DIRECT TWO-PHOTON CREATION
OF EXCITONIC MOLECULE IN CuCl

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The probability of direct excitation of excitonic molecule in the two-photon absorption process is calculated with an Hylleraas–Ore type biexciton envelope, which is variationally optimized. In the second order of perturbation, because of the resonance effect, only the exciton Γ_5 intermediate state is taken into account. The band structure at band extrema due to spin–orbit interaction is assumed. The transition probability of two-photon absorption is expressed by matrix element between the free exciton and the biexciton envelopes. The obtained probability of two-photon absorption in CuCl is about three orders of magnitude smaller when compared to that obtained by Hanamura.

PACS numbers: 71.35.–y

1. Introduction

A shallow exciton can be regarded as a bound state of an electron in the conduction band and a positive hole in the valence band. Adamowski et al. [1] and independently Akimoto and Hanamura [2] pointed out that two weakly bound excitons form a biexciton (similarly to two hydrogen atoms which form a hydrogen molecule) for any value of the electron–hole mass ratio. The existence of the biexcitons has been confirmed in CdS, CdSe [3], in CuCl, CuBr [4] by the emission spectrum under strong excitation. The Bose condensation of these excitonic molecules [5] was also observed on the emission spectrum under the picosecond laser pulse excitation. Hanamura pointed out that the two-photon absorption due to excitonic molecule is enhanced due to the same effect of giant oscillator strength as in bound exciton [6] and the resonance effect.

We now present a more detailed estimation of the two-photon absorption coefficient due to excitonic molecule. In CuCl, compared with CuBr, valence band levels Γ_7 and Γ_8 are inverted. In CuCl the uppermost valence band maximum has symmetry Γ_7. It is much more simply to consider biexciton formed with the doubly degenerate hole states Γ_7 than that formed with the fourfold degenerate states Γ_8.

In our calculations we use the biexciton envelope optimized by variational calculation.

2. Two-photon excitation probability

The transition probability for the two ω-photon excitation of an insulating crystal from its ground state $|g\rangle$ to the excited state $|\text{biex}\rangle$ with an excitonic molecule [7] is

$$W^{(2)}(\omega) = \frac{2\pi}{\hbar} A^2 \langle\text{biex}|\varepsilon \sum_j P_j \sum_i \frac{|i\rangle\langle i|}{E_{ig} - \hbar\omega} \varepsilon \sum_{j'} P_{j'}|g\rangle \delta(2\hbar\omega - E_{\text{mol}}), \quad (1)$$

where $A = (e/m)^2 (2\pi\hbar N/\kappa\omega V)$ and N is the number of ω photons in the incident beam with polarization ε, κ is a dielectric constant for frequency ω. V is the volume of the crystal and $P_j = \exp(\mathrm{i}K_0 r_j)p_j$ with p_j — the momentum of the j-th electron and K_0 — the wave number vector of light. We count the energy from the ground state $|g\rangle$. We consider the ground state of the biexciton with energy $E_{\text{mol}}(\Gamma_1)$. The intermediate states are the excitonic states $|i\rangle$. By paying attention to the resonance effect we will only need to take the lowest intermediate excitonic states with energy $E_{\text{ex}}(\Gamma_5)$.

3. Excitations in CuCl with zinc blende structure

Cuprous chloride, CuCl — the crystal with tetrahedral symmetry (group T_d) has a band structure with the top of the valence band at $k = 0$ of symmetry Γ_7 and the bottom of the conduction band at $k = 0$ of symmetry Γ_6 (we use notation of Koster et al. [8]). The conduction Bloch functions (Γ_6) can be written as

$$c_{1/2} = \phi_c|\uparrow\rangle \quad \text{and} \quad c_{-1/2} = \phi_c|\downarrow\rangle, \tag{2}$$

where ϕ_c can be identified with the $4s$-functions of Cu. The valence Bloch functions (Γ_7) are of the form

$$v_{1/2} = \psi_1|\downarrow\rangle + \psi_0|\uparrow\rangle \quad \text{and} \quad v_{-1/2} = \psi_{-1}|\uparrow\rangle - \psi_0|\downarrow\rangle, \tag{3}$$

where the top valence wave functions may be identified with $3p$-functions of Cl:

$$\psi_{\pm 1} = (1/\sqrt{3})(p_x \pm \mathrm{i}p_y), \quad \psi_0 = (1/\sqrt{3})p_z. \tag{4}$$

Here p_x, p_y, p_z are separately normalized. The states $|\uparrow\rangle$ and $|\downarrow\rangle$ are the pure spin eigenstates corresponding to $\hbar/2$ and $-\hbar/2$, respectively.

