ cm^{-2} and the corresponding average number of excitons per QD is ~0.3. Narrowband pump pulses are produced by inserting a 10-nm bandpass dielectric interference filter into the broadband pump beam. Fluence-dependence measurements confirm that the $\Delta T/T$ signal is linear in the range of excitation fluences employed in the experiments.

3. Results and Discussion

The optical absorption spectrum of the 6.1-nm-diameter CdSe QD thin-film sample, collected at 77 K, reveals well-resolved peaks at 2.04, 2.14, and 2.32 eV, which correspond to transitions to the $1S_e1S_{3/2}$, $1S_e2S_{3/2}$, and $1P_e1P_{3/2}$ excitonic states, respectively. Photoexcitation of the sample by the 6-fs laser pulses with a spectral range of 1.65–2.25 eV results in the formation of a coherent superposition of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states.

Fig. 1(a) Contour plot of the differential transmission spectra collected as a function of time delay, following broadband excitation of 6.1-nm-diameter CdSe QDs at 77 K. The data reveals strongly damped, high-frequency oscillations that are due to excitonic quantum coherence. (b) Time-resolved differential transmission signal collected in the region of the band-edge transition for temperatures of 77, 100, 120, 140, and 295 K (top to bottom). The solid lines are fits to the experimental data. (c) Radial distribution functions of the hole density reconstructed from the experimental data collected at 77 K, for time delays of 0 fs and $T_p/2$, where is the classical orbital period. For the CdSe QDs studied here, $T_p = 44$ fs and the radius $a_0 = 3.05$ nm.

The time-resolved $\Delta T/T$ spectra collected at short time delays ($t < 100$ fs) reveals a high-frequency, short-lived oscillatory feature (Fig. 1a) which is suggestive of excitonic quantum coherence. Time traces obtained in the region of the band-edge transition where the amplitude of the coherent LO phonon is a minimum show an increasingly rapid damping of the early-time oscillation with temperature (Fig. 1b). By 295 K, a monotonically decaying time trace is obtained, consistent with the population dynamics exhibited by an incoherent ensemble of CdSe QDs. The time trace recorded at 77 K can be fit to give an oscillation frequency of 851 ± 17 cm^{-1} , a damping time of 14.7 ± 1.2 fs, and an initial phase of $(0.14 \pm 0.02)\pi$ rad.

In the absence of phonon modes with such high frequencies, the origin of the short-lived oscillatory component can be attributed to coherent excitonic dynamics. This assignment is bolstered by the good agreement between the oscillation frequency ω and the energy separation between the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states of $\Delta E \sim 730$ – 750 cm^{-1} . Furthermore, the retrieved oscillation phases for all temperatures are ~ 0 rad, which implies that the exciton density distribution starts its oscillation from an extremum, as one would intuitively expect for the excitation of a coherent superposition by transform-limited laser pulses.

The damping time is found to decrease from 14.7 ± 1.2 to 11.4 ± 2.4 fs as the temperature increases from 77 to 140 K. To within experimental error, the decoherence rates exhibit a linear temperature dependence and a temperature-independent offset that accounts for as much as $\sim 70\%$ of the measured decoherence rate at 77 K. The above suggests that decoherence of the $1S_e1S_{3/2}$ – $1S_e2S_{3/2}$ superposition is only partially induced by exciton-acoustic phonon scattering. The dominant temperature-independent component could originate from exciton-exciton scattering involving the complex manifold of fine-structure states or from exciton-surface defect scattering.

A coherent superposition of excitonic states encodes the motion of exciton density. In the present work, a superposition of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states yields a hole radial wave packet. The experimental data can be used to reconstruct the time-evolution of the hole radial distribution function (Fig. 1c). The radial distribution function that is initially peaked at a radius of 1.04 nm moves to 1.76 nm in 22 fs. The corresponding charge migration rate of 0.33 Å/fs is comparable to some of the fastest electron transfer rates inferred for strongly coupled electron donor-acceptor systems. It is important to note that the observed ultrafast charge migration is driven solely by excitonic quantum coherence without the involvement of nuclear motion.

While *incoherent* acoustic phonons are found to participate in the decoherence of the $1S_e1S_{3/2}$ – $1S_e2S_{3/2}$ excitonic superposition, the experimental data also reveals the influence of the excitonic superposition on the behavior of the

Fig. 2(a) The spectral first moment $\langle \Omega^{(1)}(t) \rangle$ computed about the band-edge transition for both broadband coherent excitation (top panel) and narrowband state-selective excitation (bottom panel) of the CdSe QD sample at 77 K. Note the different span of the vertical scales. (b) AIMD trajectories of the phonon-induced fluctuations of the E_{1s} (black) and E_{2s} (red) energy gaps, as well as the difference $E_{2s} - E_{1s}$ (blue). The inset shows the FFT amplitudes of the energy gaps.

coherent phonons. The first-moment time trace $\langle \Omega^{(1)}(t) \rangle$ computed about the band-edge transition reveals oscillations that can be assigned to the coherent LO (208 cm^{-1}) and LA (18 cm^{-1}) phonons (Fig. 2a, top panel). To clarify the influence of coherent excitonic motion on coherent phonon dynamics, the first-moment time traces obtained with narrowband, state-selective excitation to the $1S_e1S_{3/2}$ state are also recorded (Fig. 2a, bottom panel). The Huang-Rhys factors S_i ($i = \text{LO}, \text{LA}$) extracted from the $\langle \Omega^{(1)}(t) \rangle$ traces show that simultaneous excitation of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ states as compared to state-selective excitation of only the $1S_e1S_{3/2}$ state leads to a one order-of-magnitude suppression of S_{LO} over the entire temperature range of 77 – 295 K. In addition, broadband excitation of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ states yields relatively temperature-invariant S_{LA} values, whereas a linear increase in S_{LA} with temperature is observed for excitation of only the $1S_e1S_{3/2}$ state.

AIMD simulations reveal that the LO-phonon-induced modulation of the E_{1s} and E_{2s} gaps occur in phase (Fig. 2b). Hence, the energy difference $\Delta E = E_{2s} - E_{1s}$, which encodes the coherent excitonic superposition, exhibits suppressed LO phonon oscillations (Fig. 2b inset). The AIMD simulations predict the suppression of the coherent LA phonon with simultaneous excitation of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ states, even though the experimental results point to an enhancement. This contradiction between experiment and theory suggests the direct involvement of excitonic motion in driving the LA phonon, an effect that is not considered in the AIMD simulations. Intuitively, the ultrafast radial charge migration that is associated with the $1S_e1S_{3/2}$ – $1S_e2S_{3/2}$ excitonic superposition impulsively alters the electronic potential along the radial direction, which in turn triggers atomic motion along the radial coordinate, i.e., the coherent LA phonon is launched.

The valence radial wave packet that is observed in this work is reminiscent of Rydberg radial wave packets that were previously observed in atoms and small molecules in the gas phase [5]. Unlike the numerous revivals exhibited by Rydberg wave packets, however, the QD excitonic superposition is found to decohere within a fraction of the classical orbit period. Possible future avenues for exploration include the quantum control of charge migration, the manipulation of atomic motion by driving nonstationary valence electron motion, as well as the gating of charge transfer in optoelectronic nanomaterials by the excitonic coherence.

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