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IR Resonant Absorption in Molecular Nanofilms

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The paper presents a theoretical research of changes of optical properties of various nanofilm molecular crystals which are caused by the presence of two parallel and close borders. We used combined analytical-numerical calculation to find the allowed energy states of excitons and their spatial distribution (per layers) along the axis perpendicular to surface planes. We determined permittivity for the observed models of these ultrathin dielectric films and explored the influence of boundary parameters on the occurrence of discrete (per frequencies) and selective (per layers) absorption. The conditions for occurrence of smallest number of resonant absorption lines have been found and their localization has been defined.

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1. Introduction

Experimental and theoretical researches of low-dimensional crystalline samples (nanostructure: ultrathin films, quantum wires and points, etc.) have been very much intensified in order to obtain fundamental information about extremely different physical and chemical properties of the material as well as due to their extensive practical (technical and technological) application in nano-, opto- and bio-electronics [1]. Something that is specific for these "tiny" structures is that the presence of close border surfaces leads to extensive changes of generally known properties of these materials as well as to the occurrence of some non-specific phenomena (a consequence of effects of dimension quantizing [2]) compared to the characteristics of appropriate "large" samples [3]. Interest in studying exciton sub-system was brought about by the fact that the excitons are "responsible" for dielectric, optical (absorption, light dispersion, luminescence), photoelectrical and other properties of crystals [4]. In this paper we observed ultrathin dielectric films (the thickness of which does not exceed a dozen of atomic planes). Typical representatives of these structures include molecular crystals in which elementary excitations — excitons — occur as a result of interaction of external electromagnetic field and electrons of crystal. Using the law of exciton dispersion and the density of their condition, relative permittivity is defined in theoretical terms, and the latter is used to analyze optical properties of the observed system.

A standard expression for the effective exciton Hamiltonian in harmonic and bosonic representation [4, 5] has the following form:

$$H = \sum_{\boldsymbol{n}} \varDelta_{\boldsymbol{n}} B^{+}_{\boldsymbol{n}} B_{\boldsymbol{n}} + \sum_{\boldsymbol{n},\boldsymbol{m}} X_{\boldsymbol{nm}} B^{+}_{\boldsymbol{n}} B_{\boldsymbol{m}}, \tag{1.1}$$

where $B^{+}_{\boldsymbol{n}}$ and $B_{\boldsymbol{n}}$ creation and annihilation exciton operators on the site of crystal lattice, $\varDelta_{\boldsymbol{n}}$ represents energy of isolated exciton on that site, and $X_{\boldsymbol{nm}}$ are matrix elements of exciton transfer from site $\boldsymbol{n}$ to site $\boldsymbol{m}$. The model presumes that the on site energy of excitons is $\approx 10^2$ times bigger than its transfer energy.

Microtheoretical analysis will be conducted by using the method of two-time temperature Green functions [6, 7] due to the convenience provided by this method. For that purpose we look at Green's function

$$G_{\boldsymbol{nm}}(t) = \left\langle\left\langle B_{\boldsymbol{n}}(t) \,\middle|\, B^{+}_{\boldsymbol{m}}(0) \right\rangle\right\rangle, \tag{1.2}$$

which satisfies the following equation of motion:

$$\mathrm{i}\hbar \frac{\mathrm{d}}{\mathrm{d}t} G_{\boldsymbol{nm}}(t) = \mathrm{i}\hbar\delta(t)\delta_{\boldsymbol{nm}} + \varDelta_{\boldsymbol{n}} G_{\boldsymbol{nm}}(t) + \sum_{\boldsymbol{l}} X_{\boldsymbol{nl}} G_{\boldsymbol{lm}}(t). \tag{1.3}$$

By full time and space Fourier transform we can obtain a form of Green's function in $\boldsymbol{k}$-space, and from its pole,

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the sought exciton dispersion law

$$\hbar\omega_{\boldsymbol{k}} = \Delta + 2\big(X_x \cos a_x k_x + X_y \cos a_y k_y + X_z \cos a_z k_z\big), \tag{1.4}$$

which, if $X_x = X_y = X_z \equiv -|X|$ and $a_x = a_y = a_z \equiv a$, can be written in non-dimensional form

$$E_{\boldsymbol{k}} \equiv \frac{\hbar\omega_{\boldsymbol{k}} - \Delta}{|X|} = R_{xy} + S_z;$$

$$R_{xy} \equiv 2\left(\cos ak_x + \cos ak_y\right); \qquad S_z \equiv 2\cos ak_z \tag{1.5}$$

and which can be presented in a graph as in Fig. 1.