In the effective mass approximation we replace the periodic parts of the Bloch functions by their values at the band extrema $c_{\pm 1/2}$ and $v_{\pm 1/2}$.

In CuCl the crystal symmetries of the biexciton states are given by the following product of irreducible representations:

$$\Gamma_6 \otimes \Gamma_7^* \otimes \Gamma_6 \otimes \Gamma_7^* = (\Gamma_2 + \Gamma_5) \otimes (\Gamma_2 + \Gamma_5) = 2\Gamma_1 + 3\Gamma_4 + \Gamma_3 + \Gamma_5. \tag{5}$$

In the total momentum classification of the exciton states, Γ_2 corresponds to $J = 0$, Γ_5 to $J = 1$. The energy of the exciton Γ_5 is increased by the electron–hole exchange interaction. In the classification of the biexciton states Γ_1 corresponds to $J = 0$, Γ_4 to $J = 1$ and $\Gamma_3 + \Gamma_5$ results from the splitting of $J = 2$.

We will consider the optical two-photon transition from the ground state $|g\rangle$ to the biexciton ground state of symmetry Γ_1. Because the optical excitations from the state $|g\rangle$ to the exciton Γ_1 ($J = 0$) are forbidden, we will take as the

intermediate states the nearest exciton states of symmetry Γ_5 $(J = 1)$. The excited two-particle (one electron and one hole) triplet states [9] can be expressed with the use of the fermion operators

$$|l, k; J = 1, J_z\rangle$$

$$= \begin{cases} a^+_{cl,1/2}a_{vk,-1/2}|g\rangle & (J_z = 1), \\ (1/\sqrt{2})(a^+_{cl,1/2}a_{vk,1/2} - a^+_{cl,-1/2}a_{vk,-1/2})|g\rangle & (J_z = 0), \\ a^+_{cl,-1/2}a_{vk,1/2}|g\rangle & (J_z = -1). \end{cases} \tag{6}$$

The operator $a^+_{cl,\pm1/2}$ creates the electron in the conduction band in the Bloch state with the wave vector l and $J_z = \pm1/2$, while $a_{vk,\pm1/2}$ annihilates the electron in the valence band in the Bloch state with the wave vector k and $J_z = \pm1/2$.

We assume the exciton Γ_5 states in the form of a linear combination

$$|\Gamma_5^{\mathrm{ex}}; K, J_z\rangle = \sum_{l,k} A_K(l, k)|l, k; J = 1, J_z\rangle. \tag{7}$$

The summation over the wave vectors l,k is limited here to $l - k = K$, the total wave vector of the free exciton center of mass. The linear coefficients $A_K(l, k)$ are the Fourier components of the envelope

$$A_K(l, k) = \frac{1}{V} \int \int \mathrm{d}^3r_1 \mathrm{d}^3r_2 \phi_K(r_2, r_2) \exp(-\mathrm{i}lr_1 + \mathrm{i}kr_2), \tag{8}$$

where ϕ_K is the free-exciton envelope function [10]

$$\phi_K(r_1, r_2) = \frac{1}{\sqrt{V}} \exp\left(\mathrm{i}KR_0^{(\mathrm{ex})}\right) \Phi_{\mathrm{ex}}(r). \tag{9}$$

The exciton envelope $\Phi_{\mathrm{ex}}(r)$ is a function of the electron–hole distance $r = |r_1 - r_2|$, $R_0^{(\mathrm{ex})} = (m_e r_1 + m_h r_2)/M$ is the position of exciton centre of mass, m_e, m_h are the electron and hole effective masses and $M = m_e + m_h$. V is the volume of the crystal.

