

Excitonic and Vibronic Spectra in 2D Molecular Quadratic Lattice*

I.J. Lalov, I. Zhelyazkov

Faculty of Physics, University of Sofia, 1164 Sofia, Bulgaria

Abstract. In this paper, we consider a model of 2D molecular crystal of square symmetry with one molecule per unit cell. Results of the studies of the linear absorption in excitonic and vibronic spectra have been summarized for the following cases: (a) charge-transfer excitons (CTEs) in quadratic lattice; (b) Frenkel excitons (FEs) in that lattice; (c) coupled CTEs and FEs in quadratic lattice. The impact of the anisotropy inside the lattice plane and perpendicular to it on the linear absorption is analytically calculated and numerically simulated. The linear absorption spectra strongly depend upon transition dipole moments of Frenkel and charge-transfer excitons and also on the availability of one-particle and many-particle exciton–phonon states. 2D Van Hove singularities in the excitonic density of states occur in the present model.

PACS codes: 71.35.Cc, 73.20.Mf, 78.20.Bh

1 Introduction

This review represents the results of theoretical studies on excitonic and vibronic spectra of 2D molecular crystal with square symmetry and with one molecule per unit cell (see Lalov and Zhelyazkov [1–3]).

Model of phenomena in a quadratic 2D network has been initially created in statistical mechanics, based on the canonical Ising model (see, e.g., Hill [4]). Studies of 2D models nowadays are also provoked by the technical opportunities for fabricating real 2D samples (like graphene) or layer quasi-2D materials. We mention the following possible realizations of 2D molecular layers of square symmetry: colloidal molecular crystals of dimers grown on square substrates [5], protein aggregates [6], amphiphilic bi-layers of the so-called L_α lamellar phase [7], *etc.*

Our papers [1–3] analyze the linear absorption in the excitonic region of the two types of excitons in molecular systems – Frenkel excitons (FEs) and charge-transfer excitons (CTEs) – and near their vibronic replicas: exciton plus one/two quantum/quanta of the intramolecular vibration. We apply the Green function

*Invited talk at the Second Bulgarian National Congress in Physics, Sofia, September 2013.

methods and the vibronic approach [8] to obtain analytical results and make numerical simulations of excitonic density of states (DOSs) and also of the absorption coefficient of light polarized in the plane of the quadratic lattice and perpendicular to it.

In the next section, we consider the spectra of CTEs in a high-symmetry (quadratic) lattice [1]. In Section 3 we apply the results of Ref. [2] to obtain the spectrum of FEs in a quadratic lattice. The coupling of Frenkel and charge-transfer excitons is handling in Section 4. Section 5 contains a conclusion and outlook.

2 Charge Transfer Excitons in a Quadratic Lattice

In a quadratic lattice with a lattice constant a the electrons of the CTEs are located on the four molecules neighbors of the positive ion (h) (see Figure 1). We denote by $C_{i,nm}$ ($C_{i,nm}^+$), where $i = 1, 2, 3, 4$, the operators of annihilation (creation) of the CTE i whose hole is located on the node (n, m) . Let J_e be the transfer integral of an electron on one of the most closer diagonal nodes, and J_h be the corresponding hole's transfer integral. The Hamiltonian in momentum space (k_1, k_2) reads

$$\begin{aligned} \hat{H}_{\text{CTEs}} = & \sum_{k,i=1-4} E_c C_{i,k}^+ C_{i,k} + J_e \sum_k [C_{2,k}^+ C_{1,k} + C_{3,k}^+ C_{2,k} + C_{4,k}^+ C_{3,k} \\ & + C_{1,k}^+ C_{4,k} + \text{h.c.}] + J_h \sum_k [C_{2,k}^+ C_{1,k} e^{i(k_2-k_1)a} + C_{3,k}^+ C_{2,k} e^{-i(k_1+k_2)a} \\ & + C_{4,k}^+ C_{3,k} e^{i(k_1-k_2)a} + C_{1,k}^+ C_{4,k} e^{i(k_1+k_2)a} + \text{h.c.}], \quad (1) \end{aligned}$$

