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Biexciton Wavefunction in Bulk CuCl Probed by Inverse Polariton Series

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We report the observation of the radiative decay of excitonic molecules, selectively excited at the wavevector $\mathbf{K}_m$, into polaritons associated with the $n = 1$s, 2s, 3s, and 4s states of the optically allowed Z_3 exciton in bulk CuCl. The $\mathbf{K}_m$ dependence of the emission series (inverse polariton series) is quantitatively explained by the bipolariton model, leading to unambiguous estimation of the relative contributions of the 2s, 3s, and 4s exciton states to the four-particle molecule wavefunction, both in sign and in magnitude. The very structure of the molecule wavefunction is highly sensitive to the above relative contributions, and, in particular, we examine the Akimoto-Hanamura and hydrogen-molecule trial wavefunctions.

An excitonic molecule (biexciton) is the bound state of two excitons in a semiconductor. Nowadays biexcitons are readily observable in a wide variety of materials owing to the improvement in experimental techniques (laser source, sample preparation, etc.), and many attractive phenomena associated with excitonic molecules have been found with potential for future applications [1, 2]. However, a complete theoretical description of the biexciton wavefunction (WF) is still challenging because it presents a complex few-body problem in the condensed phase, involving a variety of interactions such as four-particle Coulomb interaction [3, 4], effects of the underlying electronic band structure (Bloch states), spin–spin (exchange) interaction [5, 6], coupling with photons (polariton) [2, 7] and lattice (polaron), local field effects (central-cell correction), etc. In order to approach these problems experimentally, high-precision measurements of the biexciton parameters are to be performed as has been done in the case of the hydrogen molecule [8].

A monocrystal CuCl is a prototype material in the physics of excitonic molecules, due to the relatively simple valence band structure and due to the large binding energy of the molecules $E_m \approx 32$ meV [1]. Since the discovery of biexcitons in CuCl [9], high-precision hyper-Raman (biexciton-mediated) spectroscopy has been developed [6, 10] to identify the biexciton radiative decay channels, and picosecond spectroscopy has been applied to reveal the radiative lifetimes of biexcitons in the weak excitation regime [11]. As the next step, recently we have observed the inverse exciton (M) and inverse polariton (LP) series, due to the optical decay of excitonic molecules in this semiconductor [12].

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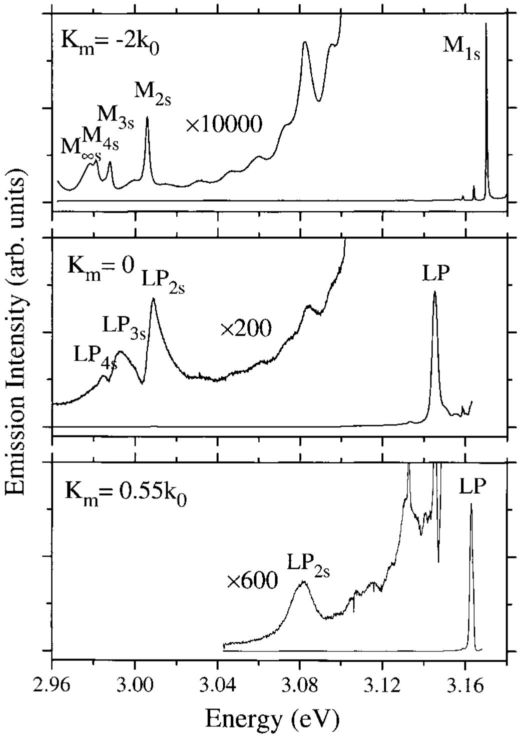

Fig. 1. Emission spectra from excitonic molecules selectively created by two-photon excitation at $\mathbf{K}_m = -2\mathbf{k}_0$ (top, the M series in the backward scattering geometry), $\mathbf{K}_m = \mathbf{0}$ and $\mathbf{K}_m = 0.55\mathbf{k}_0$ (middle and bottom, the LP series)

Figure 1 shows the M and LP series from excitonic molecules, which are generated in high-quality bulk CuCl at 2 K by wavevector selective two-photon resonant excitation [6] with two independently tunable picosecond pulse lasers [12]. The M series is the emission lines due to the biexciton radiative decay leaving behind the *n*s "mechanical" excitons, and the LP series is due to the decay leaving behind the lower-branch polaritons associated with the *n*s exciton states. Both of these series are continuously connected by changing the molecule wavevector $\mathbf{K}_m$, as shown schematically in Fig. 2. In order to explain quantitatively the relative intensity of the M and LP replicas, we analyze the multi-channel decay of excitonic molecules by the bipolariton model (BP) [2]. Note, that very recently the validity of this model has also been justified for excitonic molecules in bulk CdS and CdSe [13].

