Model of mixed Frenkel and charge-transfer excitons in donor–acceptor molecular crystals: investigation of vibronic spectra

I J Lalov¹, C Warns² and P Reineker²,³

¹ Faculty of Physics, Sofia University, Sofia 1164, Bulgaria
² Institute of Theoretical Physics, Ulm University, Albert-Einstein-Allee 11, 89069 Ulm, Germany
E-mail: peter.reineker@uni-ulm.de

New Journal of Physics 10 (2008) 085006 (25pp)
Received 26 March 2008
Published 19 August 2008
Online at http://www.njp.org/
doi:10.1088/1367-2630/10/8/085006

Abstract. The mixing of Frenkel excitons (FEs) and charge-transfer excitons (CTEs) in a molecular stack of regularly arranged donor (D) and acceptor (A) molecules is considered a model case and its vibronic line shapes have been calculated for several parameter sets. The two types of excitons (FE and CTE) are coupled linearly and quadratically with one vibrational mode of the D molecule (or of the A molecule). Using the methods of canonical transformation and of Green’s functions (at $T = 0$), as well as the vibronic approach which is applicable in the case of a narrow exciton band, the linear optical susceptibility is calculated for the three spectral regions: (a) excitonic, (b) one-phonon vibronics, and (c) two-phonon vibronics. As the study is directed to centrosymmetrical stacks, the cases of mixing of gerade excitons and of ungerade excitons have been treated separately in the calculation of the linear absorption coefficients. Because until now experimental observations of FE–CTE mixing in DA charge-transfer systems are absent, the numerical calculations have been performed for hypothetical sets of parameters which include: the parameters of CTEs in DA stacks (like anthracene–PMDA) and the parameters of FE–CTE mixing in a one-component stack (like that of PTCDA). The simulations establish the main features of the excitonic and vibronic spectra in the case of FE–CTE mixing, namely (i) the mutual influence on the positions and on the absorption intensities of all terms of the vibronic progressions stemming from FE and CTE levels; (ii) in the case of vibration of an A molecule (if the FE is assumed to be an excited electronic state of the D molecule), only one vibronic progression
is manifest and the vibronic levels closer to the FE will be most enhanced; (iii) the redistribution of the absorption intensities depends on the sign of the mixing constant and may be so strong that the terms of the two vibronic progressions could have comparable absorption; (iv) spectral lines of different shape correspond to the bound and unbound exciton–phonon states; and (v) in the case of mixing of gerade excitons its possible impact on the absorption of the ungerade CTE-combination connected with the noncentral part \( k \neq 0 \) of the Brillouin zone was established. The simulation of the FE–CTE mixing can be useful in the assignment of the linear absorption spectra and in the description of the FE–CTE–vibration coupling.

1. Introduction

The mixing of Frenkel excitons (FEs) and charge-transfer excitons (CTEs) in a molecular stack (which is a part of a three-dimensional molecular crystal) of alternating regularly arranged donor and acceptor molecules has been briefly discussed in [1] as an alternative possibility for the transfer of CTEs via FE states. In the present paper, we consider this mixing as a real (perhaps hypothetical) situation in CT systems modeling possible future experiments. Moreover, in analogy to previous papers [2]–[5], we intend to treat the one- and two-phonon vibronic satellites in the case of mixed FEs and CTEs.

The mixing of FEs and CTEs has been widely studied in one-component molecular CT crystals, e.g. polyacenes [6]–[9], perylene derivatives [10]–[12], fullerenes [13]–[15] and others. Their vibronic spectra have been investigated using various experimental techniques and theoretical approaches, see [3]–[7], [9]–[12] and others. The coupling between FEs and CTEs renormalizes the excitonic and vibronic spectra, redistributes intensities between FEs and CTEs in absorption or electro-absorption and even makes some forbidden FEs observable [8].

New Journal of Physics 10 (2008) 085006 (http://www.njp.org/)
The most widely known two-component donor (D) and acceptor (A) crystal is anthracene–PMDA \([1], [16]–[21]\). The alternatingly arranged donor (anthracene) and acceptor (PMDA) molecules create a quasi-one-dimensional molecular stack and the donor molecule resides at the inversion center between two neighboring acceptors. Its reflection spectra \([18]\) and electroreflection spectra \([19]\) contain well-resolved zero-phonon lines of the pure CTE transition and its vibronic replicas, each of them with its own structure generated by the coupling with external phonons. The spectral lines of the FEs are positioned several thousand wave numbers above the CTE region and thus the mixing of FEs and CTEs can be neglected. On the other hand, the key paper \([1]\) gives an adequate theoretical description of the CTE spectra.

In the present paper, we suppose the same one-dimensional regular arrangement of alternating D and A molecules, but the inversion symmetry is not an inherent feature of the model. Nevertheless, we pay special attention to centrosymmetrical CT media, which are more widely investigated and probably more frequently available. In the molecular stack with inversion symmetry, the mixing of FEs and CTEs must be of the same parity.

We consider the mixing of CTEs, described in \([1]\), and FEs, whose electronic excited state stems from the excitation of the neutral donor molecule (the case of a FE originating from the acceptor molecule is completely analogous). Both types of excitons are mobile: the FEs via resonance transfer of the electronic excitation between neighboring donors and the CTEs via the transfer of the hole between neighboring donors or of the electron between neighboring acceptors. In our paper, the linear optical susceptibility in the excitonic and vibronic regions is calculated considering one vibrational intramolecular mode (of the donor or of the acceptor molecule), which is linearly and quadratically coupled with FEs and CTEs. The vibronic approach introduced in \([22]\) allows us to calculate the linear absorption coefficient in the excitonic, one-phonon and two-phonon vibronic spectra.

The next section contains the theoretical model and introduces the initial Hamiltonian and its canonical transformation whereas in section 3, we calculate the optical susceptibility using Green’s functions method. In section 4, the results of numerical calculations of the absorption curves based on the analytical results of section 3 are presented. The last section contains some conclusions on the influence of FE–CTE mixing on excitonic and vibronic spectra. The appendix contains the formulae which are necessary for the calculation of the linear optical susceptibility.

### 2. Hamiltonian in the case of mixing of FEs and CTEs

In our model, the unit cell of the molecular stack of alternating regularly arranged donor and acceptor molecules contains one donor and one acceptor with \(d\) being the distance between neighboring donors (or acceptors). The non-degenerate molecular electronic excitations with excitation energy \(E_F\) of each neutral donor form a FE with \(L\) being the transfer integral between neighboring donors. We denote by \(B_n, (B_n^\dagger)\) the annihilation (creation) operator of the electronic excitation on donor \(n\) and get the following FE part of the Hamiltonian

\[
\hat{H}_FE = \sum_n E_F B_n^\dagger B_n + \sum_{n,n'} L \left( \delta_{n',n+1} + \delta_{n',n-1} \right) B_{n'}^\dagger B_n.
\]

(1)

We consider the case of two CTEs of equal excitation energy \(E_C\). Their annihilation operators are denoted by \(C_{n,\sigma}, \sigma = 1, 2\), where \(n\) is the number of the site of the ionized donor (hole), \(\sigma = 1\) stands for the CT exciton with ionized acceptor on the same pair \(n\), and the
electron of the CTE with $\sigma = 2$ is located on the neighboring acceptor in the unit cell $n - 1$. In the CTE part of the Hamiltonian, the parameter $M_e$ is the transfer integral of the electron between neighboring acceptors and $M_h$ is the corresponding transfer integral of the hole between neighboring donors \cite{1}:
\begin{equation}
H_{\text{CTE}} = \sum_{n,\sigma=1,2} E_c C_{n,\sigma}^\dagger C_{n,\sigma} + \sum_n M_e (C_{n,1}^\dagger C_{n,2} + C_{n,2}^\dagger C_{n,1}) + \sum_n M_h (C_{n,1}^\dagger C_{n+1,2} + C_{n+1,2}^\dagger C_{n,1}).
\end{equation}

The mixing between FEs and CTEs is supposed to be realized through one mechanism only, namely, the transfer of the electron from the excited neutral donor to the closest acceptors. The operator of the FE–CTE coupling reads
\begin{equation}
\hat{H}_{\text{FC}} = \sum_n (\epsilon_{e1} B_n^\dagger C_{n1} + \epsilon_{e2} B_n^\dagger C_{n2} + \text{h.c.}).
\end{equation}

