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<td><strong>Author(s)</strong></td>
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Observation of an Excitonic Quantum Coherence in CdSe Nanocrystals

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Abstract

Recent observations of excitonic coherences within photosynthetic complexes suggest that quantum coherences could enhance biological light harvesting efficiencies. Here, we employ optical pump-probe spectroscopy with few-femtosecond pulses to observe an excitonic quantum coherence in CdSe nanocrystals, a prototypical artificial light harvesting system. This coherence, which encodes the high-speed migration of charge over nanometer length scales, is also found to markedly alter the displacement amplitudes of phonons, signaling dynamics in the non-Born-Oppenheimer regime.

Keywords: Electronic coherence, quantum dots, femtosecond optical spectroscopy, electron-phonon coupling, charge migration, non-Born-Oppenheimer dynamics

TOC graphic
Recent observations of electronic and/or vibronic coherences\(^1\)\(^-\)\(^4\) in biological light harvesting complexes by ultrafast multidimensional spectroscopy have led to speculation that such phenomena are exploited to boost energy transfer efficiencies in photosynthesis.\(^5\) Quantum coherences between electronic states manifest themselves as periodic oscillations of the electronic density with time, in which the modulation frequencies scale with the energy differences between the participating eigenstates.\(^6\) Motivated by fundamental scientific interest and potential applications, studies of electronic coherences have also been extended to a variety of nanoscale artificial light harvesting systems.\(^7\)-\(^11\) Indeed, theoretical studies have put forth the possibility of harnessing electronic quantum coherences to enhance the output of solar cells.\(^12\)

Among the multitude of artificial light harvesting systems, semiconductor nanocrystals,\(^13\),\(^14\) also known as quantum dots (QDs), stand out due to their desirable optical properties\(^15\) and relatively well-established synthetic procedures.\(^16\) The latter allows exquisite control over the size and shape, and hence, the photophysical properties of these nanocrystals. High incident-photon-to-current conversion efficiencies of 8.55% have been demonstrated\(^17\) by solar cells that incorporate QDs as the photosensitizer.\(^18\) While the excited-state dynamics\(^19\),\(^20\) and the coherent phonon phenomena\(^21\),\(^22\) of semiconductor nanocrystals have been actively investigated, it is only in recent years that excitonic quantum coherence has been studied in CdSe QDs.\(^23\),\(^24\) Two-dimensional electronic spectroscopy (2DES) performed on zinc-blende CdSe QDs at ambient temperature reveals a coherent superposition between \(1S_e 1S_{3/2}\) and \(1S_e 2S_{3/2}\) excitonic states, for which a dephasing time of 15 fs is found.\(^23\) More recent 2DES measurements elucidate multi-level quantum coherences with dephasing times that extend to \(~100\) fs.\(^24\) These studies did not address the excitonic decoherence mechanism, for which physical insight is all the more critical given the disparate dephasing time scales
reported. In addition, 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 $1S_e 1S_{3/2} - 1S_e 2S_{3/2}$ excitonic superposition in wurtzite CdSe QDs. 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. Spectral signatures of excitonic coherence are clearly discerned from our low-temperature optical pump-probe data, from which an ultrafast charge 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.

The optical absorption spectrum of the CdSe QD thin-film sample collected at 77 K is shown in Figure 1. The spectrum reveals well-resolved peaks at 2.04, 2.14, and 2.32 eV, which correspond to transitions to the $1S_e 1S_{3/2}$, $1S_e 2S_{3/2}$, and $1P_e 1P_{3/2}$ excitonic states, respectively; note that the background rising towards the high-energy side of the spectrum is due to Rayleigh scattering by the thin-film sample. The optical absorption spectrum of the CdSe QDs in toluene solution at 295 K reveals a band edge of 1.99 eV (see Supporting Information), which suggests a mean diameter of 6.4 nm for the CdSe QDs. The mean diameter inferred from the band-edge absorption energy is in good agreement with that obtained from transmission electron microscopy, from which an average diameter of 6.1 ± 0.4 nm is measured (see Supporting Information).
Photoexcitation of the sample by transform-limited, broadband laser pulses of 6-fs duration and spectral range of 550 – 750 nm results in the formation of a coherent superposition of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states. The normalized differential transmission $\Delta T/T$ spectra obtained at 77 K show positive features, which correspond to ground-state bleaching and stimulated emission from the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states, as well as negative features, which can be assigned to excited-state absorption to the biexciton manifold$^{19}$ (see Supporting Information). Temporal oscillations in the time-resolved $\Delta T/T$ spectra can be assigned to coherent longitudinal-optical (LO) and longitudinal-acoustic (LA) phonons, with frequencies of 208 and 18 cm$^{-1}$, respectively. Inspection of the $\Delta T/T$ signal at short time delays ($t < 100$ fs) reveals an additional high-frequency, albeit short-lived oscillatory component (Figure 2a), which is suggestive of excitonic quantum coherence.