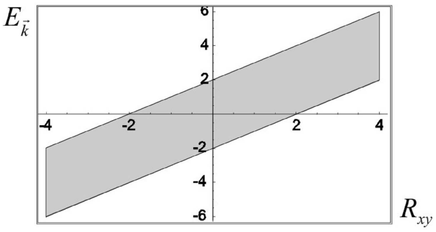

Fig. 1. Dispersion law of excitons in bulk.

Relative dielectric permittivity is defined [8, 9] by way of a general expression

$$\varepsilon^{-1}(\omega) = 1 - 2\pi\mathrm{i}F\left[G(\omega) + G(-\omega)\right] = 1 + 2F\frac{\omega_{\boldsymbol{k}}}{\omega^2 - \omega_{\boldsymbol{k}}^2}, \tag{1.6}$$

where F is a an internal structure parameter. Dependence of that permittivity is shown in Fig. 2.

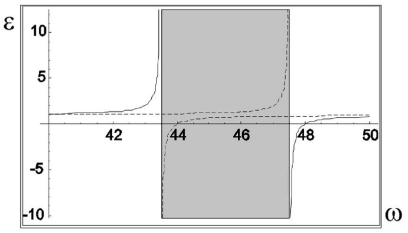

Fig. 2. Relative permittivity of bulk crystal.

In the case of the bulk we can see that energies take continual values, within a certain range of permitted energies, which results in dependence of bulk permittivity, i.e. dielectric response, makes absorption zone in which bulk will "swallow" all energies (i.e. frequencies of electromagnetic field) of exactly determined ranges.

2. Dielectric film-structure properties

Systems bounded with two parallel surfaces are called films [10, 11]. Dimensions of crystal nano-film are such that xy is unlimited, while in z-direction it has final and very small thickness $L = Na$ ($N < 10$). We will look at ultrathin (nano)crystal film (Fig. 3), which can be practically made by way of controlled reaching of massive dielectric samples [11]. Due to the existence of border surfaces, the energies of excitons on nodes and transfers of energy between border ($n_z = 0$; $n_z = N$) and their adjacent planes ($n_z = 1$; $n_z = N - 1$) are perturbed, which can be presented in the following manner [9, 11–14]:

$$\Delta_{\boldsymbol{n}} \equiv \Delta\left[1 + \left(d_0\delta_{n_z,0} + d_{\mathrm{N}}\delta_{n_z,N}\right)\right];$$

$$X_{\boldsymbol{n},\boldsymbol{n}+\boldsymbol{\lambda}} \equiv X\left[1 + \left(x_0\delta_{n_z,0} + x_{\mathrm{N}}\delta_{n_z,N-1}\right)\right];$$

$$X_{\boldsymbol{n},\boldsymbol{n}-\boldsymbol{\lambda}} \equiv X\left[1 + \left(x_0\delta_{n_z,1} + x_{\mathrm{N}}\delta_{n_z,N}\right)\right], \tag{2.1}$$

where parameter $d_{0/N}$ defines relative perturbation of site exciton energy on surfaces (boundary planes), and $x_{0/N}$ relative perturbation of exciton transfer energy in boundary layers along z-direction.

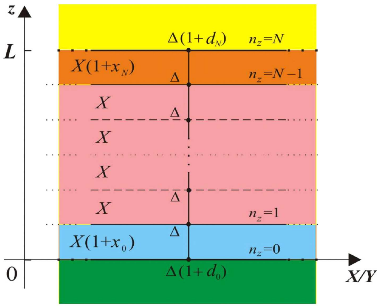

Fig. 3. Ultrathin dielectric film model.

