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Dynamics of Frenkel excitons in 2-dimensional molecular crystals

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A B S T R A C T

We investigate theoretically the linear low-temperature excitonic and vibronic absorption spectrum of Frenkel excitons in a 2-dimensional lattice with two identical, but differently oriented molecules in the unit cell. The calculation of the spectrum is based on Green's function formalism using the dynamic and dispersive approximations according to Rashba et al. and Lalov et al., respectively. With the experimental data for anthracene we find that the linear coupling between excitons and intramolecular vibrations allows for a quasi-bound state between the exciton and a single phonon, but is not able to couple an exciton and more than one phonon. The coupling is strengthened by the contribution of quadratic exciton–phonon coupling.

1. Introduction and assumptions

From the optical spectra of molecular crystals information on the electronic and vibrational degrees of freedom are derived. A well-investigated example is anthracene [1–4], where especially the vibronic spectra were considered [5–9]. Summaries are given in [2,3,5]. To simplify the theoretical approach, in [10] a 2-dimensional model of anthracene has been developed. In addition to this theoretical point of view, low dimensional structures become more and more important for the understanding of experimental realizations. Therefore, in [11] 2-dimensional models with one molecule in the unit cell for monoclinic and triclinic crystals have been investigated using the dynamic and dispersive approximations. In our investigations we consider 2-dimensional crystals with two molecules in the unit cell, see Fig. 1. For lack of space, we present here only results for 2-dimensional models of monoclinic crystals. In the numerical evaluation we use parameters for anthracene taken in part from [10,12].

The main assumptions of our calculation are the following ones: we calculate the linear absorption spectrum for a 2-dimensional crystal, modelling the (*ab*)-plane of anthracene. For the electronic excitations we consider only Frenkel excitons. The density of excitons is low enough that interactions between them can be neglected and we allow only for nearest neighbor interaction. In the exciton–phonon interaction we take into account terms being linear and quadratic in the variables of intramolecular, totally symmetric vibrations. In addition periodic boundary conditions are applied.

2. Hamiltonian and dielectric susceptibility

The Hamiltonian of a polyacene crystal in a 2-dimensional model consists of three terms

$$H = H_{\mathrm{ex}} + H_{\mathrm{ph}} + H_{\mathrm{ex-ph}} \tag{1}$$

In the nearest neighbor approximation the excitonic Hamiltonian H_{ex} is given by (see Fig. 2)

$$\begin{aligned} H_{\mathrm{ex}} = {} & E_F \sum_{\sigma} \sum_{l,m} B^{\dagger}_{\sigma,l,m} B_{\sigma,l,m} \\ & + \frac{1}{2} \sum_{\sigma} \sum_{l,m} W_{\sigma} B^{\dagger}_{\sigma,l,m} (B_{\sigma,l,m+1} + B_{\sigma,l,m-1}) \\ & + \frac{1}{2} \sum_{l,m} \Big\{ M_1 B^{\dagger}_{1,l,m} \big[B_{2,l,m} + B_{2,l-1,m-1} \big] \\ & + M_2 B^{\dagger}_{1,l,m} \big[B_{2,l-1,m} + B_{2,l,m-1} \big] + \mathrm{h.c.} \Big\} \end{aligned} \tag{2}$$

The operator $B^{\dagger}_{\sigma,l,m}$ ($B_{\sigma,l,m}$) creates (annihilates) a local electronic excitation with energy E_F at molecule (l,m) of the sublattice $\sigma = 1, 2$. The transfer matrix element W_{σ} describes the Frenkel exciton transport between molecules in the same sublattice σ, M_{σ} between molecules in different sublattices. In the case of anthracene, because of its monoclinic crystal structure, we have $M_1 = M_2 = M$ and $W_1 = W_2 = W$.