Further analysis of the early-time oscillatory signal is performed on a time trace obtained at a probe wavelength in the band-edge transition region where the amplitude of the coherent LO phonon is a minimum. In this way, the contribution of the coherent LO phonon to the signal can be neglected. The resultant time traces obtained at 77, 100, 120, and 140 K show that the early-time oscillation becomes more rapidly damped with temperature (Figure 2b). To see this trend, we note that the secondary maximum of the $\Delta T/T$ signal at 40-fs time delay, apparent at 77 K (see arrow in the top panel of Figure 2b), becomes indiscernible at 140 K. Furthermore, the appearance of the time trace at 295 K (bottom panel of Figure 2b) is qualitatively different from those recorded between 77 – 140 K: the monotonically decaying time trace collected at 295 K is consistent with the population dynamics of an incoherent ensemble of CdSe QDs. The absence of coherent dynamics at ambient temperature suggests decoherence within the <10-fs time resolution of the experiment, in agreement with the results of previous 2DES measurements.$^{25}$ To extract the damping times, the time traces are fit to the function
\[
S(t) = \frac{4 \ln 2}{\sqrt{\pi \Delta_{IRF}^2}} \exp \left( - \frac{4 \ln 2 \tau^2}{\Delta_{IRF}^2} \right) \ast \Theta(t) \times [A_1 + A_2 \cos(\omega t + \varphi) \exp(-t/\tau)],
\]

which is a convolution of a damped oscillation atop a step function with a normalized Gaussian instrument response function of FWHM \( \Delta_{IRF} \). In the expression, \( \Theta(t) \) is the Heaviside function with amplitude \( A_1 \), and \( A_2, \omega, \varphi, \) and \( \tau \) are the amplitude, frequency, phase, and damping time of the oscillation, respectively. The fits to the time traces are shown in Figure 2b and the fit parameters \( \omega, \varphi, \) and \( \tau \) are summarized in Table 1.

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>Frequency ( \omega ) / cm(^{-1} )</th>
<th>Phase ( \varphi ) / ( \pi ) rad</th>
<th>Damping time ( \tau ) / fs</th>
<th>Dephasing time ( T_{12}^{*} ) / fs</th>
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<tr>
<td>77</td>
<td>851 ± 17</td>
<td>0.14 ± 0.02</td>
<td>14.7 ± 1.2</td>
<td>15.8 ± 1.5</td>
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<td>100</td>
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<td>0.07 ± 0.02</td>
<td>14.1 ± 1.0</td>
<td>15.1 ± 1.2</td>
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<tr>
<td>120</td>
<td>753 ± 63</td>
<td>0.18 ± 0.05</td>
<td>13.8 ± 3.8</td>
<td>14.7 ± 4.2</td>
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<tr>
<td>140</td>
<td>750*</td>
<td>0.13 ± 0.04</td>
<td>11.4 ± 2.4</td>
<td>11.9 ± 2.6</td>
</tr>
</tbody>
</table>

(* The oscillation frequency at 140 K was fixed to allow the fit to converge.)

The frequencies of the oscillations observed at \( t < 100 \) fs are ~750 – 850 cm\(^{-1}\) for the range of temperatures employed in the experiments. 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 following observations.

