Biexciton versus Exciton Lifetime in a Single Semiconductor Quantum Dot

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(Received 20 July 1999)

The decay characteristics of excitons and biexcitons in one single semiconductor quantum dot (QD) are directly monitored using time- and spatially resolved photoluminescence spectroscopy. The experiments are performed on a CdSe/ZnSe QD, occupied by either one or two excitons at a time, allowing a direct comparison between the radiative lifetime of a biexciton and an exciton confined in the same QD. The rather surprising result of comparable recombination rates for both states is related to the spatial wave function distribution and the spin structure of the particles and their coupling to the photon field, i.e., the superradiance effect.

PACS numbers: 78.47.+p, 42.50.Ct, 73.20.Dx, 78.66.Hf

In solid state physics, the recombination of biexcitons (B), which can be regarded as an entity of two weakly bound excitons (X), is often discussed in a simple way of argumentation: The recombination of any of the two excitons forming the biexciton will result in its disappearance. Therefore one would expect that the biexciton lifetime, τ_2, is about half of that of the exciton, τ_1. However, although seeming intuitively convincing, this pedestrian point of view does not take into account a number of elementary points. For example, a direct radiative recombination into the ground state of the crystal, allowed for the exciton state, is optically forbidden for singlet biexcitons. Furthermore, the spin structure and the Coulomb interaction of the electrons and the holes forming the excitons and the biexcitons has to be considered. In order to discuss the coupling of an excited state of a crystal, e.g., the exciton state, to a radiation field, the concept of superradiance has to be included: If a set of 2-level systems, separated by less than the wavelength of light, are coupled to a common radiation field, the corresponding decay rate is expected to be significantly enhanced with respect to a single system. This concept was introduced by Dicke [1] already in 1954 and, only recently, two-ion superradiance has been reported from investigations of the spontaneous emission of two trapped ions [2]. In a solid, a macroscopic number of atoms are "trapped" by the interatomic interaction in a regular lattice and the radiative recombination of both single excitons and excitons "localized" in a biexciton is expected to be strongly influenced by their coherence volume [3,4]. Thus, from a theoretical point of view, a deviation from $\tau_1/\tau_2 = 2$ is expected [4,5].

In bulk or quantum wells (QWs), usually a decay time of the biexciton signal is measured, which is indeed about half of the exciton one [6,7]. However, it has to be emphasized here that this does not reflect the ratio of the radiative lifetimes, τ_2/τ_1, but is related to the fact that the exciton-biexciton system is close to thermal equilibrium and the decay time in such systems is controlled by the interplay between formation and dissociation of biexcitons [6–8]. In QWs with strong potential fluctuations, in contrast, thermal equilibrium cannot be established, resulting in a deviation from this behavior [9,10]. On the other hand, an artificially designed quantum dot (QD) with $d \approx a_X$ provides a three-dimensional (3D) confinement of excitons and biexcitons. Hence, the biexciton dissociation into a pair of excitons and, vice versa, the molecule formation from two free excitons is suppressed, giving access to the radiative recombination of biexcitons.

In order to permit an unequivocal measurement of the lifetime of both quasi-0D biexcitons and excitons in the same QD, the experiments have to be performed on one single quantum dot (SQD). Optical studies on SQDs have attracted large interest recently, allowing a sophisticated insight into various basic properties of solid state QDs [11–17]. However, despite the fundamental interest in the coupling between interacting 2-level systems and the radiation field, experimental studies of the relation between the radiative lifetimes of X and B states in the same SQD have to our knowledge not been performed up to now.

We present time-resolved photoluminescence (PL) measurements on one SQD, where only the ground state is occupied by either one or two excitons. For the experiments, we choose CdSe/ZnSe QDs, a material with a large excitonic Rydberg, thus ideally suited to study the B dynamics in semiconductor QDs. The kinetics of the X and the B emission is described quantitatively by introducing a statistical model which takes into account the discreteness of the number of excitons in the dot. This provides a unique opportunity to compare the radiative lifetime of quasi-0D biexcitons and excitons in the same QD, giving access to the impact of the spatial wave function distribution and the spin structure of the particles and the dipolar superradiance effect on the radiative lifetime of single- and two-exciton states in a SQD.

