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Biexciton effects in femtosecond nonlinear transmission of semiconductor quantum dots

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The dynamics of carrier-induced absorption changes in CdSe quantum dots are investigated with femtosecond spectroscopy. After excitation with 4-eV photons a redshift of the lowest optical transition is observed in the initial phase of carrier relaxation. This shift is attributed to a biexciton effect where two electron-hole pairs interact via the Coulomb potential.

Semiconductor nanocrystals (NC's) with dimensions in the order of the bulk exciton Bohr radius or less can be treated as quasi-zero-dimensional objects or quantum dots. The three-dimensional quantum confinement leads to a significant modification of the energy spectrum of the material. The quasicontinuous spectrum of the bulk semiconductor is replaced by a discrete spectrum of a particle in a quantum box. In the theoretical model of Efros and Efros[1] the electron energy spectrum and optical transition probabilities were calculated for a spherical NC with an infinite potential barrier by using the effective mass approximation applied to a two-band semiconductor with parabolic and isotropic valence and conduction bands. This oversimplified approach has been modified substantially during the last years to include finite-well[2,3] and image-charge[3,4] effects, Coulomb interaction,[5–7] nonparabolicity of the conduction band,[8,9] and confinement-induced mixing of valence subbands.[6,9,10]

The study of energy structure in NC's by methods of linear spectroscopy is complicated by strong inhomogeneous broadening of optical transitions arising from broad size and shape distribution of NC's in the samples available. In contrast, the discrete structure of optical transitions can be well resolved in nonlinear transmission or photoluminescence excitation spectra[11–15] due to selective excitation of NC's of a certain size.[16,17]

The mechanisms for optical nonlinearities leading to pronounced photoinduced absorption changes in NC's are a subject for intense theoretical and experimental studies. Nonlinear transmission spectra of NC's are usually dominated by strong bleaching of one-pair resonances attributed to the state filling[11–13] or/and to the trapped-carrier-induced Stark effect.[15] Coulomb interaction has a significant influence on the nonlinear absorption in NC's, since it may lead to a modification of the dipole selection rules and to a shift of the energy levels of the one- and many-electron-hole-pair states.[5–7] In particular, two-electron-hole-pair interaction (biexciton effect) leads to an energy shift of the optical transitions from one- to two-pair states. The energy of two-pair interaction can be treated as biexciton binding energy $\delta E_2 = 2E_1 - E_2$, where E_1 and E_2 are the energies of the one- and two-pair states, respectively. Theoretical studies show that quantum confinement leads to a significant increase of the biexciton binding energy with respect to bulk semiconductors.[7,17,18]

Biexciton states can be observed experimentally as additional resonances in the absorption spectra of the excited samples. In particular, the increased absorption above exciton resonance can be explained in terms of transitions involving excited-state biexcitons.[13,18] These transitions are not allowed without Coulomb interaction and can only be observed due to Coulomb-potential-induced modification of the dipole selection rules.

The excitation of the ground-state biexciton should lead to an induced-absorption feature below the lowest one-pair transition. The observation of this effect is usually complicated by the strong broadening of the quantized levels and by the state-filling-induced bleaching of the one-pair transitions. The biexciton ground state has been observed recently in low-temperature ($T = 15$ K) nonlinear-transmission spectra of CdSe quantum dots by a modified pump and probe method with an additional third "saturating" beam tuned below the pump spectral energy.[17] These measurements allowed the estimation of the biexciton binding energy which was much higher than in the bulk material, which is in agreement with theoretical predictions.[7,17,18]

In the present paper we report on the observation of the biexciton state in room-temperature femtosecond nonlinear transmission spectra of CdSe NC's excited well above the energy of the lowest optical transition. The effect of the two-pair interaction is clearly observed as a transient redshift of the lowest optical transition at the initial stage of carrier relaxation, when the corresponding levels are not occupied with electrons and holes. From the measured nonlinear transmission spectra the two-pair interaction energy (biexciton binding energy) is derived.