First, the measured oscillation frequency coincides with the \( \Delta E \sim 730 – 750 \)-cm\(^{-1}\) energy separation between the \( 1S_e 1S_{3/2} \) and \( 1S_e 2S_{3/2} \) excitonic states determined for the CdSe QD sample over the same temperature range (see Supporting Information). The good agreement between \( \Delta E \) and \( \omega \) strongly suggests that the observed oscillations originate from excitonic quantum beats. Second, 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.\textsuperscript{27, 28}

A coherent superposition of excitonic states encodes the motion of exciton density. In the present work, a superposition of the $1S_e 1S_{3/2}$ and $1S_e 2S_{3/2}$ excitonic states yields a hole radial wave packet, described by the time-dependent wave function

$$
\Psi(r,t) = c_{1s}(t)\psi_{1s}(r) \exp(-iE_{1s}t/\hbar) + c_{2s}(t)\psi_{2s}(r) \exp(-iE_{2s}t/\hbar),
$$

(2)

where $\psi_{1s}(r)$ and $\psi_{2s}(r)$ are the $1S_{3/2}$ and $2S_{3/2}$ hole radial wave functions with coefficients $c_{1s}(t)$ and $c_{2s}(t)$, respectively, and $E_{1s}$ and $E_{2s}$ are the associated eigenenergies. The hole wave functions are obtained from solving the Luttinger Hamiltonian that includes an additional spherical confinement potential.\textsuperscript{29} The coefficients $c_{ns}(t)\ (n = 1,2)$ are related to the fractional populations $f_{ns}(t)$ of the $1S_e nS_{3/2}$ states by $c_{ns}(t) = [f_{ns}(t)]^{1/2}$, where $f_{1s}(t) + f_{2s}(t) = 1$; the fractional populations are in turn determined by the spectral overlap between the sample optical absorption spectrum and the laser spectral density (see Supporting Information). Note that, in principle, $c_{1s}(t)$ and $c_{2s}(t)$ are time-dependent due to the decay of the $1S_e 2S_{3/2}$ excited state to the $1S_e 1S_{3/2}$ band-edge state with a time constant of 245 fs,\textsuperscript{20} as well as the further relaxation of the $1S_e 1S_{3/2}$ state to the ground state and/or to trap states.\textsuperscript{30}

The corresponding motion of the radial hole density is given by the expression

$$
|\Psi(r,t)|^2 = c_{1s}^2(t)|\psi_{1s}(r)|^2 + c_{2s}^2(t)|\psi_{2s}(r)|^2
$$

$$
+ 2c_{1s}(t)c_{2s}(t)\psi_{1s}(r)\psi_{2s}(r) \cos[(E_{2s} - E_{1s})t/\hbar] \exp(-t/T_{12}),
$$

(3)

where a phenomenological damping term with time constant $T_{12}$ has been introduced to account for the decoherence between the $1S_{3/2}$ and $2S_{3/2}$ hole states. In the limit that the population dynamics are slow compared to the decoherence time, i.e., $T_{12} \ll T_{1s}, T_{2s}$, where $T_{1s}$ and $T_{2s}$ are the population decay time constants of the $1S_{3/2}$ and $2S_{3/2}$ hole states,
respectively, \( c_{15}(t) \) and \( c_{25}(t) \) can be assumed to be time-independent. That is, \( c_{15}(t) = c_{15}(0) \) and \( c_{25}(t) = c_{25}(0) \), where \( c_{15}(0) \) and \( c_{14}(0) \) are determined by the initial excitation conditions to be \( c_{15}(0) = 0.849 \) and \( c_{25}(0) = 0.528 \) (see Supporting Information). In this limit, the experimentally measured damping time \( \tau \) corresponds to \( T_{12} \).

