DIRECT TWO-PHOTON CREATION OF EXCITONIC MOLECULE IN CuCl

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The probability of direct excitation of exciton 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 $\Gamma_5$ 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.

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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 $\Gamma_7$ and $\Gamma_8$ are inverted. In CuCl the uppermost valence band maximum has symmetry $\Gamma_7$. It is much more simply to consider biexciton formed with the doubly degenerate hole states $\Gamma_7$ than that formed with the fourfold degenerate states $\Gamma_8$.

In our calculations we use the biexciton envelope optimized by variational calculation.
Two-photon excitation probability

The transition probability for the two $\omega$-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

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

where $A = (e/m)^2(2\pi\hbar N/\kappa \omega V)$ and $N$ is the number of $\omega$ photons in the incident beam with polarization $e$, $\kappa$ is a dielectric constant for frequency $\omega$. $V$ is the volume of the crystal and $P_j = \exp(iK_0 r_j)p_j$ 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 $\Gamma_7$ and the bottom of the conduction band at $k = 0$ of symmetry $\Gamma_6$ (we use notation of Koster et al. [8]). The conduction Bloch functions $(\Psi_6)$ can be written as

\[ c_{1/2} = \phi_e | \uparrow \rangle \quad \text{and} \quad c_{-1/2} = \phi_e | \downarrow \rangle, \tag{2} \]

where $\phi_e$ can be identified with the 4s-functions of Cu. The valence Bloch functions $(\Psi_7)$ 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:

\[ \psi_{\pm 1} = (1/\sqrt{3})(p_x \pm ip_y), \quad \psi_0 = (1/\sqrt{3})p_z. \tag{4} \]

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, $\Gamma_2$ corresponds to $J = 0$, $\Gamma_5$ to $J = 1$. The energy of the exciton $\Gamma_5$ is increased by the electron–hole exchange interaction. In the classification of the biexciton states $\Gamma_1$ corresponds to $J = 0$, $\Gamma_4$ 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 $\Gamma_1$. Because the optical excitations from the state $|g\rangle$ to the exciton $\Gamma_1$ ($J = 0$) are forbidden, we will take as the
intermediate states the nearest exciton states of symmetry $\Gamma_5$ ($J = 1$). The excited two-particle (one electron and one hole) triplet states \cite{9} can be expressed with the use of the fermion operators

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

$$= \left\{ \begin{array}{ll}
  a_{d,1/2}^+ a_{v,k,-1/2}^- |g\rangle & (J_z = 1), \\
  (1/\sqrt{2})(a_{d,1/2}^+ a_{v,k,1/2}^- - a_{d,-1/2}^+ a_{v,k,-1/2}^-) |g\rangle & (J_z = 0), \\
  a_{d,-1/2}^+ a_{v,k,1/2}^- |g\rangle & (J_z = -1).
\end{array} \right.$$  \hspace{1cm} (6)

The operator $a_{d,\pm 1/2}^+$ creates the electron in the conduction band in the Bloch state with the wave vector $l$ and $J_z = \pm 1/2$, while $a_{v,k,\pm 1/2}^-$ annihilates the electron in the valence band in the Bloch state with the wave vector $k$ and $J_z = \pm 1/2$.

We assume the exciton $\Gamma_5$ states in the form of a linear combination

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

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

where $\phi_K$ is the free-exciton envelope function \cite{10}

$$\phi_K(r_1, r_2) = \frac{1}{\sqrt{V}} \exp \left( i K R^{(ex)}_0 \right) \Phi_{ex}(r).$$  \hspace{1cm} (9)

The exciton envelope $\Phi_{ex}(r)$ is a function of the electron–hole distance $r = |r_1 - r_2|$, $R^{(ex)}_0 = (m_e r_1 + m_h r_2)/M$ is the position of exciton center 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 $\Gamma_1$ is described by a spatial envelope function symmetrized with respect to the permutation of two electrons, as well as the permutation of two holes \cite{11, 12}. According to this symmetry we define the excited four particle singlet states symmetric in $l, l'$ and symmetric in $k, k'$:

$$|l, k, l', k'; J = 0\rangle = \frac{1}{2} \left( a_{d,l,1/2}^+ a_{d,l',-1/2}^- - a_{d,l,1/2}^+ a_{d,l',1/2}^- \right) \times \left( a_{v,k,1/2}^+ a_{v,k',-1/2}^- - a_{v,k,1/2}^+ a_{v,k',1/2}^- \right) |g\rangle.$$  \hspace{1cm} (10)