According to the BP model, we interpret the LP_{ns} and M_{ns} lines ($n = 1, 2, 3$, and 4) in terms of the scattering scheme "two incoming polaritons → excitonic molecule → two outgoing polaritons, associated with 1s and *n*s exciton states". The efficiency of the multi-branch molecule-mediated polariton

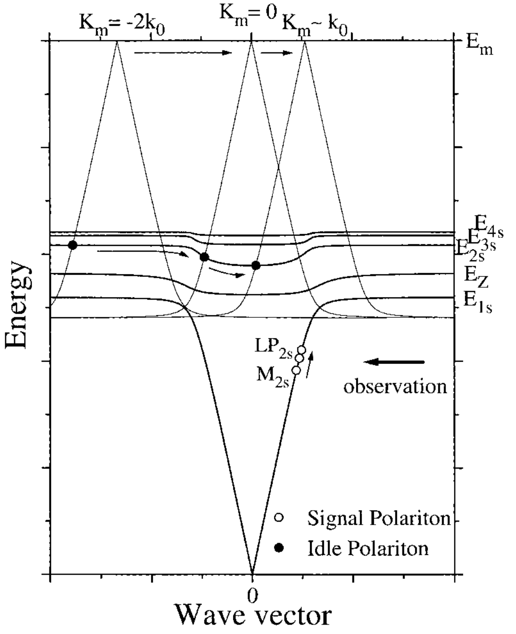

Fig. 2. Scheme of the resonant molecule-mediated polariton–polariton scattering. Open and closed circles refer to the signal and idle polaritons, respectively

scattering is determined by the Coulombic interaction between the excitonic components of the incoming and outgoing polaritons [12]. The inverse M and LP series yield a unique information on the very internal structure of the molecule WF $\Gamma_{\mathrm{m}}(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2)$, where $\mathbf{R}$ and $\mathbf{r}_{1,2}$ are the exciton–exciton and electron–hole relative coordinates, respectively. Namely, the decay rate of the excitonic molecule $\mathbf{K}_{\mathrm{m}}$ is given by [12]

$$\gamma(\mathbf{K}_{\mathrm{m}},E_1) \;=\; \frac{2\pi}{\hbar}\,\rho^{(1,2)}\,\Big|\sum_{i,j} B_i(k_1)\,B_j(k_2)\,W_{i,j}C_{i,j}\Big|^2 , \tag{1}$$

where E_1 is the energy of the signal polariton, $\mathbf{k}_1$ and $\mathbf{k}_2$ are the wavevectors of the outgoing signal and idle polaritons, $\rho^{(1,2)}$ is the joint density of polariton states, B_n is the ns excitonic component in the final-state polaritons (i.e., a generalized Hopfield coefficient for the ns exciton state), $C_{i,j} = \int \mathrm{d}\mathbf{R}\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\Gamma^{*}_{\mathrm{m}}(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2)\,\phi_i(\mathbf{r}_1)\,\phi_j(\mathbf{r}_2)$, and $W_{i,j} = E_{\mathrm{m}} - E_i - E_j$. Here, $\phi_{i=n\mathrm{s}}$ are the exciton envelope eigenfunctions, E_{m} and E_j are the binding energies of the excitonic molecule and the js exciton. While Eq. (1) is derived beyond standard second-order perturbation theory with respect to the exciton–exciton and exciton–photon interacions, it is still approximate and does not include the influence of the light field on the molecule WF.

