ON THE CALCULATION OF THE ENERGY OF MOLECULAR EXCITONS

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Abstract

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Using the simple example of an isotropic molecular crystal, one can show that the quantitative results of all works (for example, ([1–3])) in which attempts were made at a theoretical calculation of exciton bands in molecular crystals should be changed by a factor of 1.5-2.

In isotropic molecular crystals containing one molecule per unit cell, each electronic excitation E_f corresponds to an exciton band, i.e., a quasi-continuous system of levels $E_f(\mathbf{k})$, determined by the equality

$$E_f(\mathbf{k}) = E_f + D_f + \sum_{\mathbf{m}(\neq \mathbf{n})} M^f_{\mathbf{nm}} \exp\{i\mathbf{k}(\mathbf{n}-\mathbf{m})\}, \tag{1}$$

where $\mathbf{k}$ is the wave vector; $\mathbf{n}$ and $\mathbf{m}$ are lattice vectors; D_f is the change in the interaction energy of all molecules with one molecule when the latter passes into the f-th excited state; $M^f_{\mathbf{nm}}$ is the matrix element for transfer of the excitation energy from molecule $\mathbf{n}$ to molecule $\mathbf{m}$. For allowed dipole transitions it is usually assumed ([4])

$$M_{\mathbf{nm}} = \frac{d_f^2}{R^3_{\mathbf{nm}}}\{1 - 3\cos^2(\widehat{\mathbf{d}_f\mathbf{R}_{\mathbf{nm}}})\}, \tag{2}$$

where $\mathbf{d}_f$ is the electric dipole moment of the molecular transition from the ground state to the f-th excited state; $R_{\mathbf{nm}}$ is the distance between molecules $\mathbf{n}$ and $\mathbf{m}$. The sum (1) converges slowly; therefore the summation must be carried out over a sufficiently large region of the crystal. Calculations show that (1) can be represented by the formula

$$E_f(\mathbf{k}) = 4\pi(\mathbf{d}_f\mathbf{k})^2/vk^2 + \Phi_f(\mathbf{k}), \tag{3}$$

where v is the volume of the unit cell of the crystal, and $\Phi_f(\mathbf{k})$ is an analytic function of $\mathbf{k}$.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Light interacts with transverse excitons ($\mathbf{k} \perp \mathbf{d}_f$) having wave vectors $k \approx 0$. According to equality (3), the energy of such excitons is

$$E_f^{\perp}(0) = \Phi_f(0). \tag{4}$$

The energy of longitudinal excitons ($\mathbf{k} \parallel \mathbf{d}_f$) under the same conditions is equal to

$$E_f^{\parallel}(0) = 4\pi d_f^2/v + E_f^{\perp}(0). \tag{5}$$

On the other hand, the energy of longitudinal excitons (see (5)) can also be found from the condition that the phenomenological dielectric permittivity $\varepsilon(\omega)$ of the crystal vanish. The dielectric permittivity of the crystal in the frequency region close to, but not equal to, $E_f^{\perp}(0)$, neglecting absorption, is determined by the expression

$$\varepsilon(\omega) = \varepsilon_0 + 8\pi d_f^2 E_f/v\{[E_f^{\perp}(0)]^2 - \hbar^2\omega^2\}, \tag{6}$$

where ε_0 is the dielectric permittivity due to all electronic states of the molecules of the crystal except E_f. Equating the right-hand side of equality (6) to zero, we find

$$E_f^{\parallel}(0) = \{[E_f^{\perp}(0)]^2 + 8\pi^2 d_f^2 E_f/v\varepsilon_0\}^{1/2} \approx E_f^{\perp}(0) + 4\pi d_f^2/v\varepsilon_0. \tag{7}$$

The discrepancy between formulas (5) and (7) is due to the fact that formula (5) takes into account only the f-th excited state of the molecules, whereas formula (7) takes into account all electronic states. If in (6) only the f-th excited state is likewise taken into account, then $\varepsilon_0 = 1$.