The samples under investigation are thin plates (thickness $d = 280$ μm) prepared from commercially available CdS_xSe_{1-x} doped glass KC-19. Raman spectra of the samples exhibit only the CdSe-related LO-phonon peak. Therefore, the samples are considered as doped with pure CdSe. Transmission electron microscopy (TEM) examination indicates an average radius of CdSe NC's of about 5.7 nm which is close to the bulk-exciton radius in CdSe.

Time-resolved nonlinear transmission spectra are measured by using a standard femtosecond pump and probe technique. The samples are excited by femtosecond pulses obtained by frequency doubling of amplified pulses from a colliding pulse mode-locked laser. The duration of the 4-eV excitation pulse is 80–100 fs. Pump-induced transmission

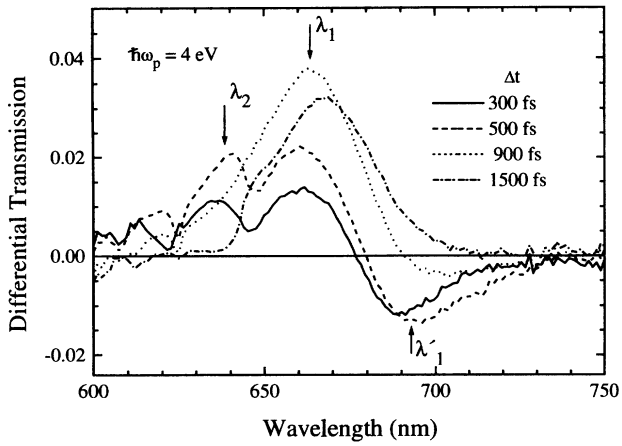

FIG. 1. DTS of the CdSe NC's ($T=300$ K) at different delay between pump and probe pulses.

changes are probed by delayed pulses of a femtosecond continuum. An optical multichannel analyzer is used to measure differential transmission spectra (DTS) $=(T-T_0)/T_0$, where T_0 and T are the transmission spectra of the unexcited and excited sample, respectively. The measurements are performed at room temperature.

Figure 1 shows that the DTS recorded between 200 and 800 fs after excitation exhibit three well-resolved features: two bleaching bands at $\lambda_1=660-670$ nm and $\lambda_2=635-640$ nm, and one band of induced absorption at $\lambda_1'=690-700$ nm. In Fig. 2 the temporal evolution of the changes of optical density, $-\Delta\alpha d$, derived from the DTS for different bands are shown. The bands λ_2 and λ_1' are characterized by extremely fast dynamics. Their amplitudes increase within the first 400–500 fs after excitation and then decay during the next 500–600 fs. The band λ_1 reaches a maximum at delay of about 800–900 fs, i.e., after the decay of the bands λ_1' and λ_2. The exponential relaxation time of the λ_1 band is about 2.5 ps. For comparison, in DTS recorded after excitation with 2-eV photons, the λ_1 bleaching occurs at low excitation fluence, while both bleaching bands (λ_1 and λ_2) are seen at higher pump intensity. However, the band λ_1' of increased absorption is not observed.[19]

We believe that the measured absorption changes can be explained by state filling and two-electron-hole-pair interaction. We have analyzed the possibility of other mechanisms for nonlinearity, for example, of trapped-carrier-induced Stark effect reported in Ref. 15. The latter effect results in a synchronous shift of all optical transitions and is characterized by a slow relaxation dynamics on the microsecond time scale.[15] This is not consistent either with the intensity dependence of the DTS (Ref. 19) or with the fast picosecond dynamics of absorption changes measured in our samples (see also Ref. 11).

