

Coherent phonons in CdSe quantum dots triggered by ultrafast electron transfer

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Abstract. The origin of coherent oscillations in CdSe quantum dots and in the CdSe/methylviologen electron transfer system is studied. In CdSe/methylviologen coherent phonons are triggered by the electron transfer from the quantum dot to methylviologen.

1 Introduction

Due to their unique properties semiconductor quantum dots (QDs) have been under intense study in various application fields such as lasing, microscopy and photovoltaics [1-3]. In a photovoltaic environment, charge extraction from the photoexcited QDs is a main challenge for their applicability. Ultrafast processes such as intraband relaxation and charge trapping can act as energy loss channels after photoexcitation of the QD.

Here we study the correlation between generation of phonons in CdSe QDs and the ultrafast interfacial electron transfer (ET) to the electron acceptor methylviologen (MV^{2+}). Coherent phonons in CdSe QDs have been studied in time domain experiments by ultrafast transient absorption (TA) spectroscopy. In these experiments the longitudinal optical (LO) and the longitudinal acoustic (LA) phonon modes have been observed at $\sim 210\text{ cm}^{-1}$ and $\sim 18\text{ cm}^{-1}$ [4]. Moreover, time domain experiments allow to characterize the ET reaction between photoexcited QDs and suitable acceptors by monitoring the exciton dynamics. Therefore, we conducted TA experiments with femtosecond time resolution ($\sim 40\text{ fs}$) on colloidal CdSe QDs in toluene and on the QD/ MV^{2+} ET system. Our results demonstrate that photoinduced coherent phonons in the pure QDs lead to a frequency modulation of the quantum dot excited-state spectrum. In contrast to that the observed oscillations in the ET system are induced by a chemical fundamental reaction (ET) in the product ground state reflecting the ultrafast nature of the ET [5].

2 Experimental

For the synthesis of CdSe QDs we slightly modified a method introduced by Nordell et al [6]. The particles diameter of 3.1 nm was determined by the spectral position of the lowest excitonic transition ($1S(e)-1S_{3/2}(h)$). Pure QDs and the QD/ MV^{2+} ET system had similar concentrations ($\sim 3 \cdot 10^{-5}\text{ M}$) in toluene. In the preparation of the ET system MV^{2+} (methylviologen dichloride hydrate, Aldrich, purity 98%) was dissolved in methanol and added to the QD colloidal solution. At a molar QD/ MV^{2+} ratio of 1:5 all MV^{2+} molecules are believed to be quantitatively adsorbed on the QD surface since MV^{2+} is poorly soluble in toluene.

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In the time-resolved experiments a pump/probe setup was employed which uses a CLARK CPA 2001 laser/amplifier system as light source operating at a repetition rate of 1 kHz at a central wavelength of 775 nm. Pump pulses at 523 nm were generated with a noncollinear optical parametric amplifier (NOPA) [7]. The excitation energies of the pump pulses were ~ 10 nJ to ensure that the sample contains mainly single excited and nonexcited QDs. According to a published procedure an averaged number of absorbed photons per QD of 0.2 was calculated [8]. White light probe pulses were generated by focusing the laser fundamental into a sapphire crystal.

3 Results and Discussion

Photoexcitation of the QDs occurred at the maximum of the $1S(e)-1S_{3/2}(h)$ transition at 523 nm. Transient traces recorded at the blue side of the $1S(e)-1S_{3/2}(h)$ absorption band ($\lambda_{\text{probe}} = 518$ nm; Figure 1(a)) exhibit instantaneous negative absorption changes due to the population of the $1S(e)$ state (state filling effect) for both samples, the pure QDs and the QD/MV^{2+} ET system. An ultrafast decay of the negative absorption is observed for QD/MV^{2+} as a consequence of an efficient ET to the molecular acceptor MV^{2+} . Since the QD-related TA signals decay nearly completely during the ET reaction it can be concluded that the cationic QD ($\text{QD}[h]$) spectrum is highly similar to the QD ground state spectrum.

