Coherent Longitudinal-Optical Ground-State Phonon in CdSe Quantum Dots Triggered by Ultrafast Charge Migration

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We observe the CdSe longitudinal-optical ground-state phonon in the electron transfer system composed of CdSe quantum dots and methylviologen directly by femtosecond absorption spectroscopy. A significant phase shift indicates that the coherent oscillations are triggered by an ultrafast charge migration, which is the consequence of an electron transfer from the photoexcited quantum dot to the molecular acceptor methylviologen. In contrast, the observed coherent phonons in isolated quantum dots stem from the frequency modulation of the quantum dot excited-state spectrum. From the probe wavelength dependence of the longitudinal-optical phonons in the electronic ground state and excited state it is possible to determine a biexciton binding energy of 35 meV.

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The fundamental processes in nanocrystalline semiconductor quantum dots (QDs) such as exciton confinement [1] or exciton relaxation dynamics [2–4] have received a great deal of interest motivated by their possible application in microscopy [5], lasing [6,7], and photovoltaics [8–10]. An important ingredient of the physical properties of QDs is the exciton-phonon coupling. Two general types of phonon modes—optical and acoustic—are known in QDs [11]. In studies on CdSe QDs longitudinal-optical (LO) [12–16], transverse [12], and surface optical [17,18], as well as longitudinal acoustic (LA) [14–16,19] phonon modes have been observed. In II-VI semiconductors the optical phonons are expected to couple to the exciton via the Fröhlich interaction, whereas acoustic phonons are coupled via the deformation potential interaction and the piezoelectric potential [11]. In time-resolved studies on QDs, coherent phonons are usually induced by ultrashort laser pulses [14,15]. In our experiments these coherent oscillations are induced by a chemical fundamental reaction (charge transfer) in the product ground state. This novel type of phonon generation inherently reflects the ultrashort nature of the charge transfer process and is not influenced by the properties of the exciting laser pulse. Recent efforts try to establish QDs as light absorbers in QD-based solar cells [8–10]. Here, an efficient charge separation after photoexcitation of the QD mediated by an acceptor is crucial [20]. However, the vibrational relaxation of highly excited QDs (hot excitons) could be a main obstacle for the construction of highly efficient QD-based solar cells. A theoretical solar-to-electric energy conversion efficiency of 66% has been determined if the loss due to cooling effects could be avoided [21].

This study deals with the correlation between the generation of phonons in CdSe QDs and the ultrafast interfacial electron transfer (ET) to the adsorbed molecular electron acceptor methylviologen (MV^{2+}) after photoexcitation of the QDs. For that purpose isolated CdSe QDs in toluene as well as the coupled system containing CdSe QDs and adsorbed MV^{2+} were investigated by time-resolved absorption spectroscopy. The ultrafast ET between QDs and MV^{2+} has been described already in several studies [20,22,23]. In order to synthesize the CdSe QDs we slightly modified a method developed by Nordell *et al.* [24]. The averaged core size of the particles was 3.1 nm, determined by the position of the lowest excitonic transition [$1S(e)$-$1S_{3/2}(h)$] at 523 nm [25,26]. Both samples had the same QD concentration of $3 \times 10^{-5} M$ in toluene. The QD/MV^{2+} coupled system was prepared by adding an excess amount of MV^{2+} dissolved in methanol at a molar ratio of 1:5. All MV^{2+} molecules are believed to bind to the QD surface since MV^{2+} is poorly soluble in toluene. Nearly complete quenching of the QD fluorescence is observed (data not shown) and explained by an efficient ET from the excited CdSe to MV^{2+}. Since MV^{2+} is not absorbing light in the visible spectral range, a Förster-type energy transfer can be excluded.

In general the transient absorption (TA) spectrum of QDs exhibits (1) bleach signals in the spectral range of QD excitonic transitions which involve populated states due to state filling and (2) positive contributions from the carrier induced redshifting of all optical transitions (photoinduced absorption) [3,4,27]. After photoexcitation intraband transitions have not been observed in the visible spectral region. Therefore the term excited-state absorption describes the absorption of QDs which already possess an exciton and not a transition into a higher excited state ($S_1 \rightarrow S_N$) as known from molecular systems [4].

