Theoretical interpretation of electro-absorption spectra for intense optical transitions

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The interaction of a light wave with a molecular crystal subjected at the same time to the influence of static electric field is analyzed. The coupling of the crystal to the radiation field is described in terms of classical electrodynamics, the molecular transition moments being represented by oscillating dipoles. The molecular parameters that enter the classical equations of motion (transition energy and oscillator strength), modified by the static electric field, are derived from the corresponding zero-field values using quantum-mechanical perturbation theory. Subsequently, the field-induced change of the absorption spectrum [electro-absorption (EA) signal] is calculated as the difference between the absorption spectra at nonzero and at zero modulating field. The approach is valid for any allowed transition, irrespective of its intensity. The results demonstrate that, while the absorption spectra of very intense transitions exhibit substantial peculiarities (such as orientational dispersion and polariton effects), the relationship between the absorption and electro-absorption spectra is always the same, regardless of the oscillator strength; specifically, the EA signal of a nondegenerate Frenkel exciton follows the first derivative of the corresponding absorption band. These conclusions are discussed in the context of recent literature on this subject.

I. INTRODUCTION

Owing to the relative weakness of intermolecular interactions, the properties of molecular crystals are largely determined by the properties of individual molecules. The electronic spectra of such crystals are usually dominated by intramolecular excitations (Frenkel excitons), only slightly modified by the crystalline environment. The influence of the surrounding molecules is mediated primarily by the resonance interaction between the excited molecule and its unexcited neighbors, giving rise to delocalization of the excitation. The importance of the resonance effects depends on the size of the transition dipole moment, being moderate for the (most common) transitions of medium oscillator strength, but having dramatic consequences for very strong transitions.

The main peculiarities of strong transitions are due, on the one hand, to the long range of the interaction between the transition dipoles, resulting in the marked influence of crystal boundaries on the bulk exciton energies, and, on the other hand, to the strong coupling between the radiation field and the exciton states of the crystal, giving rise to avoided crossings, and in consequence to the occurrence of a new kind of quasiparticles, referred to as polaritons. Experimentally, the former effect is manifested in the dependence of exciton energies on crystal orientation, while the latter is responsible for very strong reflection due to the so-called stopping bands, which are the energy intervals where light cannot penetrate into the crystal.

The interest in spectroscopy of very intense Frenkel exciton transitions in molecular crystals started about the year 1970.[1–3] At that time, some model systems, such as anthracene, were intensively studied, both theoretically and experimentally[1,2] to yield a satisfactory level of understanding of their absorption and reflection spectra.

To our knowledge, there have been no corresponding theoretical investigations dealing specifically with the electro-absorption (EA) spectra of very intense Frenkel states. At the present moment, the existing interpretations in this area are based on either of two mutually contradictory approaches, both suffering from a certain degree of arbitrariness.

One of the approaches follows from the classic interpretational paradigm, justified by a sound derivation[4,5] where no assumptions are made regarding the oscillator strength of the transition in hand. Its direct application for very strong transitions is rooted in the tacit belief that there is no reason for them to behave differently. In effect, although used in actual calculations,[6] this view has never been validated by a rigorous argument.

The other approach[7–9] invokes a new postulate, allegedly valid only for very strong transitions, and conflicting with the classic paradigm[4,5] mentioned above. This new approach has been based exclusively on intuitive arguments; no attempt to derive it in a systematic way from fundamental physical principles and equations has ever been made.

The existing interpretational ambiguity is detrimental to the future progress in this field. Over the past several years applications of EA spectroscopy are gaining considerable impact;[10–15] they need a sound theoretical basis. This demand is the motivation of the present paper.

For electronic transitions in typical inorganic crystals bonded by the strong valence interactions (covalent or ionic), theoretical foundations of electro-modulation spectroscopy are well established and are to be found, e.g., in the classic monograph by Cardona.[16] In these systems, the electro-absorption signal is composed of the contributions from the valence-to-conduction-band transitions and from Wannier-Mott excitons.

The former exhibits damped oscillatory behavior; the ensuing shape is described by the Airy function.[16,17] Although reported for some conjugated polymers,[18–20] this contribution is not detectable in organic molecular crystals, where the absorption spectrum is dominated by the Frenkel (intramolecular) excitons, and band-to-band absorption is practically

forbidden on account of the small intermolecular overlap.

In electric field the absorption bands corresponding to Wannier excitons may both shift and substantially broaden. The resultant EA contributions are governed by several factors. The binding energy of typical Wannier excitons is often comparable with the energy of the interaction with the modulating electric field;[16,21] in that case, the field strongly mixes the excitonic bound states with the unbound electron-hole continuum, leading to exciton autoionization.[21] As the spacing between the different exciton levels is even smaller than the exciton binding energy, the field-mediated coupling between the different excitonic levels is still more important; accordingly, experimentally accessible field strengths may be large enough to invalidate perturbational description. Moreover, within the strictly hydrogenic model the exciton levels characterized by different l numbers are degenerate, giving rise to linear Stark effect; this degeneracy may be lifted by crystal-symmetry effects and spin-orbit coupling[21] or by the phonon-mediated deviations from the Coulombic form of the electron-hole interaction potential.

The physics of molecular crystals is different. Most of the above complications are absent for Frenkel excitons. It should be noted that in these systems electro-absorption has been observed only for the excitations of relatively low energy, since the absorption spectrum at higher energies is too broad to produce a detectable differential signal. The energy of the interaction with the modulating field (on the order of meVs) is much smaller than the exciton binding energy (typically on the order of eV), so that exciton autoionization may be safely disregarded. Also the spacing between molecular excited states (typically tenths of an eV) exceeds the field-induced coupling by order(s) of magnitude; consequently, the effects of electric field are adequately handled by perturbation theory.

The input data needed for interpretation are different as well. Wannier excitons are characterized by the effective masses of individual charge carriers and by the dielectric constant of the crystal. In contrast, for Frenkel excitons these quantities are of no direct relevance; owing to the strong electron-hole correlation, theoretical description is based on the energies and oscillator strengths of molecular excited states, obtainable for the specific system in hand by quantum chemistry methods.

Even theoretical difficulties have a different nature for Wannier and Frenkel excitons. Apart from the coupling with the photon field which is in the focus of the present paper, Frenkel excitons are coupled to charge transfer (CT) excitons. These latter states, although in some respect reminiscent of Wannier excitons, are better characterized by specifying the relative position (in terms of lattice sites) of the electron with respect to the hole. Their mixing with one another and with Frenkel excitons is best viewed in terms of configuration interaction. The corresponding model Hamiltonian may be derived from the total many-electron Hamiltonian of the crystal by expansion with respect to the (small) intermolecular overlap integrals;[22] its actual form is specific for the crystal structure in hand. There is no simple generic description similar to that valid for Wannier excitons, but most of the ingredients necessary to parametrize the model are accessible to quantum chemistry and microelectrostatic calculations.

Accordingly, although the physical principles underlying electro-absorption spectroscopy are the same, irrespective of the peculiarities of crystal bonding and zero-field spectrum, the specific structure of the eigenstates largely determines the theoretical machinery preferred for actual calculations, which for molecular crystals is different from that previously developed for other systems.[16]

Theoretical description of Frenkel excitons may be alternatively formulated either in the Hamiltonian form or in terms of the dielectric response function.[23] The former approach is preferable for treating the coupling with CT states and was consistently used in previous microscopic calculations of the EA spectra.[22,24–26] The alternative dielectric-function formulation[23,27,28] is equivalent in principle, but clumsy in practical application in that particular context, since the nonlocal polarizability terms[23,27,28] are not easily amenable to direct evaluation by quantum chemistry (or other) methods, unless one resorts again to the Hamiltonian picture.[29] In contrast, for the interaction with the electromagnetic field the dielectric function approach is the description of choice, and will be consistently used in the present paper.