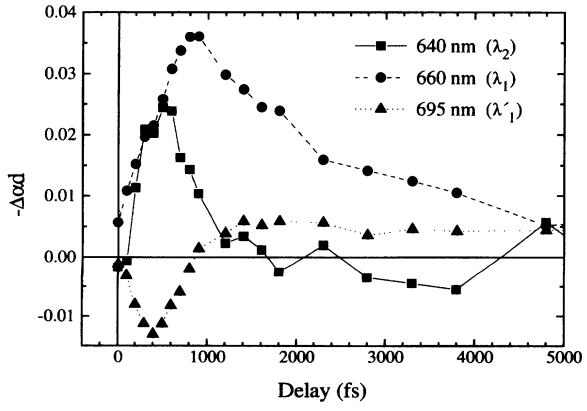

FIG. 2. Time dependence of the induced absorption changes at the maxima of the λ_1, λ_2, and λ_1' bands in the DTS.

We attribute the long-wave bleaching band λ_1 to the state-filling-induced saturation of the lowest optical transition $1s_e$-$1s_{h,3/2}$. The notations used for the electron and hole states are similar to those introduced in Refs. 9 and 10 and have the general form nL_e and $nL_{h,F}$, where L is the orbital momentum of the envelope wave function (for the hole state L is a minimum orbital momentum included in the wave function; the other one is $L+2$), F is the total momentum of the hole wave function, and n is the number of the state of the given symmetry. The pump-intensity dependence of the DTS recorded under 2-eV excitation[19] shows that the amplitude of the band λ_2 increases with excitation density after the saturation of the band λ_1 is already achieved. This indicates that the states involved in the transition associated with the λ_2 band are different from those associated with the λ_1 band ($1s$ electron and $1s_{3/2}$ hole states). The second electron state is the $1p$ state. It is only coupled to $1p$ hole states. The lowest and most intense of the corresponding optical transitions is $1p_e$-$1p_{h,3/2}$.[9] This transition can be attributed to the bleaching band λ_2 in the recorded DTS. The assignment made is consistent with calculations in Ref. 9 for transitions energies. When it is considered that the energy separation between transitions under consideration is determined mainly by the electron energies (the contribution from the difference in the hole energies is less than 10%) (Ref. 9) one obtains a NC radius of about 6 nm for the measured spacing of 99 meV between the λ_1 and λ_2 bands. This estimation is in agreement with data of TEM examination (see above).

The induced absorption below the λ_1 band recorded at small delay between pump and probe pulses indicates a redshift of the lowest transitions which we attribute to the Coulomb two-pair interaction. The observed dynamics of the DTS can be explained in the following way. The excitation photon energy exceeds by far the energies of the transitions $1s_e$-$1s_h$ and $1p_e$-$1p_h$ (here and in what follows we omit the $F=3/2$ index in the notation for the hole state). Therefore, at the initial stage of the energy relaxation, the $1s$ and $1p$ states are not occupied with carriers. From investigations of the excitation density dependence of the DTS and from the data shown, an average number of electron-hole pairs per NC less than one is estimated. During the energy relaxation the carriers (an electron and/or a hole) reach initially the respective $1p$ state saturating the $1p_e$-$1p_h$ transition. This is observed as the λ_2 bleaching band in the DTS. The two-pair interaction results in a shift of the energies for creation of a second electron-hole pair including a pair in the $|1s_e,1s_h\rangle$ state. This manifests itself as a bleaching in the range of the lowest resonance (band λ_1) and the increased absorption below it (band λ_1'). The relaxation of the carriers to the lowest $1s$ states causes the fast decay of the λ_2 and λ_1' bands and an increasing amplitude of the λ_1 band by state filling. Due to the large line width of the transitions, the latter effect results