We will conduct micro theoretical analysis of exciton sub-system in ultrathin crystalline molecular films in the same way as for the bulk — by using the same Green functions (1.2) and use the same procedure for their determination. Taking into account the boundary conditions (2.1) and the Hamiltonian (1.1) as well as the equation of motion (1.3), we arrive at the equation for requested Green's functions [11–14]. After full time, and now only partial space (xy) Fourier transform of these equations, we obtain the following:

$$G_{n_z,m_z}\left[\rho - \frac{\Delta}{|X|}\left(d_0\delta_{n_z,0} + d_{\mathrm{N}}\delta_{n_z,N}\right)\right] + G_{n_z-1,m_z}\left[1 + \left(x_0\delta_{n_z,0} + x_{\mathrm{N}}\delta_{n_z,N-1}\right)\right] + G_{n_z+1,m_z}\left[1 + \left(x_0\delta_{n_z,1} + x_{\mathrm{N}}\delta_{n_z,N}\right)\right] = \frac{\mathrm{i}\hbar}{2\pi|X|}\delta_{n_z,m_z}, \tag{2.2}$$

where a designation is introduced: $\rho = \frac{\hbar\omega - \Delta}{|X|} + 2(\cos ak_x + \cos ak_y)$. Equation (2.2) represents a system of $N + 1$ non-homogeneous algebraic-differential equations for Green's functions. As for finding of the dispersion laws we need only the poles of these functions, it is sufficient to find the determinant of the system (2.2) and equalize it with zero [11–14]. In this way we obtain $N+1$ solution $\rho \equiv \rho_\nu = \rho(\omega_\nu); \nu = 1, 2, \ldots, N+1$. As with the bulk, we will present the dispersion law of excitons in observed nanofilms in non-dimensional form

$$E^{-}_{\nu}=\frac{\hbar\omega^{-}_{\nu}\Delta}{|X|}\equiv R^{-}_{xy}\rho_{\nu}, \qquad (2.3)$$

which is in the similar form, depending on the function R_{xy}. This energy spectrum is presented in Figs. 4–6, more precisely: in Fig. 4 for non-perturbed (ideal) symmetrical five-layer film, in Figs. 5 and 6 for d-perturbed and x-perturbed five-layer film, respectively. Full lines present energy levels of excitons in observed film, while the intermittent lines designate the borders of continual energy areas of excitons in the bulk. Already at the first sight the absence of zero energies and discreteness of exciton energies in the film can be seen. The number of possible exciton conditions corresponds to the number of crystallographic planes of this film along the z-axis.

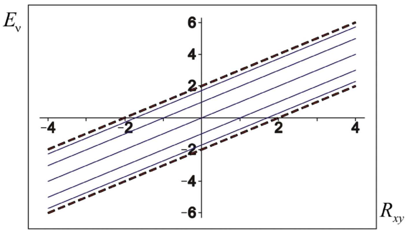

Fig. 4. The law of dispersion of ideal ($d_{0/N}=0.0$; $x_{0/N}=0.0$) five-layer film.

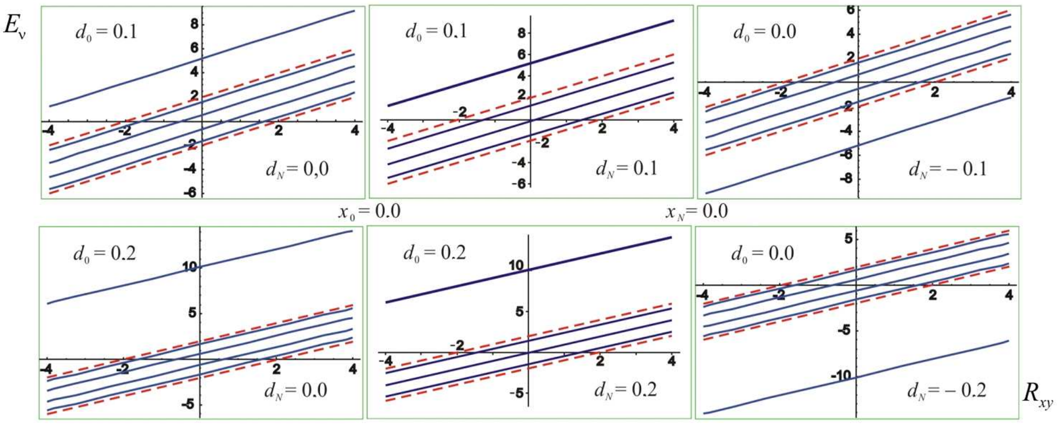

Fig. 5. Law of dispersion of d-perturbed ($x=0.0$) five-layer film.