The excitation of the QDs occurred at the maximum of the $1S(e)$-$1S_{3/2}(h)$ transition at 523 nm. Low pump pulse energy ensured that the sample contains mainly single excited and nonexcited QDs. The calculated averaged number of absorbed photons per QD was ≤ 0.2 [20,26]. Figure 1 shows the transient traces recorded at the rising

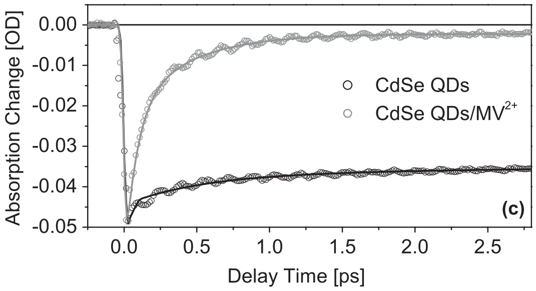

FIG. 1. Normalized transient traces at the probe wavelength $\lambda_{\text{probe}} = 518$ nm and fits (solid lines) for the two different samples after excitation of the QDs at 523 nm. (OD is optical density.)

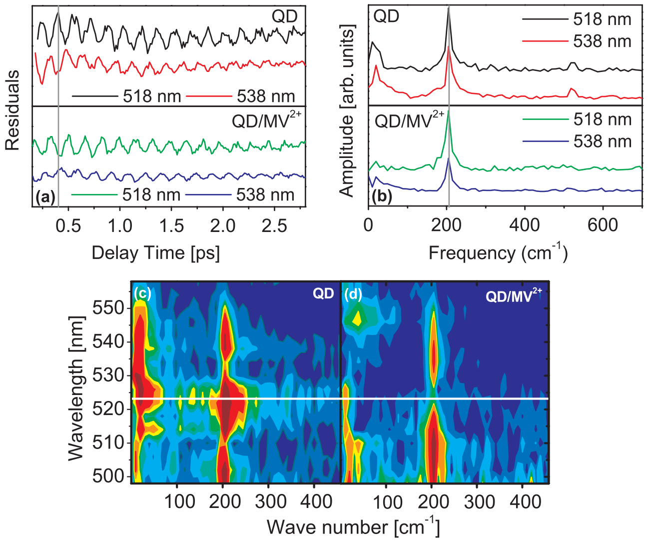

FIG. 2 (color). (a) Residual oscillations of isolated CdSe QDs and the CdSe $\mathrm{QD/MV^{2+}}$ coupled system at different λ_{probe} obtained from the subtraction of the model function from the transient data. (b) Fourier transformed data of the residuals of isolated CdSe QDs and the CdSe $\mathrm{QD/MV^{2+}}$ coupled system at different λ_{probe}. 2D representation of the Fourier transformed data for (c) isolated CdSe QDs and (d) the CdSe $\mathrm{QD/MV^{2+}}$ coupled system; the white line indicates the maximum of the lowest excitonic transition of the QDs.

edge of the $1S(e)$-$1S_{3/2}(h)$ absorption band ($\lambda_{\text{probe}} = 518$ nm). Both transient traces exhibit an instantaneous negative signal (excitonic bleach) which is dominated by the electron population in the $1S(e)$ state of the QDs [2,27]. In the case of isolated QDs the long-lived signal demonstrates the weak exciton dynamics during the first picoseconds. In contrast, an ultrafast decay of the negative signal in the coupled system can be observed as a consequence of an efficient ET from the photoexcited QD to the molecular acceptor $\mathrm{MV^{2+}}$ [28]. All QD related TA signals decay nearly completely during the ET reaction. This observation is in agreement with earlier studies of Huang *et al.* [28]. We conclude that after the ET reaction the spectrum of the cationic QD (QD[h]) has a spectrum which is highly similar to the spectrum of unexcited QD. However, to account for the remaining hole the coupled system after the ET reaction is denoted as QD[h].

