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Vibronic spectra of charge transfer excitons and of mixed charge transfer and Frenkel excitons

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Abstract

The linear absorption spectra in the excitonic and vibronic regions in the case of mixing of Frenkel excitons (FEs) and charge-transfer excitons (CTEs) have been theoretically studied for the exciton parameters of the crystals of MePTCDI and PTCDA. Two coupling parameters for the exciton–phonon coupling are introduced: the FE–phonon coupling and the CTE–phonon coupling. The main features of the vibronics in the absorption spectra are the following: (a) the existence of a doublet structure in the vibronic spectra of CTEs; (b) the vibronic levels of the FE at intermediate values of both coupling parameters are located in the continuum of the many-particle exciton–phonon states which makes its absorption line wide and flat; (c) in the case of strong coupling (coupling constants larger than 1) a doublet of bound states appears above this continuum; (d) in the case of vanishing CTE–phonon coupling the vibronics of the charge transfer excitons practically disappear in the absorption spectra.

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1. Introduction

The linear absorption spectra of molecular systems have been studied for several decades. These spectra manifest both the pure electronic excitations (excitons) and their vibronic replicas [1,2]. The studies of the vibronics of charge transfer systems exhibited the necessity to include into the consideration also the coupling between phonons and mixed Frenkel excitons (FEs) and charge transfer excitons (CTEs) [3]. This paper presents the continuation of our recent studies of vibronic spectra of the crystals of *N*,*N*′-dimethylperylene-3,4,9,10-perylenetetracarboximide (MePTCDI) and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) [4,5]. These crystals are attractive charge transfer systems and provide us with a good model for a quasi-one-dimensional molecular crystal. The short intermolecular distance inside the molecular stacks of the crystal ensures strong intermolecular interaction whereas the interstack interaction is relatively weak [6–10]. The lowest electronic excitations of both crystals exhibit the mixed nature of FEs and CTEs states [6,9]. Thus their excitonic and vibronic spectra investigated in absorption, photoluminescence, and electronic energy-loss spectroscopy have been extensively studied [10–14]. Our theoretical treatment is directed to establish connections between absorption spectra and exciton–phonon coupling in charge transfer crystals.

We calculate the linear absorption in the excitonic and one-phonon vibronic spectra using the model of strongly mixed FEs and CTEs and introducing specific exciton parameters of both crystals [6,7]. Our approach includes the so-called dynamic theory of vibronics [2]. In its linear version the total number of excitons in the crystal equals

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one and the total number of vibrational quanta is also preserved permanently. We consider the linear exciton–phonon coupling which usually is the strongest one and in the crystals MePTCDI and PTCDA it is the only coupling mechanism [8,9].

The most important extension of the model in this paper is the assumption of different values for the parameters of the linear FE–phonon coupling and the CTE–phonon coupling (in [4] the two parameters are supposed to be equal).

The organization of the paper is as follows: in Section 2 we present our calculations of the absorption coefficient as the imaginary part of the linear optical susceptibility in the excitonic and one-phonon vibronic regions. In this section we also derive the model Hamiltonian which describes the coupling between mixed FEs and CTEs and intramolecular phonons. Section 3 contains the expressions for the linear optical susceptibility and in Section 4 we show absorption curves that have been calculated using the specific data for the exciton parameters in the crystals MePTCDI and PTCDA [6,7]. In our calculations we use different sets of values for the parameters of the linear exciton–phonon coupling. In Section 5 we give some conclusions.

2. Theoretical model

We calculate the linear optical susceptibility χ_{ij} using the following expressions [1,15]:

$$\chi_{ij} = \lim_{\varepsilon\to 0}\left\{-\frac{1}{2\hbar V}[\Phi_{ij}(\omega+\mathrm{i}\varepsilon)+\Phi_{ij}(-\omega+\mathrm{i}\varepsilon)]\right\} \tag{1}$$

$$\Phi_{ij}(t) = -\mathrm{i}\Theta(t)\langle 0|\widehat{P}_i(t)\widehat{P}_j(0)+\widehat{P}_j(t)\widehat{P}_i(0)|0\rangle \tag{2}$$

$$\widehat{P} = \sum_n \widehat{P}_n \tag{3}$$

in which V is the crystal volume and $\widehat{P}_n$ the operator of the electric transition dipole moment of the exciton on site n. We calculate the Green functions (2) as averages over the ground state $|0\rangle$, taking into account the large values of the energy of the excitons and of the vibrations compared to kT.