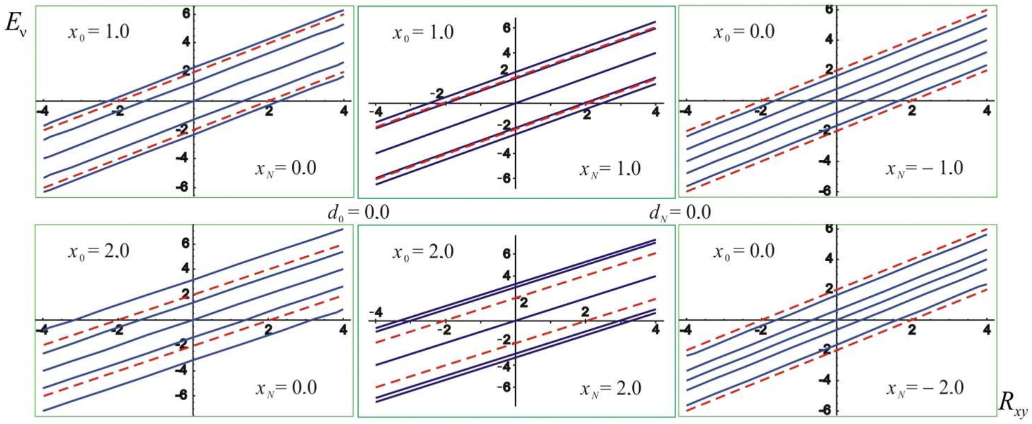

Fig. 6. Law of dispersion of x-perturbed ($d=0.0$) five-layer film.

In Fig. 5 one can see that by increasing d parameter the energy area expands in a way that one or two energy levels move toward higher energies and exit outside the bulk borders. These energy conditions are known as localized or Tamm states [4]. Based on analysis of Fig. 6 it comes out that by increasing of x parameter the spectrum is expanded and two or four energy levels exit outside the bulk borders, i.e. there is an emergence of localized conditions. Upon comparison of symmetrically (central graphs) and non-symmetrically (side graphs) perturbed films in Figs. 5 and 6, it is evident that there is a non--symmetry/symmetry of distribution of localized states and that in the case of symmetric perturbation localized levels overlap! This happens only for d-perturbation which is decisive in other cases, too.

In order to find the probability of occurrence and space distribution of exciton conditions in the film, it is necessary to calculate spectral weights of individual Green's functions. The starting point is the system of equations for Green's functions (2.2), written in matrix form

$$\hat{D}_{N+1}\tilde{G}_{N+1} = \hat{K}_{N+1}, \tag{2.4}$$

where $\hat{D}_{N+1}$ is a matrix that corresponds to the system determinant and $\tilde{G}_{N+1}$ and $\hat{K}_{N+1}$ are the vectors of Green function and of Kronecker deltas, respectively. If in (2.4) we act with inverse matrix $\hat{D}^{-1}_{N+1}$ from the left side and knowing that inverse matrix may be expressed by way of adjunct matrix D_{ik} members of which are co-factors of elements d_{ik} of direct matrix, by applying further calculations we can obtain Green's functions, in the numerators of which spectral weights $g_{n_z}\ (\rho_\nu)$, directly exist, i.e. probabilities to find exciton conditions ρ_ν [9, 11–14]:

$$G_{n_z} = -\frac{\mathrm{i}\hbar}{2\pi|X|}\sum_{\nu=1}^{N+1}\frac{g_{n_z}(\rho_\nu)}{\rho-\rho_\nu}. \tag{2.5}$$