The biexciton ground state of the symmetry Γ_1 is described by a spatial envelope function symmetrized with respect to the permutation of two electrons, as well as the permutation of two holes [11, 12]. According to this symmetry we define the excited four particle singlet states symmetric in l, l' and symmetric in k, k':

$$|l, k, l', k'; J = 0\rangle = \frac{1}{2}\left(a^+_{cl,1/2}a^+_{cl',-1/2} - a^+_{cl,-1/2}a^+_{cl',1/2}\right)$$

$$\times \left(a_{vk,1/2}a_{vk',-1/2} - a_{vk,-1/2}a_{vk',1/2}\right)|g\rangle. \tag{10}$$

We assume the biexciton ground state in the form

$$|\Gamma_1^{\mathrm{mol}}; K\rangle = \sum_{l,k,l',k'} B_K(l, k, l', k')|l, k, l', k'; J = 0\rangle. \tag{11}$$

Here the summation is limited to $l - k + l' - k' = K$, where K is the total momentum of the biexciton. The linear coefficients B_K are the Fourier components

$$B_{\boldsymbol{K}}(l, k, l', k') = \frac{1}{V^2} \int \int \int \int \mathrm{d}^3r_1 \mathrm{d}^3r_2 \mathrm{d}^3r_3 \mathrm{d}^3r_4 \psi_{\boldsymbol{K}}(r_1, r_2, r_3, r_4)$$

$$\times \exp\left(-\mathrm{i}lr_1 + \mathrm{i}kr_2 - \mathrm{i}l'r_3 + \mathrm{i}k'r_4\right), \tag{12}$$

where $\psi_{\boldsymbol{K}}$ is the biexciton wave function of the electron (1,3) and the hole (2,4) coordinates

$$\psi_{\boldsymbol{K}}(r_1, r_2, r_3, r_4) = \frac{1}{2\sqrt{V}} \exp\left(\mathrm{i}\boldsymbol{K}\boldsymbol{R}_0^{\mathrm{mol}}\right) \Psi_{\mathrm{mol}}(r, r', \boldsymbol{R}). \tag{13}$$

Here $\boldsymbol{R}_0^{\mathrm{mol}} = m_e(r_1+r_3)/2M + m_h(r_2+r_4)/2M$ is the position of biexciton centre of mass and Ψ is the biexciton ground state envelope function [10] of $r = r_3 - r_1$, $r' = r_4 - r_2$ and $\boldsymbol{R} = (r_1 + r_3 - r_2 - r_4)/2$. Introducing the factor $1/(2\sqrt{V})$ in Eq. (13) we have for the normalized biexciton state (10) the normalization condition of the envelope function Ψ: $\int \mathrm{d}^3r \int \mathrm{d}^3r' \int \mathrm{d}^3R |\Psi_{\mathrm{mol}}(r, r', \boldsymbol{R})|^2 = 1$.

4. The two-photon absorption

For the transition with absorption of light we use in the zinc blende type CuCl crystal the customary dipole approximation

$$\varepsilon \sum_{j=1}^{N} \exp\left(\mathrm{i}\boldsymbol{K}_0 r_j\right) p_j = \varepsilon \sum_{\lambda} \Big(\langle\phi_c|p|\psi_{-1}\rangle a_{c\lambda+K_0, 1/2}^+ a_{v\lambda, -1/2}$$

$$+ \langle\phi_c|p|\psi_0\rangle a_{c\lambda+K_0, 1/2}^+ a_{v\lambda, 1/2} + \langle\phi_c|p|\psi_1\rangle a_{c\lambda+K_0, -1/2}^+ a_{v\lambda, 1/2}$$

$$- \langle\phi_c|p|\psi_0\rangle a_{c\lambda+K_0, -1/2}^+ a_{v\lambda, -1/2} \Big), \tag{14}$$

where p_j is the momentum of j-th electron and $\langle\phi_c|p|\psi_{J_z}\rangle$ is the matrix element of the electron momentum p between the valence and the conduction band wave functions.

The matrix elements in Eq. (1) are evaluated, with the use of the approximation (14), as follows:

$$\langle \Gamma_5^{\mathrm{ex}}; \boldsymbol{K}, J_z | \varepsilon \sum_{j=1}^{N} \exp\left(\mathrm{i}\boldsymbol{K}_0 r_j\right) p_j | g \rangle$$

$$= \begin{cases} \delta_{\boldsymbol{K}, \boldsymbol{K}_0} \sqrt{V} \Phi_{\mathrm{ex}}(0) \langle\phi_c|\varepsilon p|\psi_{\mp 1}\rangle & \text{for} \quad J_z = \pm 1, \\ \delta_{\boldsymbol{K}, \boldsymbol{K}_0} \sqrt{V} \Phi_{\mathrm{ex}}(0) \sqrt{2} \langle\phi_c|\varepsilon p|\psi_0\rangle & \text{for} \quad J_z = 0 \end{cases} \tag{15}$$

