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# THE PHENOMENON OF RESONANT ABSORPTION IN MOLECULAR NANOSCOPIC FILM STRUCTURES

*Research paper*

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**Abstract:** This paper presents the results of a theoretical study on changes in optical properties caused by the presence of boundaries in molecular crystal nanofilms. The energy spectrum of Frenkel excitons and their spatial distribution along the confinement axis (across crystallographic layers) were determined using a combined analytical-numerical calculation. Subsequently, the relative permittivity and absorption index were determined, and the influence of boundary parameters on the occurrence of resonant - virtually monochromatic - absorption was analyzed.
**Key words:** Ultrathin films, nanostructures, Frenkel excitons, permittivity, absorption index

## INTRODUCTION

Theoretical research into low-dimensional crystal systems (nanostructures such as ultrathin films, quantum wires, quantum dots, etc.) has intensified significantly, driven not only by the need to gain fundamental insights into the radically different physicochemical properties of these materials but also by their increasingly broad and high-quality practical applications in nano-, opto-, and bio-electronics (Wood K., et al., 2008). The distinctive nature of these "tiny" - i.e., ultrathin - structures lies in the fact that the presence of nearby interfaces leads to significant alterations in the materials' well-known properties and gives rise to unique phenomena - resulting from dimensional quantization effects (Tringides M.C., et al., 2007) when compared to the characteristics of corresponding "bulk" samples (Davison S.G. & Steslicka M.,1996).

Interest in studying the exciton subsystem in molecular crystals generally stems from the fact that Frenkel excitons are responsible for the dielectric, optical (absorption, light dispersion, luminescence), and photoelectric properties, as well as other physical characteristics, of these crystals (Agranovich V.M. & Ginzburg V.L., 1979). In this paper, we examine ultrathin dielectric films (characterized by a dimension not exceeding the thickness of approximately ten interatomic planes). Typical examples of such structures are molecular crystals in which elementary excitations - Frenkel excitons - arise from the interaction between an external electromagnetic field and the crystal's electrons. The relative permittivity - and through it, all the optical characteristics of the system under study - is theoretically defined using the dispersion laws and density of states of these excitons.

## FRENKEL EXCITONS IN AN ULTRATHIN CRYSTALLINE FILM

The standard expression for the effective exciton Hamiltonian in the harmonic approximation - for instance, according to Ref. (Agranovich V.M. & Ginzburg V.L., 1979) - takes the form:

$$H = \sum_{\vec{n}} \Delta_{\vec{n}} B_{\vec{n}}^{+} B_{\vec{n}} + \sum_{\vec{n},\vec{m}} X_{\vec{n}\vec{m}} B_{\vec{n}}^{+} B_{\vec{m}} \ , \qquad (1)$$

where $B_{\vec{n}}^{+}$ and $B_{\vec{n}}$ are the exciton creation and annihilation operators, $\Delta_{\vec{n}}$ represents the energy of an isolated exciton at site $\vec{n}$, and $X_{\vec{n}\vec{m}}$ are the matrix elements for exciton transfer

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from site $\vec{n}$ to site $\vec{m}$. The model assumes that the exciton energy at a site is approximately 100 times greater than the exciton transfer energy (Agranovich V.M. & Ginzburg V.L., 1979). Systems bounded by two parallel surfaces are referred to as films (Cottam M.G. & Tilley D.R., 1989; Šetrajčić J.P., et al., 2008). The dimensions of the crystalline nanofilm model are such that it is infinite in the $XY$ plane, while it has a finite thickness of $L = N\,a$ in the $z$-direction. We consider a dielectric nanofilm (Figure 1), which can be fabricated in practice through the controlled doping of bulk samples - matrices (Šetrajčić J.P., et al., 2008). Due to the presence of boundary surfaces, the site exciton energies and the energy transfer between the boundary planes ($n_z = 0$; $n_z = N$) and their adjacent crystallographic planes ($n_z = 1$; $n_z = N - 1$) are perturbed; this can be represented as follows (Šetrajčić J.P., et al., 2008; Pelemiš S., et al., 2008; Rodić, D., et al., 2013):