Obviously, the transfer of the hole from the excited neutral donor to the neighboring donor does not create a CTE of the type under consideration. We suppose different values of the transfer integrals $\epsilon_{e1}$ and $\epsilon_{e2}$ of the electron from the excited neutral donor to the acceptor on the ‘left’ side and on the ‘right’ one because of possible different distances or different intermolecular overlap integrals. Even in the case of a molecular stack with inversion symmetry, as in anthracence–PMDA, the inclination of the normal of the molecular planes to the stack axis destroys the $D_{2h}$ site symmetry of the triples ADA (see the corresponding remark in \cite{1}). This inclination might be the reason for different values of the coupling constants $\epsilon_{e1}$ and $\epsilon_{e2}$ in (3). We stress that the transfer integrals $\epsilon_{e1}$ and $\epsilon_{e2}$ are connected with the overlap between neighboring DA pairs whereas the other transfer integrals $L$, $M_e$, $M_h$ describe jumps of the excitations at distances DD or AA which equal the size $d$ of the unit cell and are two times bigger than the distance DA. Therefore $L$, $M_e$ and $M_h$ are expected to be smaller than $\epsilon_{e1}$ and $\epsilon_{e2}$. The full Hamiltonian finally contains a phonon part $\hat{H}_{\text{ph}}$ and the operator of exciton–phonon coupling $\hat{H}_{\text{ex,phon}}$
\begin{equation}
\hat{H} = \hat{H}_{\text{FE}} + \hat{H}_{\text{CTE}} + \hat{H}_{\text{FC}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{ex,phon}}.
\end{equation}

The last two terms are expressed with different operators in the case of intramolecular modes of the D and of the A molecule, namely,
(a) vibrational mode of D
\begin{equation}
\hat{H}_{\text{ph}} = \sum_n \hbar \omega_0 a_n^\dagger a_n,
\end{equation}

\begin{equation}
\hat{H}_{\text{ex,phon}} = \sum_n B_n^\dagger B_n \hbar \left[ \xi F \omega_0 (a_n^\dagger + a_n) + \Delta \omega F a_n^\dagger a_n \right] + \sum_{n,\sigma} C_{n,\sigma}^\dagger C_{n,\sigma} \hbar \left[ \xi \omega_0 (a_n^\dagger + a_n) + \Delta \omega a_n^\dagger a_n \right]
\end{equation}
in which $\omega_0$ is the vibrational frequency of the neutral nonexcited D, $\xi$ and $\xi_F$ are dimensionless parameters of the linear exciton–phonon coupling in the ionized donor and in the excited neutral donor, respectively, and $\Delta \omega$ and $\Delta \omega_F$ are the changes of the vibrational frequency in D. The latter changes are caused by the quadratic exciton–phonon coupling and usually the ratios $|\Delta \omega/\omega_0|$ and $|\Delta \omega_F/\omega_0|$ do not exceed several percent.

\textit{New Journal of Physics 10} (2008) 085006 (http://www.njp.org/)
(b) In the case of the vibrational mode of A (the FE is excited on D):

\[ \hat{H}_{\text{ph}} = \sum_n \hbar \omega_{\text{ac}} b_n^\dagger b_n, \] (6a)

\[ \hat{H}_{\text{ex, phon}} = \sum_{n, \sigma} C_{n, \sigma}^\dagger C_{n, \sigma} \hbar \left[ \xi_{\text{ac}} \omega_{\text{ac}} (b_n^\dagger + b_n) + \Delta \omega_{\text{ac}} b_n^\dagger b_n \right]. \] (6b)

As usual, the most important linear parts of the exciton–phonon coupling can be eliminated using the canonical transformation \([2, 3, 23]\):

\[ \hat{H}_1 = e^Q \hat{H} e^{-Q} \] (7)

in which for the case (a)

\[ Q = \sum_{n, \sigma} C_{n, \sigma}^\dagger C_{n, \sigma} \xi(a_n^\dagger - a_n) + \sum_n B_n^\dagger B_n \xi_F (a_n^\dagger - a_n) \] (8a)

and for the case (b)

\[ Q = \sum_{n, \sigma} C_{n, \sigma}^\dagger C_{n, \sigma} \xi_{\text{ac}} (b_n^\dagger - b_n). \] (8b)

We introduce the vibronic operators

\[ V_n = e^Q B_n e^{-Q}, \] (9a)

\[ U_{n, \sigma} = e^Q C_{n, \sigma} e^{-Q}. \] (9b)

In the case (a) (vibrational mode of D), the transformed Hamiltonian (7) is expressed as follows (for more details, see the transformation in [22]):

\[ \hat{H}_1 = \sum_n \left( E_{\text{F}} - \hbar \omega_0 \xi_{\text{F}}^2 \right) V_n^\dagger V_n + \sum_{n, n'} L (\delta_{n', n+1} + \delta_{n', n-1}) V_{n'}^\dagger V_n + \sum_{n, \sigma} \left( E_{\text{ac}} - \hbar \omega_0 \xi_{\text{ac}}^2 \right) U_{n, \sigma}^\dagger U_{n, \sigma} \]

\[ + \sum_n M_c (U_{n, 2}^\dagger U_{n, 1} + U_{n, 1}^\dagger U_{n, 2}) + \sum_n M_b (U_{n+1, 2}^\dagger U_{n, 1} + U_{n, 1}^\dagger U_{n+1, 2}) \]

\[ + \sum_n (\epsilon_{c1} V_n^\dagger U_{n, 1} + \epsilon_{c2} V_{n+1}^\dagger U_{n, 2} + \text{h.c.}) + \sum_n \hbar \omega_0 a_n^\dagger a_n \]

\[ + \sum_{n, \sigma} \hbar (\Delta \omega_{\text{c}} V_n^\dagger V_n + \Delta \omega U_{n, \sigma}^\dagger U_{n, \sigma}) a_n^\dagger a_n \] (10)

and a corresponding expression for the case (b) (vibrational mode of A).

For the calculation of the linear optical susceptibility, we need the operator of the transition dipole moment of the system which may be represented through the operators of the transition dipole moments of the CTEs, \( \vec{\mu}_\sigma (\sigma = 1, 2) \), and of the FE, \( \vec{\mu}_{\text{F}} \):

\[ \hat{\vec{\mu}}_1 = \sum_{n, \sigma} \vec{\mu}_\sigma (C_{n, \sigma} + C_{n, \sigma}^\dagger) + \sum_n \vec{\mu}_{\text{F}} (B_n + B_n^\dagger). \] (11)

The operator \( \hat{\vec{P}}_1 \) is transformed and rewritten in the following way:

\[ \hat{\vec{P}} = \sum_n \left[ \vec{\mu}_{\text{F}} (V_n + V_n^\dagger) + \sum_{\alpha} (\vec{\mu}_\alpha + (-1)^{\sigma-1} \vec{\mu}_\alpha) (U_{n, \sigma} + U_{n, \sigma}^\dagger) \right] \] (12)
in which
\[ \tilde{\mu}_s = (\tilde{\mu}_1 + \tilde{\mu}_2)/2, \quad \tilde{\mu}_a = (\tilde{\mu}_1 - \tilde{\mu}_2)/2. \]

In the stack without inversion center, all components $\tilde{p}_F$, $\tilde{\mu}_s$ and $\tilde{\mu}_a$ may be different from zero and the linear optical susceptibility has to be calculated using the full Hamiltonian (10). But if the donor (acceptor) molecules reside at the inversion center, like anthracene in the anthracene–PMDA crystal, then the situation needs further specification. In such a case, the CTE eigenstates of the Hamiltonian can be represented by the following symmetrical and antisymmetrical combination
\[ \frac{1}{\sqrt{2}} \left( U_{n,1}^\dagger + U_{n,2}^\dagger \right) |0\rangle \quad \text{and} \quad \frac{1}{\sqrt{2}} \left( U_{n,1}^\dagger - U_{n,2}^\dagger \right) |0\rangle \]

and in linear absorption, starting from the symmetric ground state, only the last one is allowed [1, 19]. Hence in the operator (12), we have $\tilde{\mu}_s \equiv 0$. In the present paper, we treat the case of a stack with inversion center and with one DA pair in the unit cell (as is the case in the anthracene–PMDA crystal). In this situation, mixed excitations, such as FEs and CTEs, must be of the same parity. Thus, FEs which couple linearly with the symmetrical combination of CTEs must also be ‘forbidden’ (i.e. dipole non-allowed).