We assume the biexciton ground state in the form

$$|\Gamma_1^{moll}; K\rangle = \sum_{l,k,l',k'} B_K(l, k, l', k') |l, k, l', k'; J = 0\rangle.$$  \hspace{1cm} (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.
where $\psi_K$ is the biexciton wave function of the electron (1,3) and the hole (2,4) coordinates

$$
\psi_K(r_1, r_2, r_3, r_4) = \frac{1}{2\sqrt{V}} \exp \left( iK\mathbf{R}_0^{\text{mol}} \right) \Psi_{\text{mol}}(r, r', R).
$$

Here $\mathbf{R}_0^{\text{mol}} = m_e(r_1 + r_3)/2M + m_h(r_2 + r_4)/2M$ is the position of biexciton centre of mass and $\Psi$ is the biexciton ground state envelope function [10] of $r = r_3 - r_1$, $r' = r_4 - r_2$ and $R = (r_1 + r_3 - r_2 - r_4)/2$. 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 $\Psi$:

$$
\int d^3r \int d^3r' \int d^3R |\Psi_{\text{mol}}(r, r', R)|^2 = 1.
$$

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

$$
\varepsilon \sum_{j=1}^{N} \exp (iK_0 r_j) p_j = \varepsilon \sum_{\lambda} \left( \langle \phi_e | p | \psi_{-1} \rangle a_{\lambda, c_0}^{+} + \langle \phi_e | p | \psi_1 \rangle a_{\lambda, c_0}^{+} \right) \frac{1}{2} + \frac{1}{2} \frac{1}{2}
$$

$$
- \langle \phi_e | p | \psi_0 \rangle a_{\lambda, c_0}^{+} + \langle \phi_e | p | \psi_{-1} \rangle a_{\lambda, c_0}^{+} \right) ,
$$

where $p_j$ is the momentum of $j$-th electron and $\langle \phi_e | p | \psi_J \rangle$ 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:

$$
\langle I_5^{\text{ex}}; K, J_z | e \sum_{j=1}^{N} \exp (iK_0 r_j) p_j | g \rangle
$$

$$
= \left\{ \begin{array}{ll}
\delta_{K, K_0} \sqrt{\delta_{J_z}} \langle \phi_e \phi_e | \psi_{-1} \rangle | \phi_e | e p | \psi_{-1} \rangle & \text{for} \ J_z = \pm 1, \\
\delta_{K, K_0} \sqrt{\delta_{J_z}} \langle \phi_e \phi_e | \psi_0 \rangle | \phi_e | e p | \psi_0 \rangle & \text{for} \ J_z = 0
\end{array} \right.
$$

and

$$
\langle I_1^{\text{mol}}, K | e \sum_{j=1}^{N} \exp (iK_0 r_j) p_j | I_5^{\text{ex}}; K_0, J_z \rangle
$$

$$
= \left\{ \begin{array}{ll}
\delta_{K, 2K_0} I[\phi_{\text{ex}}, \Psi_{\text{mol}}] | \phi_e | e p | \psi_{-1} \rangle | \phi_e | e p | \psi_{-1} \rangle & \text{for} \ J_z = \pm 1, \\
\delta_{K, 2K_0} I[\phi_{\text{ex}}, \Psi_{\text{mol}}] | \phi_e | e p | \psi_0 \rangle | \phi_e | e p | \psi_0 \rangle & \text{for} \ J_z = 0
\end{array} \right.
$$

where for $K_0 \approx 0$ the functional of the exciton and biexciton envelopes is defined
\[ I[\Phi_{\text{ex}}, \Psi_{\text{mol}}] = 2 \sum_{l,k} B^*_{l,2K_0}(l, l - K_0, K_0, k) A_{K_0}(l, l - K_0) \]