The samples under investigation consist of a thin CdSe layer (nominal thickness = 1 monolayer) embedded in ZnSe barriers, grown by migration enhanced epitaxy on a GaAs substrate [18]. High resolution transmission electron microscopy measurements demonstrate the formation of CdSe-rich islands with a diameter $d \approx 10$ nm, i.e., comparable to the exciton diameter. The average height of about 1 nm is much less than the Bohr radius, a_X [19]. The 3D confinement of excitons in such islands has been demonstrated by PL spectroscopy and optical gain studies [19,20]. In order to select a SQD, small mesas with diameters down to 50 nm were prepared by electron beam lithography and wet chemical etching [19]. Low temperature ($T = 2$ K) time-integrated and time-resolved PL spectroscopy on SQDs were performed using a frequency doubled Ti:sapphire laser with a pulse length of 1.5 ps and a repetition rate of 82 MHz as excitation source. The PL signal is dispersed by a 0.32 m monochromator and recorded either time resolved by a streak camera with an S20 cathode or time integrated by a LN_2 cooled CCD camera. The spectral resolution is about 0.7 meV and 1.5 meV for the time-integrated mode and the time-resolved mode, respectively, and an overall time resolution of about 50 ps was obtained.

Because of the small mesa size, we have been able to select mesas with only one individual QD; i.e., any interaction between particles in different QDs is suppressed. In Fig. 1, transient PL spectra of one SQD are depicted for an excitation flux of $\Phi = 4.0\ \mu\mathrm{J\,cm^{-2}}$. The spectra consist of the emission of the single exciton (X) at $E = 2.690$ eV and the biexciton transition (B) at $E = 2.6715$ eV. The origin of the two lines has been checked carefully by density and polarization dependent experiments [14]. The large separation between the two peaks X and B, which amounts to $\Delta E_{XB} = 18.5$ meV, originates partly from the Coulomb interaction between the two excitons in the QD and partly from the exchange interaction in the single exciton state. No transient change of the line shape and the emission energy for the lines X and B is observed, indicating the absence of any marked filling of excited states [15].

However, as can be seen more clearly in Fig. 2, the relative contribution of the X and B peaks changes characteristicly with increasing time. While the rise time of the B line (<50 ps) is limited by the time resolution of the setup, its decay is monoexponential with a time constant of 310 ps. In contrast, the onset of the X line is significantly delayed, resulting in a "plateaulike" characteristics of the exciton decay curve. This behavior is in contrast to what is usually observed in bulk or high quality QWs, where biexcitons are formed by combining two excitons [7,9] and the onset of the biexciton rather than the exciton emission is delayed.

In order to describe the X and B dynamics quantitatively, one has to take into account (a) the 3D confinement, (b) the discrete number of excitons (0, 1, or 2) that are allowed in the QD because of the Pauli principle, and (c) the fact that the final state of the B recombination is

