Spectral dependence of the optical Stark effect in ZnSe-based quantum wells

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An experimental study of the optical Stark effect in ZnSe-based quantum wells using pump-probe spectroscopy is presented. The Stark shift at both the heavy-hole and the light-hole resonances is measured as a function of pump detuning for samples with different heavy-hole–light-hole separations. The coupling between the heavy hole and the light hole has to be taken into account to explain the observed dependence on the pump wavelength detuning and polarization of pump and probe pulses. For a range of samples the Stark shift behavior is characterized by the ratio of the detuning to the heavy-hole to light-hole separation; higher order Coulomb correlations play a prominent role when the ratio is less than 2.

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I. INTRODUCTION

The excitonic optical Stark effect in semiconductors has attracted considerable attention given the potential applications in developing ultrafast nonlinear optical switches.[1,2] The shift of the exciton peak following below-gap excitation by an ultrafast pulse has been reported in bulk semiconductors[3–5] and quantum wells.[6–9] Detailed experimental results and theoretical analyses have demonstrated that for a complete description of the Stark effect in semiconductors, Coulomb correlations have to be included.[10] This difference from atomic systems is highlighted in the dependence of the shift on the pump pulse detuning, which can even change sign when Coulomb interactions become important. In most cases, the exciton peak shifts to a higher energy during excitation.[6–8,10] However, Hulin and Joffre observed a red shift in a CuCl thin film, when the pump pulse was tuned slightly below the exciton to biexciton transition for parallel linearly polarized pump and probe pulses and this shift was attributed to the influence of the biexcitons.[4]

In ZnSe layers, with a relatively small biexciton binding energy of 4 meV a shift of the heavy-hole polaritons towards higher energy was reported even when pumping resonantly with the exciton-biexciton transition.[5] In semiconductor quantum wells, experimental investigations have concentrated on GaAs-based structures and have reported a blue shift of the heavy-hole resonance.[6–8] However, a red shift was observed in $In_xGa_{1-x}As/GaAs$ quantum wells for opposite circularly polarized pump and probe pulses. This was attributed to Coulomb memory effects, rather than to the existence of bound biexcitons.[9] The sign of the shift was also sensitively dependent on the detuning and the splitting between heavy hole (HH) and light hole (LH). As the detuning was increased or for samples with reduced HH to LH splitting, the magnitude of the red shift decreased and finally switched to a blue shift. The theoretical model developed to explain the experimental results showed that Coulomb correlations become dominant for a specific detuning and splitting range, and highlighted for the first time, to the best of our knowledge, the influence of light holes on the HH Stark shift.[11,12]

Most reports of the nonresonant optical Stark shift in quantum wells focus exclusively on the HH exciton Stark shift. However, for detunings large compared to the HH to LH energy separation, the LH resonance is also shifted by the pump pulse and should be taken into consideration when analyzing the experimental results. Additionally, it has been demonstrated that even when the splitting between the HH and LH resonances is larger than the pump pulse detuning, so that only the HH exciton is excited, a shift of the LH resonance could still be induced due to intervalence-band coherences.[13,14]

In this paper, we present a systematic study of the excitonic optical Stark effect in ZnSe-based quantum wells. The large HH-LH energy separation of ZnSe-based quantum well structures, compared to GaAs-based semiconductors, makes them an ideal material for the study of the Stark shifts at both HH and LH resonances. Additionally, due to the increased exciton binding energy in ZnSe-based semiconductors, Coulomb correlations are expected to play a far more important role in their nonlinear optical properties. Exploiting a range of pump pulse detuning and HH-LH splitting combinations we study the effect of Coulomb correlations on the observed Stark shifts and identify detuning regimes for which they become significant. Further we show that, apart from the HH Stark shift, the influence of Coulomb correlations can affect considerably the LH Stark shift as well.

II. SAMPLES AND SETUP

Four ZnSe-based samples with different HH to LH splitting were used in these studies. All samples were grown by molecular beam epitaxy (MBE) on a GaAs substrate. To perform transmission experiments the substrate was removed over windows larger than the beam spot size by wet chemical etching. We used a ternary multiple quantum well structure consisting of 20 periods of $Zn_{0.8}Cd_{0.2}Se$ well layers with ZnSe barriers (sample *A*) and binary multiple quantum wells of 10 periods of ZnSe with either ZnMgSSe (sample *B*) or MgS (samples *C* and *D*) barriers. MgS has a very large band gap, ≈ 5 eV and so forms an excellent barrier material with good confinement for ZnSe. The stable bulk crystal structure of MgS is rocksalt (NaCl) but the zincblende structure is

TABLE I. Detuning range of pump pulse from HH exciton resonance for each sample.