In this treatment we will strictly follow the derivation of Philpott,[30] valid for absorption and reflection spectra. As the paper addresses a controversial issue, in order to facilitate detailed verification of the results the treatment is presented in considerable detail, including some intermediate steps that have not been explicitly shown in the classic monographs.[3,30]

As in Ref. 30, in the consideration of its interaction with electromagnetic field each transition dipole moment is represented by a classical dipole. For this dipole, the equation of motion is written down and solved, using supplementary information provided by Maxwell's equations. This leads to the secular equations for the Coulombic excitons of the system, which may subsequently be applied to construct the polariton excitations.

The underlying equations of motion of classical electrodynamics are parametrized by the frequency ω and the oscillator strength f of the transition under consideration. These two quantities do not result from classical electrodynamics and have to be provided either from experiment or from a different theoretical paradigm, which in this case is molecular quantum mechanics.

The same general approach remains applicable when the system is in an external electric field **F** of low frequency. In the following we will assume that on the time scale of the light wave oscillations the external field may be approximated as static; this is manifestly valid since in typical experiments the frequencies differ at least by 12 orders of magnitude. For the sake of simplicity, we will also assume that the crystal under study consists of centrosymmetric molecules (which is the case for most systems of current interest) and contains one molecule per unit cell.

In the equation of motion for the classical dipole the slow modulating field has to be added to the driving electric field of the light wave, but upon the Fourier transformation to frequency domain the equations corresponding to different frequencies decouple from each other. In effect, the static field (zero frequency) does not contribute at all at the frequency of the optical field, so that it does not enter the final secular equation.

The static field affects the resonance position at a different level. As has already been mentioned, the equations of motion of classical electrodynamics are parametrized by the molecular frequencies and oscillator strengths, and these depend on the electric field. As all intramolecular effects, this dependence has to be treated quantum mechanically.

This will be done in Sec. II. The resultant field-modified values of molecular transition frequency and oscillator strength will be used in Sec. III to write down and solve the electromagnetic equations of motion. The obtained energies of Coulombic excitons will be used in Sec. IV to construct the polariton states. The results will be presented in Sec. V and discussed in Sec. VI.

II. MOLECULAR EXCITATIONS IN ELECTRIC FIELD

In a static electric field $\mathbf{F}$, the ground state $|0\rangle$ and the excited state $|u\rangle$ are coupled by the product $\mathbf{F} \cdot \mathbf{d}_{0u}$, where $\mathbf{d}_{0u} = \langle 0|\mathbf{d}|u\rangle$ is the transition dipole moment between the two states. This coupling is described by the familiar 2×2 Hamiltonian. In addition, each of the two states undergoes the shift of $-\frac{1}{2}\alpha_i'\mathbf{F}^2$ (where $i = 0, u$), due to the dipolar coupling to all other excited states of the system. α_i' is readily obtained from the sum-over-states expression with the terms corresponding to the states 0 and u omitted. For the sake of simplicity, these other states are taken into account merely as contributors to the molecular polarizability; only one excited state per molecule will be explicitly taken into account. In other words, the light frequency is assumed to be tuned in such a way as to probe a single nondegenerate molecular excited state.

In effect, the eigenenergies read

$$E_{u,0}(\mathbf{F}) = \frac{1}{2}\left(E_u - \frac{1}{2}\alpha_u'\mathbf{F}^2 + E_0 - \frac{1}{2}\alpha_0'\mathbf{F}^2\right)$$
$$\pm \frac{1}{2}\left[\left(E_u - \frac{1}{2}\alpha_u'\mathbf{F}^2 - E_0 + \frac{1}{2}\alpha_0'\mathbf{F}^2\right)^2\right.$$
$$\left. + 4(\mathbf{F} \cdot \mathbf{d}_{0u})^2\right]^{1/2}, \tag{1}$$

where $E_{u,0}$ are the respective energies in zero field. Accordingly, the frequency of the transition from the ground state to the excited state u reads (in atomic units where $\hbar = 1$)

$$\omega_{0u} = \left[\left(E_u - \frac{1}{2}\alpha_u'\mathbf{F}^2 - E_0 + \frac{1}{2}\alpha_0'\mathbf{F}^2\right)^2 + 4(\mathbf{F} \cdot \mathbf{d}_{0u})^2\right]^{1/2} \tag{2}$$

which for a weak electric field may be approximated to reconstitute the familiar expression

$$\omega_{0u} \cong E_u - \frac{1}{2}\alpha_u'\mathbf{F}^2 - E_0 + \frac{1}{2}\alpha_0'\mathbf{F}^2 + 2(\mathbf{F} \cdot \mathbf{d}_{0u})^2/(E_u - E_0)$$
$$= E_{0u} - \frac{1}{2}\Delta\alpha\mathbf{F}^2, \tag{3}$$

where $E_{0u} = E_u - E_0$ is the frequency of the molecular transition at zero electric field, $\alpha_{u,0} = \alpha_{u,0}' + 2(\mathbf{F} \cdot \mathbf{d}_{0u})^2/(E_u - E_0)$ is the total molecular polarizability in the appropriate electronic state, also including the contribution from the coupling between the states 0 and u, and $\Delta\alpha = \alpha_u - \alpha_0$ is the difference

between the static polarizabilities of the two states, i.e., the polarizability change upon excitation.

The other quantity needed to parametrize the relevant equations of classical electrodynamics is the oscillator strength of the transition of interest

$$f_u(0) = \frac{2m}{\hbar^2 e^2}E_{0u}|\langle 0|\mathbf{d}|u\rangle|^2. \tag{4}$$

In the following, we assume that the transition is allowed at zero field, so that $f_u(0) \neq 0$. The oscillator strength in a weak electric field is readily obtainable from perturbation theory. Then, by virtue of Eqs. (3) and (4)

$$f_u(\mathbf{F}) = \frac{2m}{\hbar^2 e^2}\left(E_{0u} - \frac{1}{2}\Delta\alpha\mathbf{F}^2\right)$$
$$\times \left|\left(\langle 0| + \sum_{t \neq 0}\langle t|\frac{\langle 0| - \mathbf{d} \cdot \mathbf{F}|t\rangle}{E_0 - E_t}\right)\right.$$
$$\left. \times \mathbf{d}\left(|u\rangle + \sum_{s \neq u}|s\rangle\frac{\langle s| - \mathbf{d} \cdot \mathbf{F}|u\rangle}{E_u - E_s}\right)\right|^2. \tag{5}$$

All terms linear in the electric field strength contain the products of the same formal structure $\langle 0|\mathbf{d}|t\rangle\langle t|\mathbf{d}|u\rangle$, which vanish by symmetry. This is a consequence of the following elementary argument.

As by assumption the optical transition between the states $|0\rangle$ and $|u\rangle$ is allowed, these states must have different parities, i.e., the excited state is of *ungerade* (u) symmetry. In the product $\langle 0|\mathbf{d}|t\rangle\langle t|\mathbf{d}|u\rangle$ the first factor vanishes unless the state $|t\rangle$ belongs to the u symmetry species, while the second factor vanishes unless the same state $|t\rangle$ belongs to the g symmetry species. These two conditions are mutually exclusive, so the product under consideration is always equal to zero.

This considerably simplifies the final formula. In addition, in the absence of magnetic field the wave functions may always be chosen as real, giving rise to real transition moments. With this assumption and after some elementary algebra, Eq. (5) may be recast into the form

$$f_u(\mathbf{F}) = f_u(0)\left(1 - \frac{\Delta\alpha\mathbf{F}^2}{2E_{0u}} + \frac{2}{|\mathbf{d}_{0u}|^2}\sum_{i,j,l=1}^{3}\langle 0|d_i|u\rangle\right.$$
$$\left. \times \sum_{t \neq 0}\sum_{s \neq u}\frac{\langle u|d_l|s\rangle\langle s|d_i|t\rangle\langle t|d_j|0\rangle}{(E_0 - E_t)(E_u - E_s)}F_jF_l\right), \tag{6}$$

where i, j, l label the Cartesian components of the corresponding vectors.