and

$$\langle \Gamma_1^{\mathrm{mol}}; \boldsymbol{K} | \varepsilon \sum_{j=1}^{N} \exp\left(\mathrm{i}\boldsymbol{K}_0 r_j\right) p_j | \Gamma_5^{\mathrm{exp}}; \boldsymbol{K}_0, J_z \rangle$$

$$= \begin{cases} \delta_{\boldsymbol{K}, 2\boldsymbol{K}_0} I[\Phi_{\mathrm{ex}}, \Psi_{\mathrm{mol}}] \langle\phi_c|\varepsilon p|\psi_{\pm}\rangle & \text{for} \quad J_z = \pm 1, \\ \delta_{\boldsymbol{K}, 2\boldsymbol{K}_0} I[\Phi_{\mathrm{ex}}, \Psi_{\mathrm{mol}}] \sqrt{2} \langle\phi_c|\varepsilon p|\psi_0\rangle & \text{for} \quad J_z = 0, \end{cases} \tag{16}$$

where for $\boldsymbol{K}_0 \approx 0$ the functional of the exciton and biexciton envelopes is defined

$$I[\Phi_{\text{ex}}, \Psi_{\text{mol}}] = 2 \sum_{l,k} B_{2K_0}^*(l, l - K_0, k + K_0, k) A_{K_0}(l, l - K_0)$$

$$\approx \int \int \mathrm{d}^3 x \mathrm{d}^3 y \, \Psi_{\text{mol}}^*(x - y, x, y/2) \Phi_{\text{ex}}(y). \tag{17}$$

Inserting matrix elements (15)–(16) into Eq. (1) we get for $K_0 \approx 0$

$$W^{(2)}(\Gamma_1^{\text{mol}}; \omega) = \frac{2\pi}{\hbar} A^2 \Big\{ \Phi_{\text{ex}}(0) \sqrt{V} I[\Phi_{\text{ex}}, \Psi_{\text{mol}}] \frac{1}{E_{\text{ex}}(\Gamma_5) - \hbar\omega}$$

$$\times \Big[\langle \phi_c | \varepsilon p | \psi_1 \rangle \langle \phi_c | \varepsilon p | \psi_{-1} \rangle + \langle \phi_c | \varepsilon p | \psi_0 \rangle^2 \Big] \Big\}^2 \delta[2\hbar\omega - E_{\text{mol}}(\Gamma_1)]. \tag{18}$$

Because of the cubic symmetry $\langle \phi_c | p_x | p_x \rangle = \langle \phi_c | p_y | p_y \rangle = \langle \phi_c | p_z | p_z \rangle$, Eq. (18) is simplified to

$$W^{(2)}(\Gamma_1^{\text{mol}}; \omega) = \frac{2\pi}{\hbar} A^2 \Phi_{\text{ex}}^2(0) V I^2[\Phi_{\text{ex}}, \Psi_{\text{mol}}]$$

$$\times \frac{4\varepsilon^4 |\langle \phi_c | p_x | p_x \rangle|^4}{9[E_{\text{ex}}(\Gamma_5) - \hbar\omega]^2} \delta[2\hbar\omega - E_{\text{mol}}(\Gamma_1)]. \tag{19}$$

We will compare $W^{(2)}$ with the transition probability of one-photon absorption due to a single exciton

$$W^{(1)}(\Gamma_5^{\text{ex}}; \omega) = \frac{2\pi}{\hbar} A V \Phi_{\text{ex}}^2(0) \frac{2}{3} \varepsilon^2 |\langle \phi_c | p_x | p_x \rangle|^2 \delta[\hbar\omega - E_{\text{ex}}(\Gamma_5)]. \tag{20}$$

5. Numerical results

The probabilities $W^{(1)}(\Gamma_5^{\text{ex}}; \omega)$ at $\omega = \omega_{\text{ex}} = E_{\text{ex}}(\Gamma_5)/\hbar$ and $W^{(2)}(\Gamma_1^{\text{mol}}; \omega)$ at $\omega = \omega_{\text{mol}} = \frac{1}{2} E_{\text{mol}}(\Gamma_1)/\hbar = \left[E_{\text{ex}}(\Gamma_2) - \frac{1}{2} E_{\text{mol}}^{\text{b}} \right]/\hbar$ with $E_{\text{mol}}^{\text{b}}$ — the binding energy of excitonic molecule, can be compared by taking the following experimental values for CuCl: $|\langle \phi_c | p_x | p_x \rangle|^2/m \approx 3$ eV [6], $\hbar\omega = 3.4$ eV and $E_{\text{ex}}(\Gamma_5) - \hbar\omega = \frac{1}{2} E_{\text{mol}}^{\text{b}} + \Delta_{\text{ex}}^{\text{exch}}$ with $E_{\text{mol}}^{\text{b}} \approx 30$ meV and $\Delta_{\text{ex}}^{\text{exch}} = E_{\text{ex}}(\Gamma_5) - E_{\text{ex}}(\Gamma_2) \approx 6$ meV [13].