Sample	Structure	HH-LH splitting (meV)	Detuning (meV)	Detuning-splitting ratio
A	(Zn,Cd)Se/ZnSe 20×4 nm wells	36	36–71	1–2
B	ZnSe/ZnMgSSe 10×5 nm wells	33	39–73	1.2-2.2
C	ZnSe/MgS 10×10 nm wells	20.5	41–86	2–4.2
D	ZnSe/MgS 10×11 nm wells	16	42–79	2.6–4.9

metastable when grown epitaxially on GaAs. The ZnSe/MgS samples presented here were grown using a novel MBE growth method using Mg and ZnS as a source of sulphur.[15] In order to limit the reaction of S with the substrate, MgS was grown on a thin ZnSe buffer layer. The ZnSe/MgS samples were then capped with a thin ZnMgSSe layer due to the hygroscopic nature of MgS. The characteristics of the samples used are shown in Table I. All samples showed clear HH and LH exciton absorption peaks in their linear absorption spectra at 4 K as shown in Fig. 1. The Stokes shift for these samples ranges from 1 meV to 10 meV. As the detuning in what follows is always much larger than this width we expect the inhomogeneous broadening to be unimportant in these particular experiments.

Nonresonant Stark shifts were measured using polarization selective pump-probe spectroscopy. The laser system consisted of a 100 fs Ti: sapphire pumped regenerative amplifier (RGA) and an optical parametric amplifier (OPA). The output of the OPA provided tuneable 120 fs pump pulses at a repetition rate of 1 kHz. A part of the RGA output beam was focused into a water cell to produce broadband white light continuum probe pulses. Polarization of pump and probe pulses was controlled by $\lambda/4$ plates. The pump pulse was always σ^+ polarized, while the probe beam was either same circular (SCP) or oppositely circular polarized (OCP) to the pump. The pump beam was focussed onto the sample in a 380 μm diameter spot. Only the central part of the excited area was probed by a 160 μm diameter probe beam. All the measurements in this work were performed with the sample kept in a He cooled cryostat at 4 K. A dual-channel optical spectrum analyzer, with a spectral resolution of 0.13 meV, was used to record the transmitted probe pulse. The temporal overlap between the pump and the probe was adjusted using a computer controlled delay stage. Changes in the transmitted probe spectrum were measured as a function of the delay between the pump and probe pulses at different pump wavelengths. The range of detuning used for each sample is shown in Table I. When the pump pulse is resonant with the HH resonance, the creation of a finite density of excitons produces a blue shift of the HH resonance.[16] Therefore, the pump pulse was tuned sufficiently below the HH resonance to minimize the generation of real *e-h* carriers either from direct overlap of the pump pulse with the HH resonance or by two photon absorption via the biexciton. The pump pulse energy was in the range of 0.2–0.7 μJ and was kept constant for each sample studied, as the detuning was varied. For the intensity range of all our experiments the Stark shift was directly proportional to the pump pulse intensity.

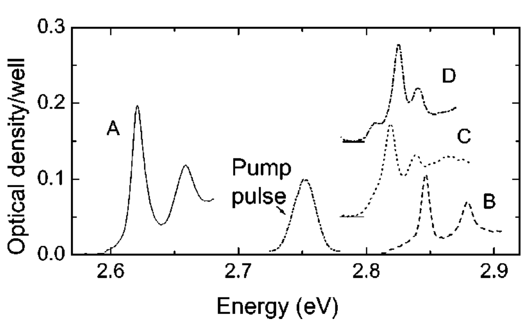

FIG. 1. Linear absorption spectra of the ZnSe-based multiple quantum wells at 4 K. Sample *A* (solid line), sample *B* (dashed line), sample *C* (dotted line), and sample *D* (dash-dot line). Spectra of samples *C* and *D* are vertically shifted for clarity. The shoulder observed below the HH resonance for sample *D* is due to the residual ZnSe buffer layer. A typical pump pulse spectrum is also shown (dash-dot-dot line).