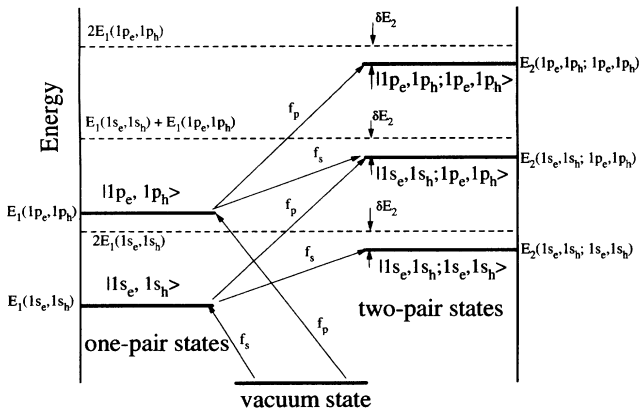

FIG. 3. The six-level model used to calculate the induced absorption changes. The arrows show the six dipole-allowed transitions coupling vacuum, two one-pair, and three two-pair states.

in the suppression of the increased absorption below lowest resonance. Thus, the DTS recorded at small delay between pump and probe pulses ($\Delta t<300-400$ fs) can be described by absorption changes caused by the occupation of the $1p_e$ and/or $1p_h$ states (the lowest $1s$ states remain empty). The DTS at long delay ($\Delta t>1$ ps) correspond to the final occupation of the $1s_e$ and/or $1s_h$ states.

The changes in the susceptibility resulting from the state filling and the Coulomb two-pair interaction in the presence of the electron-hole pair occupying the $|i_e',j_h'\rangle$ state (symbols i' and j' denote the sets of electron and hole quantum numbers, respectively) are given by

$$\Delta\chi\propto\sum_{i,j} f_{ij}\left[\frac{\delta_{ii'}+\delta_{jj'}}{\hbar\Delta\omega_{ij}+i\Gamma_{ij}} + \frac{(1-\delta_{ii'})(1-\delta_{jj'})\,\delta E_2(ij,i'j')}{(\hbar\Delta\omega_{ij}+i\Gamma_{ij})[\hbar\Delta\omega_{ij}+\delta E_2(ij,i'j')+i\Gamma_{ij}]}\right], \quad (1)$$

where $\hbar\Delta\omega_{ij}=\hbar\omega-E_{ij}$, E_{ij} and f_{ij} are the energy and oscillator strength of the optical transition resulting in the creation of the electron-hole pair in the $|i_e,j_h\rangle$ state, Γ_{ij} is the broadening of this transition, $\delta E_2(ij,i'j')$ is the interaction energy of the pairs in the $|i_e,j_h\rangle$ and $|i_e',j_h'\rangle$ states, and $\delta_{ii'}$ is the Kronecker symbol ($\delta_{ii'}$ is equal to one if $i=i'$ and to zero otherwise).

The measured DTS are modeled by taking into account the dipole-allowed transitions coupling vacuum state, two one-pair states $|1s_e,1s_h\rangle$ and $|1p_e,1p_h\rangle$ and three two-pair states $|1s_e,1s_h;1s_e,1s_h\rangle$, $|1s_e,1s_h;1p_e,1p_h\rangle$, and $|1p_e,1p_h;1p_e,1p_h\rangle$ which are schematically depicted in Fig. 3. The same broadening Γ_0 for all transitions and the same value of the interaction energy δE_2 (biexciton binding energy) for all two-pair states under consideration are assumed (the latter assumption will be discussed below). The spectra of absorption changes $\Delta\alpha$ caused by the occupation of either the $|1s_e,1s_h\rangle$ one-pair state $[\Delta\alpha_{1s}(\hbar\omega)]$ or the $|1p_e,1p_h\rangle$ state $[\Delta\alpha_{1p}(\hbar\omega)]$ are calculated by using Eq. (1) and summarized in Fig. 4.

The calculated spectra $\Delta\alpha_{1s}$ are less sensitive to the ratio $\eta=\delta E_2/\Gamma_0$ than the spectra $\Delta\alpha_{1p}$. The amplitude of the bleaching peak in the spectra $\Delta\alpha_{1s}$ attributed to the saturation of the lowest one-pair transition is practically independent of η. The two-pair interaction manifests itself as increased absorption below the $1s_e$-$1s_h$ resonance only for $\eta>1.1$. At smaller η the increased absorption is suppressed by the bleaching of the lowest one-pair transition through state filling. In contrast, the increased absorption in the spectra $\Delta\alpha_{1p}$ is observed at much lower values of η ($\eta>0.02$), and its magnitude rapidly increases with increasing η. Thus, the modeling shows that the effect of the two-pair interaction can be observed much easier in the DTS of NC's with the carriers occupying the excited rather than the ground one-pair state. This is consistent with the interpretation of the experimental data given above.