Because we have two molecules with different orientations in the unit cell, Davydov-splitting [5] occurs. The transformation of H_{ex} into the reciprocal lattice ($\vec{k} = (k_a, k_b)^{\mathrm{T}}$) reads

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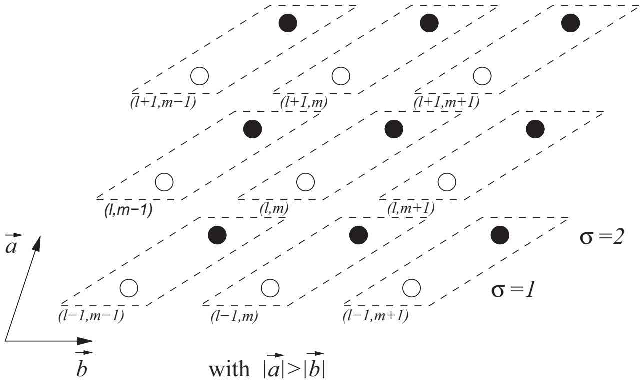

Fig. 1. (*ab*)-plane of a 2-dimensional polyacene crystal with triclinic crystal structure. The unit cells (with indices *l*, *m*) are depicted by dashed parallelograms. The bright and dark circles symbolize identical molecules with different orientations, defining the two sublattices $\sigma = 1, 2$. In the monoclinic case (such as anthracene) the crystallographic base vectors $\vec{a}$ and $\vec{b}$ are orthogonal to each other.

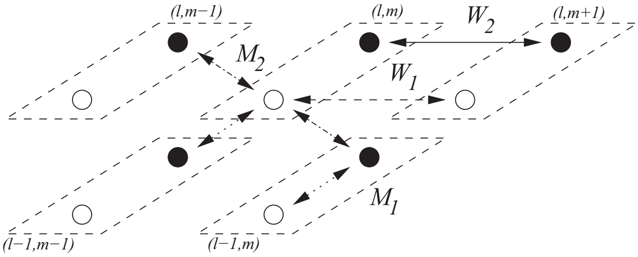

Fig. 2. Exciton transport paths with respective transfer matrix elements in a triclinic structure, within sublattice (dashed line W_1, solid line W_2) and to other sublattice (dotted line M_1, dash-dotted line M_2). Only direct nearest neighbors are taken into account. For anthracene with a monoclinic crystal structure we have $M_1 = M_2 = M$ and $W_1 = W_2 = W$.

$$H_{\rm ex} = \sum_{\sigma}\sum_{\vec{k}}(E_F + W_\sigma \cos(k_b b))B^{\dagger}_{\sigma,\vec{k}}B_{\sigma,\vec{k}} + \sum_{\vec{k}}\left\{M(\vec{k})B^{\dagger}_{1,\vec{k}}B_{2,\vec{k}} + M^{*}(\vec{k})B^{\dagger}_{2,\vec{k}}B_{1,\vec{k}}\right\} \tag{3}$$

with (for a monoclinic structure)

$$M(\vec{k}) = e^{i((k_a a + k_b b)/2)}\, 2M\cos\left(\frac{k_a a}{2}\right)\cos\left(\frac{k_b b}{2}\right) \tag{4}$$

The solution of the time-independent Schrödinger equation gives the two energy bands

$$E_{1/2} = E_F + \frac{(W_1 + W_2)\cos(k_b b)}{2} \pm \frac{1}{2}\sqrt{(W_1 - W_2)^2\cos^2(k_b b) + 4|M(\vec{k})|^2} \tag{5}$$

and the Davydov splitting $\Delta E|_{\vec{k}=0} = 4M$ (monoclinic case).

The phononic Hamiltonian $H_{\rm ph}$ is

$$H_{\rm ph} = \hbar\omega_0 \sum_{\sigma}\sum_{l,m} a^{\dagger}_{\sigma,l,m}a_{\sigma,l,m} \tag{6}$$

The operator $a^{\dagger}_{\sigma,l,m}$ ($a_{\sigma,l,m}$) creates (annihilates) a quantum of an intramolecular, totally symmetrical vibration of frequency ω_0 (internal phonon).

The coupling between the Frenkel excitons and the intramolecular phonons is described by

$$H_{\rm ex-ph} = D\hbar\omega_0 \sum_{\sigma}\sum_{l,m} B^{\dagger}_{\sigma,l,m}B_{\sigma,l,m}(a^{\dagger}_{\sigma,l,m} + a_{\sigma,l,m}) + E\hbar\omega_0 \sum_{\sigma}\sum_{l,m} B^{\dagger}_{\sigma,l,m}B_{\sigma,l,m}\left(a^{\dagger}_{\sigma,l,m} + a_{\sigma,l,m}\right)^2 \tag{7}$$

consisting of a linear and quadratic term in the vibrational variables. The dimensionless coupling constant *D* determines the shift of the equilibrium position after the electronic excitation; *E* is responsible for the change of the vibrational frequency after excitation.