III. RESULTS

Figure 2 shows an example of the absorption spectra for different detunings for the (Zn,Cd)Se/ZnSe sample and for pump pulse energy of 0.56 μJ. Pronounced shift and bleaching of both HH and LH resonances are evident. The peak positions of the HH and LH are determined by calculating

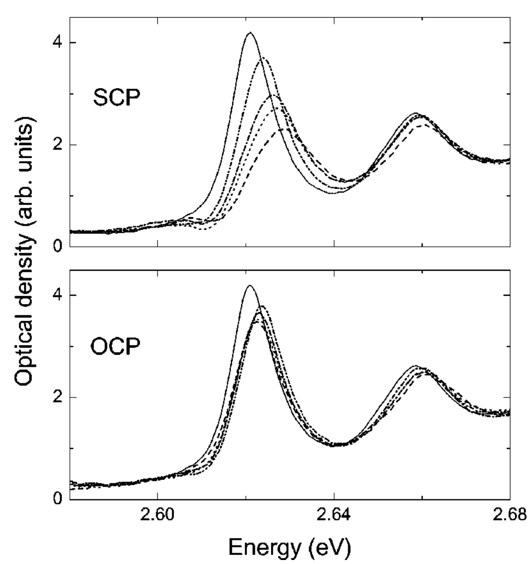

FIG. 2. Absorption spectra for the (Zn,Cd)Se/ZnSe multiple quantum wells for SCP and OCP configurations and different pump pulse detunings: 36 meV (dashed line), 46 meV (dotted line), 56 meV (dash-dot line), 71 meV (dash-dot-dot line). The solid line corresponds to the linear absorption spectrum.

the first moment of the measured spectrum around the peak, and the Stark shift is calculated as a difference of the shifted peak position to the peak position in the linear absorption. The spectra shown in Fig. 2 correspond to a zero pump-probe delay, which produces the maximum HH shift for each detuning. The time-dependent behavior of the absorption saturation and the energy shift was monitored for ≈ 1 ps around zero pump-probe delay, with a step of 27 fs. In all cases, the time response of the induced energy shift and absorption saturation of both HH and LH resonances was observed to closely follow the pump pulse profile. Moreover, the shift reduced to zero for pump-probe delays >250 fs. Therefore, there were no residual effects from incoherent processes.

There were pronounced differences between the samples when we examine the detuning and polarization dependence of the Stark shift. As the HH-LH separation is not the same for the investigated samples, the effect of the HH-LH splitting variation needs to be considered, in order to explain the observed differences. We introduce the ratio of the detuning of the pump center wavelength from the HH resonance to the HH-LH separation (Table I), and we find that the behavior of the four samples can be categorized into the two following groups. Samples *A* and *B*, where the detuning to splitting ratio is in the range 1–2, show similar detuning and polarization dependence. Samples *C* and *D*, where this ratio is in a higher range (2–5), show a different behavior.

Figures 3 and 4 show the observed energy shift at zero delay as a function of detuning for the HH and LH and for both polarizations. As we are interested in the spectral dependence of the Stark shift and the shift is directly proportional to the pulse intensity we can choose a slightly different pulse energy E_p in each sample to maintain a good signal-to-noise ratio.

At the HH resonance, opposite circularly polarized pump and probe pulses cause an increase of the shift with increasing detuning for a small detuning to splitting ratio (samples *A* and *B*), whereas for samples *C* and *D* the shift decreases as detuning is increased. For SCP the shift decreases with increasing detuning for all samples (Fig. 3). The described behavior can also be seen in the absorption spectra presented in Fig. 2 for sample *A*. At the LH resonance, the shift in all cases shows a decrease with increasing detuning. However the actual value of the shift for the two polarizations is different. For samples *A* and *B* the shift is similar for both circular polarization configurations. This behavior is modified for higher detuning to splitting ratio (samples *C* and *D*) where the OCP LH shift is always higher than the corresponding SCP shift (Fig. 4).