Let us rewrite the transformed operator of the FE–CTE coupling (3) given in the fourth line of (10) in the following way:
\[ \hat{H}_{1,FC} = \sum_n \left[ \varepsilon' V_n^\dagger (U_{n,1} + U_{n,2}) + \varepsilon'' V_n^\dagger (U_{n,1} - U_{n,2}) + \text{h.c.} \right], \]

where $\varepsilon' = (\varepsilon_{e1} + \varepsilon_{e2})/2$ and $\varepsilon'' = (\varepsilon_{e1} - \varepsilon_{e2})/2$. The FE–CTE mixing is possible when the FEs and CTEs (see equation (14)) have the same parity. Hence, two different cases, I and II, show up.

**Case I.** For gerade FEs with symmetry of the symmetrical CTE combination $(U_{n,1}^\dagger + U_{n,2}^\dagger)|0\rangle$ the coupling constant $\varepsilon''$ vanishes, i.e. $\varepsilon'' \equiv 0$. Their transition dipole moment $\tilde{p}_F$ vanishes due to symmetry reasons, see the analogous arguments below in equation (14). Thus, in the absorption coefficient, a part proportional to $|\mu_s|^2$ will be non-vanishing only. But the symmetry ‘forbidden’ excitations, namely $(U_{n,1}^\dagger + U_{n,2}^\dagger)|0\rangle$ and the gerade FE, will weakly influence the absorption spectrum via their coupling with the antisymmetrical part $(U_{n,1}^\dagger - U_{n,2}^\dagger)|0\rangle$. The coupling between the gerade and the ungerade excitons vanishes at the values of the excitonic quasi-momentum $k$ near the center of the Brillouin zone, i.e. for $k = 0$, but it is nonzero in the other parts of the Brillouin zone. We recall that in the vibronic absorption spectra all values of the quasi-momentum $k$ are seen (but not in the excitonic one), see [8].

**Case II.** For ungerade FEs with symmetry of the antisymmetrical CTE combination $(U_{n,1}^\dagger - U_{n,2}^\dagger)|0\rangle$ the coupling constant $\varepsilon'$ vanishes, i.e. $\varepsilon' \equiv 0$, due to symmetry reasons. Since the symmetry allows the components $\tilde{p}_e$ and $\tilde{\mu}_a$, the absorption is expected to be significant and strongly dependent on the mixing between FE and the ungerade CTE combination. In our further calculations, we treat the cases I and II separately.

### 3. Linear optical susceptibility in the case of mixing Frenkel and CTEs

The linear optical susceptibility $\chi_{ij}$ can be calculated with the help of the following formulae [23, 24]:
\[ \chi_{ij} = \lim_{\varepsilon \to 0} \left\{ -\frac{1}{2}\left[ \Phi_{ij}(\omega + i\varepsilon) + \Phi_{ij}(-\omega + i\varepsilon) \right] \right\} \]

*New Journal of Physics* 10 (2008) 085006 (http://www.njp.org/)
with
\[ \Phi_{ij}(t) = -i \Theta(t) \langle 0| \hat{P}_i(t) \hat{P}_j(0) + \hat{P}_j(t) \hat{P}_i(0)|0 \rangle, \]
where \( V \) is the volume of the crystal and \( \hat{P} \) is the operator (12). Green’s functions (17) have been calculated as an average over only the ground state \( |0\rangle \) taking into account the large values of \( E_F, E_C, \hbar \omega_0 \gg kT \).

For the evaluation of Green’s functions, we need the Fourier components in the frequency and momentum space of functions of the type
\[ G_{n,\sigma\sigma_1}(t) = -i \Theta(t) \langle 0| T_{n,\sigma}(t) \sum_{n_1} T^\dagger_{n_1,\sigma_1}(0)|0 \rangle \]
(18) in which the operators \( T_{n,\sigma} \) are the vibronic operators (9a) and (9b). We calculate Green’s functions (18) using the standard procedure of differentiation of (18) with respect to time and using the Hamiltonian (10). We obtain an infinite chain for the Fourier components of Green’s functions (18) with an increasing number of vibrational quanta, namely with
(a) \( \langle 0| T_{n,\sigma}(t) \rangle \),
(b) \( \langle 0| a_{n_2} T_{n,\sigma}(t) \rangle \),
(c) \( \langle 0| a_{n_1} a_{n_2} T_{n,\sigma}(t) \rangle \),
etc. In the calculations of the chain, we follow the approach proposed in [22] considering the transfer integrals as small in comparison with the energy of the vibrational quantum and of the excitons
\[ |L|, |M_k|, |M_h|, |\varepsilon_e| \ll \hbar \omega_0, E_F, E_C. \]
(19)
In this case of narrow exciton bands, the transfer integrals govern the fine structure of the excitonic and vibronic bands, but they can be neglected in calculations of the following steps of the ladder (a), (b), (c), . . . . For example, if we are interested in one-phonon vibronic spectra, we calculate Green’s functions of type (b) including all terms of the Hamiltonian (10). In these equations, Green’s functions with two phonon operators (of type (c)) enter and we neglect in the calculations for the functions (c), (d), . . . all transfer terms of the Hamiltonian. If we are interested in two-phonon vibronic spectra, then all transfer terms will be included in the equations for Green’s functions of type (c), but they will be neglected in the equations of the neighboring steps of the ladder (b), (d), (e), . . . . For the susceptibility \( \chi_{xy} \) in the two cases I and II (introduced at the end of section 2), we find the expressions given in the following two subsections.

### 3.1. The case of gerade FEs (case I)

In the case of a gerade FE which couples with the gerade (symmetrical) CTE combination \((U_{n_1}^1 + U_{n_2}^1)|0\rangle\), i.e. in the case of \( \varepsilon'' \equiv 0 \) in (15), we obtain
\[ \chi_{xy} = -\frac{1}{\hbar v} \mu_a^{(x)}(G_1 - G_2) \]
(20) in which \( v \) is the volume of the unit cell of the crystal and the function \( G_1 - G_2 \), connected with the antisymmetrical combination in (14), namely with the components \( \langle 0|[U_{n,1}(t) - U_{n,2}(t)] \sum_{n_1} (U_{n_1,1}^1(0) - U_{n_1,2}^1(0))|0 \rangle \), has been calculated for 0-, 1-, and 2-phonon vibronic
spectra using continued fractions. We have

1. for the excitonic region

\[ G_1 - G_2 = \frac{2}{\omega - (E_c - M_e - M_h)/\hbar - \Omega_{0c}(1)}, \]  

where \( \Omega_{0c}(1) \) is expressed through the continued fraction following from the recursion

\[ \Omega_{0c}(n) = \frac{n \omega_{a1}}{\omega - E_c/\hbar - \omega_{oc} - \Omega_{0c}(n+1)} \]  

and

\[ \omega_{oc} = \omega_0 + \Delta\omega, \quad \omega_{a1} = \xi \omega_{oc}. \]

2. For one-phonon vibronic spectra, we get

\[ G_1^{(1)} - G_2^{(1)} = \frac{2}{\omega - (E_c - M_e - M_h)/\hbar - (\omega_{a1}^{2(1)}/1 - M_3^{(1)})} \]  

with

\[ M/\hbar = \Delta\omega + \Omega_{0c}(2) - \Omega_{ic}(1) \]

in which \( \Omega_{ic}(n) \) can be represented by the recursion

\[ \Omega_{ic}(n) = \frac{n \omega_{a1}}{\omega - E_c/\hbar - (n+1)\omega_0 - n\Delta\omega - \Omega_{ic}(n+1)}. \]  

The definitions of \( \gamma_3^{(i)}, i = 1, 2 \) and some other functions introduced below are given in the appendix.

3. For two-phonon vibronic spectra, we have

\[ G_1^{(2)} - G_2^{(2)} = \frac{2}{\omega - (E_c - M_e - M_h)/\hbar - (\omega_{a1}^{2(2)}/1 - M_3^{(2)})} \]  

with

\[ F = \hbar[2\Delta\omega + \Omega_{0c}(3) - \Omega_{2c}(1)]. \]

where

\[ \Omega_{2c}(n) = \frac{n \omega_{a1}}{\omega - E_c/\hbar - (n+2)\omega_0 - n\Delta\omega - \Omega_{2c}(n+1)}. \]

Furthermore, we still introduce quantities needed in deriving an additional contribution to the susceptibility stemming from the coupling between the FE and the vibrations. They are

(a) the continued fractions \( \Omega_{0F}(n), \Omega_{1F}(n) \) and \( \Omega_{2F}(n) \) following formulae (22), (25), and (28) with the replacements

\[ \omega_{0c} \rightarrow \omega_1 = \omega_0 + \Delta\omega_F, \quad \omega_{a1} \rightarrow \omega_a = \omega_1 \xi_F, \quad E_c \rightarrow E_F, \quad \xi \rightarrow \xi_F, \quad \Delta\omega \rightarrow \Delta\omega_F \]

and

(b) the quantities \( M_F \) and \( F_F \) analogous to \( M \) and \( F \) (see formulae (24) and (27) with the replacements (29)).