We consider excitations in a linear stack of periodically arranged molecules $n = 1,2,\ldots,N$ and begin with the Hamiltonian [4,8,9]

$$\widehat{H} = \widehat{H}_{\mathrm{ex}} + \widehat{H}_{\mathrm{phon}} + \Delta\widehat{H} \tag{4}$$

$\widehat{H}_{\mathrm{ex}}$ is the Hamiltonian of mixed FEs and CTEs [6–8]:

$$\begin{aligned}\widehat{H}_{\mathrm{ex}} = {} & \sum_n E'_{\mathrm{F}} B_n^{\dagger}B_n + \sum_{nn'} L'(\delta_{n',n+1}+\delta_{n',n-1})B_n^{\dagger}B_{n'} \\ & + \sum_{n,\sigma=1,2} E'_{\mathrm{C}} C_{n\sigma}^{\dagger}C_{n\sigma} + \sum_{n,\sigma=1,2}\varepsilon'_{\mathrm{e}}[B_n^{\dagger}C_{n\sigma}+C_{n\sigma}^{\dagger}B_n] \\ & + \sum_n \varepsilon'_{\mathrm{h}}[B_n^{\dagger}C_{n+1,2}+B_n^{\dagger}C_{n-1,1}+\mathrm{h.c.}]\end{aligned} \tag{5}$$

where B_n ($B_n^{\dagger}$) is the annihilation (creation) operator of a FE on molecule n, E'_{F} is the excitation energy of FEs and L' is the transfer integral between neighboring molecules n and $n\pm 1$, $C_{n\sigma}$ are the annihilation operators of CTEs of type $\sigma = 1, 2$ whose hole is based on site n and the electron is located on site $n+1$ ($\sigma = 1$) and on site $n-1$ ($\sigma = 2$), E'_{C} is the excitation energy of CTEs. As a consequence of the inversion symmetry of the system, both types of CTEs have equal excitation energy (and we neglect the transfer of CTEs as a whole). The quantities $\varepsilon'_{\mathrm{e}}$ and $\varepsilon'_{\mathrm{h}}$ represent charge-transfer integrals of the electron and of the hole between the molecule n with the FE and its neighbors.

We consider the vibronics with one effective intramolecular vibrational mode of frequency ω_0 and a_n as operator of annihilation of one vibrational quantum on molecule n. Thus the phonon part $\widehat{H}_{\mathrm{phon}}$ is expressed as

$$\widehat{H}_{\mathrm{phon}} = \sum_n \hbar\omega_0 a_n^{\dagger}a_n \tag{6}$$

In our approach the operator $\Delta\widehat{H}$ of the linear exciton–phonon coupling is introduced as follows [1,2,4,8]:

$$\begin{aligned}\Delta\widehat{H} = {} & \sum_n \hbar\omega_0\xi B_n^{\dagger}B_n(a_n^{\dagger}+a_n) \\ & + \sum_{n,\sigma}\hbar\omega_0\xi_1 C_{n\sigma}^{\dagger}C_{n\sigma}\cdot[a_n^{\dagger}+a_n+a_{n+\sigma_1}^{\dagger}+a_{n+\sigma_1}]\end{aligned} \tag{7}$$

with $\sigma_1 = +1$ if $\sigma = 1$; $\sigma_1 = -1$ if $\sigma = 2$.

The dimensionless parameters ξ and ξ_1 describe the displacement of the equilibrium positions of the nuclei in the excited (ionized) molecule and express the coupling between the FE and the intramolecular vibration (ξ) and between the CTE and the vibration (ξ_1). In principle the vibrational quantum can be excited on the positive ion (hole) or on the negative ion and these two different electronic states have a different impact on the intramolecular vibration (non-equal values of ξ_1). For the sake of simplicity we take only one parameter ξ_1 of the CTE–phonon coupling. This, however, is not a principal limitation. But we stress again the main difference between the studies in paper [4] in which the equality $\xi = \xi_1$ is a basic assumption and the present work in which $\xi \neq \xi_1$.

We can eliminate the operator (7) using the canonical transformation [1,4,16]:

$$\widehat{H}_1 = \mathrm{e}^{Q}\widehat{H}\mathrm{e}^{-Q} \tag{8}$$

where

$$\begin{aligned}Q = {} & \xi\sum_n B_n^{\dagger}B_n(a_n^{\dagger}-a_n) \\ & + \xi_1\sum_{n,\sigma} C_{n\sigma}^{\dagger}C_{n\sigma}[a_n^{\dagger}-a_n+a_{n+\sigma_1}^{\dagger}-a_{n+\sigma_1}]\end{aligned} \tag{9}$$

We are interested in the linear case only, in which the concentration of the excitons is low and thus the following relations hold true:

$$\widehat{N}_{\mathrm{ex}} = \sum_{n,\sigma}(B_n^{\dagger}B_n + C_{n\sigma}^{\dagger}C_{n\sigma}) = 1 \tag{10}$$

$$\begin{aligned}& B_n^{\dagger}B_nB_{n'}^{\dagger}B_{n'} = B_n^{\dagger}B_n\delta_{n,n'} \\ & C_{n\sigma}^{\dagger}C_{n\sigma}C_{n'\sigma'}^{\dagger}C_{n'\sigma'} = C_{n\sigma}^{\dagger}C_{n\sigma}\delta_{n,n'}\delta_{\sigma\sigma'} \\ & B_n^{\dagger}B_nC_{n'\sigma'}^{\dagger}C_{n'\sigma'} = 0\end{aligned} \tag{11}$$