We now discuss these results in the context of the current understanding. Two nonlinear effects, phase-space filling and Coulomb interactions, govern the optical Stark shift in semiconductors.[10] The latter can be further divided into a first-order term and higher-order Coulomb correlation terms incorporating bound and unbound two-exciton states. In our experimental conditions, the pump pulse simultaneously excites both HH and LH resonances and therefore the coupling between HH and LH excitons also needs to be taken into account. To the best of our knowledge a complete theory

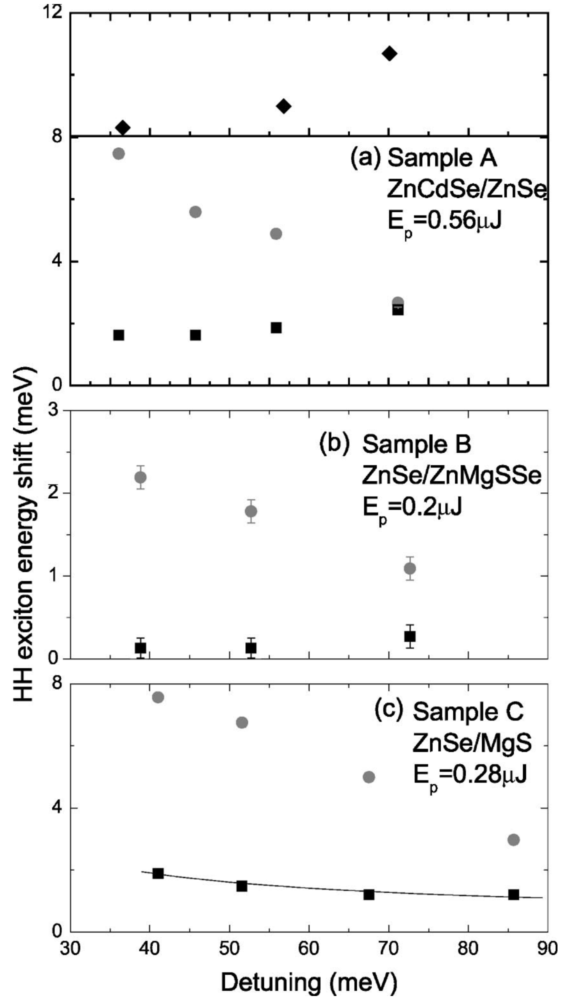

FIG. 3. Measured heavy-hole energy shifts as a function of detuning Δ_{HH} for SCP (gray circular symbols) and OCP (black square symbols) configurations (a) Sample *A*, (b) Sample *B*, (c) Sample *C*. Fitted dependence of the OCP HH shift ΔE_{ocp} on the detuning: $\delta E_{ocp}(\text{meV}) = 0.15 + 102/\Delta_{LH}$ [Top of (a): Measured maximum heavy-hole energy shifts as a function of detuning for OCP at $T = 160$ K].

including all these effects at both resonances is not available at present. Previous theoretical studies have considered the HH shift[11,12] as influenced by the light-hole but not vice versa. However, combining the polarization dependence of the Hartree-Fock (Pauli blocking and first-order Coulomb) contributions and the observed behavior at a variety of detuning to splitting ratios we can identify the influence of Coulomb correlations. In the following we analyze the results of Figs. 3 and 4 in more detail in an attempt to identify the various underlying contributions to the observed Stark shifts.

We first consider Figs. 3(a) and 3(b), which show the HH shift dynamics for a low detuning to splitting ratio. The relevant energy-level diagram and the allowed transitions for different polarizations are shown in Fig. 5. Below resonance excitation by a σ^+ pump pulse couples the $m = -1/2$ electron states with the $m = -3/2$ HH states and the $m = 1/2$ electron states with the $m = -1/2$ LH states with