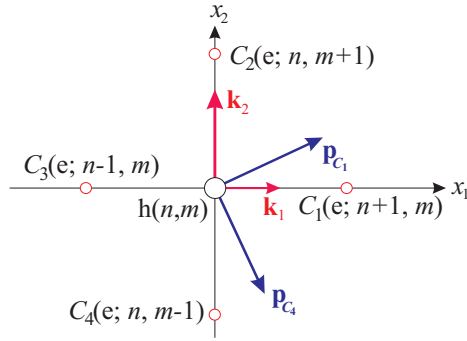


Figure 1: Unit cell of a quadratic lattice and CTEs with a hole on the node (n, m) ; a being the lattice constant. The electron e is located on the node $(n + 1, m)$ for CTE1, $(n, m + 1)$ for CTE2, etc. The components of the transition dipole moments parallel to the layer are mutually perpendicular and equal, *i.e.*, $|\mathbf{p}_{C1}| = |\mathbf{p}_{C2}| = |\mathbf{p}_{C3}| = |\mathbf{p}_{C4}| = p$.

where E_c is the excitation energy of all CTEs.

We consider one vibrational intramolecular mode of frequency ω_0 and operator of annihilation a_{nm} of one vibrational quantum on a (n, m) -molecule linearly coupled with the electron and the hole of CTEs (with coupling parameter ξ). The convenient canonical transformation eliminates the terms of the linear CTEs–phonon coupling and we obtain the Hamiltonian (1) in which operators $C_{i,k}$ are replaced by the operators

$$U_{i,k} = \exp(Q)C_{i,k} \exp(-Q), \quad (2)$$

where

$$Q = \sum_{nm, i=1-4} \xi C_{i,nm}^+ C_{i,nm} (a_{nm}^+ - a_{nm} + a_{(nm)+\sigma_i}^+ - a_{(nm)+\sigma_i}) \quad (3)$$

with σ_i being a position vector of the CTE's electron relative to its hole (nm) .

The linear optical susceptibility χ_{ij} can be calculated by using the Green function methods (see Agranovich [9]) and the following expressions for the operator of transition dipole moment:

(a) Inside the plane of the lattice ($\chi_{xx} = \chi_{yy}$ components)

$$\hat{P}_{\parallel} = p_{\parallel} [(U_{1,0} - U_{3,0}) \hat{x} + (U_{2,0} - U_{4,0}) \hat{y} + \text{h.c.}], \quad (4)$$

$$\chi_{xx} = \chi_{yy} = -\frac{2p_{\parallel}^2}{v} G_3(\omega), \quad (5)$$

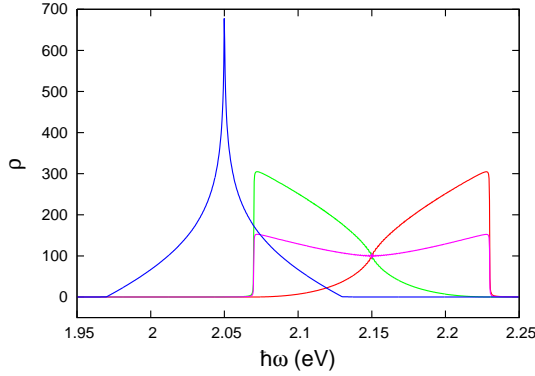


Figure 2: CTEs density of states ρ_z ($E_c = 2.15$ eV) and ρ_x ($E_c = 2.05$ eV) for $|J_e| = |J_h| = 0.02$ eV. ρ_z : red curve for $J_e = J_h = 0.02$ eV, green curve for $J_e = J_h = -0.02$ eV, purple curve for $J_e = -J_h = 0.02$ eV. ρ_x : blue curve for $|J_e| = |J_h| = 0.02$ eV.

where v is the volume occupied by one molecule and $G_3(\omega)$ is a Green function having different expressions in the excitonic and vibronic spectra (we use the vibronic approach [8]).