The sum over states in the above expression may be thought of as an off-diagonal (in the basis of zero-field eigenstates) matrix element of third-order hyperpolarizability (coupling the ground state with the excited state u). The "diagonal" hyperpolarizabilities (expectation values) are small as a rule, and their off-diagonal analog should be at least as small as they are. In effect, the last term in the above equation is expected to provide only a marginal correction. This expectation is supported by the following argument.

An elementary rearrangement transforms Eq. (6) to yield

$$f_u(\mathbf{F}) = f_u(0)\left\{ 1 - \frac{\Delta\alpha\mathbf{F}^2}{2E_{0u}} + \frac{2}{|\mathbf{d}_{0u}|^2} \right.$$

$$\times \sum_{i,j,l=1}^{3} \sum_{t\neq 0} \sum_{s\neq u} \left[\frac{\langle 0|d_i|t\rangle\langle t|d_j|0\rangle}{E_0 - E_t} \right]$$

$$\left. \times \left[\frac{\langle u|d_l|s\rangle\langle s|d_i|u\rangle}{E_u - E_s} \right] \times F_j F_l \frac{\langle 0|d_i|u\rangle\langle s|d_i|t\rangle}{\langle 0|d_i|t\rangle\langle s|d_i|u\rangle} \right\}, \quad (7)$$

where the terms in square brackets are readily identified as contributions to the sum-over-states expressions for the corresponding polarizability components.

It is now expedient to introduce the constant

$$R = \sum_i \left[\frac{\langle 0|d_i|u\rangle\langle s|d_i|t\rangle}{\langle 0|d_i|t\rangle\langle s|d_i|u\rangle} \right]_{av}, \quad (8)$$

where av denotes averaging over the states s and t of the molecule. This allows one to rewrite Eq. (7) in the approximate form

$$f_u(\mathbf{F}) = f_u(0)\left(1 - \frac{\Delta\alpha\mathbf{F}^2}{2E_{0u}} + \frac{R}{2|\mathbf{d}_{0u}|^2}\alpha_0\alpha_u\mathbf{F}^2 \right), \quad (9)$$

where α_u and α_0 are the directionally averaged polarizabilities in the uth excited state and in the ground state, respectively, (alternatively, this could be expressed in terms of individual Cartesian components of the corresponding polarizability tensors).

The importance of the last term in Eq. (9) depends on the value of the constant R. The contributions from individual states to the average of Eq. (9) are expected to have different signs, which in the first approximation may be considered random. The averaging of Eq. (9) is extended over all the electronic states of the molecule, so that the number of terms is very large, while the negative and positive contributions should be more or less equally probable. Hence, considerable cancellations are expected to occur. As the averaging is done over two sets of states (s and t), the cancellations should be pretty complete, resulting in a small value of R. (A similar mechanism accounts for the generally small values of the hyperpolarizabilities.) Accordingly, most of the numerical estimates to follow will be done for the limiting case $R=0$.

Of course, the above argument is not valid for a forbidden transition, where $f_u(0)=0$, and the last term in Eq. (9) is singular. In that case the appropriate formula for the perturbed value of the oscillator strength should be obtained directly from Eq. (5), which is not pursued here because the present paper is focused on the properties of very intense transitions.

III. INTERACTION WITH LIGHT WAVES

In the standard consideration of the coupling between a molecular exciton located at site s and the radiation field,[30] the transition dipole moment $\mathbf{d}_{su}=\langle 0|\mathbf{d}_s|u\rangle$ is represented by a classical oscillating dipole $\mathbf{d}_{su}(t)$. Its equation of motion[30] in the electric field $\mathbf{E}'(\mathbf{r},t)$

$$\left[\frac{\partial^2}{\partial t^2} + \omega_{0u}^2(\mathbf{F}) \right]\mathbf{d}_{su}(t) = \frac{e^2 f_u(\mathbf{F})}{m}\hat{\mathbf{d}}_{su}\hat{\mathbf{d}}_{su}\cdot\mathbf{E}'(\mathbf{r}_s,t) \quad (10)$$

is parametrized by the frequency $\omega_{0u}(\mathbf{F})$ and the oscillator strength $f_u(\mathbf{F})$ of the transition under consideration. These two quantities depend on the slowly varying ("static") external electric field $\mathbf{F}$ according to the results of the preceding section. Note that the static field is also added at the right-hand side of Eq. (10).

Strictly following the classic derivation of Ref. 30, the part of the electric field $\mathbf{E}'(\mathbf{r},t)$ which oscillates with the frequency ω of exciting light is then decomposed into the field of a free electromagnetic wave and the combined field of all the oscillating dipoles. Subsequently, Maxwell's equations are used to relate the fields to the current and charge density. This is most conveniently done in terms of the scalar potential $\varphi(\mathbf{r},t)$ and vector potential $\mathbf{A}(\mathbf{r},t)$.

In the Coulomb gauge

$$\boldsymbol{\nabla}\cdot\mathbf{A}(\mathbf{r},t) = 0, \quad (11)$$

Maxwell's equations for the transverse part

$$\left(\boldsymbol{\nabla}^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} \right)\mathbf{A}(\mathbf{r},t) = -\frac{4\pi}{c}\mathbf{j}^{\perp}(\mathbf{r},t) \quad (12)$$

and for the longitudinal part

$$\boldsymbol{\nabla}^2\varphi(\mathbf{r},t) = -4\pi\rho(\mathbf{r},t) \quad (13)$$

of the field [Eqs. (94),(95) of Ref. 30] are uncoupled[31] and may be solved separately.

The sources of the field are given by [Eqs. (82),(83) of Ref. 30]

$$\mathbf{j}(\mathbf{r},t) = \frac{\partial}{\partial t}\mathbf{P}(\mathbf{r},t) + c\,\boldsymbol{\nabla}\times\mathbf{M}(\mathbf{r},t), \quad (14)$$

$$\rho(\mathbf{r},t) = -\boldsymbol{\nabla}\cdot\mathbf{P}(\mathbf{r},t), \quad (15)$$

where $\mathbf{P}$ is the electric polarization vector of the medium. It can be expressed in terms of oscillating electric dipoles $\mathbf{d}_{su}(t)$ [Eq. (84) of Ref. 30]:

$$\mathbf{P}(\mathbf{r},t) = \sum_{su}\mathbf{d}_{su}(t)\delta(\mathbf{r}-\mathbf{r}_s). \quad (16)$$

Following Philpott[30] we neglect magnetic polarization $\mathbf{M}$, as the magnetic effects are of no interest here. Equation (13) can be easily solved (Appendix A), yielding the longitudinal electric field

$$\mathbf{E}^{\|}(\mathbf{r}_s,t) = -\boldsymbol{\nabla}\varphi(\mathbf{r}_s,t) = -\frac{4\pi}{\nu_0}\sum_{s'u'}\mathbf{T}_{ss'}\mathbf{d}_{s'u'}(t) + \mathbf{F}, \quad (17)$$

where

$$\mathbf{T}_{ss'} = \frac{\nu_0}{4\pi}(1-\delta_{ss'})\frac{(\mathbf{1}-3\hat{\mathbf{R}}_{ss'}\hat{\mathbf{R}}_{ss'})}{|\mathbf{R}_{ss'}|^3} \quad (18)$$

denotes the dipole tensor ($\delta_{ss'}$ appears here, because at $\mathbf{r}=\mathbf{r}_s$ the field due to the dipoles $\mathbf{d}_{su}(t)$ must be omitted) and $\mathbf{R}_{ss'}=\mathbf{r}_s-\mathbf{r}_{s'}$.