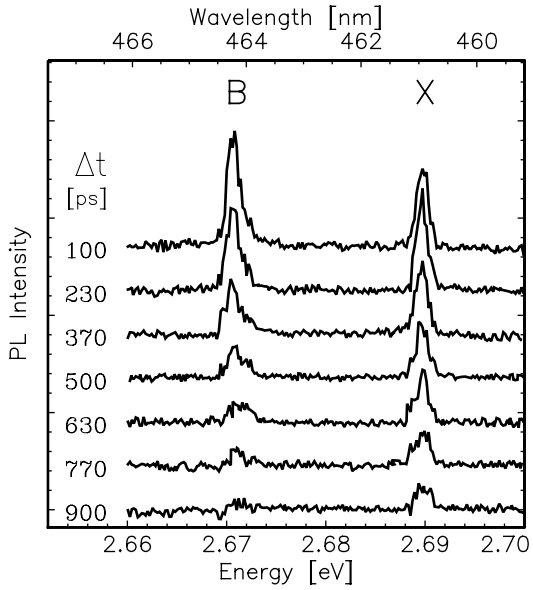

FIG. 1. Transient PL spectra of one single CdSe/ZnSe quantum dot including single exciton (X) and biexciton (B) emission. The excitation flux was $\Phi = 4.0\ \mu\mathrm{J\,cm^{-2}}$.

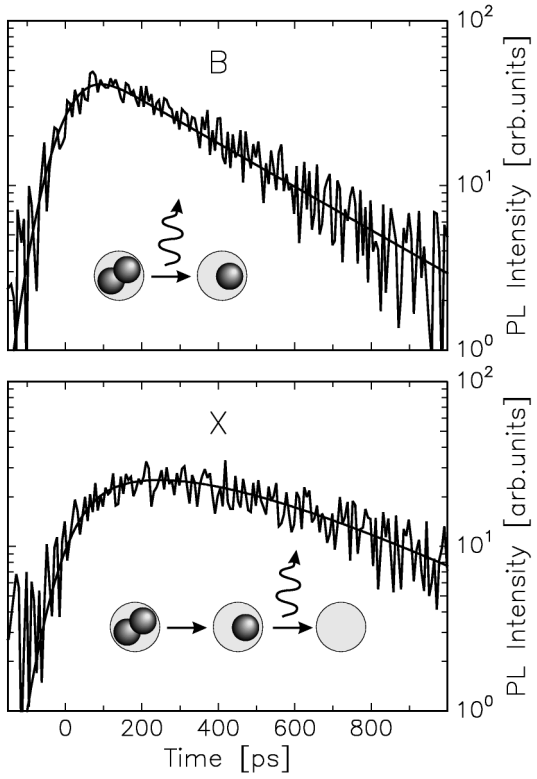

FIG. 2. Decay characteristics of the single exciton (X) and the biexciton (B) transition. The solid lines represent model calculations as discussed in the text.

an optically allowed (bright) exciton state. Because of exchange interaction, the excitons are split into optically allowed (bright, $X^\star$) states with spin $J = \pm 1$ and optically forbidden (dark, X^o) states with spin $J = \pm 2$. The spin flip time between $X^\star$ and X^o states, τ_{1s}, is expected to be in the range of several ns, i.e., much longer than the bright exciton lifetime [21].

Although in the present experiments the excitation was performed above the ZnSe barrier band gap, neither a PL signal from the ZnSe barrier nor from any embedding CdZnSe layer is observed. This indicates an efficient carrier capture into the SQD and a relaxation into the dot ground state occurring on a time scale much less than our time resolution of 50 ps. Therefore these relaxation processes can be neglected in our calculations. Moreover, neither biexciton formation nor biexciton dissociation have to be taken into account due to the 3D confinement in the QD. This results in an elegant analytical expression for the time evolution of the probabilities for the population of the B and X states, w_2 and w_1, respectively:

$$\frac{dw_2}{dt} = -\frac{w_2}{\tau_2}, \qquad \frac{dw_1}{dt} = -\frac{w_1}{\tau_{1t}} + \frac{w_2}{\tau_2} \tag{1}$$

with $1/\tau_{1t} = 1/\tau_1 + 1/\tau_{1s}$, where τ_1 and τ_2 are the $X^\star$ and the B radiative recombination times, respectively. Here we have taken into account that radiative transitions from the two exciton states are allowed only into the bright exciton state of the QD.