A model function consisting of a sum of exponentials convoluted with a Gaussian (considering the cross correlation time of 40 fs) was used to fit the excitonic contribution of the transient signal. Since the excitonic bleach is dominated by the electron population in the $1S(e)$ state, its decay can be directly related to the ET reaction in the $\mathrm{QD/MV^{2+}}$ couple. Two time constants were necessary to describe the decay dynamics of the excitonic bleach signal of the coupled system. Such multiphasic behavior in charge transfer systems containing QD-acceptor couples has already been observed in former investigations [29]. We obtained an amplitude weighted average time constant for the decay of the bleach signal in the presence of $\mathrm{MV^{2+}}$ of $\langle \mathrm{ET} \rangle \approx 100$ fs. Additionally, the transient traces of both investigated samples (Fig. 1) show a periodic modulation of the transient absorption signal, which can be unambiguously assigned to the appearance of coherent phonons [14,15]. The oscillation of the transient signal is even more obvious from the residuals shown in Fig. 2(a). Here, the model function was subtracted from the transient data. For both systems, the residuals show a phase shift of π going from $\lambda_{\text{probe}} = 518$ nm to $\lambda_{\text{probe}} = 538$ nm in the transient absorption signal. It is assumed that coherent phonons influence the electronic states of QDs via the Fröhlich interaction, leading to a frequency modulated dynamic spectrum, which explains the observed phase shift by π [14,30]. In the case of isolated QDs, either stimulated emission (SE), the photoinduced absorption, or both can be frequency modulated. Surprisingly, the coherent phonons observed for the $\mathrm{QD/MV^{2+}}$ coupled system are still present even after the exciton is separated by the ultrafast ET to the $\mathrm{MV^{2+}}$ ($\langle \mathrm{ET} \rangle \approx 100$ fs). Since the QDs are not in their excited state after the ET reaction, we conclude that the observed coherent phonon has to stem from the cationic ground-state QD. Interestingly, there is also a phase shift between the coupled system and the isolated QDs at the same wavelength [cf. Fig. 2(a)].

Fourier transformed (FT) data of the residual oscillations measured for the isolated QDs show a dominant high frequency mode at 206 $\mathrm{cm^{-1}}$ and a low frequency mode at 19 $\mathrm{cm^{-1}}$ for both investigated λ_{probe} [Fig. 2(b)]. The high frequency mode is in very good agreement with cw Raman experiments on CdSe clusters which have found the LO phonon at 205 $\mathrm{cm^{-1}}$ [13]. A recent time-resolved study of CdSe QDs showed the LO and the LA phonon at 209 and 18.4 $\mathrm{cm^{-1}}$, respectively [14,16]. Here we assign the low frequency mode at 19 $\mathrm{cm^{-1}}$ of the isolated QDs to the LA phonon. Fourier transformed data of the residual oscillations recorded for the $\mathrm{QD/MV^{2+}}$ coupled system at $\lambda_{\text{probe}} = 518$ nm and $\lambda_{\text{probe}} = 538$ nm also yield a strong peak at 206 $\mathrm{cm^{-1}}$ due to the LO phonon, whereas the

LA phonon is suppressed [Fig. 2(b)]. The 2D Fourier transformed spectra in Figs. 2(c) and 2(d) demonstrate the probe wavelength dependence of the observed phonon modes in isolated QDs and the QD/MV^{2+} coupled system. The presence of MV^{2+} leads to a remarkable change of the spectral characteristics of the LO phonon mode at $\approx 200\ \mathrm{cm}^{-1}$. At the $1S(e)$-$1S_{3/2}(h)$ linear absorption maximum (white line at 523 nm), a minimum is observed whereas the isolated QDs exhibit a maximum at that spectral position.

The spectral dependence of the LO phonon in Fig. 2(c) directly reflects the absorption properties of electronically excited QD (QD$^*[e, h]$), which are dominated by the electrons in the $1S(e)$ state. In general, strong frequency modulation of transient absorption should be observed at spectral positions where the derivative of the absorption of the oscillating species is large. In the case of the pure QD the oscillating species is the QD$^*[e, h]$. In QD$^*[e, h]$ the positions of all optical transitions change due to the biexciton induced level shifting. Therefore, the strongest frequency modulation in the transient signal of the isolated QDs is expected to be at the spectral positions where the derivative of the absorption of QD$^*[e, h]$ is large [cf. schematic representation in Fig. 3(a)]. Since the pump pulses in our experiments are not negatively chirped, a significant impulsive resonant Raman contribution is ruled out [31,32].