It is important to note that observations of coherent dynamics by ensemble-averaged pump-probe measurements are complicated by inhomogeneous dephasing.\(^{31}\) In the present work, inhomogeneity of the optical response arises primarily from the finite size dispersity of the CdSe QD sample. In a recent 2DES study, the influence of size dispersion was effectively eliminated by analyzing the dephasing of the zero-quantum coherence at a specific coherence energy, thereby yielding the decoherence time for only a narrow subset of QD sizes.\(^{24}\) Here, we account for inhomogeneous dephasing by considering the normal distribution of oscillation frequencies \( \omega = (E_{2s} - E_{15})/\hbar \) that arises from the size-dependence of \( E_{2s} \) and \( E_{15} \) (see Supporting Information).\(^{32}\) According to our estimates, the experimentally measured \( T_{12} = 14.7 \pm 1.2 \) fs at 77 K corresponds to a homogeneous dephasing time of \( T_{12}^* = 15.8 \pm 1.5 \) fs (see Table 1). This result is supported by AIMD simulations performed on a 1.3-nm-diameter \( \text{Cd}_{33}\text{Se}_{33} \) model cluster, which yield a decoherence time of 17 fs at 77 K for the \( 1S_e1S_{3/2} - 1S_e2S_{3/2} \) excitonic superposition. While the use of a QD with smaller radius \( R \) in the simulations constitutes an approximation, given that higher acoustic phonon frequencies\(^{21}\) (\( \omega_a \sim R^{-1} \)) and stronger electron-phonon coupling via the deformation potential\(^{33}\) (\( S \sim R^{-2} \)) would predict shorter decoherence times, we note that the computed \( 1S_e1S_{3/2} - 1S_e2S_{3/2} \) energy gap of the model QD (0.08 eV) is similar to the experimental value of 0.09 eV. As a result, the amplitude of the phonon-induced fluctuations for the model QD is expected to be commensurate with that of the experimental system.\(^{34}\) According to linear response theory,\(^{35}\) the computed dephasing time should therefore be directly comparable to the experimental results.
The experimental data can be used to reconstruct the time-evolution of the hole radial distribution function (Figure 3). 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.\textsuperscript{36-38} In the present work, the observed ultrafast charge migration is driven solely by excitonic quantum coherence without the involvement of nuclear motion. Furthermore, because the radial distribution function at the moment of coherent photoexcitation is governed by the relative phases of the $1S_e 1S_{3/2}$ and $1S_e 2S_{3/2}$ excitonic states, and as phase coherence is lost, this initial radial distribution function asymptotically evolves into that given by the relative populations of the $1S_e 1S_{3/2}$ and $1S_e 2S_{3/2}$ states, the rate of charge migration can be increased simply by reducing the decoherence time. In the present system, for example, the initial and asymptotic hole densities are peaked at 1.04 nm and 1.67 nm, respectively. Hence, a shortened decoherence time of 1 fs would yield a charge migration rate of 2 Å/fs. A corollary to this point is that coherent charge migration can be expected as long as the initial and asymptotic charge density distributions are different, even when the decoherence time is ultrashort.

Examining the temperature-dependence of the excitonic decoherence provides insight into the decoherence mechanism. In bulk semiconductors, carrier decoherence occurs via carrier-carrier and carrier-phonon scattering.\textsuperscript{39, 40} In the case of semiconductor QDs, three-pulse photon-echo measurements reveal optical dephasing rates that scale linearly with sample temperature $T$.\textsuperscript{41, 42} In the limit $k_B T \gg \hbar \omega_a$, where $k_B$ is the Boltzmann constant and $\omega_a$ is the frequency that characterizes the quasi-continuum of acoustic phonons, the linear temperature dependence suggests exciton-phonon scattering involving low-frequency, incoherent acoustic phonons as the dominant dephasing mechanism. Such linear scaling has also been observed, for example, in the case of GaAs quantum wells,\textsuperscript{43} carbon nanotubes,\textsuperscript{44}
and dye molecules in the condensed phase.\textsuperscript{45} Within experimental error, our temperature-dependent $T_{12}$ values follow the linear relation $1/T_{12}(T) = \Gamma_{12}(T) = \Gamma_{12}(0) + aT$, where $\Gamma_{12}(0) = 45 \pm 8 \text{ ps}^{-1}$ is the temperature-independent offset and $a = 0.22 \pm 0.09 \text{ ps}^{-1}\text{K}^{-1}$ is the slope (Figure 4). It is evident that $\Gamma_{12}(0)$ dominates the decoherence rates that are obtained in the 77 – 140-K range, with the temperature-dependent term $aT$ accounting for only $\sim 30\%$ of the measured decoherence rate. This result suggests that decoherence of the $1S_e 1S_{3/2} - 1S_e 2S_{3/2}$ excitonic superposition in the 77 – 140-K temperature range is only partially induced by acoustic phonons. Possible origins of $\Gamma_{12}(0)$ include exciton-exciton scattering between the two excitonic states that comprise the superposition,\textsuperscript{46} as well as scattering that involve surface defects.\textsuperscript{42} The former could be enhanced by the complex exciton fine structure of the wurtzite CdSe QDs,\textsuperscript{47} whereas the latter is conceivable for the ligand-capped QDs examined here. Finally, while we caution against the direct comparison between optical dephasing rates and intraband dephasing rates, which is not meaningful,\textsuperscript{48} we note that the slope $a$ obtained from our experiments is $\sim 4\times$ larger than the value of $a \sim 0.06 \text{ ps}^{-1}\text{K}^{-1}$ obtained for the optical dephasing rates of similar-sized CdSe QDs.\textsuperscript{42} The origin of this discrepancy is unknown and requires a systematic study over a wider temperature range.

