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Energy renormalization and binding energy of the biexciton

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We deduce the energy renormalization of the biexciton resonance in ZnSe quantum wells from polarization and intensity dependent pump-probe spectroscopy in the coherent regime. We confirm that the biexciton renormalization is exactly what one would expect from a compound particle of two excitons in opposite circular polarization states. Since the biexciton binding is measured with respect to the exciton resonance one has to consider the renormalization of the latter resonance as well. We present an exact method to determine the real biexciton binding energy using the low-excitation extrapolation of the exciton-to-biexciton transition energy.

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I. INTRODUCTION

The biexciton resonance is one of the fundamental many–particle effects occurring in optically pumped semiconductors.[1] Since the first predictions[2,3] and observations[4,5] of biexcitons in semiconductors, a variety of both theoretical and experimental reports about different aspects of biexcitons has been published especially on low-dimensional structures. At first, mainly GaAs-based heterostructures were examined[6,7] despite their small biexciton binding energy.[8–11] With the rising quality of II-VI compound semiconductors such as ZnSe-based heterostructures, the importance of biexcitons for the interpretation of the nonlinear optical properties of semiconductor nanostructures became more obvious. Because of the larger binding energies the biexciton resonance could be clearly separated from the exciton resonance and the influences of continuum states could often be excluded. This made the discussion much easier. In the coherent regime the long overlooked importance of biexcitons was proved by several experimental and theoretical groups.[12–15] In ZnCdSe heterostructures, with binding energies in the order of 30 meV, a biexciton gas was even proposed as ground state of the highly excited system.[16] Lately, biexcitons in quantum dots are treated as a candidate for an entangled-photon source,[17,18] one of the main ingredients for quantum cryptography.

Two of the most investigated biexcitonic properties are the selection rules for biexcitonic contributions to the signal in coherent spectroscopy[15,19,20] and the biexciton binding energy.[8,11,15,21,22] The binding energy was deduced in many different ways, for example from photoluminescence data by a line shape analysis or from four-wave mixing data by a beat-frequency analysis.[8,21,22] In principle, the use of exciton-biexciton quantum beats should be more accurate in the determination of the binding energy, because a lineshape fit can be omitted. But attention is demanded whatever method is used, because of the high pump intensity needed to see a biexcitonic signal. Such excitation conditions evoke higher-order Coulomb correlation effects and thus renormalization of all resonances.[23]

We could recently show that the renormalization of the exciton resonance in ZnSe based heterostructures depends strongly on the pump fluence, on the degree of temporal coherence, and on the polarization configuration of pump and probe pulses.[24,25] The interaction of linearly polarized excitons even depends strongly on the enclosed angle, i.e., the coherent phase between the circular spin eigenstates.[26] Extending this evaluation of the so called excitation-induced shift[25,27] from the exciton resonance to the exciton-biexciton transition, we are able to deduce the renormalization of the biexciton resonance. To the best of our knowledge, there is no current theory treating these renormalizations in a consistent way. But by measuring experimentally both the coherent exciton and biexciton renormalizations, we present a method to determine the biexciton binding energy in a very reliable and accurate way.

II. INVESTIGATED SAMPLES AND EXPERIMENTAL METHODS

We investigate a ZnSe/ZnMgSSe multiple quantum well (MQW) with ten periods of 8 nm well and 11 nm barrier width grown by molecular beam epitaxy. The sample shows a long excitonic dephasing time of about 15 ps (Refs. 25,28) in the low excitation limit and a small Stokes shift between photoluminescence (PL) and PL excitation spectra. From these findings and from temperature dependent PL measurements[26] we can conclude that localization plays only a minor role in the sample. The hh-lh splitting of 22 meV and the exciton binding energy of about 21 meV allows the resonant excitation of the hh exciton, without the influence of simultaneously excited light-hole or continuum states.