The integral $I = I[\Phi_{\text{ex}}, \Psi_{\text{mol}}]$ is equal to the square root of the ratio of the oscillator strengths due to the transition of the biexciton-free exciton and to the recombination of the free exciton. We take the value $I \approx 4$ obtained by one of the authors [14] with the optimized envelope Ψ_{mol}. Function Ψ_{mol} was approximated by the Hylleraas–Ore [15, 16] wave function ψ of electron–hole distances r_{ij}. All the distances are expressed in units of exciton Bohr radius $a_0 = \kappa_0^2/\mu e^2$, where κ_0 is crystal's dielectric constant and $\mu = m_e m_h/(m_e + m_h)$ is the reduced mass of the exciton. The envelope is $\Psi_{\text{mol}} = \psi F/S$ with $\psi = 2 \exp\left[-(s_1 + s_2)/2)\right] \cosh[\beta(t_1 - t_2)/2]$, where $s_1 = k(r_{12} + r_{14})$, $s_2 = k(r_{32} + r_{34})$, $t_1 = k(r_{12} - r_{14})$, $t_2 = k(r_{32} - r_{34})$, F/S is the function of the hole–hole distance $\rho = r_{24}$ introduced by Brinkman et al. [11]: $F(\rho) = (\rho/A)^n \exp(-\rho/A) + C \exp(-B\rho/A)$ and $S^2(\rho) = \int \psi^2 \mathrm{d}^3 r_1 \mathrm{d}^3 r_2$. The variational parameters of $\Psi_{\text{mol}}(k, \beta, A, B, C, n)$ depend on the ratio of effective masses $\sigma = m_e/m_h$ (for CuCl $\sigma = 0.02$).

The exciton envelope Φ_{ex} was taken in the form of the hydrogen-like wave function $\Phi_{ex}(r) = \exp(-r)/\sqrt{\pi}$. We have obtained the ratio of the probabilities $W^{(2)}/W^{(1)} = 3.5 \times 10^{-18}$ cm³ N/V. Our result is smaller than that previously obtained by Hanamura $W^{(2)}/W^{(1)} = 3 \times 10^{-15}$ cm³ N/V. In comparison with an ordinary two-photon absorption due to a single electron excitation there are two enhancement factors determining direct two-photon absorption probability $W^{(2)}$ (19): $I^2[\Phi_{ex}, \Psi_{mol}]$, which corresponds to the oscillator strength [14], and the second one, which comes from the resonance effect $1/[E_{ex}(\Gamma_5) - \hbar\omega]^2$. $I[\Phi_{ex}, \Psi_{mol}]$ obtained with the use of the optimized envelope [14] is about 10 times smaller compared to that estimated by Ueta [6]. The resonance denominator, corrected by the electron–hole exchange term is twice greater than that used in [6].

Therefore at the dye laser of tunable frequency above the photon density $N/V = 10^{17}$ cm⁻³, the two-photon absorption coefficient at $\omega = \omega_{mol}$ is expected to be as strong as a single excitation absorption at $\omega = \omega_{ex}$.

We note that time of biexciton decay corresponding to the oscillator strength of biexciton into exciton transition estimated with simple envelope used by Hanamura was too small [16, 17]. Therefore the smaller value of the integral $I[\Phi_{ex}, \Phi_{mol}]$ and thus, the smaller than previously estimated value of $W^{(2)}/W^{(1)}$ seems to be more appropriate.

We also estimated the ratio $W^{(2)}/W^{(1)}$ in case of CuBr crystal. Taking the electron to hole mass ratio $\sigma = 0.01$ [11] we got $W^{(2)}/W^{(1)} \approx 10^{-18} \div 10^{-17}$ cm³ N/V, which is close to the result obtained for CuCl.

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