

Charged Frenkel biexcitons in organic molecular crystals

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It is known that the energy of the lowest electronic transition in neutral molecules of anthracene, tetracene and other polyacenes is blue shifted in comparison with the corresponding transition energy in mono-valent molecular ions. This effect in molecular crystal may be responsible for the attraction between molecular (Frenkel) exciton and charge carrier. Due to this attraction the bound state of Frenkel exciton and free charge (charged Frenkel exciton) may be formed [5]. As we demonstrate below, the same mechanism can be responsible for formation of charged biexciton (bound state of two Frenkel excitons and a charge carrier). One-dimensional lattice model is used which corresponds to J -aggregates and is also a good approximation for quasi-one-dimensional crystals. Calculations are performed for molecular crystals like tetracene where at low temperature the exciton band is much narrower than that of the charge carrier.

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Investigations of physical properties of molecular crystals in conditions when both excitons and charge carriers are present in a crystal have a long history (see, e.g. [1]). It was shown, for example, that exciton can transfer its energy to a charge, either a trapped one, causing its detrapping, or to a free one, which is then excited to a higher conducting state. This direction of investigations has recently received new impulse after high quality crystals made of various molecular compounds were grown and it was shown that these crystals demonstrate high carrier's mobility [2]. Band-like motion of delocalized charge carriers has been clearly observed at low temperatures in molecular crystals of various polyacenes and oligothiophenes. One may expect that different effects of exciton-charge interactions can be investigated in such crystals.

Interaction of a charge carrier with exciton can arise due to different physical mechanisms. One is the Coulomb interaction [3] caused by a change of the polarizability of a molecule upon its excitation. This interaction decreases with distance r between exciton and charge carrier as r^{-4} and is very anisotropic. Another mechanism is due to the fact that the excitation energy of an ionized molecules may differ from that of the neutral molecule by some negative amount $-\Delta$ ($\Delta > 0$); see, e.g. [4]. This leads to a contact exciton-charge interaction and to formation of bound states of a Frenkel exciton and a free charge carrier [5]. Such "charged" excitations might be important for applications, since the motion of these quasi-particles, and hence transport of their energy, can be controlled by external electric field.

In this paper we demonstrate that the bound states of two Frenkel excitons and one charge carrier can also be formed due to short-range interaction of the above mentioned nature. For definiteness we shall consider negatively charged biexcitons formed by two Frenkel excitons and an electron with the use of experimental data for negative molecular ions [4].

We consider a one-dimensional lattice with one molecule in elementary cell labeled by index n and introduce the creation and annihilation operators B_n^\dagger, B_n for excitons and c_n^\dagger, c_n for electrons. We confine ourselves to the case of "heavy" excitons with the width of the energy band much narrower than that of the electron. According to [2] such situation takes place, for example, for singlet excitons in tetracene at low temperature where excitonic hopping matrix element V_{exc} is about 50 cm^{-1} whereas electronic hopping matrix element V is about 350 cm^{-1} . For such molecular structures we can use the adiabatic approximation and neglect in the first order approximation the motion of excitons. Such adiabatic approximation may be even better for triplet excitons in molecular crystals for which the hopping matrix element is about $5\text{--}10 \text{ cm}^{-1}$. Thus, in this approximation we have to find the solution of the one-particle Schrödinger equation for an electron moving in the potential created by two excitons located at two different sites of the lattice. The Hamiltonian of the system can be written in the form

$$H = E_0 \sum_n B_n^\dagger B_n + \epsilon_0 \sum_n c_n^\dagger c_n - V \sum_n \left(c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n \right) - \Delta \sum_n B_n^\dagger B_n c_n^\dagger c_n, \quad (1)$$

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where we take into account only nearest-neighbor interaction, E_0 is the energy of exciton and ϵ_0 of the electron, V is electron's hopping matrix element ($V > 0$), $\Delta > 0$ is the constant of exciton-electron interaction. The wave function has the form

$$|3\rangle = \sum_p \psi_p B_n^\dagger B_m^\dagger c_p^\dagger |0\rangle, \quad (2)$$

where $|0\rangle$ is the "vacuum" state without any quasi-particles, excitons are located at the sites n and m . Substitution of (2) and (1) into the Schrödinger equation $H|3\rangle = E|3\rangle$ yields the system

$$E' \psi_p = V (\psi_{p+1} + \psi_{p-1}) - \Delta (\delta_{mp} + \delta_{np}) \psi_p, \quad (3)$$

$$E' = E - 2E_0 - \epsilon_0$$

for the energy E and electron amplitudes ψ_p . It can be easily solved for any n and m . At $p \rightarrow \pm\infty$ the wave function ψ_p decays exponentially $\sim \exp(-\kappa|p|)$ and the energy E is connected with κ by simple formula

$$E = 2E_0 + \epsilon_0 - 2V \cosh \kappa. \quad (4)$$

The parameter κ is determined by the equation

$$(\Delta/V) \cosh(\kappa N/2) = \exp[\kappa N/2] \sinh \kappa, \text{ even states}, \quad (5)$$

$$(\Delta/V) \sinh(\kappa N/2) = \exp[\kappa N/2] \sinh \kappa, \text{ odd states},$$

where $N = |m - n|$; $\psi_m = \psi_n$ for even electronic states and $\psi_m = -\psi_n$ for odd states.