While \textit{incoherent} acoustic phonons are found to participate in the decoherence of the $1S_e 1S_{3/2} - 1S_e 2S_{3/2}$ excitonic superposition, the experimental data also reveals the influence of the excitonic superposition on the behavior of the \textit{coherent} phonons of CdSe QDs. Two types of coherent phonon modes are known to exist in CdSe quantum dots\textsuperscript{22} – the coherent LO phonon (208 cm\textsuperscript{-1}) and the coherent LA phonon (18 cm\textsuperscript{-1}). In the present work, the $\Delta T/T$ time traces reveal that broadband (Figure 5a) and narrowband (Figure 5b) excitation predominantly launch the coherent LA and LO phonons, respectively. Further insight into the effect of the $1S_e 1S_{3/2} - 1S_e 2S_{3/2}$ superposition on the coherent phonon dynamics can be
obtained from analyzing the first-moment time trace $\langle \Omega^{(1)}(t) \rangle$ computed about the band-edge transition (Figure 5c). The first moment $\langle \Omega^{(1)} \rangle$ of a differential transmission spectrum is related to the energy gap between the bands which are optically coupled by the probe pulse.\textsuperscript{49} Considering the contributions from both LO and LA phonons, $\langle \Omega^{(1)}(t) \rangle$ can be fit to the expression

$$\langle \Omega^{(1)}(t) \rangle = A_{\text{LO}} \cos(\omega_{\text{LO}}t + \varphi_{\text{LO}}) \exp(-t/\tau_{\text{LO}})$$

$$+ A_{\text{LA}} \cos(\omega_{\text{LA}}t + \varphi_{\text{LA}}) \exp(-t/\tau_{\text{LA}}),$$

where $A_{\text{LO}}, \omega_{\text{LO}}, \varphi_{\text{LO}},$ and $\tau_{\text{LO}}$ ($A_{\text{LA}}, \omega_{\text{LA}}, \varphi_{\text{LA}},$ and $\tau_{\text{LA}}$) correspond to the amplitude, frequency, phase, and damping time of the LO (LA) phonon, respectively (see Supporting Information). 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 $1S_{1/2}-1S_{3/2}$ state are also recorded (Figure 5c). The $\langle \Omega^{(1)}(t) \rangle$ traces obtained under the two different excitation conditions reveal qualitative differences: excitation of the $1S_{1/2}-1S_{3/2}$ superposition drives predominantly the coherent LA phonon whereas state-selective excitation mostly yields the coherent LO phonon.

The observed suppression of the coherent LO phonon and the enhancement of the coherent LA phonon can be further quantified by computing their corresponding Huang-Rhys factors $S_i$ ($i = \text{LO, LA}$).\textsuperscript{50} The Huang-Rhys factor characterizes the exciton-phonon coupling strengths and can be extracted from the $\langle \Omega^{(1)}(t) \rangle$ oscillation amplitude by the relation\textsuperscript{51} $A_i = 2\omega_i S_i$. Several observations can be made about the $S_{\text{LO}}$ and $S_{\text{LA}}$ values measured over the temperature range of 77 – 295 K (Figures 5b and 5c). First, it is evident that simultaneous excitation of the $1S_{1/2}-1S_{3/2}$ and $1S_{3/2}-2S_{3/2}$ states as compared to state-selective excitation of only the $1S_{1/2}-1S_{3/2}$ state leads to a one order-of-magnitude suppression of $S_{\text{LO}}$ over the entire temperature range of 77 – 295 K. Second, broadband excitation of the $1S_{1/2}-1S_{3/2}$ and
$1S_e 2S_{3/2}$ states yields relatively temperature-invariant $S_{LA}$ values, whereas a linear increase in $S_{LA}$ with temperature is observed for excitation of only the $1S_e 1S_{3/2}$ state. The latter observation can be rationalized in terms of a linearly increasing phonon occupation number in the electronic ground state with temperature, which in turn launches an excited-state vibrational wave packet with a larger nuclear displacement amplitude upon photoexcitation.\(^{52}\) From the experimental data, it can be deduced that the intrinsic Huang-Rhys factor for the LA phonon, accessed in the low-temperature limit and therefore independent of the phonon occupation number, is larger for coherent excitation of the $1S_e 1S_{3/2}$ and $1S_e 2S_{3/2}$ states than for selective excitation of the $1S_e 1S_{3/2}$ state.