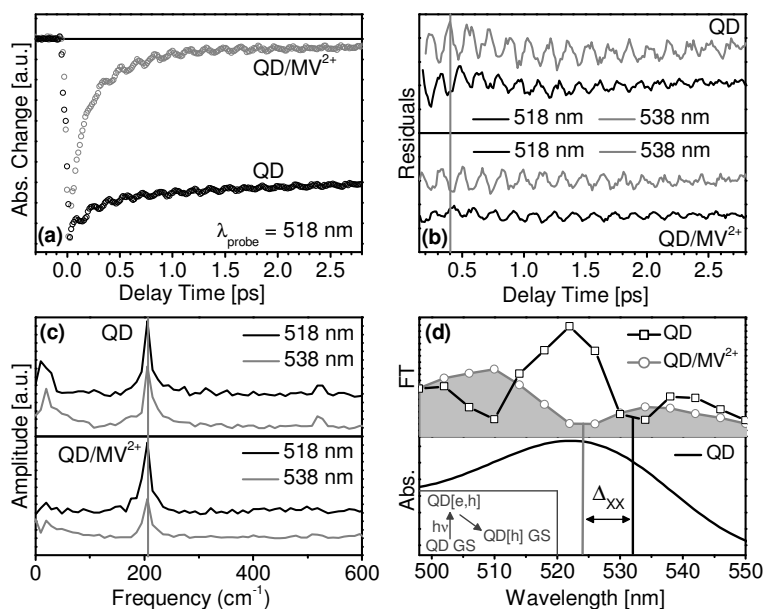


Fig. 1. (a) Transient absorption traces and (b) residual oscillations of CdSe QD and CdSe QD/MV²⁺ after photoexcitation at 523 nm. (c) Fourier transformed data of the residual oscillations. (d) Fourier transformed amplitudes at 206 cm⁻¹ and different λ_{probe} . Inset: reaction scheme for CdSe QD/MV²⁺ (GS denotes electronic ground state).

The decay of the QD-related TA signals could be described satisfactorily with a model function consisting of a sum of two exponentials convoluted with a Gaussian. We obtained an amplitude weighted average time constant for the ET reaction of ~ 100 fs. In contrast, the negative TA signal detected for the pure QDs has weak decay dynamics indicative for a very slow exciton recombination process. Furthermore, the transient traces in Figure 1(a) show significant oscillation patterns. In the ET system the oscillations are still present after the ET reaction. The subtraction of the electronic contribution of the TA signal led to the residuals shown in Figure 1(b). For both

samples, the residuals exhibit a phase shift of π going from the blue side ($\lambda_{\text{probe}} = 518 \text{ nm}$) to the red side ($\lambda_{\text{probe}} = 538 \text{ nm}$) of the $1S(e)-1S_{3/2}(h)$ absorption band. Therefore, we conclude that the observed coherent phonons modify the electronic level structure of the QDs leading to a frequency modulated dynamic spectrum.

Fourier transformation (FT) of the residuals in Figure 1(b) resulted in the FT data depicted in Figure 1(c). A dominant mode at 206 cm^{-1} and a low frequency mode at 19 cm^{-1} is detected for the pure QD. The two modes have been observed in earlier time resolved studies on colloidal CdSe QD and were assigned to the LO and LA phonon [4]. The FT data for the QD/MV²⁺ ET system also exhibit the LO phonon at 206 cm^{-1} whereas the low frequency mode is suppressed.

Interestingly, the spectral dependence of the phonon amplitude is significantly different in the samples under investigation (cf. Figure 1(d)). In general strong frequency modulation of the TA signal can be expected, where the slope in the absorption spectrum of the oscillating species is large. For CdSe/MV²⁺ a minimum in the FT amplitude spectrum at 206 cm^{-1} is observed at 524 nm which is nicely correlated with the QD absorption maximum (which is equivalent to a minimum slope). Stronger FT amplitudes are observed in the spectral region where the slope in the absorption spectrum is large. Therefore, we conclude that the LO phonon modulates the QD[h] ground state spectrum. In the FT amplitude spectrum of pure QDs the minimum is red shifted and now appears at 532 nm . The shift demonstrates, that the $1S(e)-1S_{3/2}(h)$ absorption band undergoes a biexcitonic level shifting of 8 nm . Therefore, we conclude that the LO phonon modulates the QD excited-state spectrum of the pure QD. From the biexcitonic level shifting we calculate a biexciton binding energy of 35 meV . Interestingly, a phase shift between the oscillations measured for pure QD and for QD/MV²⁺ at the same probe wavelength is observed (cf. Figure 1(b)). It indicates, that coherent oscillations are triggered differently, namely by photoexcitation in the case of pure QDs and by the ultrafast ET reaction in QD/MV²⁺ (cf. reaction scheme in Figure 1(d)).

4 Conclusions

TA experiments on colloidal CdSe QD revealed that coherent phonons lead to frequency modulation of the QD excited-state spectrum. In contrast, the LO phonon modulates the QD[h] ground state spectrum in the CdSe QD/MV²⁺ ET system. The coherent LO phonon in the electronic ground state of the cationic QD is triggered by the ET associated ultrafast charge migration. We conclude that the observed LO phonon is an intrinsic property of the investigated ET system and therefore independent of the characteristics of the optical pump pulse.

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