For the case $N = 1$, when excitons are separated by one lattice constant, these equations are solved explicitly to give

$$\exp \kappa = \begin{cases} \Delta/V + 1, & \text{even states,} \\ \Delta/V - 1, & \text{odd states,} \end{cases} \quad (6)$$

and, hence, the energy of these states are given by

$$E = \begin{cases} 2E_0 + \epsilon_0 - \Delta - V - V^2/(\Delta + V), & \text{even states,} \\ 2E_0 + \epsilon_0 - \Delta + V - V^2/(\Delta - V), & \text{odd states.} \end{cases} \quad (7)$$

On the other hand, in the limit of large $\kappa N \gg 1$ any equation (5) gives

$$\exp \kappa = \frac{\Delta}{2V} + \sqrt{\left(\frac{\Delta}{2V}\right)^2 + 1} \quad (8)$$

and thus the energy for both types of states becomes

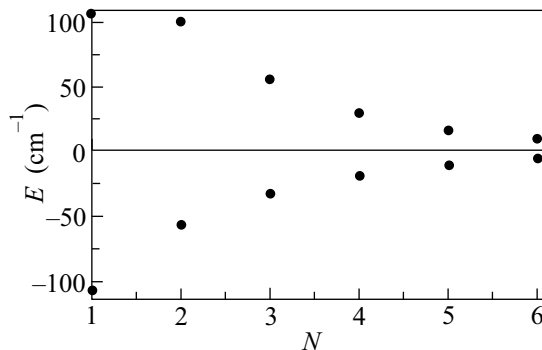
$$E = 2E_0 + \epsilon_0 + E' = 2E_0 + \epsilon_0 - \sqrt{\Delta^2 + 4V^2}. \quad (9)$$

Due to degeneracy of these states, this energy coincides with the energy of partially dissociated state which consists of a charged exciton (bound state of exciton and electron) and a free exciton separated considerably from each other. Correction to formula (9) shows an exponential dependence of the spectrum on N

$$E = 2E_0 + \epsilon_0 - \sqrt{\Delta^2 (1 \pm 2e^{-\kappa(N+1)}) + 4V^2}, \quad (10)$$

$$N \gg 1/\kappa,$$

going to the energy (9) from below for even states and from above for odd states. Subtraction of energy (9) from that given by Eq. (4) gives the binding energy of charged biexciton states for finite N .



Dependence of charged biexciton energy on distance between excitons. Zero energy corresponds to the dissociated state consisting of charged and uncharged excitons at infinite distance between them

For estimations we use typical values of $V = 300 \text{ cm}^{-1}$ [2] and $\Delta = 400 \text{ cm}^{-1}$ (anthracene) and $\Delta = 800 \text{ cm}^{-1}$ (tetracene) [4]. Dependence of binding energies $E_b = E(N) - E(\infty)$ on N for tetracene case is shown in Figure. We see from this Figure that the even charged biexciton states have the energies less than the energy (9) of partially dissociated state, whereas the odd states have the energies greater than the energy of partially dissociated states. Hence, only even states are stable with respect to dissociation to charged and free excitons. Obviously, corrections to adiabatic approximation will destroy the states with large N . Number of states with small N which can be observed experimentally depends crucially on the parameters of a crystal. In particular, in case of parameters chosen above the binding energy of biexciton with $N = 1$ is about $\simeq 100 \text{ cm}^{-1}$ what is greater than the width δ of lowest energy excitonic resonance $\delta \lesssim 20 \text{ cm}^{-1}$ (see, e.g. [6]). The differences of binding energies for the states with $N = 1$ and 2 are about 50 cm^{-1} . Hence, at least these two states can be probably observed in spectroscopic

experiments. The considered states must give contribution into biexcitonic part of all optical nonlinearity, and this contribution is controlled by concentration of free charge carriers. Formation of such states have to lead to dependence of carriers' mobility on exciton concentration in molecular crystals (anthracene, tetracene) doped by mono-valent ions and having a dark conductivity as well as carriers arising due to injection by means of field effect transistors (see [2]).

The theory of charged biexcitons with taking into account motion of excitons will be published later.

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1. M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, Oxford University Press, New York and Oxford, 1999.
 2. C. Kloc, P. G. Simpkins, T. Siegrist, and R. A. Landise, *J. Cryst. Growth* **182**, 416 (1997); J. H. Schoen, C. Kloc, and B. Batlog, *Phys. Rev.* **B61**, 10803 (2000).
 3. V. M. Agranovich and A. A. Zakhidov, *Chem. Phys. Lett.* **68**, 86 (1979).
 4. G. J. Hoitink, N. H. Velthorst, and P. J. Zandstra, *Mol. Phys.* **3**, 533 (1960).
 5. V. M. Agranovich, D. M. Basko, F. Bassani et al., *Chem. Phys.* (2001, submitted).
 6. H. C. Wolf, *Z. Naturforsch.* **A13**, 414 (1958).