$$\Delta_{\vec{n}} \equiv \Delta\ \left[1 + d\left(\delta_{n_z,0} + \delta_{n_z,N}\right)\right];\quad X_{\vec{n},\vec{n}+\vec{\lambda}} \equiv X\ \left[1 + x\left(\delta_{n_z,0} + \delta_{n_z,N-1}\right)\right];\quad X_{\vec{n},\vec{n}-\vec{\lambda}} \equiv X\ \left[1 + x\left(\delta_{n_z,1} + \delta_{n_z,N}\right)\right], \quad (2)$$

which effectively constitute the boundary conditions, where the parameter $d$ defines the perturbation of the exciton energy at the boundary surface sites, and the parameter $x$ defines the perturbation of the exciton transfer energy in the boundary layers along the $z$-direction.

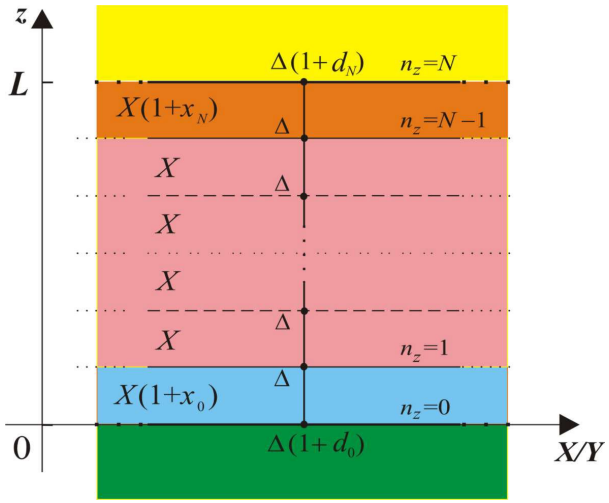



***Fig. 1**. Schematic of the ultra-thin dielectric film model*

We conduct a micro-theoretical analysis of the exciton subsystem of an ultrathin (crystalline) molecular film using the method of time- and temperature-dependent Green's functions; thus, we consider the following Green's function (Mahan G., 1990): $G_{\vec{n}\vec{m}}(t) = \left\langle\left\langle B_{\vec{n}}(t)\middle|B^{+}_{\vec{m}}(0)\right\rangle\right\rangle$, which satisfies the following equation of motion:

$$i\hbar\frac{d}{dt}G_{\vec{n}\vec{m}}(t) = i\hbar\delta(t)\delta_{\vec{n}\vec{m}} + \Delta_{\vec{n}}G_{\vec{n}\vec{m}}(t) + \sum_{\vec{l}} X_{\vec{n}\vec{l}}\,G_{\vec{l}\vec{m}}(t). \quad (3)$$

We then apply a full temporal Fourier transform, along with partial spatial Fourier transforms, to these equations, obtaining:

$$G_{n_z,m_z}\left[\rho - \frac{\Delta}{|X|}d\left(\delta_{n_z,0} + \delta_{n_z,N}\right)\right] + G_{n_z+1,m_z}\left[1 + x\left(\delta_{n_z,0} + \delta_{n_z,N-1}\right)\right] + G_{n_z+1,m_z}\left[1 + x\left(\delta_{n_z,1} + \delta_{n_z,N}\right)\right] = \frac{i\hbar}{2\pi|X|}\delta_{n_z,m_z}, \quad (4)$$

where the following notation is introduced: $\rho = \dfrac{\hbar\omega - \Delta}{|X|} + 2\left(\cos ak_x + \cos ak_y\right)$.