The transverse part of the electric field is given by the vector potential

$$\mathbf{E}^{\perp}(\mathbf{r},t) = -\frac{1}{c}\frac{\partial}{\partial t}\mathbf{A}(\mathbf{r},t). \tag{19}$$

Substituting Eqs. (17) and (19) into the equation of motion (10) yields

$$\sum_{s'u'}\left[\left(\frac{\partial}{\partial t}+\omega_{0u}^2(\mathbf{F})\right)\delta_{ss'}\delta_{uu'}+\frac{4\pi e^2 f_u(\mathbf{F})}{m\nu_0}(\hat{\mathbf{d}}_{su}\hat{\mathbf{d}}_{su})T_{ss'}\right]\mathbf{d}_{s'u'}(t)$$
$$=\frac{e^2 f_u(\mathbf{F})}{m\nu_0}(\hat{\mathbf{d}}_{su}\hat{\mathbf{d}}_{su})\left(\mathbf{F}-\frac{1}{c}\frac{\partial}{\partial t}\mathbf{A}(\mathbf{r}_s,t)\right) \tag{20}$$

while Eq. (14) allows one to rewrite Eq. (12) in the form

$$\left(\boldsymbol{\nabla}^2-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{A}(\mathbf{r},t)=-\frac{4\pi}{c}\frac{\partial}{\partial t}\mathbf{P}^{\perp}(\mathbf{r},t). \tag{21}$$

For a crystal in a static electric field, interacting at the same time with the monochromatic driving field of frequency ω all dynamical quantities have only two Fourier components in frequency domain: the static component (denoted by the subscript S) and the optical component (denoted by the subscript D). Upon Fourier transformation to frequency domain the equations corresponding to different frequencies decouple from each other. For zero frequency, the corresponding equation reconstitutes the standard result describing the static polarization of the dielectric:

$$\sum_{s'}[\mathbf{1}\delta_{ss'}+4\pi\boldsymbol{\alpha}_s(0)T_{ss'}]\mathbf{P}_{s'S}=\boldsymbol{\alpha}_s(0)\mathbf{F}, \tag{22}$$

$$\boldsymbol{\nabla}^2\mathbf{A}_S(\mathbf{r})=0. \tag{23}$$

The part of the field that is relevant to optical phenomena is readily singled out at the optical frequency

$$\sum_{s'}[\mathbf{1}\delta_{ss'}+4\pi\boldsymbol{\alpha}_s(\omega)T_{ss'}]\mathbf{P}_{s'D}=\frac{i\omega}{c}\boldsymbol{\alpha}_s(\omega)\mathbf{A}_D(\mathbf{r}_s), \tag{24}$$

$$\left(\boldsymbol{\nabla}^2+\frac{\omega^2}{c^2}\right)\mathbf{A}_D(\mathbf{r})=i\frac{4\pi}{c}\omega\mathbf{P}_D^{\perp}(\mathbf{r}), \tag{25}$$

where we have introduced the polarizability tensor

$$\boldsymbol{\alpha}_s(\omega)=\frac{e^2}{m\nu_0}\sum_u\frac{f_u}{\omega_{0u}^2-\omega^2}\hat{\mathbf{d}}_{su}\hat{\mathbf{d}}_{su} \tag{26}$$

and polarization per unit cell

$$\mathbf{P}_{si}=\frac{1}{\nu_0}\sum_u\mathbf{d}_{sui}, \tag{27}$$

where $i=S,D$. Equations (24),(25) show explicitly that the static field does not contribute at optical frequency, and consequently affects crystal absorption and reflection merely via the field-induced changes of the molecular transition frequency ω_{0u} and oscillator strength f_u.

Following Ref. 30, the above equations may be readily solved for a crystal with one molecule per unit cell in the absence of light waves, i.e., when the driving field vanishes, $\mathbf{A}_D(\mathbf{r},t)=0$. This yields the frequencies of Coulombic excitons as the roots of the equation

$$\det|\mathbf{1}+4\pi\boldsymbol{\alpha}(\omega)\cdot\mathbf{T}(\mathbf{k})|=0, \tag{28}$$

where

$$\mathbf{T}(\mathbf{k})=\sum_n\mathbf{T}_{nn'}\exp[i\mathbf{k}\cdot(\mathbf{r}_n-\mathbf{r}_{n'})] \tag{29}$$

is the lattice sum representing the Fourier transform of the dipole tensor.

For a single exciton branch (one allowed molecular transition) the solution is

$$\omega^2(\mathbf{F})=\omega_{0u}^2(\mathbf{F})+\omega_0^2 f_u(\mathbf{F})T(\mathbf{k}) \tag{30}$$

yielding the approximate energy of the exciton

$$E(\mathbf{F})=E_{0u}(\mathbf{F})+\frac{4\pi}{\nu_0}|\mathbf{d}_u(\mathbf{F})|^2 T(\mathbf{k})-\cdots$$
$$\cong E_{0u}+\frac{4\pi}{\nu_0}|\mathbf{d}_{0u}|^2 T(\mathbf{k})-\frac{1}{2}\left[\Delta\alpha-\frac{4\pi}{\nu_0}R\alpha_0\alpha_u T(\mathbf{k})\right]\mathbf{F}^2, \tag{31}$$

where $T(\mathbf{k})=\hat{\mathbf{d}}_u\cdot\mathbf{T}(\mathbf{k})\cdot\hat{\mathbf{d}}_u$.

This shows that for $R=0$ the effect of the static electric field consists in shifting the exciton energy according to Eq. (3), in perfect agreement with the classic argument of Ref. 4. The term proportional to R is expected to be a small correction.

Following the standard practice,[30,32] the lattice sum may be split into the analytic and nonanalytic (direction-dependent) part

$$T(\mathbf{k})=t(0)+(\hat{\mathbf{k}}\cdot\hat{\mathbf{d}})^2. \tag{32}$$

Substituting Eq. (32) into Eq. (31) one can easily see that the nonanalyticity of the lattice sum leads to the dependence of the exciton energy on the direction of wave vector $\mathbf{k}$.

IV. POLARITON EFFECTS

For an infinite crystal and a finite driving transverse field $\mathbf{A}_D(\mathbf{r},t)$ we assume the vector potential of the form

$$\mathbf{A}(\mathbf{r})=\mathbf{A}_0\exp(i\mathbf{k}\cdot\mathbf{r}), \tag{33}$$

where $\mathbf{k}$ is a vector from the first Brillouin zone and $\mathbf{A}_0$ is perpendicular to $\mathbf{k}$. It means that only the coupling of excitons (with wave vector $\mathbf{k}$) to photons with the same wave vector is taken into account; the coupling to photons with wave vectors $\mathbf{k}+\mathbf{K}$, where $\mathbf{K}$ is any reciprocal lattice vector (different from null vector) is ignored. As mentioned by Philpott (Ref. 30), this approximation holds extremely well in the visible and ultraviolet range.

After the Fourier transformation to $\mathbf{k}$ space, Eqs. (24) and (25) describing the part of the fields that oscillates with optical frequency assume the form

$$[\mathbf{1}+4\pi\boldsymbol{\alpha}(\omega)T(\mathbf{k})]\mathbf{P}_0=\frac{i\omega}{c}\boldsymbol{\alpha}(\omega)\mathbf{A}_0, \tag{34}$$

$$\left(\frac{\omega^2}{c^2} - \mathbf{k}^2\right)\mathbf{A}_0 = i\frac{4\pi}{c}\omega(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}})\mathbf{P}_0, \qquad (35)$$

where the amplitude of polarization is given by $\mathbf{P}_0 = (\nu_0)^{-1}\Sigma_u\mathbf{d}_u$, and $\mathbf{d}_u$ is defined as $\mathbf{d}_{su} = \mathbf{d}_u\exp(i\mathbf{k}\cdot\mathbf{r}_s)$.