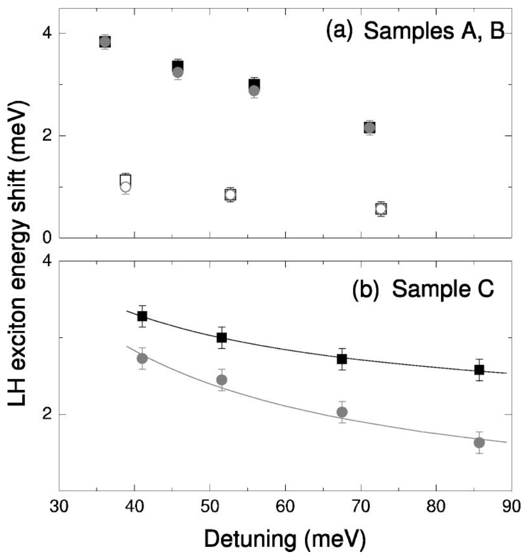

FIG. 4. Measured light-hole energy shifts as a function of detuning from the HH resonance Δ_{HH} for SCP (gray circular symbols) and OCP (black square symbols) polarization configurations (a) Samples *A* (solid symbols) and *B* (open symbols) (b) Sample *C*. Fitted dependence of the SCP LH shift: $\delta E_{scp}(\text{meV}) = 0.18 + 160/\Delta_{LH}$ (gray line) and the OCP LH shift: $\delta E_{ocp}(\text{meV}) = 2 + 55/\Delta_{HH}$ (black line) on the pump pulse detuning.

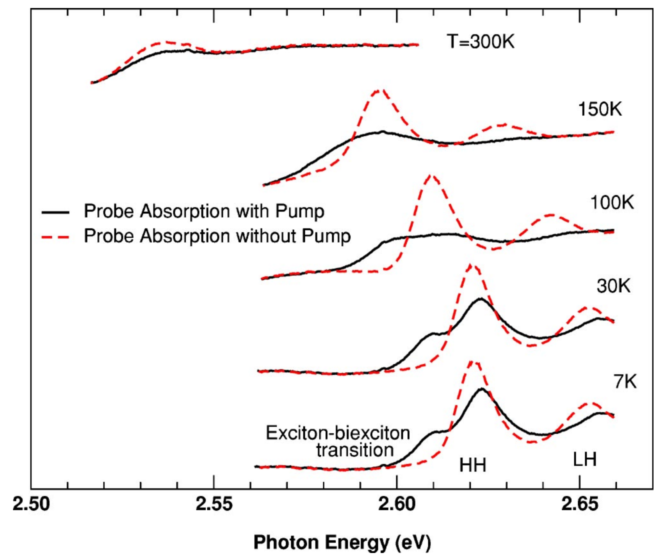

FIG. 6. Temperature dependence of the biexciton absorption for the ZnCdSe/ZnSe quantum well structure. The absorption spectra (solid lines) were obtained for OCP configuration under HH resonant pump pulse excitation. Linear absorption spectra (dashed lines) are also shown.

a ratio of oscillator strengths of 3:1. A σ^+ polarized white light continuum pulse probes the same HH transition, which would blue shift due to phase space filling. The effect from this process is expected to be the dominant one.[12] On the other hand a σ^- polarized probe pulse probes the $\Delta m = -1$ HH transition, which means that Pauli blocking and first-order Coulomb terms due to HH excitation are zero. However, excitation of the $m = 1/2$ electron states due to LH transition will blue shift the resonance to higher energies although this blue shift would be less compared to the SCP case. The observed shift will also have contributions from higher-order Coulomb correlation terms. As shown in Figs. 3(a) and 3(b) the blue shift for OCP increases with increasing detuning. Since the Pauli blocking term would always cause a blue shift decreasing with increasing detuning the observed increase implies that there are also terms producing a red shift, which decays faster than the blue shift. Higher-order Coulomb correlations are known to cause such a red shift[12] and we expect that here too the main contributions to the Stark shift are from the LH Pauli blocking and HH higher-order Coulomb correlations. The contributions from the Coulomb interaction terms at the LH are not expected to be significant in this detuning regime, as we show later.

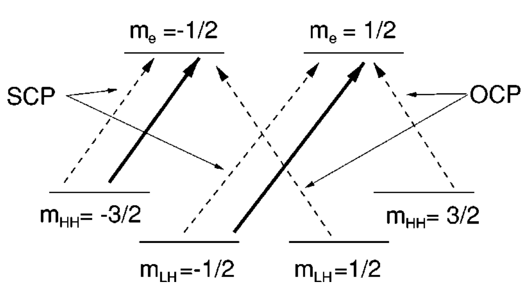

FIG. 5. Simplified energy level diagram and transitions induced by a σ^+ polarized pump (solid thick arrows) and a σ^+ (SCP) or σ^- (OCP) probe beam (dashed arrows).