Equation (4) represents a system of $N+1$ inhomogeneous algebraic-difference equations for the unknown Green's functions. However, since only the poles of these functions are required to determine the dispersion law, it suffices to find the determinant of the system and set it to zero. In this way, we obtain $N+1$ solutions: $\rho \equiv \rho_\nu$; $\nu = 1, 2, 3, \ldots, N+1$.

## PERMITIVITY OF NANOFILMS

To determine the occurrence probabilities and spatial distribution of exciton states in the film, it is necessary to calculate the spectral weights of the individual Green's functions. One approach is to start with the system of equations for the Green's functions (4), but written in matrix form:

$$\hat{D}_{N+1}\widetilde{G}_{N+1} = \hat{K}_{N+1}, \tag{5}$$

where $\hat{D}_{N+1}$ is the matrix corresponding to the system's determinant, and $\widetilde{G}_{N+1}$ and $\hat{K}_{N+1}$ are the vectors of the Green's functions and Kronecker deltas, respectively. By applying the inverse matrix $\hat{D}_{N+1}^{-1}$ to equation (5) from the left - and knowing that the inverse matrix can be expressed in terms of the adjugate matrix, whose entries $D_{ik}$ are the cofactors of the elements $d_{ik}$ of the original matrix-further calculation yields the Green's functions. The spectral weights $g_{n_z}(\rho_\nu)$ - i.e., the probabilities of finding exciton states $\rho_\nu$ (Šetrajčić J.P., et al., 2008; Pelemiš S., et al., 2008; Rodić, D., et al., 2013; Šetrajčić, I.J., 2018) - appear directly in the numerators of these functions:

$$G_{n_z} = -\frac{i\hbar}{2\pi|X|}\sum_{\nu=1}^{N+1}\frac{g_{n_z}(\rho_\nu)}{\rho-\rho_\nu}. \tag{6}$$

To determine the dynamic permittivity of the film, we will use the general expression (Dzialoshinski I.E. & Pitaevski L.P., 1959), while strictly accounting for the fact that the Green's functions - and consequently the permittivity - depend on the (number, i.e., position of) the crystallographic planes $n_z$ of the symmetric film:

$$\varepsilon_{n_z}^{-1}(\omega) = 1 - 2\pi i\, F\,\left[G_{n_z}(\omega) + G_{n_z}(-\omega)\right], \tag{7}$$

where $F$ is the structure factor [4,5]. Substituting the expression for the Green's functions (6) yields:

$$\varepsilon_{n_z}^{-1}(\omega) = 1 - \frac{\hbar F}{|X|}\sum_{\nu=1}^{N+1}\sum_{s=+,-}\frac{g_{n_z}^{\nu}}{\rho_s-\rho_\nu}, \tag{8}$$

where: $\rho_\pm = \frac{\mp\hbar\omega-\Delta}{|X|} + 2\left(\cos ak_x + \cos ak_y\right)$; after some analytical rearrangement, expression (8) becomes:

$$\varepsilon_{n_z}(\omega) = \left\{1 - \frac{2\hbar F}{|X|}\sum_{\nu=1}^{N+1} g_{n_z}^{\nu}\,\frac{\rho_\nu - \frac{\Delta}{|X|} - 2\left(\cos ak_x + \cos ak_y\right)}{\left(\frac{\hbar\omega}{|X|}\right)^2 - \left[\rho_\nu - \frac{\Delta}{|X|} - 2\left(\cos ak_x + \cos ak_y\right)\right]^2}\right\}^{-1}. \tag{9}$$

This expression represents the dependence of the relative dynamic permittivity on the frequency of the initial electromagnetic excitation - that is, the dielectric response of the observed symmetric molecular film to an external electromagnetic field. Figure 2 illustrates the dependence of the relative dynamic permittivity on the reduced energy of the external electromagnetic radiation for a five-layer film.

All the figures show the dependence of permittivity on the reduced frequency of the external electromagnetic field for the outer (boundary) surfaces, the first inner layers, and the central crystallographic plane. The appearance of resonant peaks is evident; their number and arrangement depend significantly on the boundary perturbation parameters.