Solving Eq. (35) for $\mathbf{A}_0$ and substituting the result into Eq. (34) leads to the equation for $\mathbf{P}_0$. Nontrivial solutions of this equation exist only if

$$\det\left|(1 - n^2)\mathbf{1} + [\mathbf{1} + 4\pi\boldsymbol{\alpha}(\omega)\mathbf{T}(\mathbf{k})]^{-1}4\pi\boldsymbol{\alpha}(\omega)(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}})\right| = 0, \qquad (36)$$

where $n = c|\mathbf{k}|/\omega$ is the refractive index. Equation (36) is the polariton dispersion relation.

For a crystal with one molecule per unit cell and all transitions polarized along the same direction $\hat{\mathbf{d}}$, Eq. (36) can be simplified using the formula

$$[\mathbf{1} + 4\pi\boldsymbol{\alpha}(\omega)\mathbf{T}(\mathbf{k})]^{-1}\boldsymbol{\alpha}(\omega) = [1 + 4\pi\alpha(\omega)T(\mathbf{k})]^{-1}\alpha(\omega)\hat{\mathbf{d}}\hat{\mathbf{d}}, \qquad (37)$$

where $\alpha(\omega) = \hat{\mathbf{d}}\cdot\boldsymbol{\alpha}(\omega)\cdot\hat{\mathbf{d}}$. Then the refractive index for photons linearly polarized along $\hat{\mathbf{e}}_\lambda$ can be calculated:

$$[n_\lambda(\omega,\mathbf{k})]^2 = 1 + \frac{4\pi\alpha(\omega)(\hat{\mathbf{e}}_\lambda\cdot\hat{\mathbf{d}})^2}{1 + 4\pi\alpha(\omega)T(\mathbf{k})}. \qquad (38)$$

For the ordinary ray, the photon polarization vector $\hat{\mathbf{e}}_\lambda$ is orthogonal to vectors $\hat{\mathbf{k}}$ and $\hat{\mathbf{d}}$, while for the extraordinary ray it lies in the plane of the vectors $\hat{\mathbf{k}}$ and $\hat{\mathbf{d}}$.

After adding some phenomenological damping, the polarizabilty becomes complex:

$$\alpha_s(\omega) = \frac{e^2}{m\nu_0}\sum_u\frac{f_u}{\omega_{0u}^2 - \omega^2 - i\omega\gamma_u} \qquad (39)$$

and so does the refractive index. Its imaginary part can then be related to the extinction coefficient

$$\varepsilon = \frac{2\omega\,\text{Im}[n(\omega,\mathbf{k})]}{c}. \qquad (40)$$

V. RESULTS AND DISCUSSION

Equation (40) has been applied to simulate the absorption spectrum (Fig. 1) of a model crystal, and subsequently to calculate the electro-absorption signal as the difference between the absorption spectrum at nonzero and at zero-electric field. The spectra are shown for several values of the angle θ between the wave vector and the transition dipole moment, representing different crystal orientations.

The input data (Table I) roughly mimic the situation in sexithiophene (6T), being based on the parametrization used previously in the interpretation[6] of the experimental EA spectrum of this crystal. Of course, this mimicry has to be taken with a grain of salt, because the unit cell of the model crystal used in these calculations contains one molecule, while that of sexithiophene contains four molecules. However, our present objective is not to reproduce in any detail the spec-
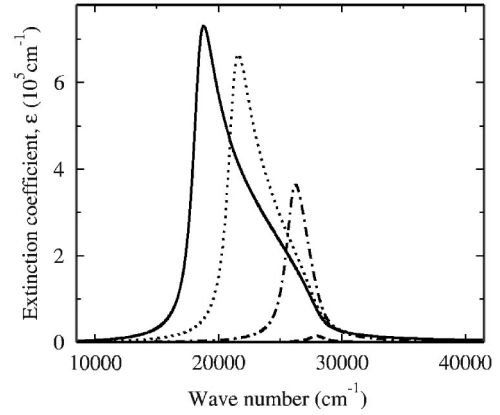

FIG. 1. Calculated absorption spectra for $\theta = 90°$ (solid line), $60°$ (dotted line), $30°$ (dash-dot line), and $5°$ (dashed line).

trum of a specific crystal, but to illustrate the salient features of the coupling between the excitons and photons. Thus, the effects of Davydov splitting are out of our present scope, so that this simplified picture of the crystal is sufficient for our purposes.

The assumed electric field of 23 kV/cm is typical of experiments reported in the literature.[7] The parameter R is not known for sexithiophene, but on general grounds is expected to be small (see Sec. II). Therefore, the EA signal calculated for $R = 0$ is expected to be reasonably realistic. This expectation is reinforced by the finding that for the R values up to about 0.3 the signal does not change qualitatively, and the quantitative differences grow rather slowly with increasing R.

The dependence of the electro-absorption spectrum on the angle θ (Fig. 2) is a consequence of the changes in the absorption spectrum (Fig. 1); the latter exhibits normal orientational dispersion, resulting from the directional dependence of the lattice sum of Eq. (32). For all angles the EA signal evidently follows the first derivative of the absorption spectrum, reconstituting the well-known result of the earlier phenomenological approaches,[4,5] based on the following (classic) argument.

The absorption spectrum (dependence of the extinction coefficient on photon energy E) may be represented as $\varepsilon(E) = f(E_c)s(E - E_c)$, where f is the oscillator strength of the transition in hand, dependent on the transition energy E_c, and

TABLE I. Input parameters for the calculation of the model spectra.

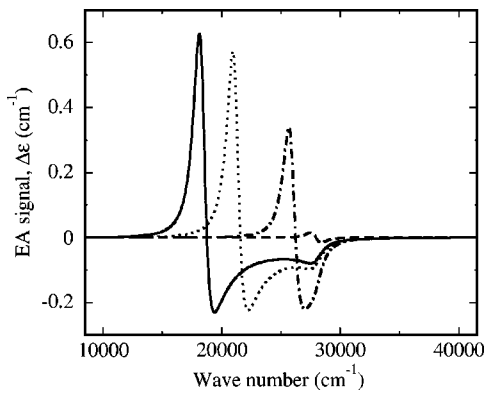| Parameter	Value
$\omega_u(0)$	20 330 cm^{-1}
$|\mathbf{d}_{0u}(0)|$	2.0 eÅ
ν_0	530 Å^3
$t(0)$	-0.17
γ	1500 cm^{-1}
$\mathbf{F}$	23 kV/cm
$\Delta\alpha$	80 Å^3
α_0	93 Å^3

FIG. 2. Electro-absorption spectra calculated with $R=0$ for $\theta = 90°$ (solid line), $60°$ (dotted line), $30°$ (dash-dot line), and $5°$ (dashed line).

s is the shape function, centered at E_c. The small shift ΔE_c of the transition energy, induced by (weak) electric field, gives rise to absorption change, which may be approximated as

$$\Delta\varepsilon(E) = s(E-E_c)\frac{\partial f(E_c)}{\partial E_c}\Delta E_c + f(E_c)\frac{\partial s(E-E_c)}{\partial E_c}\Delta E_c.$$

$$(41)$$

For allowed transitions, the first term is normally negligible (which is also the case in our present calculations), while in the second term the differentiation with respect to E_c may be replaced by differentiation with respect to E, to yield the derivative of the (measured) absorption spectrum with respect to photon energy

$$\Delta\varepsilon(E) \cong f(E_c)\frac{\partial s(E-E_c)}{\partial E_c}\Delta E_c$$

$$= -f(E_c)\frac{\partial s(E-E_c)}{\partial E}\Delta E_c$$

$$= -\frac{\partial\varepsilon(E)}{\partial E}\Delta E_c.$$

$$(42)$$

Substituting the expression for the shift from Eq. (3), one recovers the familiar expression[4,5]

$$\Delta\varepsilon = -\frac{\partial\varepsilon}{\partial E}\Delta E_c = \frac{1}{2}\frac{\partial\varepsilon}{\partial E}\Delta\alpha\mathbf{F}^2.$$

$$(43)$$

Consequently, the signal is proportional to the first derivative of the absorption spectrum, and the prefactor in this dependence is governed by the polarizability change between the ground and excited electronic state of the molecule, which exactly agrees with the EA spectrum of Fig. 2 calculated numerically. The positive lobe of the first derivative precedes the negative lobe on the energy scale, since the energy shift is negative. These results reconstitute the common wisdom existing in the field, and were to be expected.