In case I (gerade FEs, gerade symmetrical CTE combination) the coupling constant \( \varepsilon' \) enters only via the expression for the functions \( \gamma_3^{(i)}, i = 1, 2 \) (see equation (15) with \( \varepsilon'' = 0 \)) and the mixing of FEs and CTEs does not influence the absorption spectra strongly.
3.2. The case of ungerade FEs (case II)

In the case of an ungerade FE which couples with the ungerade (antisymmetrical) combination \((U_{n1}^T - U_{n2}^T)|0\rangle\), i.e. \(\varepsilon' \equiv 0\) in (15), but \(\varepsilon'' \neq 0\) we have

\[
\chi_{xy} = -\frac{1}{v} \frac{1}{\alpha_{11}\alpha_{22} - 2\alpha_{12}^2} \left\{ p_F^{(x)} p_F^{(y)} \alpha_{22} + 2\mu_a^{(x)} \mu_a^{(y)} \alpha_{11} + 2\alpha_{12} \left[ \mu_a^{(x)} p_F^{(y)} + \mu_a^{(y)} p_F^{(x)} \right] \right\}. 
\]

(30)

We orient the \(x\)-axis along the vector \(\vec{p}_F\) and introduce the angle \(\phi\) between the vectors \(\vec{p}_F\) and \(\vec{\mu}_a\) (in the crystal anthracene–PMDA the transition dipole moment \(\vec{\mu}_a\) is oriented along the stack axis) as well as the ratio \(a = |\mu_a/p_F|\). Then the linear optical susceptibility can be represented as

\[
\chi_{xx} = -\frac{p_F^2}{v} \frac{1}{\alpha_{11}\alpha_{22} - 2\alpha_{12}^2} \left[ \alpha_{22} + 4a\alpha_{12} \cos \phi + 2a^2\alpha_{11} \cos^2 \phi \right]. 
\]

(31)

The functions \(\alpha_{11}, \alpha_{22}\) and \(\alpha_{12}\) in expressions (30) and (31) also in case II have been calculated for the excitonic, one-phonon vibronics and two-phonon vibronics regions. They are represented in the following two subsections for the cases II.1 and II.2 of the vibrational mode on the acceptor (vibrational mode A) and of the vibrational mode on the donor (vibrational mode D), respectively.

3.2.1. Vibrational mode on the acceptor (case II.1). In the case of vibronic spectra with the vibrational mode on the acceptor molecule (the FE is the collective electronic excitation of the donor and thus \(\xi_F = 0\), \(\Delta \omega_F = 0\), \(\omega_a = 0\)), we have

\[
\alpha_{11} = \hbar \omega - (E_F + 2L), \tag{32a}
\]

\[
\alpha_{12} = \varepsilon'', \tag{32b}
\]

whereas \(\alpha_{22}\) is expressed by different formulae, namely: for the excitonic region

\[
\alpha_{22} = \hbar(\omega - \Omega_0c(1)) - (E_c - M_e - M_h) \tag{32c}
\]

for the one-phonon vibronic spectrum

\[
\alpha_{22} = \hbar \omega - (E_c - M_e - M_h) - \frac{\hbar\omega_a c_{\gamma(1)}}{1 - M\gamma(1)} \tag{32d}
\]

and for the two-phonon vibronic spectra

\[
\alpha_{22} = \hbar \omega - (E_c - M_e - M_h) - \omega - \frac{\hbar\omega_a^2}{\hbar - \omega_a c_{\gamma(1)}} - 2\varepsilon''/\omega - (\hbar\omega - E_F - \hbar\omega_a c_{\gamma(2)}/(1 - F\gamma(2)). \tag{32e}
\]

3.2.2. Vibrational mode on the donor (case II.2). In the case of vibronic spectra with the vibrational mode at the donor molecule both the FE and the CTE are interacting directly with the vibrations and we get

1. for the excitonic region

\[
\alpha_{11} = \hbar \omega - (E_F + 2L) - \hbar\Omega_{0F}(1), \tag{33a}
\]

\[
\alpha_{12} = \varepsilon'', \tag{33b}
\]

\[
\alpha_{22} = \hbar(\omega - \Omega_0c(1)) - (E_c - M_e - M_h), \tag{33c}
\]
2. for the one-phonon vibronic spectra

\[
\alpha_{11}^{(1)} = \hbar \left[ \omega - \frac{(E_F + 2L) + \omega_0^2}{D_{11}} \left( \beta^{(1)} + MT^{(1)} \right) \right], \\
\alpha_{12}^{(1)} = \varepsilon'' \left[ 1 + \frac{\hbar^2 \omega_0 \omega_a}{D_{11}} \alpha \right], \\
\alpha_{22}^{(1)} = \hbar \left[ \omega - \frac{(E_c - M_c - M_h) + \omega_0^2}{D_{11}} \left( \gamma^{(1)} + MF T^{(1)} \right) \right],
\]

\[ D_{11} = 1 - M_F \beta^{(1)} - M \gamma^{(1)} - M M_F T^{(1)}, \tag{35} \]

and

3. for the two-phonon vibronic spectra

\[
\alpha_{11}^{(2)} = \hbar \omega - E_F - 2L - \frac{\hbar^2 \omega_0^2}{D_{12}} \left( \hbar \omega - E_c - \omega_0 - \frac{2 \omega_0^2}{D_4} \lambda_1 \right), \\
\alpha_{12}^{(2)} = \varepsilon'' \left[ 1 + \frac{\hbar^2 \omega_0 \omega_a}{D_{12}} \left( 1 + \frac{2}{D_4} \omega_0 \omega_a \alpha \right) \right], \\
\alpha_{22}^{(2)} = \hbar \omega - (E_c - M_c - M_h) - \frac{\hbar^2 \omega_a^2}{D_{12}} \left( \hbar \omega - E_F - \omega_0 - \frac{2 \omega_0^2}{D_4} \lambda_F \right),
\]

in which

\[ D_4 = 1 - F_F \beta^{(2)} - F \gamma^{(2)} - FF_T T^{(2)}, \tag{37} \]

\[ D_{12} = \left( \hbar \omega - E_F - \omega_0 - \frac{2 \omega_0^2}{D_4} \lambda_F \right) \left( \hbar \omega - E_c - \omega_0 - \frac{2 \omega_0^2}{D_4} \lambda_1 \right) - 2 \varepsilon'' \left( 1 + \frac{2 \alpha^{(2)} \omega_0 \omega_a}{D_4} \right)^2. \tag{38} \]

In these expressions, we have

\[ \lambda_1 = \gamma^{(2)} + F_T T^{(2)}, \quad \lambda_F = \beta^{(2)} + F T^{(2)}, \quad T^{(i)} = 2 \varepsilon'' \alpha^{(i)2} - \beta^{(i)} \gamma^{(i)}, \quad i = 1, 2. \tag{39} \]

Parameters which are not defined here are presented in the appendix.

4. Numerical calculations of the absorption coefficient

4.1. Parameter values for the numerical evaluation

We calculate the linear absorption coefficients via the imaginary part of equation (20), i.e. via the imaginary part of Green’s functions (21), (23) and (26) for gerade excitons and as the imaginary part of the expression (30) for ungerade excitons. We provide the frequency \( \omega \) with an imaginary addend \( i \delta \) which is related to the final width of the excitonic and vibrational states and we put \( \delta = 2 \, \text{cm}^{-1} \). This value was obtained from the experimental studies of the well-known CT-crystal anthracene–PMDA (see [1, 16, 18, 19, 21]). According to these references, the lowest excited electronic states have presumably a CTE nature and the levels of the FEs are far above the CTE levels [18, 20]. Thus, FE–CTE mixing is not treated in the interpretation.
of the linear absorption in this DA crystal. This mixing was observed and studied, however, in one-component CT-systems, like the crystals of MePTCDI and PTCDA. That is why in our numerical calculations we use partly the excitonic and vibrational parameters of the anthracene–PMDA crystal, of the one-component PTCDA crystal and another rather hypothetical set of parameters and add, if necessary, the data for a possible mixing with FEs.