To be able to perform absorption measurements without introducing strain, the sample was mounted on a C-oriented sapphire plate and the GaAs substrate was chemomechanically removed. The sample was kept at $T=5$ K in a helium flow cryostat. Excitation source was the frequency doubled output of a femtosecond Ti:sapphire laser with a repetition rate of 76 MHz. The pulses—temporal FWHM of about 130 fs and spectral FWHM of 12 meV—were broad enough to measure the absorption of the exciton resonance and the exciton-biexciton transition simultaneously, when exciting

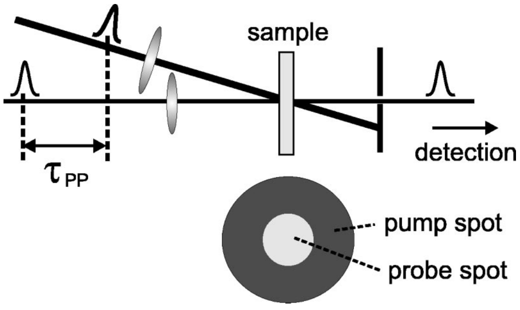

FIG. 1. Schematic pump-probe setup.

resonantly into the exciton resonance. Note that the intensity of the probe pulse was three orders of magnitude lower than the weakest applied pump pulse. Thus no direct two-photon absorption to the biexciton state could be observed, even in the case of linearly polarized probe pulses.

In order to evaluate the intensity dependent energy renormalization of the biexciton state, we used a standard femtosecond pump-probe setup as depicted in Fig. 1. The transmission of the probe pulse was measured spectrally resolved by the combination of a grating spectrometer and a nitrogen cooled CCD camera. From the transmitted signal the optical density of the sample (see Fig. 2) was calculated, using the integrated form of Beer′s law

$$\alpha d = \ln \frac{I_0}{I_T}. \tag{1}$$

I_0 denotes the incident laser intensity, I_T the transmitted intensity, α the absorption coefficient, and d the total MQW thickness. Both the pump and probe pulses were taken from the same initial laser pulse and could be delayed with respect to each other via computer controlled delay stages. The pulses were focused onto the sample at a small angle. To ensure that we probe a region of uniform photo excitation, we defocused the pump-beam spot to excite a much larger area than the probe spot ($\varnothing = 50\ \mu$m). The polarization of both beams could be chosen independently to investigate different polarization configurations. For the investigation of coherent exciton-exciton interaction in dependence of the optical orientation or alignment (for details see Ref. 24), we used the following four configurations: same circular polarization (SCP), opposite circular polarization (OCP), same linear polarization (SLP) and orthogonal linear polarization (OLP). For the examination of the biexciton renormalization only the SLP and OCP cases[19,20] are important, because only for this configurations a contribution of the exciton-biexciton transition to the signal exists. Nevertheless we need the information of the exciton renormalization in the SCP case also in order to gain more insight into the biexciton energy shift in the OCP case.

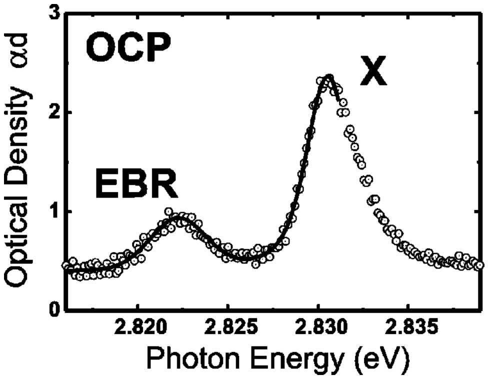

FIG. 2. Optical density. Both the exciton resonance and the exciton-biexciton transition are clearly visible. The line is a combination of a Gaussian fit to the EBR and a Voigt fit to the low energy side of the exciton line.

Before going into details of the extraction of the biexciton renormalization and binding energy, we have to discuss the direct measurable quantities like the position of the exciton-biexciton resonance (EBR) in the optical-density spectrum. In Fig. 2 the optical density in the energy region of interest is shown. The exciton absorption and the absorption peak originating from the EBR can be seen. We extract the position of the EBR by a gaussian line shape analysis and the position of the exciton resonance by a Voigt fit. For details of the Voigt fitting procedure see Ref. 24.

III. RESULTS AND DISCUSSION

Having in mind our goal to learn more about the density dependent renormalization of the biexciton state and the biexciton binding energy, it is useful to plot the energy shift and not the transition energy. As reference point we use the energetic EBR position for the lowest pump fluence for which a transition to the biexciton can bee observed and evaluated. For reasons of clarity the shift of the exciton resonance for this pump fluence is also set to zero. In Fig. 3 the results of this analysis are shown for both the SLP and the OCP case. The open boxes represent the energy renormalization of the exciton resonance and the dots the shift of the EBR. In addition to the OCP shift and the SCP shift of the exciton resonance (dashed line) in (b), the excitonic shift for the SLP case is indicated (dotted line) for comparison. While the exciton resonance is shifting strongly in the SLP case [Fig. 3(a)], the transition energy of the EBR is not affected by the pump fluence at all. In the OCP case the exciton renormalization is much weaker than in the SLP configuration[24] but interestingly the EBR shifts to lower energies. This different behavior in the SLP and OCP configurations gives the clue for the understanding of the renormalization of the biexciton state.