When determining dynamic permittivity of film we will use the general expression (1.6), only taking strict account that Green's functions, as well as permittivity, depends on the number, i.e. the position of crystallographic planes of symmetric film n_z:

$$\varepsilon^{-1}_{n_z}(\omega) = 1 - 2\pi\mathrm{i}F\left[G_{n_z}(\omega) + G_{n_z}(-\omega)\right]$$

$$= 1 - \frac{\hbar F}{|X|}\sum_{\nu=1}^{N+1}\sum_{s=+,-}\frac{g^{\nu}_{n_z}}{\rho_s-\rho_\nu}, \tag{2.6}$$

where F is the same structural factor as in (1.6), and

$$\rho_\pm = \frac{\mp\hbar\omega - \Delta}{|X|} + 2\left(\cos ak_x + \cos ak_y\right).$$

This expression represents dependence of relative dynamic permittivity on the frequency of initial electromagnetic excitation, i.e. dielectric response of the observed symmetrical molecular film to external electromagnetic field. Dependences of relative dynamic permittivity on the reduced energy of external electromagnetic radiation for five-layer film are presented in Fig. 7.

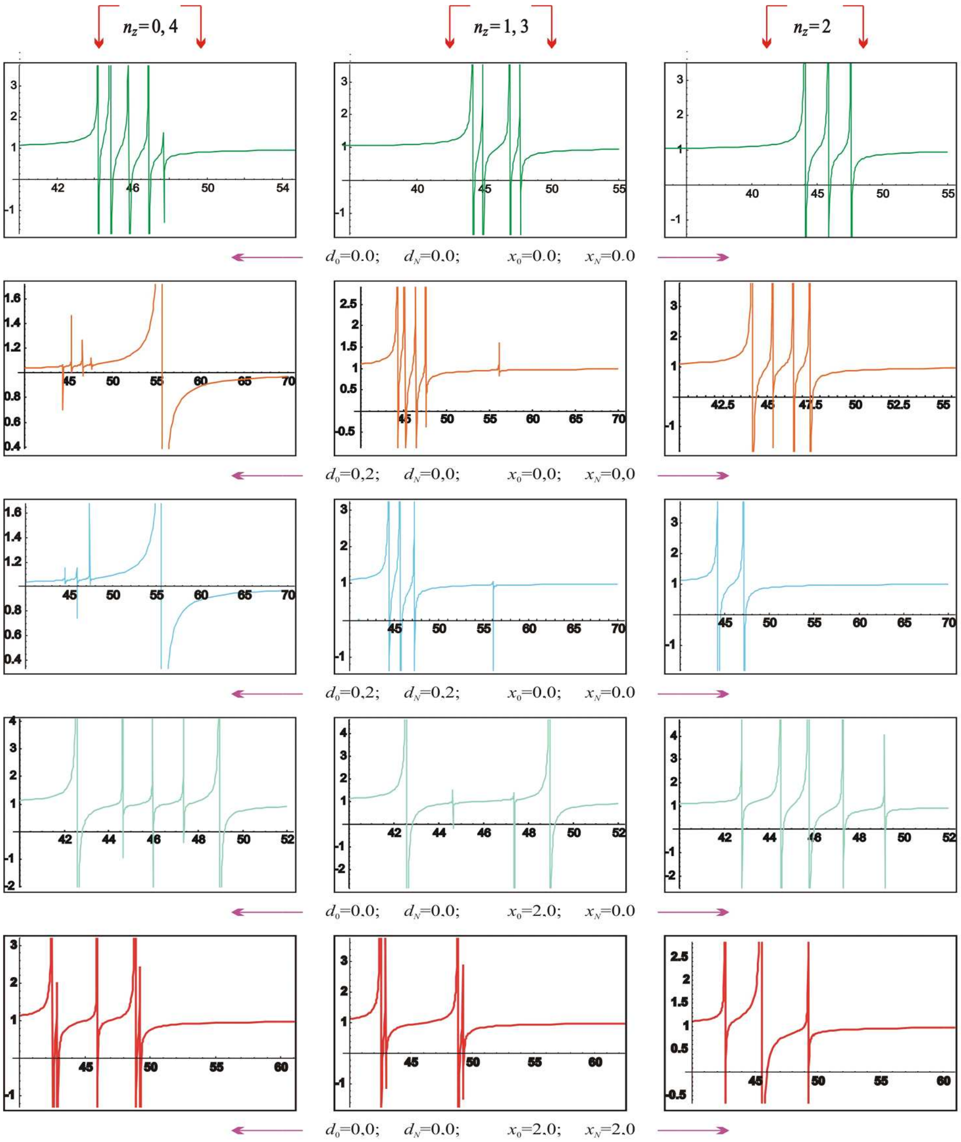

Fig. 7. Relative permittivity of perturbed five-layer film depending on reduced frequency.