(b) Perpendicular to the plane (z -axis)

$$\hat{P}_\perp = p \sum_{i=1-4} (U_{i,0} + U_{i,0}^+), \quad (6)$$

$$\chi_{zz} = -\frac{4p^2}{v} G_1(\omega). \quad (7)$$

Functions $G_3(\omega)$ and $G_1(\omega)$ in the vibronic spectrum at $\omega_0 = 0$, $\xi = 0$, describe the corresponding density of states (for detail see Refs. [1, 2]):

$$\rho_x = \rho_y = -\pi \text{Im} G_3(\omega + i\delta) \text{ and } \rho_z = -2\pi \text{Im} G_1(\omega + i\delta) \text{ with } \delta \rightarrow +0. \quad (8)$$

Figure 2 illustrates CTEs density of states. Function ρ_x manifests mirror symmetry relative to the level E_c and one saddle Van Hove point of DOS (logarithmic in 2D models). Figure 3 demonstrates the positions of the CTE absorption maxima (the lowest maxima) and the positions of the first two vibronics. Lineshape of the excitonic and vibronic maxima is Lorentzian in the case of relatively small transfer integrals, $|J_e|, |J_h| \leq 0.01$ eV. If the magnitudes of transfer integral increase the excitonic maxima preserve their Lorentzian lineshape but the maxima of the linear absorption in vibronic spectra are wider and structureless that correspond to unbound (many particle) propagation of the CTEs and the quanta of the intramolecular vibrations (see Figure 4).

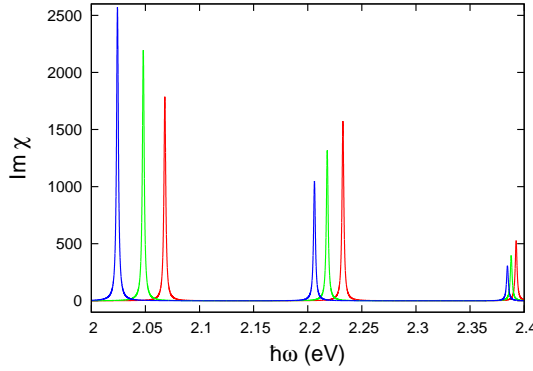


Figure 3: Absorption spectra of CTEs (the lowest maxima) and position of the first two vibronics for $\xi^2 = 0.6$. Red curves correspond to $J_e + J_h = 0.02$ eV, green curves to $J_e + J_h = 0$, blue curves describe the case $J_e + J_h = -0.02$ eV ($\text{Im} \chi_{zz}$). The excitonic maxima of χ_{xx} coincide with the green peaks.

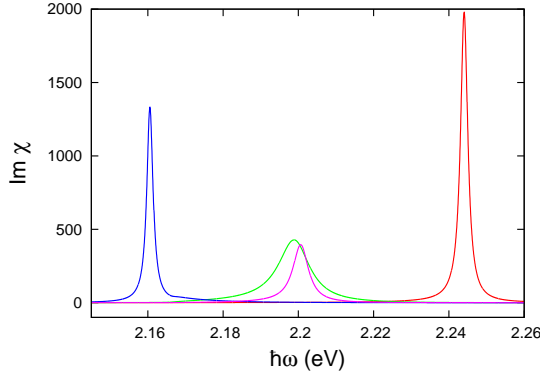


Figure 4: Linear absorption in the vibronic region, $E_c + \hbar\omega_0$, at $\xi^2 = 0.6$. $\text{Im } \chi_{zz}$: red curve for $J_e = J_h = 0.02$ eV; green curve for $J_e = -J_h = 0.02$ eV; blue curve for $J_e = J_h = -0.02$ eV. $\text{Im } \chi_{xx}$: purple curve for $J_e = J_h = 0.02$ eV.