The absorption leading to a signal at the EBR is a coherent process involving two photons—more exactly a coherent material polarization evoked by photon one and a second photon. We know the energies of both contributing photons from the measured optical density. Information about the biexciton renormalization, which is not directly accessible, can be gained by introducing a simple level scheme. If we sketch the shifts of the exciton and the EBR in such a level scheme[19] (see Fig. 4) and use the measured exciton renormalization as input, we can deduce the renormalization of the biexciton state for a given pump fluence and polarization just by keeping the distance between exciton and biexciton level at the EBR transition energy. On the left hand side of Fig. 4 the unshifted exciton and biexciton levels are depicted

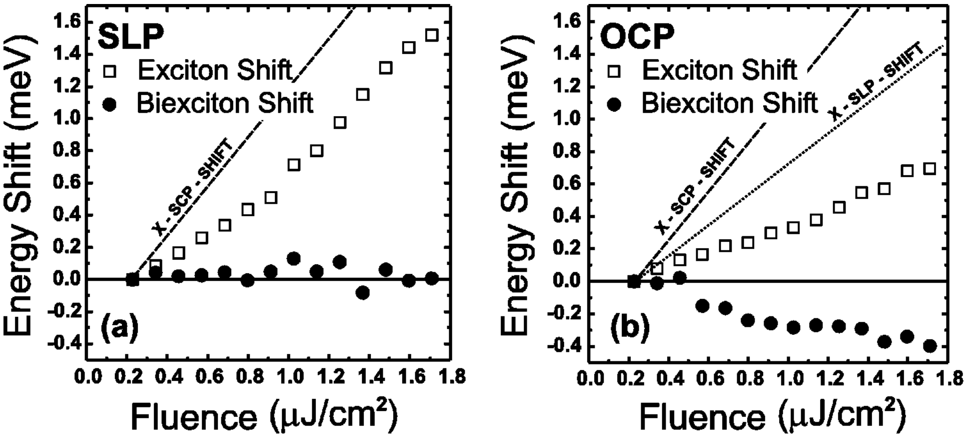

FIG. 3. Density dependent shift of the exciton transition and the exciton-biexciton transition. The shifts for the lowest pump fluence for which the EBR can be evaluated are set to zero. The excitonic shifts are indicated as open boxes, the shifts of the EBR as dots. The SCP shift of the exciton is indicated as dashed line and in (b) additionaly the SLP shift as dotted line.

as well as the optical transitions due to circularly polarized photons. For a linearly polarized pump pulse, both the $|+1\rangle$ and the $|-1\rangle$ exciton resonances (a) are excited and renormalized by the same energy ΔE_{SLP} (b). For a σ^{+} polarized pump pulse (c) only the $|+1\rangle$ exciton polarization is excited and shifts by ΔE_{SCP} (d). The $|-1\rangle$ excitons shift by a much smaller amount ΔE_{OCP}, but this is not important for the further discussion. In the SLP configuration the probe pulse consists of both $|\sigma^{+}\rangle$ and $|\sigma^{-}\rangle$ photons. For the exciton-to-biexciton transition, both types of photons couple the renormalized exciton resonance (shifted by ΔE_{SLP}) to the renormalized biexciton resonance. Since the experiment revealed that the EBR transition energy does not change, the biexciton level has to shift by exactly the same energy ΔE_{SLP} as the exciton levels.

On first sight the situation for the OCP case seems to be a bit more complicated, but it turns out to be very similar. Starting point for the σ^{-} photons of the probe pulse is the shifted $|+1\rangle$ exciton level at an energy of $E_{|+1\rangle}+\Delta E_{\mathrm{SCP}}$. Assuming that the biexciton level shifts roughly as in the SLP case, the photon evoking the EBR transition has to be of lower energy than in case (b). As a result the EBR in the pump & probe absorption should shift to the red with increasing pump intensity, as is indeed observed in the experiment [see Fig. 3(b)].

Summarizing these arguments we can conclude that the biexcitonic polarization is interacting with a test exciton exactly as a mixed polarization state of 50% $|+1\rangle$ and 50% $|-1\rangle$ excitons. This interpretation is consistent with the experimental findings of Langbein *et al.*,[29] who reported similar scattering rates for excitons and biexcitons in a FWM experiment using collinear polarized excitation pulses.