In order to explain the inverse series, it is practically enough to retain four leading terms in Eq. (1) as $\gamma(\mathbf{K}_{\mathrm{m}},E_1) = (2\pi/\hbar)\,\rho^{(1,2)}\,|B_1(k_1)B_1(k_2)W_{1,1}C_{1,1} + B_1(k_1)\,B_2(k_2)\,W_{1,2}C_{1,2} + B_1(k_1)\,B_3(k_2)\,W_{1,3}C_{1,3} + B_1(k_1)\,B_4(k_2)\,W_{1,4}C_{1,4}|^2$. Other terms, which include $B_{n=2,3,4}(k_1)$, can be neglected because $B_{n=2,3,4}(k_1)$ (the 2s, 3s, and 4s excitonic components of the signal 1s lower-branch polariton) are nearly zero. For the $\mathrm{M}_{n\mathrm{s}}$ emission lines the idle polariton is exciton-like and, therefore, except for $B_n(k_2) \approx 1$ and $B_1(k_1) \approx 0.4$ all other generalized Hopfield coefficients $B_n(k_{1,2})$ are negligible. Consequently, the intensity of the $\mathrm{M}_{n\mathrm{s}}$ replica is proportional to $|C_{1,n}|^2$. In this way we estimate $|C_{1,n}/C_{1,1}|$ from the relative intensities $I_{\mathrm{M}_{n\mathrm{s}}}/I_{\mathrm{M}_{1\mathrm{s}}}$ of the $\mathrm{M}_{n\mathrm{s}}$ lines [12]. With $\mathbf{K}_{\mathrm{m}}$ increasing from $-2\mathbf{k}_0$ toward zero, as shown in Fig. 2, $|B_{n\mathrm{s}}(k_2)|$ decreases while $|B_{1\mathrm{s}}(k_2)|$ increases (the wavenumber $k_0 \approx 4.4\times10^5$ cm^{-1} corresponds to degenerate two-polariton excitation of the molecules with $\mathbf{K}_{\mathrm{m}} = 2\mathbf{k}_0$). As a result, at $\mathbf{K}_{\mathrm{m}} = \mathbf{0}$ the two terms $B_{1\mathrm{s}}(k_1)\,B_{1\mathrm{s}}(k_2)\,W_{1,1}C_{1,1}$ and $B_{1\mathrm{s}}(k_1)\,B_{n\mathrm{s}}(k_2)\,W_{1,n}C_{1,n}$ become comparable in magnitude and interfere with each other. This quantum interference determines the intensity of the $\mathrm{LP}_{n\mathrm{s}}$ lines at $\mathbf{K}_{\mathrm{m}} = \mathbf{0}$. Therefore, the signs of $C_{1,n}$ can be determined. In Fig. 3 we show the result of our analysis: the K_{m} dependence of the relative intensities $I_{\mathrm{LP}_{n\mathrm{s}}}/I_{\mathrm{LP}_{1\mathrm{s}}}$ in comparison with those calculated by Eq. (1) with explicit evaluation of $C_{1,n}$ (the normalization is given by $C_{1,1} = 1$). The agreement between the theory and experiment is very good. Note that in this procedure we use no free fitting parameters.

The internal molecule wavefunction $\Gamma(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2)$ is constructed in terms of a deformed ground-state exciton WF ϕ_1^{d} and an envelope wavefunction Ψ as $\Gamma = \Gamma_{\mathrm{direct}} + \Gamma_{\mathrm{exchange}} = \Psi(\mathbf{R})\,\phi_1^{\mathrm{d}}(\mathbf{r}_1)\,\phi_1^{\mathrm{d}}(\mathbf{r}_2) + \Psi(\mathbf{R}')\,\phi_1^{\mathrm{d}}(\mathbf{r}_1')\,\phi_1^{\mathrm{d}}(\mathbf{r}_2')$, where $\mathbf{R}'$, $\mathbf{r}_1'$, and $\mathbf{r}_2'$ are obtained from $\mathbf{R}$, $\mathbf{r}_1$, and $\mathbf{r}_2$ by exchange of the positions of two constituent electrons. As listed in Table II of Ref. [12], the Akimoto-Hanamura (A-H) WF yields $C_{1,2}^{\mathrm{direct}} > 0$ and $C_{1,2}^{\mathrm{exchange}} < 0$. The sign of $C_{1,n} = C_{1,n}^{\mathrm{direct}} + C_{1,n}^{\mathrm{exchange}}$ is determined by the balance between the direct (positive) and exchange (negative) contributions. Furthermore, the very small absolute values of $C_{1,n}$ ($n = 2,3,4$), obtained from the experimental data, clearly indicate a large degree of cancellation between the radial deformation of the excitonic orbits and the exchange effect. According to our experimental data, $C_{1,n}$ ($n = 2,3,4$) are negative for excitonic molecules in CuCl (see Fig. 3).

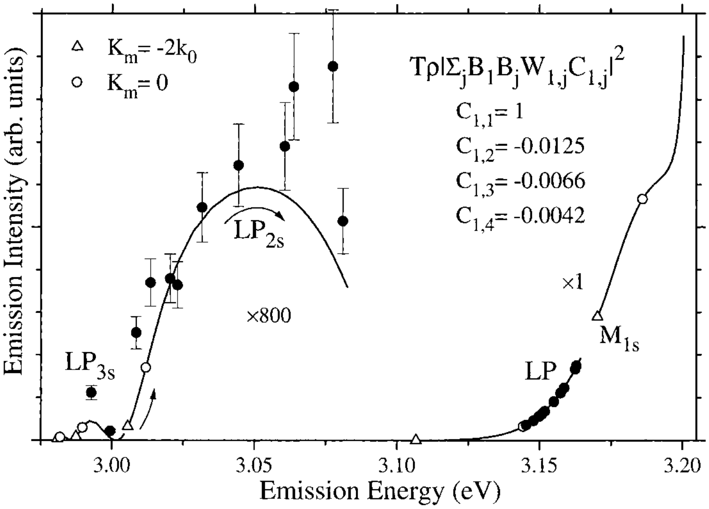

Fig. 3. Solid curves: the $\mathbf{K}_m$ dependence of the biexciton emission intensities calculated by Eq. (1) with $C_{1,1} = 1$, $C_{1,2} = -0.0125$, $C_{1,3} = -0.0066$, and $C_{1,4} = -0.0042$. A minor correction due to the sample transmission $T(E)$ is included. Closed circles: the relative intensities of the LP$_{ns}$ ($n = 2$, 3, and 4) lines normalized by $I_{\mathrm{LP}_{1s}}$. The error bars indicate the uncertainty in estimation of the frequency-integrated intensities. The arrows show the change of the molecule wavevector $\mathbf{K}_m$ from $-2\mathbf{k}_0$ (open triangles) to $\mathbf{k}_0$ (open circles), in accordance with Fig. 2