The following two intramolecular vibrations are used in our simulations of the linear absorption:

(i) We use the vibration of the acceptor molecule PMDA in the anthracene–PMDA crystal, introduced by the notation A, of frequency $\omega_0 = 634 \text{ cm}^{-1}$ ([16, 18, 19], see also [25]). The exciton–phonon coupling in the ion of PMDA is not well described but by using data of the electroreflectance spectra of [19], we estimate the linear coupling constant as $\xi^2 = 0.5$ and combine it with two values of the shift of the vibrational frequency due to the quadratic exciton–phonon interaction in the excited ion: $\Delta \omega = 0$ and $-20 \text{ cm}^{-1}$.

(ii) We use the vibration of the ionized donor molecule of anthracene (and other polyacenes). We introduced this vibration by the notation D, its frequency is $\omega_0 = 1400 \text{ cm}^{-1}$, and the frequency shifts in the neutral excited molecule and in the ion of anthracene are $\Delta \omega_D = \Delta \omega = 0$. For the value of the linear CTE–phonon coupling, we use $\xi^2 = 1.05$ proposed in [7] and based on an estimation from earlier works. For the constant of the linear FE–phonon coupling $\xi_F$, the following two values have been used in the calculations:

$$\xi_F^2 = \xi^2 = 1.05 \quad \text{and} \quad \xi_F^2 = 0.9.$$  

(The value of $\xi_F^2 = 0.9$ for the FE on anthracene was assumed in [23, 26].)

The same vibrational frequency is taken for the hypothetical donor of the PTCDA crystal [10]–[12]. Our calculations have been performed using the data of the FE–CTE mixing in this crystal and for the same value of $\xi^2 = 1.05$ of the linear CTE–phonon coupling (as well as for the other values).

Taking into account the transfer of the electron and hole of the CTE and of the FE to the second neighboring molecules (since the first neighbors in DA-systems are of different types), we put the value of the transfer integrals $M_e = M_h$ to $10$–$20 \text{ cm}^{-1}$, and of $L$ to $25$–$40 \text{ cm}^{-1}$. The mixing between FE and CTE is supposed to be the result of the transfer of one electron from the excited neutral donor to the neighboring acceptor. Thus the mixing constants $\varepsilon'$ and $\varepsilon''$ are assumed to have higher values than the transfer integrals $M_e$, $M_h$, and $L$, and are taken as (see [11])

$$\varepsilon', \varepsilon'' = 100, 200, \pm 350, \pm 500 \text{ cm}^{-1}.$$  

The values of the excitation energy $E_c$ of the CTE has been assumed as

$$E_c = 18 632 \text{ cm}^{-1},$$  

which gives in the calculations in [25] the CTE line at the position 18 320 cm$^{-1}$ as observed in the crystal anthracene–PMDA [1, 16, 18, 19]. (In those calculations the mixing with the FE is neglected.) In our calculations we use the values

$$E_F = 19 000 \text{ cm}^{-1} \quad \text{and} \quad 19 500 \text{ cm}^{-1}.$$
Table 1. Exciton parameters in the calculations of case I, excitation energies and transfer integrals in cm$^{-1}$.

| Excitation energy $E_c$ | Transfer integrals $E_F$, $M_e = M_h$, $L$, $\epsilon'$ |
|-------------------------|----------------------------------------------------------|
| 18 632                  | 19 500, 20, 40, 0; 200; 500                              |

The values $E_c = 17 330$ cm$^{-1}$ and $E_F = 17 890$ cm$^{-1}$ obtained in [11, 27] for the FE-CTE mixing in the one-component CT-crystal of PTCDA have also been used in two of our hypothetical cases in DA-systems. The value of $E_F - E_c$ in other cases is of the same order of magnitude.

In the case of the mixing with ungerade FE two transition dipole vectors, $\vec{p}_F$ and $\vec{\mu}_a$, contribute to the linear optical susceptibility (29). We put the ratio $a = |\mu_a/p_F| = 0.15$ (see estimations in [11]) and the value of the angle between them $\phi = 30^\circ$ (which has no essential impact on the susceptibility (30)).

4.2. Numerical calculations of the absorption coefficient in the case I of mixing gerade CT and F excitons

As stated in the last paragraph of section 3.1, the FE–CTE mixing in the case of the gerade excitons (case I) does not influence the vibronic absorption spectra strongly. The calculations based on the formulae (20), (21), (23) and (26) and using the parameters of tables 1 and 2 confirm this conclusion. The calculated vibronic spectra with vibration $A$ (at the acceptor) fully coincide with the calculations in [25], where the case of pure CTEs has been investigated. These calculations do not exhibit any impact of FE–CTE mixing on the vibronic spectra. We, therefore, do not show these spectra and display in figures 1 and 2 the excitonic and vibronic spectra with vibration D only. The linear absorption in the region of the CTE and its four satellites which create a vibronic progression is shown in figure 1 on a logarithmic scale. The absorption curves correspond to the ungerade CTE combination (see case I in section 2) governed by Green’s function $G_1 - G_2$ and they are almost identical for various values of the mixing constant $\epsilon'$. The only observable result of the mixing of gerade CTEs and FEs is shown in figure 2 in which the one-phonon vibronic peak splits at $\epsilon' = 200$ cm$^{-1}$. The absorption in this spectral region corresponds to many-particle (unbound) states of the CTE and the quantum of intramolecular vibration which are excited on different molecules. The lineshape which is non-Lorentzian and the spectral width of approximately 20 cm$^{-1}$ confirm the manifestation of a many-particle continuum. Our calculations in [25] give as tentative width of the many-particle continuum $2(M_e + M_h)\exp(-\xi^2)$. We repeat that the splitting inside the continuum is connected with the non-central part $k \neq 0$ of the Brillouin zone. The splitting could be measured more easily in the case of figure 2(b) in which the two maxima of the doublet have equal intensities. We note that increasing the mixing by using $\epsilon' = 500$ cm$^{-1}$ results in a vanishing of the splitting despite of the slight deformation of the red absorption curve in figure 2(a) near 19 940 cm$^{-1}$.
Table 2. Vibrational and vibronic parameters in the model of FE–CTE mixing.

| Vibration | $\omega_0$ in the non-excited molecule (cm$^{-1}$) | Linear coupling constants | Frequency shift |
|-----------|-------------------------------------------------|----------------------------|-----------------|
|           |                                                | FE–phonon $\xi^2$ | CTE–phonon $\xi^2$ | FE $\Delta\omega$ | Ion $\Delta\omega$ |
| A         | 634                                             | 0                          | 0.5             | 0               | 0; –20             |
| D         | 1400                                            | 1.05; 0.9                  | 1.05; 0.53      | 0               | 0                 |

Figure 1. Influence of the FE–CTE mixing on the excitonic and vibronic spectra in the case I of gerade FEs with vibration D on the donor and with $\xi^2_F = 1.05$, $\xi^2 = 0.9$ for various values of the mixing parameter $\varepsilon'$, calculated using (23), logarithmic scale.

4.3. Numerical calculations of the absorption coefficient in the case II of mixing of ungerade CT and F excitons

In the case II, the calculations of the linear absorption are based on formula (31) and we have to consider the following two situations:

II.1 The case of vibronics with vibration A: formulae (32a)–(32e).

II.2 The case of vibronics with vibration D: formulae (33a)–(39).

The exciton parameters for the calculated spectra are listed in table 3. For the vibrational parameters, we again use the values of table 2.

4.3.1. Vibrational mode A on the acceptor (case II.1). In the case of vibronics with vibration on the acceptor molecule the vibronic progression originates from the energy level $E_c$ of the CTE only ($E_c \approx 18\ 300$ cm$^{-1}$ in figure 3(a)) and not from the level $E_F \approx 19\ 500$ cm$^{-1}$. In the
Figure 2. Influence of the FE–CTE mixing on the excitonic and vibronic spectra in the one-phonon vibronic range in the case I of gerade FEs with vibration D on the donor, with $\xi^2 = 1.05$, $\xi_F^2 = 0.9$ (a) and $\xi_F^2 = 1.05$ (b) for various values of the mixing parameter $\epsilon'$, calculated using (23). (a) $\xi_F^2 = 0.9$. (b) $\xi_F^2 = 1.05$.