Using the canonical transformation $\widetilde{H} = e^{S}He^{-S}$ [8,13] with

$$S = \sum_{\sigma}\sum_{l,m} \tau B^{\dagger}_{\sigma,l,m}B_{\sigma,l,m}\left[(a_{\sigma,l,m})^2 - (a^{\dagger}_{\sigma,l,m})^2 + \theta(a_{\sigma,l,m} - a^{\dagger}_{\sigma,l,m})\right] \tag{8}$$

the terms being linear in the phonon variables can be eliminated from *H* by choosing the transformation parameters τ and θ appropriately. This condition leads to

$$\tau = -\frac{1}{2}\ln\sqrt[4]{1 + 4E}, \quad \theta = -\frac{2D}{1 + 4E}\frac{\sqrt[4]{1 + 4E}}{1 - \sqrt[4]{1 + 4E}} \tag{9}$$

The total Hamiltonian then becomes

$$\begin{aligned}\widetilde{H} = {} & \tilde{E}_F \sum_{l,m}\sum_{\sigma} V^{\dagger}_{\sigma,l,m}V_{\sigma,l,m} \\ & + \sum_{l,m}\sum_{\sigma}\frac{W_\sigma}{2}V^{\dagger}_{\sigma,l,m}\left(V_{\sigma,l,m+1} + V_{\sigma,l,m-1}\right) \\ & + \sum_{l,m}\left\{V^{\dagger}_{1,l,m}\left[\frac{M_1}{2}\left(V_{2,l,m} + V_{2,l-1,m-1}\right) + \frac{M_2}{2}\left(V_{2,l-1,m} + V_{2,l,m-1}\right)\right] + \text{h.c.}\right\} \\ & + \hbar\omega_0 \sum_{l,m}\sum_{\sigma} a^{\dagger}_{\sigma,l,m}a_{\sigma,l,m} \\ & + \hbar\Delta\omega \sum_{l,m}\sum_{\sigma} V^{\dagger}_{\sigma,l,m}V_{\sigma,l,m}a^{\dagger}_{\sigma,l,m}a_{\sigma,l,m}\end{aligned} \tag{10}$$

$V_{\sigma,l,m} = e^{S}B_{\sigma,l,m}e^{-S}$ is called the vibronic operator [2,5]. The vibronic energy $\tilde{E}_F = E_F - \xi^2\hbar\omega_0 + \hbar\Delta\omega/2$ with $\xi = -\tau\theta$ consists of the local excitation energy, diminished by the Franck–Condon energy and $\Delta\omega = \omega_0(\sqrt{1 + 4E} - 1)$. The latter quantity is small and negative-valued in most polyacene crystals [14,15]. In the framework of linear response theory [16,17] we calculate the tensor of the linear dielectric susceptibility $\chi_{\alpha\beta}(\omega)$, whose imaginary part is proportional to the absorbed energy. It is given by

$$\chi_{\alpha\beta}(\omega) = \lim_{\varepsilon\to 0}\frac{i}{\hbar V}\left\{\Phi_{\alpha\beta}(\omega + i\varepsilon) - \Phi^{*}_{\alpha\beta}(-\omega + i\varepsilon)\right\}$$

$$\text{with} \quad \Phi_{\alpha\beta}(\omega + i\varepsilon) = \int_0^{\infty}\Phi_{\alpha\beta}(t)e^{i(\omega + i\varepsilon)t}\,dt$$

$$\text{and} \quad \Phi_{\alpha\beta}(t) = \langle\hat{P}^{\alpha}(t)\hat{P}^{\beta}(0)\rangle_0 = \langle 0|\hat{P}^{\alpha}(t)\hat{P}^{\beta}|0\rangle \tag{11}$$

$\Phi_{\alpha\beta}(t)$ is called the retarded response function, $\Phi_{\alpha\beta}(\omega)$ its spectral representation, and α, β are the cartesian tensor components, *V* is the crystal volume in the (*ab*)-plane. The operator $\vec{\hat{P}}$ represents the total transition dipole moment of the Frenkel excitons, which in the 2-dimensional model can be written as

$$\vec{\hat{P}}_F = \sum_{\sigma}\sum_{l,m}\vec{p}_\sigma(\hat{V}^{\dagger}_{\sigma,l,m} + \hat{V}_{\sigma,l,m}), \tag{12}$$