The first image at the top, containing three graphs, shows the permittivity of an ideal ultrathin film consisting of four interatomic layers. The second and third rows of Figure 2 display the dependence of dynamic permittivity on the reduced frequency of the external electromagnetic field for a four-layer dielectric film, where the parameter $\Delta$ is varied via the perturbation $d_0$ (or $d_N$).

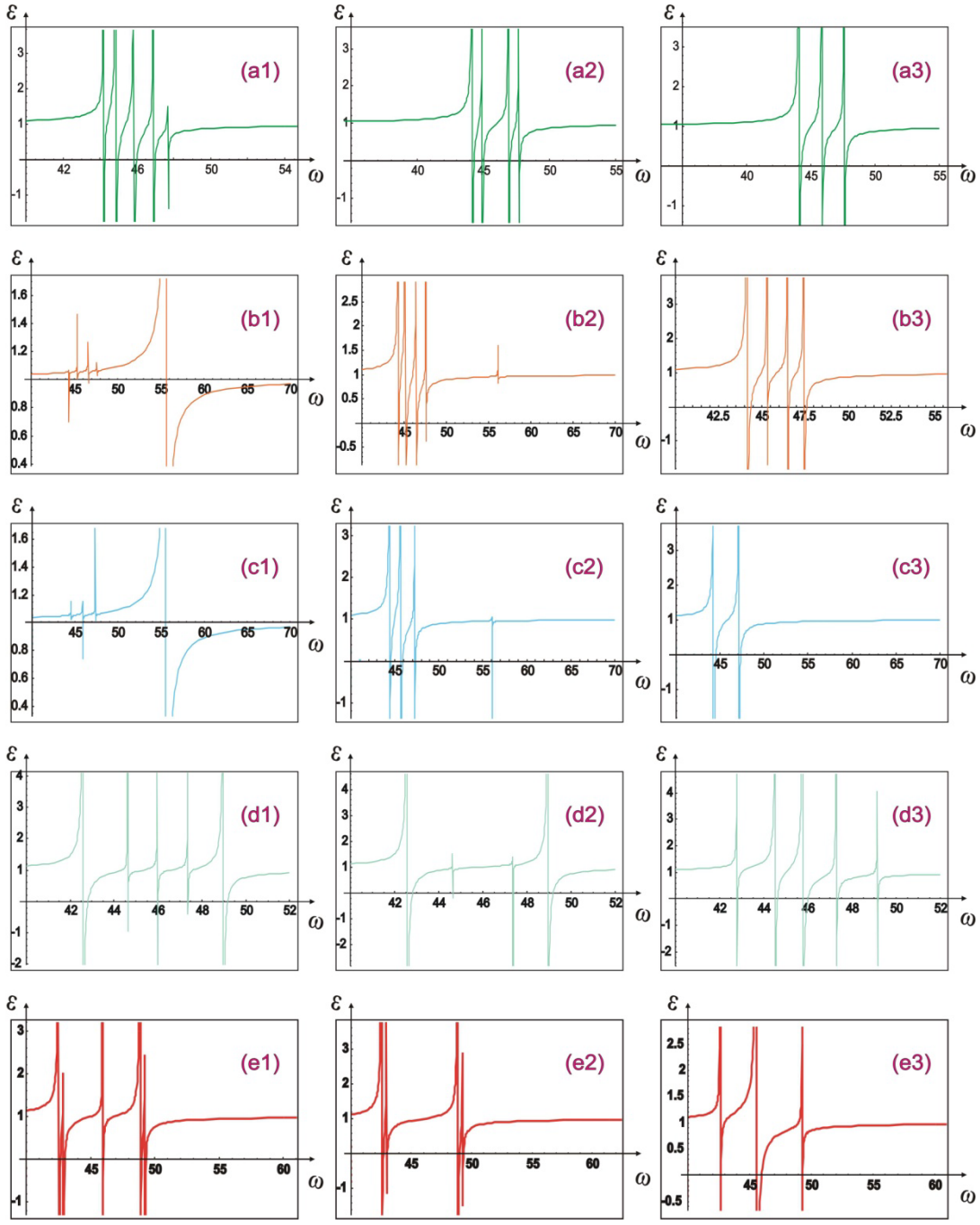



***Figure 2*** *– Relative permittivity ε of the perturbed film as a function of reduced frequency $\omega$:*

HORIZONTAL (change in energy parameters):
(a1-3): $d_0 = 0{,}0$; $d_N = 0{,}0$; $x_0 = 0{,}0$; $x_N = 0{,}0$;
(b1-3): $d_0 = 0{,}2$; $d_N = 0{,}0$; $x_0 = 0{,}0$; $x_N = 0{,}0$;
(c1-3): $d_0 = 0{,}2$; $d_N = 0{,}2$; $x_0 = 0{,}0$; $x_N = 0{,}0$;
(d1-3): $d_0 = 0{,}0$; $d_N = 0{,}0$; $x_0 = 2{,}0$; $x_N = 0{,}0$;
(e1-3): $d_0 = 0{,}0$; $d_N = 0{,}0$; $x_0 = 2{,}0$; $x_N = 2{,}0$;

VERTICAL (layers/planes):
boundary (1a–e): $n_z = 0$ and 4;
inner (2a–e): $n_z = 1$ and 3;
central (3a–e): $n_z = 2$

This demonstrates that the number of resonant peaks (where $\varepsilon(\omega_r) \rightarrow \pm\infty$) depends not only on the number - or position - of the atomic plane ($n_z$) for which the permittivity is calculated, but also on the value of the parameter $d_{0/N}$. Increasing this parameter leads to a broadening of the absorption zone, and the dominant resonant peak is observed only at the film boundary ($n_z = 0$ or $n_z \equiv N = 4$). The fourth and fifth rows of Figure 2 show the dependence of the dynamic permittivity $\varepsilon$ on the reduced energy of a four-layer dielectric film for a given parameter $x_{0/N}$. It is readily apparent that the number of resonant permittivity peaks differs across the layers - i.e., $\varepsilon = \varepsilon\,(n_z)$ - but also depends on the value of the parameter $x_{0/N}$.