3 Frenkel Excitons in a Quadratic Lattice

Two types of dipole active FEs exist in a quadratic lattice:

(a) Nondegenerate FEs whose transition dipole moment p_z is perpendicular to the layer. The operator \hat{P}_z and the Hamiltonian are correspondingly [2, 3]:

$$\hat{P}_z = p_z (V_{z,0} + V_{z,0}^+), \quad (9a)$$

$$\hat{H}_{F,z} = \sum_k \{E_F + 2W [\cos(k_1 a) + \cos(k_2 a)]\} V_{z,k}^+ V_{z,k}. \quad (9b)$$

(b) Degenerate FEs polarized in the plane of the lattice ($p_{x,y} = p_F$) for whom

$$\hat{P} = p_F (V_{x,0} \hat{x} + V_{y,0} \hat{y} + \text{h.c.}), \quad (10a)$$

$$\begin{aligned} \hat{H}_{F,x,y} = & \sum_k \{E_{F1} + 2W_1 [-2 \cos(k_1 a) + \cos(k_2 a)]\} V_{x,k}^+ V_{x,k} \\ & + \sum_k \{E_{F1} + 2W_1 [\cos(k_1 a) - 2 \cos(k_2 a)]\} V_{y,k}^+ V_{y,k}, \end{aligned} \quad (10b)$$

where $V_{x,k}$, $V_{y,k}$, and $V_{z,k}$ are canonically transformed operators of annihilation of FEs [see Eqs. (2) and (3)] with corresponding directions of their transition dipole moments. Quantities W , $W_1 > 0$ being the intermolecular transfer integrals of FEs have been calculated in dipole approximation.

Calculations of the components χ_{zz} and $\chi_{xx} = \chi_{yy}$ done in the approach of Section 2 allow to find analytical expressions which contain complete elliptic

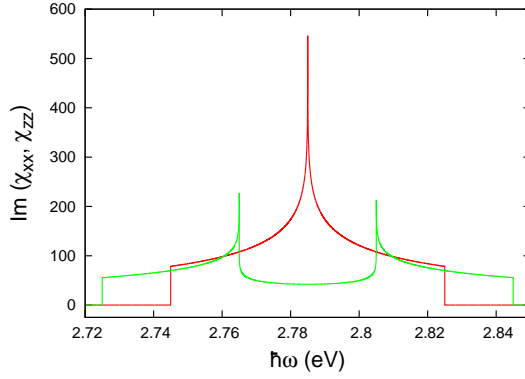


Figure 5: Densities of state of FEs in a quadratic lattice, $E_F = 2.785$ eV, $W = W_1 = 0.02$ eV; the red curve depicts ρ_z , and the green one ρ_x .

integrals $K(k)$ [see paper [2], Section 3, with $W_a = W_b$ for the Hamiltonian (9b) and $W_b = -2W_a$ for (10b)].

Figure 5 illustrates the Frenkel exciton's DOS. Van Hove singularities manifest themselves at the edges of the excitonic band (flat nonzero behavior of DOS in 2D models) and logarithmic saddle points. The absorption curves in Figure 6 have been calculated using the parameters of the lowest excitonic peak of naphthalene (its real crystal structure does not manifest square symmetry). The Lorentzian excitonic peaks appear below 3.85 eV. The vibronic absorption is governed by the linear and quadratic exciton–phonon coupling and it

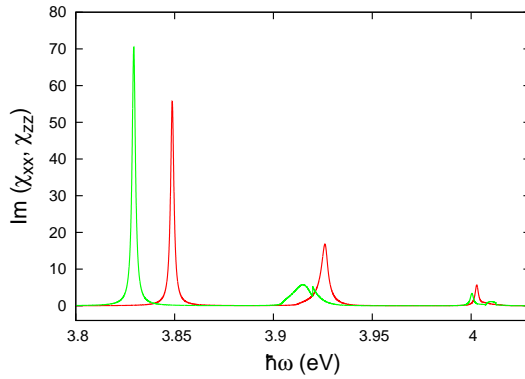


Figure 6: Linear absorption spectra of the quadratic-lattice model of naphthalene: $E_F = 3.87$ eV, $\hbar\omega_0 = 0.09$ eV, $\xi_F^2 = 0.4$, $W = 0.01$ eV; the red curve depicts $\text{Im}\chi_{zz}$, and the green one $\text{Im}\chi_{xx}$.

is manifested itself inside the continua near 3.94 eV (first vibronic) and near 4.01 eV (second vibronic). Those absorption bands correspond to many-particle unbound exciton–phonon states. The lineshape of the red curve describes a quasi-bound state with nearly Lorentzian lineshape but being wide and asymmetric due to the coupling with many-particle continuum.