AIMD simulations reveal that the LO-phonon-induced modulation of the $E_{1s}$ and $E_{2s}$ gaps occur in phase, signifying similarly signed electron-LO phonon coupling matrix elements for the $1S_e 1S_{3/2}$ and $1S_e 2S_{3/2}$ states (Figure 5d). In this case, the energy difference $\Delta E = E_{2s} - E_{1s}$, which encodes the coherent excitonic superposition, exhibits suppressed LO phonon oscillations (Figure 5d inset). In agreement with experiment, the simulation results show that phase-coherent excitation of the $1S_e 1S_{3/2}$ and $1S_e 2S_{3/2}$ states leads to a $\sim$10-fold suppression of the LO phonon mode. These results mirror qualitatively the previously observed suppression of the radial breathing mode (RBM) coherent phonon following the simultaneous excitation of the $E_{11}$ and $E_{22}$ transitions of single-walled carbon nanotubes by broadband, few-cycle laser pulses.\(^{53}\) On the other hand, the AIMD simulations predict the suppression of the coherent LA phonon with simultaneous excitation of the $1S_e 1S_{3/2}$ and $1S_e 2S_{3/2}$ 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 $1S_e 1S_{3/2}$–
$1S_e 2S_{3/2}$ 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 observed temperature-independence of $S_{LA}$ can be attributed to the persistence of coherent charge migration even at elevated temperatures. Similar launching of coherent phonons by ultrafast charge transfer has been observed.\textsuperscript{54, 55} In the resonant coupling regime, Bloch oscillations in semiconductor quantum wells have been shown to drive coherent LO phonons adiabatically.\textsuperscript{56}

The direct observation of coherent valence electron motion represents one of the holy grails in femtochemistry and attosecond physics.\textsuperscript{27, 57} Compared to coherent exciton migration in photosynthetic light harvesting complexes,\textsuperscript{1-4} or to charge migration that has been predicted for ionized molecules,\textsuperscript{58-60} the relative simplicity of the electronic structure of QDs makes them an attractive platform for visualizing coherent electron motion. Pioneering investigations of excitonic coherences in zinc blende-type CdSe QDs by 2DES spectroscopy, however, yielded largely disparate compositions of the excitonic superpositions and decoherence times despite similar experimental conditions.\textsuperscript{23, 24} In the present work, optical pump-probe spectroscopy performed on a highly monodisperse sample of wurtzite-type CdSe QDs reveals unambiguous spectral signatures of quantum coherence between the $1S_e 1S_{3/2}$ and $1S_e 2S_{3/2}$ exciton states. The high signal-to-noise ratio afforded by our experimental data allows the first reconstruction of ultrafast charge migration in a nanoscale system that is driven solely by excitonic quantum coherence. We note that the charge migration distance can be controlled by spectral shaping of the excitation laser pulse. For example, photoexcitation of an equal population of the $1S_e 1S_{3/2}$ and $1S_e 2S_{3/2}$ excitonic states would extend the inner and outer turning points of the radial wave packet to 0.97 nm and 1.98 nm, respectively. Unlike conventional donor-acceptor charge transfer, however, it is important to note that the charge migration observed herein involves the center-of-mass motion of the hole.
distribution within a single CdSe nanocrystal, which preserves its overall electrical neutrality at all times.