Solving this equation system, the X and B dynamics can be described quantitatively (see solid lines in Fig. 2). As can be seen from Eqs. (1), the decay of the line B directly reflects the radiative lifetime of the two exciton state. By fitting the experimental curve we obtain $\tau_2 = 310$ ps. For the single exciton state, $\tau_{1t} = 290$ ps is extracted from our data, which includes both, the $X^\star$ radiative lifetime τ_1 and its spin flip time τ_{1s}, into the dark state [22]. In order to separate these two contributions, density dependent experiments have been performed. Figure 3 displays the time-integrated intensity ratio of the B and the X lines, I_B/I_X, as a function of the excitation flux Φ. In the low excitation limit, the QD occupation probability is low; i.e., the dot is either unoccupied or occupied by one electron-hole pair per laser pulse, resulting in an emission spectrum controlled by the single exciton (see inset of the figure). With increasing excitation flux Φ the B line appears, rising superlinearly in intensity.

The linear dependence of $I_B/I_X(\Phi)$ obtained for low Φ saturates at high excitations. The value of $I_B/I_X = 1$ in the high excitation limit originates from the suppression of the recurring process: the QD is occupied by two excitons for each excitation cycle, and each biexciton recombination creates a single exciton, subsequently recombining without being able to form again a biexciton.

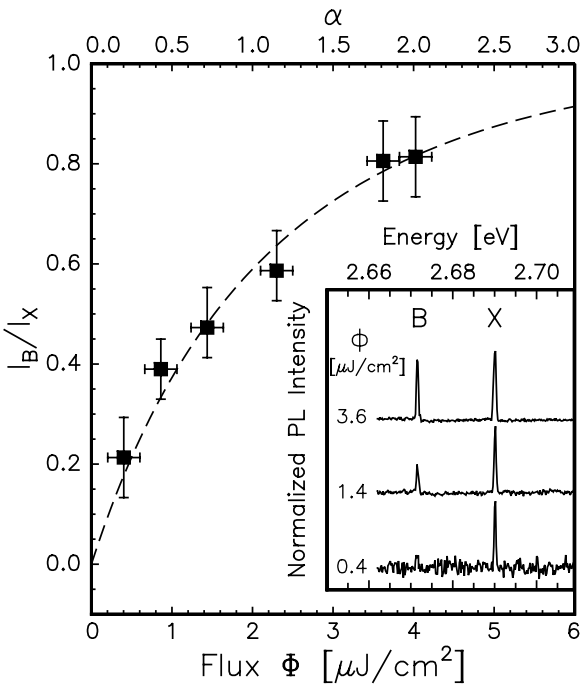

FIG. 3. Ratio of the time-integrated intensity I_B/I_X as a function of the excitation flux Φ. Experiment: symbols; theory according to Eqs. (2): dashed line. In the inset, time-integrated PL spectra are depicted for different Φ.

For a quantitative description of $I_B/I_X(\Phi)$, we have used a statistical treatment [8,23], taking into account the accumulation of the data over several minutes, i.e., several billions of subsequent laser pulses. Assuming a Poisson distribution for the number of electron-hole pairs generated for subsequent laser pulses, we obtain the probability $w_{i0}(\Phi)$ $(i = 0, 1, 2)$ that the QD is initially occupied by either zero, one, or two excitons:

$$w_{00} = e^{-\alpha}, \quad w_{10} = \alpha e^{-\alpha}, \quad w_{20} = 1 - w_{00} - w_{10}, \tag{2}$$

where α corresponds to the average number of electron-hole pairs per excitation pulse created within the QD capture cross section; i.e., α is proportional to Φ.

The dashed line in Fig. 3 shows that the calculated dependence $I_B/I_X(\Phi)$ describes the experimental data rather well [24]. According to Eqs. (1) and (2), the ratio I_B/I_X should reach $(\tau_{1s} + \tau_1)/\tau_{1s}$ in the limit of high excitation. From the fact that the experimental value of I_B/I_X approaches 1, one can deduce that the $X^\star$ radiative lifetime τ_1 is much shorter than its spin relaxation time τ_{1s} into the dark state. This leads to the remarkable result of $\tau_1 \approx \tau_{1t} = 290$ ps, i.e., a radiative exciton lifetime which is comparable to the biexciton one $\tau_2 = 310$ ps. Hence, the ratio τ_1/τ_2 is strongly different from the commonly accepted value of 2.