4 Coupling of Frenkel and Charge Transfer Excitons in Quadratic Lattice

In this Section, we consider the problem of coupling of CTEs studied in Section 2 (but in the case $J_e = J_h = 0$) and two types of FEs examined in the previous Section. The crucial issue is the form of FE–CTEs coupling terms in the Hamiltonian. Symmetry analysis (see the Appendix in Lalov and Zhelyazkov [3]) yields the following coupling terms:

(a) Nondegenerate case (component χ_{zz})

$$\hat{H}_{\text{FE-CTEs}} = D_e \sum_{k, i=1-4} \left(U_{i,k}^+ V_{z,k} + U_{i,k} V_{z,k}^+ \right) + D_h \sum_k \left[\left(U_{1,k}^+ e^{ik_1 a} + U_{2,k}^+ e^{ik_2 a} + U_{3,k}^+ e^{-ik_1 a} + U_{4,k}^+ e^{-ik_2 a} \right) V_{z,k} + \text{h.c.} \right], \quad (11)$$

where D_e and D_h are corresponding electron's and hole's transfer integrals, and, note, the operator of transition dipole moment is a sum of operators (6) and (9a). The linear optical susceptibility is

$$\chi_{zz} = -\frac{1}{v(\alpha_{11}\alpha_{22} - 4\alpha_{12}^2)} [p_z^2\alpha_{22} + 8p_z p\alpha_{12} + 4p^2\alpha_{11}], \quad (12)$$

where functions α_{11} , α_{22} , α_{12} have been separately calculated for the excitonic and vibronic spectra [3].

(b) Degenerated case (components $\chi_{xx} = \chi_{yy}$)

$$\hat{H}_{\text{FE-CTEs}} = \varepsilon_e \sum_k \left[\left(U_{1,k}^+ - U_{3,k}^+ \right) V_{x,k} + \left(U_{2,k}^+ - U_{4,k}^+ \right) V_{y,k} + \text{h.c.} \right] + \varepsilon_h \sum_k \left[\left(U_{1,k}^+ e^{ik_1 a} - U_{3,k}^+ e^{-ik_1 a} \right) V_{x,k} + \left(U_{2,k}^+ e^{ik_2 a} - U_{4,k}^+ e^{-ik_2 a} \right) V_{y,k} + \text{h.c.} \right], \quad (13)$$

where ε_e and ε_h represent electron's and hole's transition integrals from the neutral excited molecule to the neighbor molecules. The operator of transition dipole moment is a sum of operators (4) and (10a) and the components $\chi_{xx} = \chi_{yy}$ take the form

$$\chi_{xx} = \chi_{yy} = -\frac{1}{v(\beta_{11}\beta_{22} - 2\beta_{12}^2)} \left[p_{\text{F}}^2\beta_{22} + 4p_{\parallel}p_{\text{F}}\beta_{12} + 2p_{\parallel}^2\beta_{11} \right]. \quad (14)$$

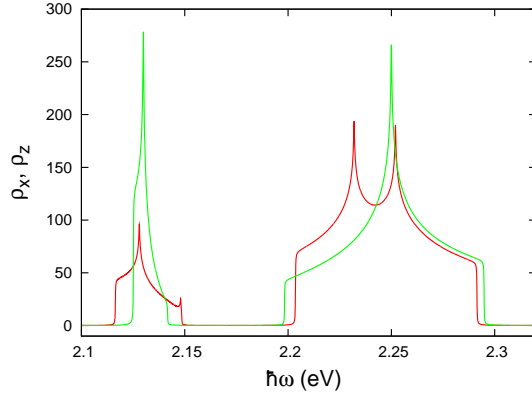


Figure 7: Excitonic DOS in the case of FE-CTEs coupling for $E_F = 2.23$ eV, $E_c = 2.15$ eV, $W = W_1 = 0.01$ eV, $\varepsilon_e = -0.02$ eV, and $\varepsilon_h = -0.01$ eV. The red curve depicts the excitonic ρ_x DOS and the green one corresponds to ρ_z .