The valence radial wave packet that is observed in this work is reminiscent of atomic Rydberg radial wave packets that were previously generated with picosecond pulses. 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. Variable temperature measurements reveal that the decoherence originates predominantly from electronic factors – exciton-exciton scattering, exciton fine structure, and defect scattering – rather than the presence of the phonon bath. This observation suggests that efforts to achieve extended decoherence times should focus on engineering the excitonic structure of QDs and minimizing the number of defect sites. Another possible avenue for further exploration is to investigate how the decoherence of the excitonic superposition is affected by the presence of coherent phonons that are simultaneously generated by the excitation pulse.

Through the observation of coherent LO and LA phonons in the present work, we have elucidated the effect of excitonic coherence and the associated ultrafast charge migration on the behavior of the phonons. This result paves way for the coherent control of atomic motion via the optical manipulation of valence electron densities. In addition, when applied to donor-acceptor motifs in which the CdSe QD serves as either the hole donor or acceptor, the ultrafast charge migration that occurs within the CdSe nanocrystal can potentially be harnessed to gate charge transfer on ultrashort time scales.

Methods

Sample preparation. Colloidal wurtzite-type CdSe QDs are synthesized following literature procedure before they are dispersed in a poly(methyl methacrylate) (PMMA) matrix and spin-coated onto a 1.5-mm-thick fused silica window. The average diameter of the QDs is 6.1
nm with 6% rms dispersity, as determined by transmission electron microscopy (see Supporting Information). The narrow size dispersity, further evidenced by the well-resolved features in the absorption spectrum (Figure 1), is critical in allowing the observation of spectral signatures of excitonic quantum coherence.

**Optical pump-probe spectroscopy.** The optical pump-probe setup employs few-cycle pulses in the visible and pulse-to-pulse measurements of the differential transmission spectra. The details of the apparatus can be found in ref. 68. For the study reported herein, multiphoton intrapulse interference phase scan (MIIPS) is incorporated to characterize and compensate for the residual high-order dispersion of the broadband laser pulses,68 thereby furnishing transform-limited ~6-fs pulses in the 550 – 750-nm spectral range for experiments (see Supporting Information). The typical excitation fluence is 0.4 mJ cm$^{-2}$ and the corresponding average number of excitons$^{19}$ per QD is $\langle N \rangle \sim 0.3$. Fluence-dependence measurements confirm that the $\Delta T/T$ signal is linear in the range of excitation fluences employed in the experiments (see Supporting Information). Narrowband pump pulses are produced by inserting a 10-nm bandpass dielectric interference filter into the broadband pump beam. Pump and probe pulses are orthogonally polarized to suppress contributions from scattering and coherent artifacts, which could otherwise obfuscate the short-lived excitonic coherence signal. In addition, coherent artifacts from the PMMA matrix are eliminated by subtracting the measured response of a pure PMMA sample from the signal of the QD sample (see Supporting Information).69 Accurate determination of time-zero is accomplished via linear spectral interferometry between pump and probe pulses (see Supporting Information).70

**Ab initio molecular dynamics simulations.** The Cd$_{33}$Se$_{33}$ cluster with a diameter of 1.3 nm was constructed using bulk wurtzite lattice. Recent experiments$^{71}$ have shown that such “magic” size cluster is one of the smallest stable CdSe QDs that support a crystalline-like core.$^{72,73}$ These properties make Cd$_{33}$Se$_{33}$ an excellent model for studying electronic and
vibrational properties of semiconductor QDs. The cluster geometry was optimized using \textit{ab initio} density functional theory with a plane wave basis, as incorporated in the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{74} The PBE functional\textsuperscript{75} with projector-augmented-wave (PAW) pseudopotentials\textsuperscript{76} was employed in a converged plane wave basis. The simulations were performed in a periodically replicated cubic cell with at least 8 Å of vacuum between QD replicas. The fully optimized structure was then heated to the desired temperatures with repeated velocity rescaling. 3-ps-long microcanonical MD trajectories were generated using the Verlet algorithm with the 1-fs time step and Hellmann-Feynman forces. The decoherence time was obtained with the semiclassical optical response formalism,\textsuperscript{35} which allows one to use the MD simulation. The pure-dephasing time is associated with fluctuations of the energy levels due to coupling of the electronic degrees of freedom to phonons. The fluctuations in the energy levels are best characterized in terms of correlation functions. The pure-dephasing function is defined as,

\[
D(t) = \exp(i\omega t) \langle \exp\left(-\frac{i}{\hbar} \int_0^t \Delta E(\tau) d\tau\right) \rangle.
\]  