The influence of all molecular electronic states distinct from the f-th one on the exciton band (1) can be taken into account phenomenologically if, when writing the matrix element (2), one allows for the fact that the molecules $\mathbf{n}$ and $\mathbf{m}$ are in a medium with dielectric constant ε_0.

Fig. 1

Fig. 2

Then, instead of (2), we have

$$M_{\mathbf{nm}} = \frac{d_f^2}{\varepsilon_0 R_{\mathbf{nm}}^3} \left\{1 - 3\cos^2\left(\widehat{\mathbf{d}_f R_{\mathbf{nm}}}\right)\right\}.$$

In this case formulas (3)–(5) are transformed respectively into the form

$$E_f(\mathbf{k}) = \frac{4\pi(\mathbf{d}_f\mathbf{k})^2}{\varepsilon_0 v k^2} + \frac{1}{\varepsilon_0}\Phi_f(\mathbf{k}), \tag{8}$$

$$E_f^{\perp}(0) = \frac{1}{\varepsilon_0}\Phi_0(0), \qquad E_f^{\parallel}(0) = \frac{4\pi d_f^2}{v\varepsilon_0} + E_f^{\perp}(0), \tag{9}$$

and the contradiction with equality (7) disappears. Comparison of expressions (8) and (1) shows that the effect of the polarizability of the crystal due to molecular electronic states not taken into account in calculating expression (1) reduces to a decrease of the band width by a factor of ε_0.

This result is also qualitatively preserved in anisotropic crystals, if one takes into account the tensor character of ε_0, which can change the polarization ratios of the components of Davydov multiplets in crystals containing two or more molecules in the unit cell.

In the work of Sheka and one of the authors of the present paper (^{3}), the dependence of the exciton energy on the magnitude and direction of the exciton quasimomenta in two energy bands of an anthracene crystal, corresponding to the first electronic excitation of the molecule ($E_f = 25570$ cm^{-1}), was calculated (without taking into account the effect indicated above). According to the experimental data of Brodin and Marisova, for two polarizations of light parallel respectively to the a and b axes in an anthracene crystal, the values of ε_0 differ little from each other and are approximately equal to 2.5. Taking these values

and using the calculations of (3), we obtain the dependence, shown in Fig. 1, of the exciton energy for three directions of the wave vector. In doing so it was assumed that $E_f = 25570$ cm^{-1}, the oscillator strength of the transition $F = 0.23$; $\varepsilon_0 = 2.5$; $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are the basis vectors of the elementary cell; $\mathbf{k}_c$ is the wave vector perpendicular to the plane ab; $\mathbf{k}_a$ is perpendicular to bc, and $\mathbf{k}_b$ is perpendicular to ac. $\mathbf{P}_1$ and $\mathbf{P}_2$ are vectors determining the polarization of the exciton states.

The energies of the exciton states shown in Fig. 1 were obtained under the assumption that the effective region of interaction between molecules is very large. Figure 2 gives the exciton energy at small values of k_c for three values of the radii R_0 of the effective interaction region. Curves 1 and 2 are for $R_0 = 1$ μ; curves 1′ and 2′ are for $R_0 = 0.1$ μ, and curves 1″ and 2″ are for $R_0 = 0.05$ μ. The maxima of the absorption curves should correspond to the intersections of these curves with the vertical arrows at cQ_a and cQ_b, corresponding to photon wave vectors of polarizations a and b. Comparing the energy difference $\Delta = E(Q_a) - E(Q_b)$ with the experimental (6) value 220 cm^{-1} mm, we find that the theory is in approximate agreement with experiment if one assumes that the radius of the effective interaction region between molecules is greater than or equal to 0.1 μ. In work (3), which did not take into account the role of ε_0, it was asserted that the radius of the effective interaction region is ~ 0.05 μ.

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Note: Figure translations are in progress. See original paper for figures.