Functions β_{11} , β_{22} , β_{12} correspond to functions α_{ij} but with different expressions. In Sections 2 and 4 we have numerically calculated the integrals and have found DOSs and absorption curves.

In Figure 7 are shown the results of excitonic DOS's simulations. Owing to the FE-CTEs coupling, two excitonic bands arise near the levels of E_F and E_c . Van Hove singularities, typical for 2D models, exhibit, too. The same splitting can be observed in the excitonic spectra of both polarizations (see Figure 8). Figure 8

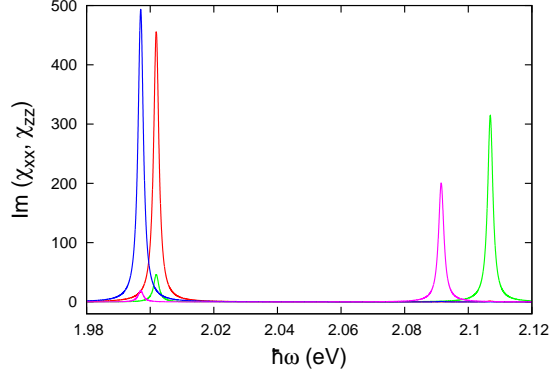


Figure 8: Linear absorption excitonic spectra with $E_F = 2.23$ eV, $E_c = 2.15$ eV, $\hbar\omega_0 = 0.17$ eV, $W = W_1 = 0.01$ eV, $D_e = \varepsilon_e = -0.02$ eV, $D_h = \varepsilon_h = -0.01$ eV, $\xi_F = 0.9$, and $\xi = 0.64$. The red ($\text{Im}\chi_{zz}$) and purple ($\text{Im}\chi_{xx}$) curves are derived at $p_z = p_F = 0$ while the green ($\text{Im}\chi_{zz}$) and blue ($\text{Im}\chi_{xx}$) curves at $p = h = 0$.

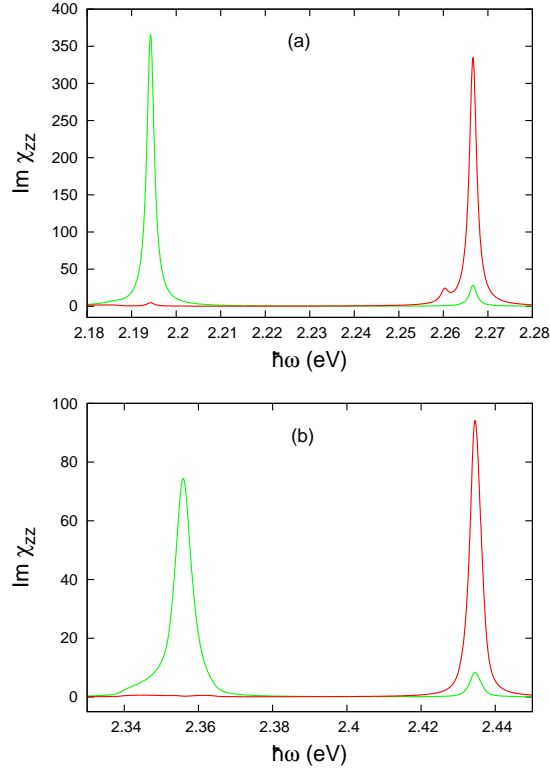


Figure 9: Vibronic absorption spectra at $E_F = 2.23$ eV, $E_c = 2.15$ eV (for other parameters see Figure 8) polarized normally to the lattice plane. The green curve is calculated for $p = 0$, and the red one for $p_z = 0$. Panel (a): One-phonon vibronic spectra. Panel (b): Two-phonon vibronic spectra.

allows to estimate also the role of transition dipole moments of FEs (blue and green curves) and that of CTEs (red and purple curves).