The quantities $C_{1,n}$ ($n > 1$) are very sensitive to the internal structure of the molecule WF. This is demonstrated in Table 1, where the total energy, the binding energy, and $C_{1,n}$ are calculated for the hydrogen molecule WF taken from Ref. [8]. The first column in Table 1 refers to the number of terms used in the trial WF. This number is a measure of the convergence toward an optimal approximation of the hydrogen molecule WF. The convergence of $C_{1,2}$ and $C_{1,3}$ is much slower than that of the energies and $C_{1,1}$. This is because the energies and $C_{1,1}$ depend only on the gross features of the WF,2) while $C_{1,2}$ and $C_{1,3}$ are characterized by the intricate details of the WF. As shown in this calculation, the hydrogen molecule is a good illustration how by using $C_{1,n>1}$ one can study the very structure of the wavefunction, although the inverse series does not exist for the hydrogen molecule so that in this case $C_{1,n}$ are not measurable quantities.

Table 1

Convergence of the energies and $C_{1,n}$ as the number of terms in the hydrogen molecule wavefunction, specified in Ref. [8], is increased. The values are normalized by those of the 50-term wavefunction

number of terms	total energy	binding energy	$C_{1,1}$	$C_{1,2}$	$C_{1,3}$
12	0.99978	0.99810	0.99988	1.08887	1.06513
24	0.99990	0.99933	1.00009	1.00297	1.00588
50	1	1	1	1	1

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2) In a crude approximation, $\Gamma_m(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2) \simeq \Psi(\mathbf{R})\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2)$ and $C_{1,1}$ is given by $C_{1,1} = \int \mathrm{d}\mathbf{R}\,\Psi(\mathbf{R})$.

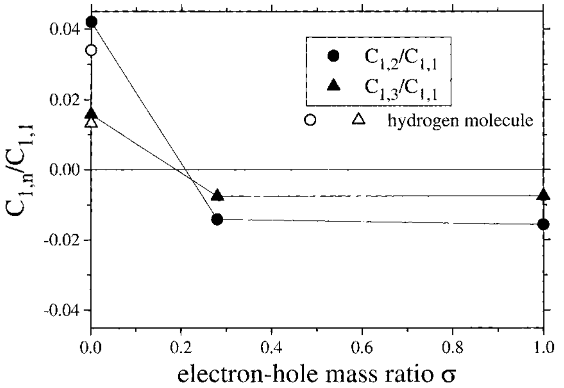

Fig. 4. The σ (electron–hole mass ratio) dependence of $C_{1,n}/C_{1,1}$ calculated with the A-H WF for $\sigma = 0$, 0.28, and 1. The lines connecting the points are only guides to the eye. For $\sigma = 0$, the values calculated by the 50-term hydrogen-molecule WF [8] are also displayed

In order to check whether the negative sign is a common characteristic of the molecule WFs, we have calculated the ratio $C_{1,n}/C_{1,1}$ for the A-H trial WF [3] as a function of the electron–hole mass ratio σ. Figure 4 shows the results for $\sigma = 0$ (hydrogen molecule), $\sigma = 0.28$ (appropriate for CuCl), and $\sigma = 1$ (positronium molecule). The negative sign of $C_{1,n=2,3}$ found from the experimental data is indeed consistent with the numerical evaluations. Figure 4 also indicates that $C_{1,2}$ and $C_{1,3}$ change the sign at $0 \leq \sigma \leq 0.25$. This means that the structures of the hydrogen molecule WF and excitonic molecule WF are different.

While $C_{1,n=2,3,4}/C_{1,1}$ evaluated for the A-H WF at $\sigma = 0.28$ agree reasonably with those determined from the experimental data, the calculated molecule binding energy is much smaller than the experimentally detected $E_m = 32$ meV. Furthermore, the A-H trial wavefunction does not include many interactions mentioned in the introduction. In spite of the simple (isotropic, nondegenerate) band structure in bulk CuCl, the molecule wavefunction is affected by (i) the polaron effect and (ii) the central-cell corrections, because of the highly polar nature of CuCl and due to the small exciton Bohr radius, respectively. We are studying these problems to resolve the remaining discrepancies between the experimental and theoretical results.

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