All figures present dependences of permittivity on reduced frequency of external electromagnetic field for external (border) surfaces, for the first internal and central crystallographic plane. Occurrence of resonant peaks is visible, the number and distribution of which is very much dependent on boundary perturbation parameters.

Figure 7 with 3 graphs represents permittivity of ideal ultrathin film with 4 inter-atom layers (addressed in more detail in [12]). The second and the third row in Fig. 7 present dependences of dynamic permittivity on reduced frequency of external electromagnetic field for four-layer dielectric film when parameter $\mathit{\Delta}$ is changed by perturbation of d_0 (or d_{N}). This clearly demonstrates that the number of resonant peaks (ensuing when $\varepsilon(\omega_{\mathrm{r}}) \to \pm\infty$) depends on the number, i.e. position of atomic plane n_z, for which permittivity is calculated, as well as on the value of parameter $d_{0/N}$. When that parameter is increased, the expanding of the absorption area occurs, and the dominant resonant peak can be seen only on the border surface of the film ($n_z = 0$ or $n_z \equiv N = 4$). This is an expected result, because the analysis of spectral weights of exciton conditions [12] shows that it is exactly at this point that probability of finding excitons in localized condition is the biggest.

In the fourth and the fifth row (or column), Fig. 7, dependences of dynamic permittivity ε upon reduced energy of four-layer dielectric film are presented, when the parameter is $x_{0/N}$. It is easily seen that the number of resonant peaks of permittivity is different for different layers, i.e. $\varepsilon = \varepsilon\ (n_z)$, but that it also depends on the values of parameter $x_{0/N}$. When the value of this parameter increases, symmetrical expansion of the absorption area toward higher and lower energy values for all layers occurs, as well as the termination of individual resonant peaks depending on the place (film layer) for which permittivity is being determined. For instance, all resonant peaks exist only for border ($n_z = 0$ and 4) and for the central plane ($n_z = 2$), while in other planes they are terminated.

This implies that the influence of parameter d is evidently much “stronger” and that it also “shifts” the whole energy and selects optical picture of observed film structures.

3. Conclusion

The results of these analyses have shown significant differences in dispersion law (microscopic, i.e. quantum properties) and in dielectric response (macroscopic, and also dimension-quantum properties) of excitons between bulk and ultrathin film structures as a consequence of film limitation along the z-direction and existence of parameter perturbation on surfaces and boundary layers of the structure.

- The energy spectra of excitons in ultrathin film are discrete with the number of levels which is equal to the number of film layers. Increase in the energy of excitons on boundary layers, i.e. nodes moves the spectrum toward higher energies, while the increase in energy transfer between boundary layers and their adjacent internal layers expands the spectrum symmetrically toward higher and lower energies. The existence of localized (Tamm’s) states is possible, and its probability grows rapidly with the increase of border perturbation parameters.

- Dielectric response of the film shows the property of selectivity, i.e. occurrence of discrete resonant absorption peaks at exactly specified energies, the number and distribution of which is directly dependent on the number of the layers in the film and the number of perturbation parameters. These properties give an advantage to the films compared to bulk structures (dielectric response of which is continual in certain energy spans), because in that case the films can be used as certain filters of external radiation.

  Compared to non-symmetrical film, with symmetrically perturbed film the effects are doubled or paired. This means that localization will always appear at two or 4 energy levels, but that single-selective absorption (ideal filter) will never occur, in the way which is possible with non-symmetrical film. Here two close absorption peaks are least possible, i.e. the least transparency is for bichrome beam (of two not so different wave lengths).

Acknowledgments

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