(5)

where the angular brackets denote thermal averaging. The dephasing function can be approximated using the second-order cumulant expansion as,

\[
D(t) = \exp(-g(t)),
\]  

(6)

where

\[
g(t) = \frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} \langle \Delta E(\tau) \Delta E(0) \rangle d\tau_2.
\]  

(7)

The method based on the cumulant expansion shows better numerical convergence than the direct expression eq. 5, which involves averaging of an oscillating function. Both direct and cumulant methods have shown excellent agreement with experiment for several systems.\textsuperscript{77-79}

The data reported here are based on the cumulant expansion.
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Supporting Information

Sample characterization by TEM and variable-temperature UV/vis spectroscopy, details of laser pulse compression and data processing to remove artifacts and determine time-zero, fluence-dependence measurements, time-resolved differential transmission spectra collected up to 5-ps time delay, estimation of size-dispersity-induced inhomogeneous dephasing, parameters used in the construction of the hole wave functions, and fit parameters obtained from the time-domain analysis of the spectral first moment. This material is available free of charge via the Internet at http://pubs.acs.org.
References


Figure 1. Linear absorption spectrum of the CdSe QD thin-film sample (black line) and the spectra of the broadband (blue line) and narrowband (red line) laser pulses. The absorption spectrum can be fit to a sum optical transitions to the three lowest excitonic states (dashed lines), in addition to Rayleigh scattering (dotted line). The spectrum of the broadband laser pulse excites predominantly the transitions to the two lowest-energy excitonic states. The inset shows the excitonic level diagram denoted with the optical transitions observed in the absorption spectrum.
Figure 2. (a) Contour plot of the differential transmission spectra collected as a function of time delay following excitation of 6.1-nm-diameter wurtzite-type 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 for the 77 – 140-K time traces are fits to Eq. (1). The $\Delta T/T$ time trace collected at 295 K is fit to a convolution of the instrument response function with an exponential decay and an offset. The arrow in the top panel denotes the secondary maximum of the $\Delta T/T$ signal that is apparent at 77 K.
Figure 3. Radial distribution functions $r^2|\Psi(r,t)|^2$ of the hole density reconstructed from the experimental data collected at 77 K for the time delays (a) 0 fs, (b) $T_p/4$, (c) $T_p/2$, (d) $3T_p/4$, (e) $T_p$, and (f) 100 fs, where $T_p = \hbar/(E_{2s} - E_{1s})$ is the classical orbital period. For the CdSe QD studied here, $T_p$ corresponds to 44 fs. The plot at 100 fs is representative of the asymptotic hole density. The radius of the QD $a_0$ is 3.05 nm in the present work.
Figure 4. The measured excitonic decoherence rates (black squares) exhibits a linear dependence on temperature with an offset. The decoherence rate computed by AIMD simulations at 77 K is also shown (red circle).
Figure 5. (a) $\Delta T/T$ signal as a function of time delay for a probe photon energy of 1.98 eV, obtained following the phase-coherent excitation of the $1S_e 1S_{3/2}$ and $1S_e 2S_{3/2}$ states. The inset shows the FFT power spectrum, which reveals oscillation frequencies that can be assigned to the LA and LO phonons of the CdSe QD. (b) $\Delta T/T$ signal as a function of time delay for a probe photon energy of 2.01 eV, obtained following the selective excitation of the $1S_e 1S_{3/2}$ state. The inset shows the FFT power spectrum, which reveals oscillation frequencies that can be assigned to the LA and LO phonons of the CdSe QD. (c) The spectral first moment 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. (d) Huang-Rhys factor $S_{LO}$ obtained at different temperatures for the LO phonon. (e) Huang-Rhys factor $S_{LA}$ obtained at different temperatures for the LA phonon. The increase in $S_{LA}$ with temperature, observed with
narrowband excitation, is described by a linear fit (dashed line). (f) 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. The peaks at 60, 120, 170, and 230 cm$^{-1}$ can be assigned to the TA, LA, TO, and LO phonon, respectively.$^{80}$