To further analyze the origin of the higher-order Coulomb correlations, the contributions from the exciton-biexciton resonance need to be considered. For the (Zn,Cd)Se/ZnSe quantum wells (sample *A*) pump-probe measurements under resonant excitation found a relatively high binding energy for the biexcitons (13 meV) and the question arises whether they may play an important role in the Stark shift dynamics.[17] To check this we repeated both the resonant pump-probe measurements and the Stark shift measurements as a function of temperature. As shown in Fig. 6, under HH resonant excitation, the distinct exciton-biexciton peak visible for OCP at low temperatures disappears at 150 K, indicating that bound biexcitons do not form at this temperature. Therefore the Stark shift measurements were repeated at 160 K for this sample where the exciton-biexciton transition is homogeneously broadened. As shown in Fig. 3(a) the Stark shift behavior remained essentially the same at 160 K. Therefore we conclude that bound biexcitons do not play a prominent role here. In the $In_xGa_{1-x}As$ quantum wells it was found that Coulomb memory effects and not the biexcitons make a major contribution to the observed red shift.[9]

Turning to sample *C* [Fig. 3(c)], where the detuning to HH-LH splitting ratio is higher than that for the other two samples, the behavior of the Stark shift for the OCP configuration as a function of detuning changes and the shift decreases with increasing detuning. The reduced detuning of the pump from the LH resonance (Δ_{LH}) will enhance the effect of light holes on heavy holes. The decay of the shift shows a Δ_{LH}^{-1} dependence, which is characteristic of the Pauli blocking contribution due to the influence of the LH excitons.[12] The contribution of first-order Coulomb terms and higher-order Coulomb correlations appears to be much less at large detuning. This supports our earlier statement that Coulomb interaction contributions from the LH do not significantly contribute to the observed shifts at the HH because of the larger detuning from the pump wavelength. The second ZnSe/MgS sample (sample *D*) shows essentially the same behavior and the plots are not shown.

Now we consider the shifts of the LH resonance. As in the case of HH, we can again categorize the samples according to the detuning to splitting ratio. We use the same phenomenological explanation as for the HH case based on the contributions from Pauli blocking and Coulomb interactions. The Pauli blocking effect can be discussed on the basis of the polarization selection rules presented in Fig. 5. Remembering that the pump pulse is σ^+ polarized, a σ^+ probe pulse couples the $m=1/2$ electron states with the $m=-1/2$ LH states, whereas a σ^- probe pulse would couple the $m=-1/2$ electron states with $m=1/2$ LH states. Therefore, Pauli blocking occurs in the case of SCP as the same transition is pumped and probed. For OCP it occurs due to the coupling of the $m=-3/2$ heavy-hole transition with the $m=-1/2$ electron states. Overall, the shift induced by Pauli blocking would always be higher for OCP than for SCP due to the higher oscillator strength and smaller detuning of the HH transition. The effect of Coulomb interactions involving the light holes can be considered very small for the detuning range of the experiment. However, the influence of heavy holes on light holes cannot be restricted only to the Pauli blocking effect, as Coulomb terms from the heavy holes cannot be neglected in this case. To our knowledge, there is no theoretical analysis available for evaluation of the Stark shift of the LH resonance including all the above phenomena. However, evidence of the significance of the Coulomb-induced nonlinearities comes from the observation that for a reduced detuning to splitting ratio, equal shifts are obtained at the LH resonance for both SCP and OCP [Fig. 4(a)]. When the detuning to splitting ratio becomes higher, Pauli blocking again dominates over Coulomb correlations, similar to the HH resonance case. The difference in the magnitude of the blue shifts as expected by the selection rules for SCP and OCP is experimentally produced, with the shifts decaying in inverse proportion to the detuning [Fig. 4(b)].

IV. CONCLUSIONS

In conclusion, we report a systematic study of the nonresonant Stark shift in ZnSe multiple quantum wells. Using pump-probe spectroscopy with a broadband ultrashort probe pulse enabled the measurement of the shift at the light hole as well as at the heavy hole. For the samples studied, higher-order Coulomb correlations play a strong role for a pump detuning to splitting ratio between 1 and 2. At the HH this leads to an increase in the Stark shift with increasing detuning when the pump and probe pulses are of opposite circular polarization, whereas for same circular polarizations the shift decreases with increasing detuning. At the LH the shifts turn out to be equal for both polarization configurations. Our results show that the ZnSe system is well suited for further study of exciton-photon coherent interactions in the presence of Coulomb correlations.

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