It should be noted that the transition dipole moment of the molecular state to which the exciting light is tuned enters the overall $\mathbf{F}$-induced shift on exactly the same footing as the transition dipoles of other excited states do, i.e., only via the corresponding contribution $4(\mathbf{F}\cdot\mathbf{d}_{0u})^2/(E_u-E_0)$ to the mo-

lecular polarizability. In this expression, the transition dipole moment appears in the *second power*, and its contribution is weighted by the inverse of the energy gap between the ground and the excited electronic state. It should be emphasized that there is no term *linear* in the transition dipole moment.

This observation is important in view of the recent controversial interpretation of the electro-absorption spectrum of sexithiophene.[7–9] The interpretation is based on the assumption that the resonance position depends linearly on the transition dipole moment from the ground state to the relevant excited state. In this way, the transition moment, which is an *off-diagonal* matrix element of the dipole moment operator (and hence, strictly speaking, has no classical counterpart), is treated as if it were an expectation value, i.e., a *diagonal* matrix element of the dipole moment operator. Even without the derivation we have presented, it is obvious on quantum-mechanical grounds that the difference between the *eigenenergies* of the two relevant electronic states (defining the position of the optical resonance) *must not* depend linearly on *any* off-diagonal matrix element of *any* operator.

This conclusively determines the shape of the signal due to a Frenkel state as the first derivative of the absorption spectrum, in contrast to the second-derivative shape, invoked in Ref. 7. In fact, the second-derivative shape emerges as a result of the off-diagonal coupling by the dipole moment operator between two closely spaced electronic states. This is illustrated by the following argument.

Let the position of the ground state serve as energy zero. Suppose that in the absence of electric field two excited electronic states $|1\rangle$ and $|2\rangle$ have the energies E_1 and E_2, respectively, and that the off-diagonal matrix element $\mathbf{d}=\langle 1|\mathbf{d}|2\rangle$ of the dipole moment operator does not vanish. Then in the electric field the two states are coupled according to the Hamiltonian

$$\begin{pmatrix} E_1 & \mathbf{d}\cdot\mathbf{F} \\ \mathbf{d}\cdot\mathbf{F} & E_2 \end{pmatrix}$$

$$(44)$$

with the eigenenergies

$$E_\pm = \tfrac{1}{2}(E_1+E_2) \pm \tfrac{1}{2}\sqrt{(E_1-E_2)^2 + 4(\mathbf{d}\cdot\mathbf{F})^2}.$$

$$(45)$$

In the absence of electric field the corresponding optical transitions would be observed in absorption at energies E_1 and E_2. It is readily seen that, owing to the dipole coupling, in the electric field the lower state exhibits a redshift and the upper state exhibits a blueshift, yielding a first-derivative and an "inverted" first-derivative (with negative lobe preceding the positive lobe) EA signal, respectively. In general, these signals could be well separated on energy scale. In the special case when the spectral widths of the transitions to these states markedly exceed the difference E_1-E_2, the two signals fuse to yield a second-derivative shape. This usually happens for charge transfer states, as is discussed in Appendix B.

It is clear on this view that the coupling (by the transition dipole moment) of an isolated Frenkel state to the ground state cannot produce a second-derivative EA signal, as postulated in Refs. 7–9. In the first place, in this case there is only *one* optical transition: from the ground state to the ex-

cited state, while in order to get a second-derivative shape *two* closely spaced transitions, shifting apart, are necessary. Second, the spectral shift is due exclusively to the second-order perturbational correction to transition energy, governed by the polarizability change [see Eq. (43)]. As stated above, the transition dipole moment enters this expression in the *second* power. In Ref. 7 it is the unphysical assumption that the shift is proportional to the *first* power of the transition dipole moment that gives rise to a (nonexistent in reality) pair of closely spaced states (with the transition moments oriented "upfield" and "downfield") that shift apart in the electric field. The second-derivative signal shape is an artifact of the applied model, where the off-diagonal transition dipole moment is confused with the corresponding expectation value.

For similar reasons the amplitude of the corresponding EA signal, calculated with the same assumption, seemingly agrees with experiment.[7] In the correct expression, the dipole coupling between the ground state and the excited state in hand contributes to the observed EA signal via the corresponding term in the polarizability change between the two states. If this term is separated out (as is done for argument's sake in the derivation of Sec. II), the corresponding transition dipole moment $\mathbf{d}_{0u}$ is weighted by the factor $\mathbf{F} \cdot \mathbf{d}_{0u}/(E_u - E_0)$; the (large) denominator containing the energy separation between the two coupled states makes this contribution quite small. In the numerical estimates[7] of the shift induced by the electric field this weighting factor is disregarded, based on an (invalid) intuitive argument, where the induced dipole moment is identified directly with the transition dipole moment rather than with the corresponding weighted contribution. The absence of the weighting factor results in the shift of the resonance position being overestimated by several orders of magnitude, so that it seems to account correctly for the size of the observed spectral shift.

Although large values of the parameter R seem rather unlikely in real systems, its influence on the EA spectrum has also been tested. For $R=0$, the effect of electric field is due exclusively to the change of the molecular transition frequency ω_{0e} on the left-hand side of Eq. (7); the correction due to the change of the oscillator strength on the right-hand side of this equation vanishes for centrosymmetric molecules. As shown in Sec. II, the leading contribution to this latter change results from the second-order correction to zero-field eigenenergies, is quadratic in the electric field strength and is governed by the polarizability change. In the transformation from Eq. (30) to the final expression for the exciton energy given by Eq. (31) this term is exactly compensated by the same factor in the energy of the molecular transition, which enters in the denominator.

This is no longer true when R is not negligibly small. The EA signal predicted for $R=1$ (which is probably unphysically large) is displayed in Fig. 3. The obtained signal shapes are unusual; some deviate significantly from the first derivative of the absorption spectrum, but still they never resemble the second derivative. To the best of our knowledge, signal shapes similar to those shown in the figure have never been experimentally observed for an allowed transition, in keeping with our tentative expectation that R is generally small.
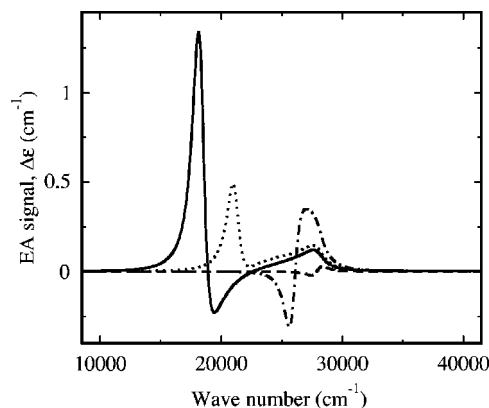

FIG. 3. Electro-absorption spectra calculated with $R=1$ for $\theta = 90°$ (solid line), 60° (dotted line), 30° (dash-dot line), and 5° (dashed line).