In general, τ_1/τ_2 depends on both the spin structure of the X and B states and their spatial wave functions which

govern the coupling to the photon field, i.e., the dipolar superradiance effect. Taking into account these effects, we have calculated the radiative lifetimes of excitons and biexcitons considering the finite extension of the QDs. Because of numerical limitations, calculations on biexcitons, which include the full geometry of the QDs, are hardly accessible. Thus, in order to demonstrate the basic physics behind the biexciton recombination process, an asymmetric QD with $L_Y, L_Z < a_X$ was assumed as a first approximation. The lateral size L_X has been varied between $0.5a_X$ and $3a_X$ and infinite barriers have been used for the calculations.

As a main result, our calculations show an increase of the spatial separation of the hole wave functions with increasing L_X, while in contrast the electron wave functions are almost homogeneously distributed in the dot. In close analogy, e.g., to the spatial separation of the protons in an H_2 molecule, this is a direct consequence of the different masses for electrons and holes and has an important impact on the radiative lifetimes of biexcitons: As the annihilation of a $|+\frac{3}{2}\rangle$ ($|-\frac{3}{2}\rangle$) hole with an $|+\frac{1}{2}\rangle$ ($|-\frac{1}{2}\rangle$) electron is forbidden, a spatial separation of the holes results in an increase of the biexciton lifetime, because only closely lying electron-hole pairs with antiparallel spins are able to couple to the radiation field. For example, the ratio $\tau_1/\tau_2 \approx 2$ calculated for $L_X < a_X$ decreases to ≈ 1.4 for $L_X = 3a_X$.

Taking into account the fact that in our dots both the disk-shaped geometry as well as the penetration of the wave functions into the barrier region due to the finite barrier height are expected to reduce τ_1/τ_2 further, it is quite obvious that the experimentally found ratio $\tau_1/\tau_2 \approx 1$ can indeed be explained by these arguments.

This becomes even more clear, if the limits of extremely large, i.e., $d \gg a_X$, and very small, i.e., $d \ll a_X$, disk-shaped QDs are discussed. In the case of $d \gg a_B \gg a_X$, where a_B corresponds to the biexciton size, the framework of the effective molecule model can be applied [4]. Here, the biexciton state can be represented as

$$B_{2K} = \frac{1}{\sqrt{2}} \sum_k \{c_k^\star X_{K-k}^\star X_{K+k}^\star + c_k^o X_{K-k}^o X_{K+k}^o\}, \quad (3)$$

where $2K$ is the B wave vector. Taking into account the internal spin structure, i.e., the fact that electrons and holes with parallel spins cannot recombine, one immediately obtains

$$\tau_2^{-1}(2K) = \sum_k |c_k^\star|^2 \tau_1^{-1}(K - k). \quad (4)$$

In this limit, $\tau_1/\tau_2 \approx a_B^2/d^2 < 1$, i.e., a biexciton lifetime even larger than the exciton one, is found [4]. In contrast, in the limit of $d \ll a_X$, Coulomb interaction induced corrections to the electron and hole wave functions in the confining potential are negligible and we obtain $\tau_2^{-1} = 2\tau_1^{-1} = 2\tau_0^{-1}$, where τ_0 corresponds to the band-to-band transition time.

We thank T. Kümmell for the preparation of the mesa structures. The financial support of the work by the Deutsche Forschungsgemeinschaft in Würzburg in the frame of the Sonderforschungsbereich 410 is gratefully acknowledged. V. D. K acknowledges the financial support from Würzburg University and the NATO grant, and N. A. G acknowledges the support of the A. v. Humboldt Foundation.

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