We can use the dependence of the CdSe QD and CdSe QD/MV^{2+} FT amplitude spectra at $206\ \mathrm{cm}^{-1}$ [Fig. 3(b)] to assign the LO phonons to a certain contribution of the transient signal. After the ET reaction in the CdSe QD/MV^{2+} coupled system the coherent phonon modulates the QD$[h]$ electronic ground-state spectrum. This is clearly indicated by (1) the large amplitudes in the spectral region where the derivative of the QD linear absorption is high and (2) the minimum at $\lambda_{\mathrm{probe}} \approx 524$ nm which is nicely correlated with the QD absorption maximum [cf. Fig. 3(b)]. The spectral dependence of the LO phonon in QD$[h]$ is illustrated in Fig. 3(a). Based on the nearly complete decay of QD TA signal during the ET reaction, we assume that the absorption of the unexcited QD and QD$[h]$ are identical. The coherent oscillations in the QD$[h]$ can be interpreted by a polaron which is generated in the ET reaction. The polarization field of the hole leads to a polarization or deformation of the crystal lattice which triggers the observed LO phonon. In contrast, the FT amplitude spectrum at $206\ \mathrm{cm}^{-1}$ of isolated QDs in Fig. 3(b) exhibits a first minimum at $\lambda_{\mathrm{probe}} \approx 532$ nm. The shift of 10 nm compared to QD$[h]$ clearly indicates that the maximum of the $1S(e)$-$1S_{3/2}(h)$ transition in QD$^*[e, h]$ undergoes the biexciton induced level shifting and the modulation of the QD excited-state spectrum is observed. The magnitude of the biexciton level shifting is governed by the biexciton binding energy (Δ_{XX}). In former investigations the ratio between state filling associated bleaching and photoinduced absorption has been applied to determine the biexciton binding energy. The obtained binding energy values varied between the different studies ($\approx$ 13–30 meV) [14,27,33,34]. Since the biexciton binding energy is determined by the shift of the excitonic transitions due to the presence of an exciton, we can directly estimate a Δ_{XX} value of 35 meV [cf. Fig. 3(c)] from our time-resolved experiments which is qualitatively consistent with the values mentioned above.

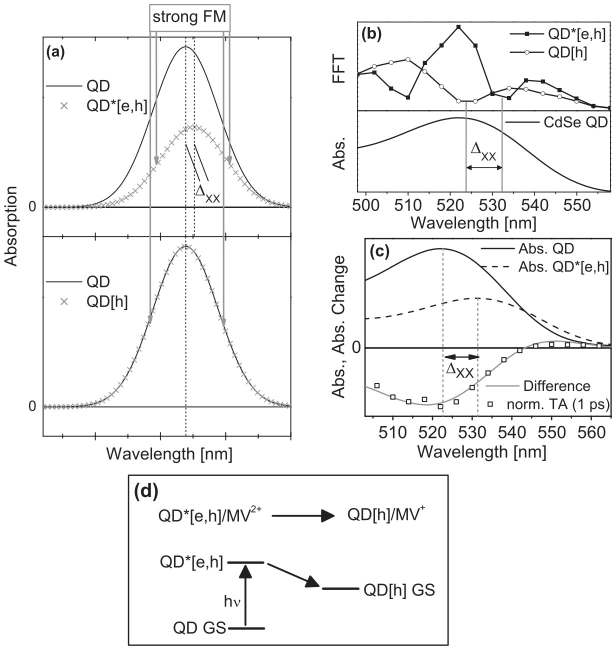

FIG. 3. (a) Schematic representation of the spectral dependence of frequency modulation (FM); Δ_{XX} is the biexciton binding energy. (b) FT amplitudes at $206\ \mathrm{cm}^{-1}$ and different λ_{probe} obtained from FT for isolated CdSe QDs and the CdSe QD/MV^{2+} coupled system (upper graph); absorption of unexcited QD and QD$[e, h]$ (lower graph). (FFT represents fast Fourier transform.) (c) Simple model to estimate the biexciton binding energy Δ_{XX}; the normalized TA signal is reconstructed by the difference of QD linear absorption and a shifted QD $*$ $[e, h]$ absorption. (d) Energy scheme for the CdSe QD/MV^{2+} coupled system. (GS is ground state.)