VI. CONCLUSIONS

The interpretational paradigm of electro-absorption spectroscopy as applied to molecular crystals, was developed in the last two decades of the past century.[4,5] It was based on the expansion of the absorption intensity in power series with respect to the modulating electric field, and led to the conclusion that for centrosymmetric crystal consisting of centrosymmetric molecules the Frenkel states give rise to first-derivative EA signals, with the amplitude governed by the polarizability change between the ground and excited electronic state, whereas the CT states give rise to second-derivative EA signals, with the amplitude governed by the dipole moment of the corresponding localized CT configurations. Some exceptions to this latter rule may be encountered and more complicated cases may emerge when quantum-mechanical mixing between the different localized configurations (Frenkel and CT) is included, but the gist of the original intuitive picture remains valid.[22,24–26]

Recently, the applicability of the above interpretational paradigm to very intense transitions has been challenged.[7–9] According to the new approach, for such a transition the transition dipole moment, which is an off-diagonal matrix element of the corresponding operator, should be treated as if it were a permanent dipole moment, which is an expectation value (a diagonal matrix element) of this operator. In effect, a very intense Frenkel transition was predicted to produce a second-derivative EA signal, contrary to the expectation based on the classic argument.[4,5]

Among other conceptual problems the new approach created, it has been unclear how the new paradigm (claimed to be valid for very strong transitions) should match to the classic paradigm, valid for weaker transitions, and how this conceptual gap could be bridged for the transitions of intermediate oscillator strength. In contrast to the classic paradigm, based on a well-defined (and hence verifiable) derivation, the new *ad hoc* approach has been based on purely intuitive notions, not amenable to formal mathematical verification. The present paper presents a systematic derivation of the electro-absorption signal, valid for any nondegenerate Frenkel transition irrespective of its absorption intensity. The derivation is open to complete formal scrutiny. The present

paper shows that the EA signals of all optical transitions, regardless of their oscillator strength, are subject to exactly the same classic interpretational rules,[4,5] i.e., that very strong transitions exhibit no peculiarities that would justify treating them as exceptional.

Admittedly, the absorption and reflectance spectra of very intense states have some specific features. Owing to the strong interaction between the transition dipoles, the energies of Coulombic excitons depend on the direction of the wave vector, which results in the dependence of the absorption and reflection spectra on crystal orientation.[1–3] Moreover, the strong coupling between the radiation field and the excitons produces polariton states, responsible for the occurrence of (metallically reflecting) stopping bands.[30]

It should be emphasized that the contentions expressed in the present work do not apply to the published experimental spectra of sexithiophene.[7–9] These spectra are extremely valuable; the single crystal spectrum[7] is the first EA spectrum of an organic single crystal that has ever been measured, and represents a major breakthrough in electro-absorption spectroscopy. However, as has been demonstrated above, the original interpretation of the spectra is not tenable.

The faulty interpretational approach[7–9] led to the incorrect conclusion that the EA spectra of the sexithiophene single crystal and films were dominated by Frenkel excitations, with no observable contribution from charge transfer states. This conclusion is not valid. The observed EA signals evidently exhibit second-derivative shape,[7–9] which, as demonstrated above, is ruled out unless contributions from CT excitons are involved.

Theoretical calculations,[6] based on a microscopic Hamiltonian, have quantitatively reproduced the sexithiophene EA signal, and confirmed the CT provenance of a majority of the observed spectral features. As the underlying theoretical approach[6] explicitly accounts for the mixing between the Frenkel and CT states, the eigenstates are no longer assigned as purely Frenkel or purely CT, but may still be characterized by the dominant contribution that defines their actual provenance; their vibronic replicas are also included in the model, as well as other low-energy intramolecular excitations. The treatment invokes no assumptions regarding the shape of the EA signal, which is calculated directly as the difference between the absorption spectrum at nonzero- and zero-electric field.

The experimental EA spectrum of the sexithiophene crystal[7–9] interpreted in Ref. 6 was measured for the light polarized along the b crystal axis. Owing to the peculiar arrangement of the molecules in the unit cell, the corresponding Davydov component of the lowest Frenkel exciton has extremely low intensity, which makes the CT states (polarized along this direction) discernible also in the absorption spectrum. Apparently, quaterthiophene[33] is an analogous case. In other molecular crystals (such as, e.g., polyacenes[4,5,25,34,35]) the eigenstates of CT parentage are rarely observable in absorption spectroscopy, being masked by vibronic satellites of the lowest Frenkel transition. It is usually the large sensitivity of the CT states to electric field that amplifies their contribution to electro-absorption, making it comparable to Frenkel contributions.

Accordingly, in most cases the observed EA signal of CT origin could be identified by its second-derivative shape, but

was not directly attributable to the bands actually observed in absorption spectroscopy. In effect, if the EA spectrum was not calculated from a microscopic model (as was done in Refs. 6, 22, and 24–26), but simulated by plain fitting, the energies of CT excitons had to be introduced as free parameters and there was no cross-check on their values. Sexithiophene is exceptional in the sense that its b-polarized absorption spectrum provides an additional verification of the applied theoretical approach (notably, confirming the calculated positions of the CT states); for this reason, the interpretation is in this case especially important conceptually.

The same physical mechanisms are expected to be operative in a variety of other interesting systems, such as other oligothiophenes, perylene derivatives,[24] etc. Electro-absorption spectroscopy is a useful tool to investigate these cases, especially in view of its ability to probe the charge transfer states, vital for the process of charge carrier generation and consequently for (opto)electronics. We hope that the elimination of interpretational ambiguity will facilitate and encourage further applications of this valuable experimental technique.

APPENDIX A

The solution of the Poisson equation (13) is[31]

$$\varphi(\mathbf{r},t) = \int_{R^3} \frac{\rho(\mathbf{r}',t)}{|\mathbf{r} - \mathbf{r}'|} d^3 r' + \varphi_0(\mathbf{r},t), \tag{A1}$$

where $\varphi_0(\mathbf{r},t)$ denotes the solution of the Laplace equation, chosen in such a way as to satisfy the boundary conditions which in this case are embodied in the presence of external static electric field $\varphi_0(\mathbf{r},t) = -\mathbf{F} \cdot \mathbf{r}$. Upon substitution from Eqs. (15),(16),(A1) becomes

$$\varphi(\mathbf{r},t) = -\sum_s \mathbf{d}_s(t) \cdot \int_{R^3} \frac{\boldsymbol{\nabla}\,\delta(\mathbf{r}' - \mathbf{r}_s)}{|\mathbf{r} - \mathbf{r}'|} d^3 r' - \mathbf{F} \cdot \mathbf{r}$$

$$= \sum_s \mathbf{d}_s(t) \cdot \int_{R^3} \delta(\mathbf{r}' - \mathbf{r}_s)\,\boldsymbol{\nabla}\left(\frac{1}{|\mathbf{r} - \mathbf{r}'|}\right) d^3 r' - \mathbf{F} \cdot \mathbf{r}$$

$$= \sum_s \frac{\mathbf{d}_s(t) \cdot (\mathbf{r} - \mathbf{r}_s)}{|\mathbf{r} - \mathbf{r}_s|^3} - \mathbf{F} \cdot \mathbf{r}. \tag{A2}$$

APPENDIX B

In centrosymmetric systems, the linear dependence of the energy eigenvalues on the off-diagonal matrix element of the dipole moment operator may emerge only for the states that at zero field are (quasi) degenerate.[36,37] This happens for charge-transfer (CT) states, as will be demonstrated below.

For a pair of molecules A and B let us take as the basis set the localized CT configurations $|A^+B^-\rangle$ and $|A^-B^+\rangle$. In this basis, the Hamiltonian reads

$$\begin{pmatrix} E_{CT} + \mathbf{F} \cdot \mathbf{d} & W \\ W & E_{CT} - \mathbf{F} \cdot \mathbf{d} \end{pmatrix}, \qquad (B1)$$

where $W = \langle A^+B^- | H | A^-B^+ \rangle$ represents the matrix element that governs the exchange of the charges between the two molecules. In the classical approximation, W is disregarded. Then, owing to the linear dependence of the energies on the perturbation $\mathbf{F} \cdot \mathbf{d}$, in an electric field one of the states undergoes a redshift and the other one a blueshift, producing, according to Eq. (43), a first-derivative and an "inverted" first-derivative EA signal, respectively. The two CT states split, but in electric fields used in actual experiments this splitting is much smaller than the spectral width of the corresponding transitions. Consequently, the two first derivatives fuse to yield a second-derivative shape of the EA signal, with the amplitude proportional to the dipole moment d.