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

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

\[ W^{(2)}(I_1^{\text{mol}}; \omega) = \frac{2\pi}{\hbar} A^2 \left\{ \Phi_{\text{ex}}(0) \sqrt{I[\Phi_{\text{ex}}, \Psi_{\text{mol}}]} \frac{1}{E_{\text{ex}}(I_5^3) - \hbar \omega} \right\} \]

\[ \times \left[ (\langle \phi_c | e_p | \psi_1 \rangle (\langle \phi_c | e_p | \psi_1 \rangle + (\langle \phi_c | e_p | \psi_0 \rangle)^2) \right]^2 \delta(2\hbar \omega - E_{\text{mol}}(I_1^1)). \] (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

\[ W^{(2)}(I_1^{\text{mol}}; \omega) = \frac{2\pi}{\hbar} A^2 \Phi_{\text{ex}}^2(0) V I^2[\Phi_{\text{ex}}, \Psi_{\text{mol}}] \]

\[ \times \frac{4\varepsilon^4}{9\sqrt{E_{\text{ex}}(I_5^3) - \hbar \omega}^2} \delta(2\hbar \omega - E_{\text{mol}}(I_1^1)). \] (19)

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

\[ W^{(1)}(I_5^{\text{ex}}; \omega) = \frac{2\pi}{\hbar} A V \Phi_{\text{ex}}^2(0) \frac{2}{3} \varepsilon^2 \langle \langle \phi_c | p_x | p_x \rangle \rangle^2 \delta(\hbar \omega - E_{\text{ex}}(I_5^3)). \] (20)

5. Numerical results

The probabilities \( W^{(1)}(I_5^{\text{ex}}; \omega) \) at \( \omega = \omega_{\text{ex}} = E_{\text{ex}}(I_5^3)/\hbar \) and \( W^{(2)}(I_1^{\text{mol}}; \omega) \) at \( \omega = \omega_{\text{mol}} = \frac{1}{2} E_{\text{mol}}(I_1^1)/\hbar = [E_{\text{ex}}(I_2^2) - \frac{1}{2} E_{\text{mol}}^b]/h \) with \( E_{\text{mol}}^b \) — the binding energy of excitonic molecule, can be compared by taking the following experimental values for CuCl: \( \langle \langle \phi_c | p_x | p_x \rangle \rangle^2/m \approx 3 \text{ eV} \) [6], \( \hbar \omega = 3.4 \text{ eV} \) and \( E_{\text{ex}}(I_5^3) - \hbar \omega = \frac{1}{2} E_{\text{mol}}^b + \Delta_{\text{exch}}^b \) with \( E_{\text{mol}}^b \approx 30 \text{ meV} \) and \( \Delta_{\text{exch}}^b = E_{\text{ex}}(I_5^3) - E_{\text{ex}}(I_2^2) = 6 \text{ meV} \) [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 \( \Psi_{\text{mol}} \). Function \( \Psi_{\text{mol}} \) was approximated by the Hylleraas–Ore [15, 16] wave function \( \psi \) of electron–hole distances \( r_{ij} \). All the distances are expressed in units of exciton Bohr radius \( a_0 = \kappa_0/\mu \), where \( \kappa_0 \) 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 \( \psi = 2 \exp[-(s_1 + s_2)/2] \cosh[b(t_1 - t_2)/2] \), 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 \( \rho = r_{34} \) introduced by Brinkman et al. [11]: \( F(\rho) = (\rho/A)^\beta \exp(-\rho/A) + C \exp(-B\rho/A) \) and \( S^2(\rho) = \int \psi^2 d^3r_1 d^3r_2 \). 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 $\Phi_{\text{ex}}$ was taken in the form of the hydrogen-like wave function $\Phi_{\text{ex}}(r) = \exp(-r)/\pi$. We have obtained the ratio of the probabilities $W(2)/W(1) = 3.5 \times 10^{-18}$ cm$^3$ N/V. Our result is smaller than that previously obtained by Hanamura $W(2)/W(1) = 3 \times 10^{-15}$ cm$^3$ 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): $I^2[\Phi_{\text{ex}}, \Psi_{\text{mol}}]$, which corresponds to the oscillator strength [14], and the second one, which comes from the resonance effect $1/(E_{\text{ex}}(\Gamma_5) - \hbar\omega)^2$. $I[\Phi_{\text{ex}}, \Psi_{\text{mol}}]$ 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 $\omega = \omega_{\text{mol}}$ is expected to be as strong as a single excitation absorption at $\omega = \omega_{\text{ex}}$.

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 $I[\Phi_{\text{ex}}, \Phi_{\text{mol}}]$ 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 $W(2)/W(1) \approx 10^{-18} \div 10^{-17}$ cm$^3$ N/V, which is close to the result obtained for CuCl.

References