In Fig. 3(b) a second minimum is observed at $\lambda_{\mathrm{probe}} \approx$ 510 nm for the isolated QDs which may reflect the contribution of another higher lying QD transition. Since the stimulated emission is not observed in transient absorption studies on small QDs, we do not consider its contribution in our further interpretation [6].

The biexciton binding energy in the isolated QDs can also be estimated by a simple model introduced by Klimov [27]. Here the transient signal is calculated from the difference of the QD linear absorption and a shifted absorption spectrum corresponding to the singly excited QD (QD$^*[e, h]$). The extent of the shift is adjusted in such a way that the difference reproduces the transient absorption signal of the isolated QDs at $\tau_{\mathrm{delay}} = 1$ ps. The amplitude of the shifted absorption spectrum is half the amplitude of the linear absorption to account for the twofold degeneracy of the $1S(e)$ state. The results of this procedure are depicted in Fig. 3(c). The obtained maximum of the $\mathrm{QD}^*[e, h]$ spectrum is 532 nm and therefore nicely reproduces our results found for the spectral dependence of the observed LO phonons [cf. Fig. 3(b)].

In a former time-resolved study on oxazine 1, coherent ground-state phonons have already been observed [31]. Here, the ground-state phonons were generated by a two field interaction where the first field generates a wave packet on the excited-state potential energy surface which then starts to propagate. The second field projects the wave packet back to the ground-state potential energy surface where the wave packet continues to propagate. In the case of the $\mathrm{QD}/\mathrm{MV}^{2+}$ coupled system, the photoexcited QD is not transferred back to the ground state by a second field but by the ET reaction to the electron acceptor. Subsequently, the wave packet propagates in the electronic ground state of the QD cation. Therefore, the observed coherence in $\mathrm{QD}[h]$ is triggered by the electron transfer associated ultrafast charge migration. It should be emphasized that in contrast to standard pump-probe studies here the observed phonon is an intrinsic property of the investigated ET system. After photoexcitation of a single $\mathrm{QD}/\mathrm{MV}^{2+}$ couple the ground-state phonon is generated independently of the optical pump pulse. Interestingly, the residual oscillations of the isolated QDs and the coupled system at the same λ_{probe} [Fig. 2(a)] are phase shifted. This phase shift is most probably a consequence of the ET reaction, which converts the photoexcited QD to a positively charged particle in its electronic ground state and thereby induces the ground-state oscillation. Since the ET time in the coupled system is in the range or shorter than one oscillation period ($\approx$ 160 fs), the phase shift cannot be observed during the measurement but is already present at very short delay times. Similar to our results, recent reports have shown that ultrafast charge migration can indeed be a source for coherent phonons [19,35].

For the determination of energy loss channels after photoexcitation of the QD in a QD-based ET system, it is interesting to know how strong the LO phonons are coupled to the ET reaction. The coupling strengths can be quantified by the Huang-Rhys parameter. According to a procedure of Sagar *et al.* [14] the Huang-Rhys parameter can be directly determined by the oscillation amplitude A_{osc} [26]. For both $\mathrm{QD}^*[e, h]$ and $QD[h]$ a Huang-Rhys parameter S_{LO} of 0.012 for the LO phonon can be calculated. Sagar *et al.* found a comparable S_{LO} of 0.016 for CdSe QD with a diameter of $\approx$ 3.1 nm. Our results demonstrate that the coupling strength between the LO phonon and the ET reaction is comparable to the coupling strengths of the phonon to the exciton. Therefore, it can be expected that the ET reaction itself acts as an energy loss channel. The different behavior of the LO and LA phonon after adding the acceptor can possibly be explained by different coupling strengths of the phonons to the ET process.

In conclusion, the results reveal a novel type of vibrational coherence in QD and QD/acceptor systems. Many studies on the ultrafast charge transfer in QD-based ET systems utilize the bleach recovery signals, which are not necessarily exclusively related to the ET. However, the coherent phonons studied in our work are directly connected to the ET product state. A detailed understanding of the coherent coupling between ET and solid-state vibrations could be a prerequisite for the design of more efficient QD-based solar cells.

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