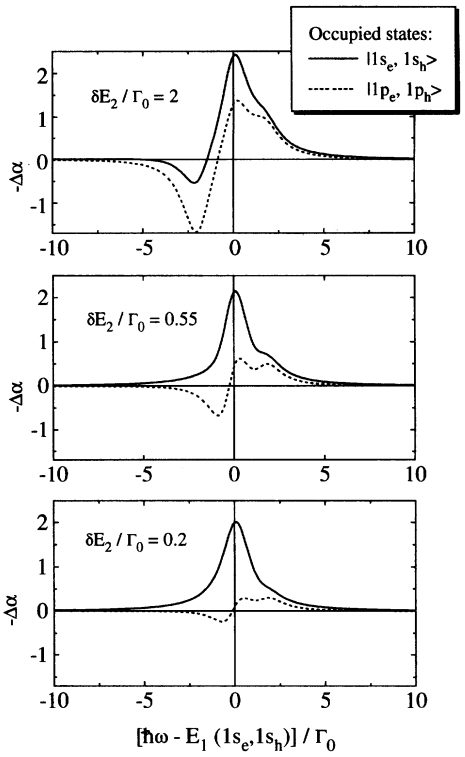

FIG. 4. Calculated absorption changes resulting from the occupation of either the $|1s_e,1s_h\rangle$ state (solid line) or the $|1p_e,1p_h\rangle$ state (dashed line) for different values of the ratio $\delta E_2/\Gamma_0$. The separation between two lowest one-pair transitions $\Delta E_{1s,1p}=E_1(1p_e,1p_h)-E_1(1s_e,1s_h)$ is taken as 1.7 Γ_0 (derived from the measured DTS).

We have used the calculated spectra $\Delta\alpha_{1s}$ and $\Delta\alpha_{1p}$ to fit the measured DTS at small ($\Delta t<400$ fs) and large ($\Delta t>1$ ps) delays, respectively, as shown in Fig. 5. The parameters involved in the fitting procedure are the energies of the one-pair transitions $E_1(1s_e,1s_h)$ and $E_1(1p_e,1p_h)$, the oscillator strengths f_s and f_p for the transitions resulting in the creation of the electron-hole pairs in the $1s$ and $1p$ states, respectively (see Fig. 3), the broadenings of the transitions Γ_0 and the two-pair interaction energy δE_2. The energies $E_1(1s_e,1s_h)$ and $E_1(1p_e,1p_h)$ are chosen as corresponding to the spectral positions of the λ_1 and λ_2 bleaching band, respectively. The broadening is obtained by fitting the DTS recorded at relatively long delay ($\Delta t\approx 1$ ps) with the spectrum $\Delta\alpha_{1s}$ which has been shown to be not strongly dependent of the interaction energy δE_2. The ratio of the oscillator strengths f_s and f_p is determined by comparison of the amplitudes of the bleaching bands λ_1 and λ_2 in the DTS at