Table 3. Exciton parameters in the calculations of case II in units of cm$^{-1}$.

| Case     | Excitation energy | Transfer integrals |
|----------|-------------------|--------------------|
|          | $E_c$             | $E_F$              | $M_h = M_h$ | $L$   | $\epsilon''$ |
| II.1.1   | 18 632            | 19 500             | 10         | 25    | 0; 100; 200   |
| II.1.2   | 18 632            | 19 000             | 20         | 40    | 0; 200; ±350  |
| II.2.1   | 18 632            | 19 500             | 10         | 25    | 0; 100; 200; 500 |
| II.2.2   | 18 632            | 19 000             | 20         | 40    | 0; 200; 500   |
| II.2.3   | 17 330            | 17 890             | 15         | 40; 150 | 0; ±350; ±500 |

absence of mixing, i.e. $\epsilon'' = 0$, a strong absorption maximum at $E_F$ and very weak maxima at $E_c + n\hbar\omega_0$ ($n = 0, 1, 2, \ldots$) can be seen (see figure 3(a) with logarithmic ordinate scale for $\epsilon'' = 0$). The weak CTE absorption is related to the small transition dipole moment of the CTE, $a^2 \approx 0.02$ in (31) for $\epsilon'' = 0$. The FE–CTE mixing shifts the vibronic lines and redistributes the absorption intensities. As can be seen in figure 3(a) for $\epsilon'' = 200$ cm$^{-1}$ the biggest enhancement caused by the mixing will be observed for the vibronic satellite which is closest to the FE-level. In figure 3(a), this is the two-phonon vibronics near 19 500 cm$^{-1}$ which borrows intensity from the FE. At the same time, the CTE absorption line near 18 300 cm$^{-1}$ and the first vibronic replica near 18 900 cm$^{-1}$ would be practically invisible in absorption. An assumed frequency shift $\Delta\omega$ influences the position of the vibronics only (compare the green and red curves in figure 3(a)). It is interesting to note that a very weak signal can appear at about 20 300 cm$^{-1}$, which is shifted from the strong red maximum at $\hbar\omega_0$ and corresponds to the excitation of the FE on the donor molecule and of one vibrational quantum on the acceptor molecule. The FE–CTE mixing creates a weak spectral doublet in the region of 20 000–20 500 cm$^{-1}$. Figure 3(b) illustrates some details of the redistribution of the absorption near the $E_F$-line for a smaller value of the coupling parameter, i.e. for $\epsilon'' = 100$ cm$^{-1}$.

Figure 4 was calculated for case II.1.2 of closer resonant conditions since the difference $E_F - E_c = 368$ cm$^{-1}$ is smaller than in the previous case II.1.1 (with a difference of 868 cm$^{-1}$).
Figure 3. Influence of the FE–CTE mixing on the excitonic and vibronic spectra in the case II.1.1 (see table 3) of ungerade excitons with vibration A on the acceptor for $\xi^2 = 0.5$, various values of the quadratic exciton–phonon coupling $\Delta \omega$ and of the mixing parameter $\varepsilon''$. (a) $\varepsilon'' = 0$ and $200 \text{ cm}^{-1}$, logarithmic scale. (b) $\varepsilon'' = 0$ and $100 \text{ cm}^{-1}$.

Figure 4. Influence of the FE–CTE mixing on the excitonic and vibronic spectra in the case II.1.2 of table 3 (closer to resonance) of ungerade excitons with vibration A on the acceptor for $\xi^2 = 0.5$, various values of the quadratic exciton–phonon coupling $\Delta \omega$ and of the mixing parameter $\varepsilon''$, logarithmic scale.

The FE–CTE mixing now enhances two vibronics with one and two phonons which borrow intensity from the FE by one to two orders of magnitude.

Figure 5 concerns the same case II.1.2, but for larger values of the mixing constant $\varepsilon'' = \pm 350 \text{ cm}^{-1}$. The stronger mixing shifts the excitonic levels far from the non-mixed FE
Figure 5. Influence of the FE–CTE mixing on the excitonic and vibronic spectra in the case II.1.2 of table 3 (closer to resonance) of ungerade excitons with vibration A on the acceptor for $\xi_F^2 = 0.5$, various values of the quadratic exciton–phonon coupling $\Delta \omega$ and for the mixing parameters $\varepsilon'' = 0$ cm$^{-1}$, $\pm 350$ cm$^{-1}$, logarithmic scale.

level near 19 050 cm$^{-1}$ (blue maximum) and can enhance the CTE absorption maximum and several vibronic satellites of the CTE. At the same time, the change of the sign of $\varepsilon''$ does not shift the positions of the excitonic and vibronic levels, since the denominator of (31) is an even function of $\varepsilon''$. However, this change can induce a big redistribution of the absorption (compare the red and the green curves in figure 5).

4.3.2. Vibrational mode D on the donor (case II.2). The case of vibronics with the vibrational quanta of the donor vibration is more complicated because the vibration is coupled to the FE and to the CTE. The simulations of the absorption spectra confirm their sensitivity on the values of the mixing constant $\varepsilon''$ and on the constants of the linear exciton–phonon coupling.

Figure 6 treats the case II.2.1 (see table 3 and vibration D in table 2, the value of the coupling constant $\xi_F$ is taken as $\xi_F^2 = 0.9$). In general, the absorption spectra (see figure 6(a)) contain the excitonic regions of the CTE line near 17 100 cm$^{-1}$ and of the intense FE line near 18 300 cm$^{-1}$ and also the region of the vibronic satellites, i.e. one-phonon vibronic spectra (see figure 6(b)), two-phonon vibronics (see figure 6(c)), three-phonon vibronics in the region 21 200–22 600 cm$^{-1}$ and less intensive vibronics above those wave number regions. The two vibronic progressions start, therefore, with the CTE line and the FE line, respectively. The positions of the lines of the second progression are less sensitive to the mixing constant $\varepsilon''$ than the lines of the first progression which start near 17 000 cm$^{-1}$ (then the first vibronics are at 18 600 cm$^{-1}$, etc). The positions of the absorption lines of the first progression are shifted with increasing $\varepsilon''$ to higher frequencies, especially in the case of figures 6(b) and (c) and
Figure 6. Influence of the FE–CTE mixing on the excitonic and vibronic spectra in the case II.2.1 of ungerade excitons with vibration D on the donor for $\xi_2 = 1.05$, $\xi_2 \xi = 0.9$ and for various values of the mixing parameter $\varepsilon''$. (a) Excitonic and vibronic range. Absorption in the excitonic region (17 000–18 500 cm$^{-1}$) and in the vibronic spectra with up to 4 satellites are calculated using (30) and (33a)–(33c). (b) Range of one-phonon vibronic absorption spectra. One-phonon vibronic spectra are calculated using (30), (34a)–(34c) and (35). (c) Range of two-phonon absorption spectra. Two-phonon vibronic spectra are calculated using (30), (36a)–(39).
borrow intensity from the closest terms of the second progression starting with the FE. The redistribution of the intensity increases with increasing $\varepsilon''$. The shape of the absorption lines is Lorentzian and they correspond to bound exciton–phonon states.

The absorption spectra in figure 7 are calculated with the data of case II.2.2 and the data of vibration $D$ with $\xi^2_F = \xi^2 = 1.05$. The dominant structure is the vibronic progression connected with the FE (strong blue, red and green curves) which begins with the absorption line of the FE near 18 000 cm$^{-1}$). In this case, the CTE absorption line (red curve around 17 000 cm$^{-1}$) will only be enhanced by the FE–CTE mixing, whereas its vibronic satellites near 18 500, 20 000 and 21 500 cm$^{-1}$ show negligible absorption. Similar results have been obtained for the same excitonic and vibrational parameters, but for $\xi^2_F = 0.9$.

The absorption spectra of case II.2.3 are presented in figures 8 and 9, calculated for $L = 40$ cm$^{-1}$, $\varepsilon'' = \pm 350$ cm$^{-1}$ and $L = 150$ cm$^{-1}$, $\varepsilon'' = \pm 500$ cm$^{-1}$, respectively. The relatively small difference $E_F - E_c$ and the larger values of the mixing constant $\varepsilon''$, which are close to the mixing constants observed in the one-component crystal PTCDA [27] do not allow to assign the absorption maxima as stemming mainly from the FE or the CTE. The excitonic as well as the vibronic maxima show up in pairs and the excitonic and vibronic pairs are well separated from each other. The redistribution of the absorption intensity caused by the change of sign of the mixing parameter $\varepsilon''$ can be seen in more detail in figures 8(b) and (c) and in figure 9. We emphasize the complicated structure of the upper partner of the vibronic pair. This structure, better expressed in two-phonon spectra, see figures 8(c) and 9(b), corresponds to the unbound, many-particle exciton–phonon states. The larger value for the transfer parameter $L$ of the FE (figure 9 with $L = 150$ cm$^{-1}$ compared to figure 8 with $L = 40$ cm$^{-1}$) changes neither the structure of the vibronic spectra nor the width of the one-phonon many-particle band near 18 200 cm$^{-1}$. However, the two-phonon band near 19 600 cm$^{-1}$ is broadened (compare figures 8(c) and 9(b)).
Figure 7. Influence of the FE–CTE mixing on the excitonic and vibronic spectra in the case II.2.2 of ungerade excitons with vibration D on the donor for $\xi^2 = \xi_F^2 = 1.05$ in the excitonic and vibronic range, logarithmic scale.