## RESULTS AND DISCUSSION

Increasing the value of this parameter results in a symmetrical broadening of the absorption zone toward higher and lower energy values across all layers, as well as the suppression of certain resonant peaks, depending on the specific location (film layer) for which the permittivity is determined. For instance, all resonant peaks are present only in the boundary planes ($n_z = 0$ and $4$) and the central plane ($n_z = 2$), whereas they are suppressed in the other planes.

This demonstrates the significantly stronger influence of parameter $d$, which shifts the entire energy profile and determines the optical characteristics of the film structures under observation.

## CONCLUSION

The results of these analyses revealed significant differences in the excitonic dielectric response between bulk and film structures, resulting exclusively from the film's confinement along the $z$-axis and the presence of parameter perturbations at the structure's interfaces and boundary layers.

a) The film's dielectric response exhibits selectivity - specifically, the appearance of discrete resonant absorption peaks at precise energy levels, with their number and distribution determined by the number of layers in the film and the perturbation parameters. These characteristics give films an advantage over bulk structures (which possess a continuous dielectric response across a specific energy range), as films can serve as specific filters for precise external electromagnetic radiation frequencies.

b) Compared to an asymmetric film, a symmetrically perturbed film exhibits doubled or paired effects. This implies that localization will always occur at two or four energy levels, yet single-selective absorption (an ideal filter) - which is possible with an asymmetric film - will never be achieved. In this case, the minimum configuration involves two closely spaced absorption peaks; essentially, minimum transparency occurs for a bichromatic beam (comprising two wavelengths that are not widely separated).

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