How can we deduce the real biexciton binding energy from the above presented data? The biexciton binding energy is defined as the energy difference between two unbound excitons and the same excitons bound to a biexciton state. In our picture this would be the difference between the energy position of the exciton resonance and the EBR. Looking at this distance in Fig. 5 we notice that it is not a constant, i.e., the biexciton binding energy would be a function of excitation intensity. In any type of experiment to determine the

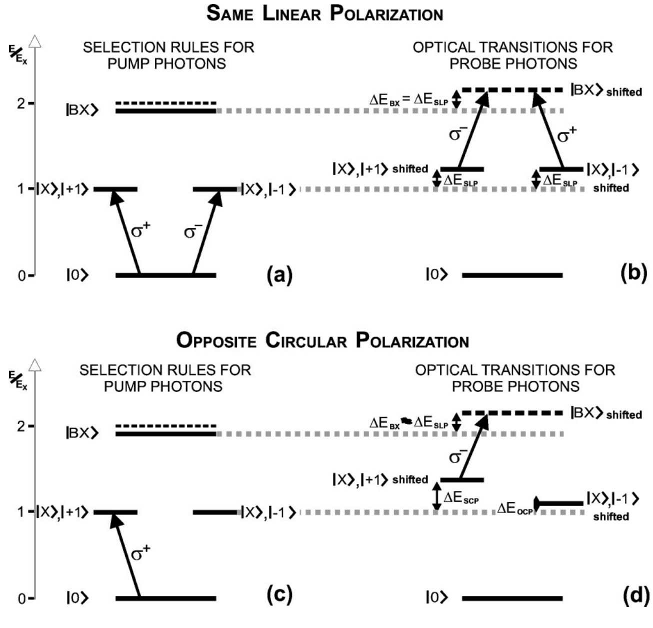

FIG. 4. Level scheme of the transitions in our pump-probe absorption experiment in a circular polarization basis. Arrows indicate excitonic transitions due to impinging photons. Details are explained in the text.

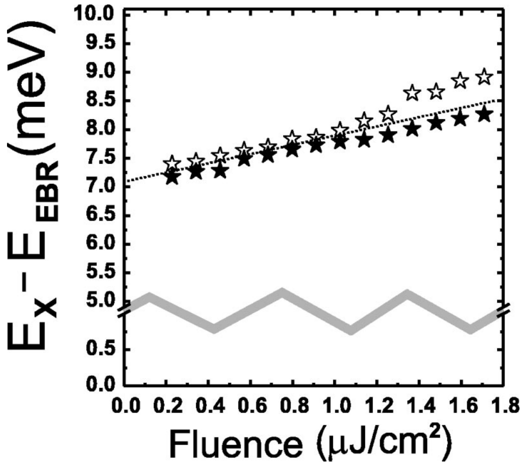

FIG. 5. Energy difference between the exciton resonance and the exciton-biexciton transition. The indicated line is a guide to the eye showing the extrapolation to zero pump fluence, i.e., the real biexciton binding energy. Open symbols: SLP, filled symbols: OCP.

biexciton binding energy one has to keep in mind that the involved energy states are renormalized because of the unavoidable high excitation intensities. The only safe way to measure the binding energy is an intensity-dependent experiment including an extrapolation to zero intensity. In our case this is very simple, because we get a more or less linear dependency of the energy difference between the exciton resonance and the EBR. The linear extrapolation versus zero pump fluence leads to the real biexciton binding energy of $E_{\mathrm{BX}}^{\mathrm{bind}}=(7.1\pm0.1)$ meV. This idea is supported by the fact that the same result is deduced from two independent experiments with different polarization configurations, where the exciton resonance and the EBR are shifting in totally different ways (Fig. 5).

IV. CONCLUSIONS

In conclusion, we have presented a method to determine the intensity dependent energy renormalization of the biexciton state. We find that the biexciton renormalization is independent of the polarization of the exciting laser pulses and reflects the nature of the biexciton as compound particle of two excitons with different optical orientation. Thus, biexcitonic polarization interacts with an excitonic test polarization exactly as the mixture of the unbound excitonic polarizations would do. In addition, we demonstrate that a measurement of the biexciton binding energy based on the difference between the exciton and exciton-to-biexciton transition can only be deduced from an extrapolation to low excitation.

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