The values of the excitonic parameters of cases II.2.2 and II.2.3 are similar and the more essential difference consists in the values of the linear CTE–phonon constant $\xi$, which in the case II.2.2 (figure 7) is equal to $\xi_F$, whereas in the case II.2.3 (figures 8(a)–(c) and 9) its value is $\xi^2 = 0.53 \approx \xi_F^2/2$. Obviously, in the case $\xi = \xi_F$ the vibronic replicas of the CTE are suppressed in figure 7, while in the case $\xi = \xi_F/\sqrt{2}$, the absorption intensities of the two components of the vibronic pair are comparable. The same suppression $\xi = \xi_F$ has been obtained in the calculations in some of our previous papers on a similar topic [4, 5].

The last example treats the molecule of PTCDA as a possible component in a two-component DA-system\(^4\). The data which we use in the calculations are the following (all parameters in cm\(^{-1}\)):

\[
\begin{align*}
E_c &= 17\,330; & E_F &= 17\,890; & M_e = M_h &= 15; \\
L &= 100; & \varepsilon'' &= 0, \pm 350; \\
\omega_0 &= 1400; & \Delta\omega &= \Delta\omega_F = 0; \\
\xi_F &= 0.82, \quad [10]; & \xi &= \xi_F/\sqrt{2}, \quad [10, 11].
\end{align*}
\]

The structure of the absorption spectra in figure 10(a) is similar to that of figure 8(a). The excitons (near 17 000 cm\(^{-1}\)) and the vibronic satellites form pairs of absorption maxima whose intensity depends on the value and the sign of $\varepsilon''$. The one-phonon vibronics in the case of no FE–CTE mixing creates two many-particle bands (blue line in figure 10(b)): the lower and

\(^4\) We are grateful to one of the referees for the remark that the molecule PTCDA is more promising as an electron acceptor. Our formulae, however, also hold for the full exchange of the parameters for donors and acceptors.

New Journal of Physics 10 (2008) 085006 (http://www.njp.org/)

19
Figure 8. Influence of the FE-CTE mixing on the excitonic and vibronic spectra in the case II.2.3 of ungerade excitons with vibration D on the donor for $\xi^2 = 0.53$, $\xi_F^2 = 1.05$, $L = 40 \text{ cm}^{-1}$ for various values of $\varepsilon''$ in the excitonic and vibronic range. (a) Excitonic region (16 000–17 000 cm$^{-1}$), one-phonon vibronic spectra (near 18 000 cm$^{-1}$), two-phonon vibronics (19 000–20 000 cm$^{-1}$) and three-, four-phonon vibronics (higher wave numbers) for $\varepsilon'' = +350 \text{ cm}^{-1}$ (upper part) and $\varepsilon'' = -350 \text{ cm}^{-1}$ (lower part), logarithmic scale. (b) One-phonon vibronic spectra calculated using (30), (34$a$)–(34$c$) and (35). (c) Two-phonon vibronic spectra calculated using (30), (36$a$)–(39).
Figure 8. Continued.

Figure 9. Influence of the FE–CTE mixing on the excitonic and vibronic spectra in the case II.2.3 of ungerade excitons with vibration D on the donor for \( \xi^2 = 0.53, \xi^2_F = 1.05, L = 150 \text{ cm}^{-1} \) and for various values of \( \varepsilon'' \) in the one- and two-phonon vibronic ranges. (a) One-phonon vibronic spectra. (b) Two-phonon vibronic spectra.

weaker continuum corresponds to the one-phonon vibronic of the CTE, whereas the stronger (blue) continuum is the vibronic spectrum of the unbound FE and vibrational quantum. The width of this continuum is approximately \([22, 25] 2L \exp(-\xi_f^2)\). The linear FE–phonon coupling \( \xi_f = 0.82 \) is not strong enough to bind the FE and the vibrational quantum. But the additional FE–CTE mixing shifts the doublet of the absorption maxima outside these bands and thus their line shape is Lorentzian. The structure of the splitting between the maxima of the two-phonon
Figure 10. Influence of the FE–CTE mixing on the excitonic and vibronic spectra in the case II.2.3 of ungerade excitons (see table 3, but with \( L = 100 \text{ cm}^{-1} \)) with vibration D on the donor for \( \xi = \xi_\text{F}/\sqrt{2} \), \( \xi_\text{F} = 0.82 \) and for various values of \( \varepsilon'' \). (a) Absorption (logarithmic scale) in the excitonic and vibronic region for \( \varepsilon'' = +350 \text{ cm}^{-1} \) (upper part) and \( \varepsilon'' = -350 \text{ cm}^{-1} \) (lower part). (b) One-phonon vibronic spectra.

vibronic spectra (in the region of 19 500–20 000 cm\(^{-1}\)) are similar to those in the one-phonon spectra.

5. Conclusions

In this paper, we studied a model case for the mixing between Frenkel excitons (FEs) and charge-transfer excitons (CTEs) in a two-component donor-acceptor (DA) charge-transfer (CT)-system. Our theoretical model contains two types of excitons (FEs and CTEs) which, on the one hand, are coupled to each other and, on the other hand, are also coupled to one vibrational mode of the acceptor (A) or of the donor (D) molecule. Due to lack of experimental realization up to now, we construct the parameter set for our numerical calculations using the excitonic and vibrational parameters of real DA-systems and combine them with some data on FE–CTE mixing in one-component CT-systems (like the crystal of PTCDA). Our main attention is directed to centrosymmetrical CT-media in which the mixing FEs and CTEs must have the same parity. Thus, two different cases have been considered: mixing of gerade excitons (case I) and mixing of ungerade excitons (case II). As we consider the case in which the FE is the electronic excitation of the D molecule (the case of the FE being the electronic excitation of the A molecule is analogous), the vibronics with the vibration of the A molecule and of the D molecule need a somewhat different treatment.

The main results from the modeling of FE–CTE mixing can be qualitatively expressed as follows:

(i) As usual, the FE–CTE mixing causes a shift and a splitting of the excitonic and vibronic spectra:

(a) the FE–CTE mixing redistributes the absorption intensity from the FEs to CTEs and their vibronic satellites;
(b) the mixing generates spectral doublets in the excitonic and the vibronic spectra (figures 2–5, 7–9);
(c) the mixing can change the shape of the absorption lines causing the binding of excitons and vibrations and the appearance of the Lorentzian maxima instead of the non-Lorentzian continua (figures 8–10);
(d) in the case of strong mixing, it is practically impossible to distinguish the origin (FE or CTE) of the excitonic and vibronic lines.

(ii) In the case of the vibration at the acceptor (A) only one vibronic progression is manifest and its spectral lines which are closest to the lines of the FE would be most enhanced by the mixing.

(iii) In the case of vibration at the donor (D) two vibronic progressions which start from the CTE and from the FE level, respectively, would be manifest. Their absorption intensities could be of comparable magnitude, but sometimes the terms of one progression can be suppressed, see figure 7, especially at $\xi_F = \xi$. The sign of the mixing parameter $\varepsilon''$ is very important for the distribution of the intensity between the terms of the two vibronic progressions.

(iv) The FE–CTE mixing acts as another coupling factor for binding the excitons and phonons. Thus, in most cases, the lineshape of the simulated absorption lines is Lorentzian which corresponds to the bound exciton–phonon states. The lineshape of a small number of the simulated vibronic lines is non-Lorentzian. They are wider as compared to the width $\delta$ of the excitonic levels which we used in the calculations. These spectral lines correspond to unbound (many-particle) exciton–phonon states.