In Figures 9 and 10 one sees the vibronic absorption spectra in the one-phonon region, 2.15–2.28 eV, [Figure 9(a)] as well in the two-phonon region, 2.34–2.45 eV, [Figure 9(b)]. The FE–CTEs coupling causes two-fold splitting of the vibronic spectra. Another effect can be observed: whereas one-phonon vibronic spectra correspond to one-particle (bound) exciton–phonon states, two-phonon vibronic spectra, especially those near 2.35 eV, demonstrate unbound states. Obviously, the exciton–phonon coupling is relatively weak to bind the excitons with two phonons (in the case of relatively small values of the parameters ξ and ξ_F).

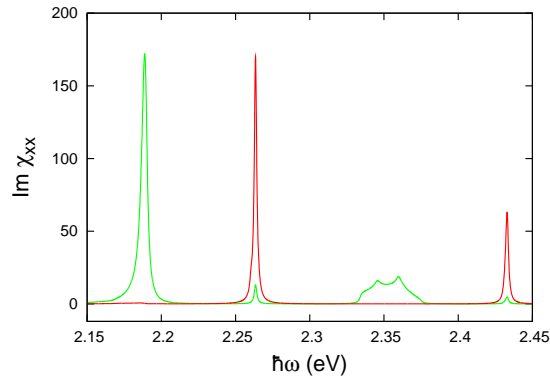


Figure 10: Vibronic absorption spectra polarized in the lattice plane. For the parameters and colors see Figure 9.

5 Conclusion and Outlook

This short review of papers [1–3] shows some feature of the collectivization of CTEs and FEs in the case of two-dimensional lattice of high symmetry. The analytical formulas and numerical simulations emphasize the role of the anisotropy of the linear optical properties inside the plane of the lattice and perpendicular to it. The axis of the 4th order transforms four CTEs, on one hand, and two (x, y) Frenkel excitons, one the other hand, into physically identical quasiparticles. Their symmetry governs the FEs–CTEs coupling terms.

We simulate the excitonic DOS which can be essential in some linear and non-linear phenomena. The studies of the absorption coefficients demonstrate the splitting of the excitonic and vibronic spectra caused by the anisotropy along with by the FEs–CTEs coupling. The absorption spectra in the case of relatively weak exciton–phonon coupling, especially in two-phonon vibronics, exhibit in the continua of many-particle bands.

Studies of excitations in quadratic lattice can be extended for the case of hexagonal 2D lattice as well for a lattice with two molecules in unit cell, like the graphene model.

References

- [1] I.J. Lalov and I. Zhelyazkov (2012) *Bulg. J. Phys.* **39** 282.
- [2] I.J. Lalov and I. Zhelyazkov (2013) *Chem. Phys.* **410** 71.
- [3] I.J. Lalov and I. Zhelyazkov (2013) *Chem. Phys.* **423** 127.
- [4] T.L. Hill (1956) *Statistical Mechanics*, McGraw Hill, New York.
- [5] R. Agra, F. van Wijland, and F. Trizac (2004) *Phys. Rev. Lett.* **93** 018304.

Excitonic and Vibronic Spectra in 2D Molecular Quadratic Lattice

- [6] J. Higo and K. Nagayama (1993) *J. Chem. Phys.* **99** 9156.
- [7] I.W. Hamley (2007) *Introduction to Soft Matter*, Revised Edition, John Wiley, Chichester.
- [8] I.J. Lalov and I. Zhelyazkov (2007) *Phys. Rev. B* **75** 245435.
- [9] V.M. Agranovich (2009) *Excitations in Organic Solids*, Oxford University Press, New York.