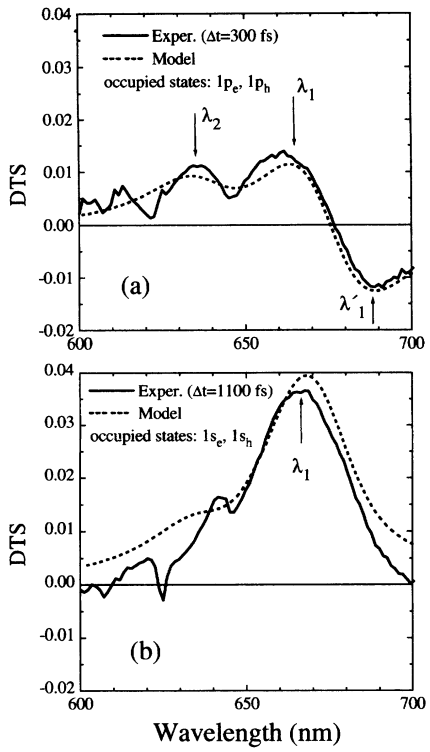

FIG. 5. Comparison of measured (solid line) and calculated (dashed line) DTS asuming the occupation of either excited (a) or ground (b) one-pair state.

small delays ($\Delta t<400$ fs) with the amplitudes of the respective bands in the spectra $\Delta\alpha_{1p}$. The value of δE_2 is determined by comparison of the calculated amplitudes for the induced absorption in $\Delta\alpha_{1p}(\hbar\omega)$ and the bleaching in $\Delta\alpha_{1s}(\hbar\omega)$ with the corresponding amplitudes in the measured DTS. As shown above this ratio is very sensitive to the value of δE_2. By this fitting procedure we find $\delta E_2=2\epsilon_x$, $\Gamma_0=3.6\epsilon_x$, $E_1(1s_e,1s_h)-E_g=6.2\epsilon_x$, $E_1(1p_e,1p_h)-E_g=12.4\epsilon_x$, $f_p=0.1f_s$, where $\epsilon_x=16$ meV and $E_g=1.751$ eV are the exciton binding energy and the band gap energy in bulk CdSe, respectively.

Notice that although three different two-pair interaction energies $\delta E_2(1s_e,1s_h;1s_e,1s_h)$, $\delta E_2(1s_e,1s_h;1p_e,1p_h)$, and $\delta E_2(1p_e,1p_h;1p_e,1p_h)$ are included in the expressions for spectra $\Delta\alpha_{1s}$ and $\Delta\alpha_{1p}$ (these energies have been assumed as equal to each other) the experimental data and the fit give in fact only one interaction energy, namely, that for the pairs in the $|1s_e,1s_h\rangle$ and $|1p_e,1p_h\rangle$ states. Two other interaction energies only have a little effect on the calculated spectra and cannot be derived by the fitting procedure.

The obtained value of δE_2 is much higher than the biexciton binding energy in bulk CdSe,[20] indicating a strong attractive interaction of the electron-hole pairs in NC's. This is in agreement with calculations in Refs. 7, 17, and 18. These calculations show that the interaction energy of the pairs in $1s$ states in NC's with a radius of about the bulk-exciton radius in CdSe is in the order of the bulk-exciton binding energy. A large value of the interaction energy derived from the recorded DTS is consistent with measurements in Ref. 17 which give for δE_2 a value in the range from $0.8\epsilon_x$ to $1.4\epsilon_x$ depending of the average radius of NC's. At the same time, it should be noted that interaction energy determined in Ref. 17 is associated with the $|1s_e,1s_h;1s_e,1s_h\rangle$ state while the value measured in the present paper is related to the biexciton in the $|1s_e,1s_h;1p_e,1p_h\rangle$ state.

In conclusion, we have studied the dynamics of nonlinear transmission of CdSe quantum dots excited by femtosecond pulses well above the energy of the lowest optical transition. The spectra of absorption changes recorded at small delay between pump and probe pulses exhibit induced absorption below the lowest one-pair resonance. This is explained by the energy shift of the transitions from one- to two-electron-hole-pair states caused by the two-pair Coulomb interaction. The nonlinear transmission at larger delay is dominated by state-filling-induced bleaching of the lowest one-pair transition. The DTS at small and large delays, respectively, can be well reproduced by calculated spectra assuming occupation of either the excited or ground one-pair states. From this modeling we obtain a value of the two-pair interaction energy of 32 meV.

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