(v) We now pay attention to the case I in which the mixing of gerade FEs and CTEs can influence the linear absorption of ungerade CTEs, described by Green’s function $G_1 - G_2$. In centrosymmetric media, this effect can be non-vanishing only in the non-central part $k \neq 0$ of the Brillouin zone which can be active in the vibronic spectra (but not in the spectra of pure excitons). This can produce a splitting of some absorption maxima which creates spectral doublets inside many-particle bands.

(vi) In the case of large transfer parameters $\varepsilon''$, compared to the spacing $|E_F - E_c|$ between the levels of the mixing excitons several spectra doublets of comparable absorption show up in a pronounced manner in the vibronic region.

For future studies, on the one hand it will be very stimulating to find a real two-component (DA) CT-system in which CTE and FE-levels are close to each other. This could make the model of mixing more realistic with more precise data for the mixing constants and for the other parameters. On the other hand, this can allow to describe and predict the linear and nonlinear processes in CT-systems in which FEs and CTEs are active. Another direction of future studies may be to analyze both theoretically and experimentally the case of a combination band in which the mixed FE and CTE can create vibronics with the combination of one D and one A vibration.

Acknowledgments

The support of this work by the Deutsche Forschungsgemeinschaft in the framework of the SFB 569 is gratefully acknowledged. I J Lalov thanks the University of Ulm for its hospitality, the
Case II: 

\( R_i = \sqrt{b_i^2 - c_i^2}, \quad t_{1,2}^{(i)} = b_i \pm R_i, \quad i = 1, 2, \) 

\[ \rho^{(i)} = \frac{1}{8LMcMhR_i} \left[ \sigma(t_2^{(i)}) - \sigma(t_1^{(i)}) \right], \quad (A.6) \]

\[ \rho_1^{(i)} = \frac{1}{8LMcMhR_i} \left[ t_2^{(i)} \sigma(t_2^{(i)}) - t_1^{(i)} \sigma(t_1^{(i)}) \right], \quad (A.7) \]

\[ \rho_2^{(i)} = \frac{1}{8LMcMhR_i} \left[ 2 + \frac{1}{R_i} \left[ (t_2^{(i)})^2 \sigma(t_2^{(i)}) - (t_1^{(i)})^2 \sigma(t_1^{(i)}) \right] \right], \quad (A.8) \]

\[ \sigma(t) = \begin{cases} -1/\sqrt{t^2 - 1}, & \text{if } |t + \sqrt{t^2 - 1}| < 1, \\ +1/\sqrt{t^2 - 1}, & \text{if } |t + \sqrt{t^2 - 1}| > 1. \end{cases} \quad (A.9) \]

Case I: \((\varepsilon' \neq 0, \varepsilon'' = 0)\)

\[ \gamma_3' = \left[ \hbar \omega_{\text{c}} (\hbar \omega_{\text{c}} - M_c) - 2\varepsilon'' \right] \rho^{(i)} - \left[ 2L(\hbar \omega_{\text{c}} - M_c) + \hbar \omega_{\text{c}} M_h \right] \rho_1^{(i)} + 2LM_h \rho_2^{(i)}, \quad (A.10) \]

\[ b'_i = \frac{1}{4LM_cM_h} \left[ \hbar \omega_{\text{c}} M_c + L \left( \hbar^2 \omega_{\text{c}}^2 - M_c^2 - M_h^2 \right) + \varepsilon'' M_h \right], \quad (A.11) \]

\[ c'_i = \frac{1}{4LM_cM_h} \left[ \hbar \omega_{\text{c}} \left( \hbar^2 \omega_{\text{c}}^2 - M_c^2 - M_h^2 \right) - 2\varepsilon'' (\hbar \omega_{\text{c}} + M_c) \right], \quad (A.12) \]

Case II: \((\varepsilon' = 0, \varepsilon'' \neq 0)\)

\[ \omega^{(i)} = (\hbar \omega_{\text{c}} - M_c) \rho^{(i)} - M_h \rho_1^{(i)}, \quad (A.13) \]

\[ \beta^{(i)} = \left[ (\hbar \omega_{\text{c}})^2 - M_c^2 - M_h^2 \right] \rho^{(i)} - 2M_h \rho_1^{(i)}, \quad (A.14) \]

\[ \gamma^{(i)} = \hbar \omega_{\text{c}} (\hbar \omega_{\text{c}} - M_c) \rho^{(i)} - \left[ 2L(\hbar \omega_{\text{c}} - M_c) + \hbar \omega_{\text{c}} M_h \right] \rho_1^{(i)} + 2LM_h \rho_2^{(i)}, \quad (A.15) \]

\[ b'_i = \frac{1}{4LM_cM_h} \left[ \hbar \omega_{\text{c}} M_c + L \left( \hbar^2 \omega_{\text{c}}^2 - M_c^2 - M_h^2 \right) - \varepsilon''^2 M_h \right], \quad (A.16) \]

\[ c'_i = \frac{1}{4LM_cM_h} \left[ \hbar \omega_{\text{c}} \left( \hbar^2 \omega_{\text{c}}^2 - M_c^2 - M_h^2 \right) - 2\varepsilon''^2 (\hbar \omega_{\text{c}} - M_c) \right]. \quad (A.17) \]
References

[1] Haarer D, Philpott M R and Morawitz H 1975 *J. Chem. Phys.* **63** 5238
[2] Lalov I J, Supritz C and Reineker P 2005 *Chem. Phys.* **309** 189
[3] Lalov I J and Zhelyazkov I 2006 *Chem Phys.* **321** 223
[4] Lalov I J and Zhelyazkov I 2006 *Phys. Rev. B* **74** 035403
[5] Lalov I J, Supritz C and Reineker P 2007 *Chem. Phys.* **332** 108
[6] Sebastian L, Weisser G, Peter G and Bässler H 1981 *Chem. Phys.* **61** 125
   Sebastian L, Weisser G, Peter G and Bässler H 1983 *Chem. Phys.* **75** 103
[7] Petelenz P, Slawik M, Yokoi K and Zgierski M 1996 *J. Chem. Phys.* **105** 4427
[8] Slawik M and Petelenz P 1997 *J. Chem. Phys.* **107** 7114
[9] Siebrand W and Zgierski M Z 1983 *Organic Molecular Aggregates* ed P Reineker, H Haken and H C Wolf (Springer Series in Solid-State Sciences vol 49) (Berlin: Springer) p 136
[10] Hennessy M H, Soos Z G, Pascal R A Jr and Girlando A 1999 *Chem. Phys.* **245** 199
[11] Hoffmann M, Schmidt K, Fritz T, Hasche T, Agranovich V M and Leo K 2000 *Chem. Phys.* **258** 73
[12] Hoffmann M and Soos Z G 2002 *Phys. Rev. B* **66** 024305
[13] Jeglinski S, Vardeny Z V, Moses D, Srdanov V I and Wudl F 1992 *Synth. Met.* **49–50** 557
[14] Pichler K, Friend R H, Romanov W J, Mertvoy H and Fischer J E 1992 *Synth. Met.* **51** 257
[15] Pac B, Petelenz P, Eilmes A and Munn R W 1998 *J. Chem. Phys.* **109** 7932
[16] Haarer D 1974 *Chem. Phys. Lett.* **27** 91
[17] Haarer D 1977 *J. Chem. Phys.* **67** 4076
[18] Brillante A and Philpott M R 1980 *J. Chem. Phys.* **72** 4019
[19] Elschnier A and Weisser G 1985 *Chem. Phys.* **98** 465
[20] Merski J and Eckhardt C J 1981 *J. Chem. Phys.* **75** 3705
[21] Port H and Hartschuh A 2004 *J. Lumin.* **110** 315
[22] Lalov I J and Zhelyazkov I 2007 *Phys. Rev. B* **75** 245435
[23] Davydov A S 1971 *Theory of Molecular Excitons* (New York: Plenum)
[24] Agranovich V M 1983 *Spectroscopy and Exciton Dynamics of Condensed Molecular Systems* ed V M Agranovich and R M Hochstrasser (Amsterdam: North-Holland) p 83
[25] Lalov I J, Supritz C and Reineker P 2008 *Chem. Phys.* Online at http://dx.doi.org/10.1016/j.chemphys.2008.05.002
[26] Broude V L, Rashba E I and Sheka E F 1985 *Spectroscopy of Molecular Excitons* (Berlin: Springer)
[27] Schmidt K, Leo K and Agranovich V M 2002 *Organic Nanostructures: Science and Applications* ed V M Agranovich and G C La Rocca (Amsterdam: IOS Press) p 521

*New Journal of Physics* **10** (2008) 085006 (http://www.njp.org/)