As demonstrated in the past quantitative reproductions of the EA signals of several systems,[22,25,26] the classical approach discussed above is insufficient to rationalize some features of the experimental spectra; the quantum mechanical off-diagonal interactions (dependent on intermolecular overlap) that govern charge transfer between the molecules turn out to have crucial importance. In the simplistic dimer model underlying Eq. (B1), they are modeled by the charge-exchange term W.

Accordingly, in the following W is no longer neglected. Then, upon transformation to the symmetry-adapted basis $|CT^\pm\rangle = 2^{-1/2}(|A^+B^-\rangle \pm |A^-B^+\rangle)$, the Hamiltonian of Eq. (B1) becomes

$$\begin{pmatrix} E_{CT} + W & \mathbf{F} \cdot \mathbf{d} \\ \mathbf{F} \cdot \mathbf{d} & E_{CT} - W \end{pmatrix}. \qquad (B2)$$

It is readily seen that in this representation the Hamiltonian is diagonal at zero-field, its diagonal elements representing the zero-field eigenenergies, and that the dipole moment operator is in this basis *off-diagonal* (since $\mathbf{d} = \langle A^+B^- | \mathbf{d} | A^+B^- \rangle = \langle CT^+ | \mathbf{d} | CT^- \rangle$).

Yet, in the limit of very weak intermolecular interaction $W \to 0$, the eigenvalues

$$E_\pm = E_{CT} \pm \tfrac{1}{2}[W^2 + (\mathbf{F} \cdot \mathbf{d})^2]^{1/2} \qquad (B3)$$

still depend linearly on the perturbation $\mathbf{F} \cdot \mathbf{d}$ and hence on the dipole moment $\mathbf{d}$ which in the basis of the zero field eigenstates is *off diagonal*. In effect, the interaction with the electric field again pushes the two eigenstates apart, giving rise to a pair of first-derivative signals (one simple and one inverted). As previously, the spectral widths of the two states are much larger than the field-induced shifts, so that the two first-derivative signals fuse to yield a second derivative.

Based on Eq. (B3) it is readily seen that in fact the electric field *always* pushes the two eigenstates apart, irrespective of the actual value of W. Consequently, even for substantial values of the zero-field splitting $2W$ the signal will retain the second-derivative shape, as long as the splitting is markedly smaller than the spectral width. For CT states this is the typical situation, since the off-diagonal CT interactions, being limited by intermolecular overlap, are usually not very large. However, there are exceptions:[22,25,26] in some systems (fullerene being a prime example[26]), the off-diagonal CT terms add and yield a cumulative splitting exceeding the spectral width. In that case, the two eigenstates of CT origin may give rise to a resolved pair of first-derivative EA signals (one simple and one inverted).

Based on the classic argument,[4,5] first-derivative EA signals are usually attributed to Frenkel excitons and second-derivative signals to CT states. Apart from the issue of the mixing between the Frenkel and CT states (which is beyond the scope of the present work, but has been exhaustively treated in other papers[22,24,25]) the above results show that a CT state, although typically expected to exhibit a second-derivative EA signal, may in some instances produce a first-derivative signal. On the contrary, a nondegenerate Frenkel state is always bound to produce a first-derivative signal [as follows from Eqs. (3) and (43)], but never a second-derivative signal.

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[1] L. B. Clark and M. R. Philpott, J. Chem. Phys. **53**, 3790 (1970).

[2] M. R. Philpott, J. Chem. Phys. **54**, 111 (1971).

[3] V. M. Agranovich, *Theory of Excitons* (Nauka, Moscow, 1968) (in Russian).

[4] L. Sebastian, G. Weiser, and H. Bässler, Chem. Phys. **62**, 125 (1981).

[5] L. Sebastian, G. Weiser, G. Peter, and H. Bässler, Chem. Phys. **75**, 103 (1983).

[6] M. Andrzejak, P. Petelenz, M. Slawik, and R. W. Munn, J. Chem. Phys. **117**, 1328 (2002).

[7] S. Möller, G. Weiser, and F. Garnier, Phys. Rev. B **61**, 15749 (2000).

[8] S. Möller, G. Weiser, and F. Garnier, Synth. Met. **116**, 305 (2001).

[9] S. Möller and G. Weiser, Synth. Met. **122**, 41 (2001).

[10] R. K. Swamy, S. P. Kutty, J. Titus, S. Khatavkar, and M. Thakur, Appl. Phys. Lett. **85**, 4025 (2004).

[11] P. R. Bangal, D. M. K. Lam, L. A. Peteanu, and M. Van der Auweraer, J. Phys. Chem. B **108**, 16 834 (2004).

[12] W. Stampor, J. Mezyk, and J. Kalinowski, Chem. Phys. **305**, 77 (2004).

[13] E. Jalviste and N. Ohta, J. Chem. Phys. **121**, 4730 (2004).

[14] K. Yanagi, T. Kobayashi, and H. Hashimoto, Phys. Rev. B **67**, 115122 (2003).

[15] M. Knupfer, T. Schwieger, H. Peisert, and J. Fink, Phys. Rev. B **69**, 165210 (2004).

[16] M. Cardona, *Modulation Spectroscopy* (Academic, New York, 1969).

[17] D. E. Aspnes, Phys. Rev. **147**, 554 (1966).

[18] G. Weiser and A. Horvath, Chem. Phys. **227**, 153 (1996).

[19] A. Horvath, G. Weiser, C. Lapersonne-Meyer, M. Schott, and S. Spagnoli, Phys. Rev. B **53**, 13507 (1996).

[20] G. Weiser, J. Lumin. **110**, 189 (2004).

[21] C. B. Duke and M. E. Alferieff, Phys. Rev. **145**, 583 (1966).

[22] P. Petelenz, M. Slawik, K. Yokoi, and M. Z. Zgierski, J. Chem. Phys. **105**, 4427 (1996).

[23] R. W. Munn and P. Petelenz, in *Organic Electronic Materials: Conjugated Polymers and Low Molecular Weight Organic Solids*, edited by R. Farchioni and G. Grosso, Vol. 41 of Springer Series in Materials Science (Springer-Verlag, Berlin, 2001), p. 327.

[24] G. Mazur, P. Petelenz, and M. Slawik, J. Chem. Phys. **118**, 1423 (2003).

[25] M. Slawik and P. Petelenz, J. Chem. Phys. **107**, 7114 (1997); **111**, 7576 (1999).

[26] B. Pac, P. Petelenz, M. Slawik, and R. W. Munn, J. Chem. Phys. **109**, 7932 (1998).

[27] R. W. Munn and T. Luty, Chem. Phys. **81**, 41 (1983).

[28] T. Luty and C. J. Eckhardt, J. Chem. Phys. **81**, 520 (1984).

[29] P. Petelenz, Chem. Phys. Lett. **215**, 607 (1993).

[30] M. R. Philpott, in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley, New York, 1973), Vol. 23, pp. 227–341.

[31] J. D. Jackson, *Classical Electrodynamics, Second Edition* (Wiley, New York, 1975).

[32] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).

[33] S. Tavazzi, A. Borghesi, M. Laicini, and P. Spearman, J. Chem. Phys. **121**, 8542 (2204).

[34] P. J. Bounds and W. Siebrand, Chem. Phys. Lett. **75**, 414 (1980).

[35] P. J. Bounds, P. Petelenz, and W. Siebrand, Chem. Phys. **63**, 303 (1981).

[36] P. Petelenz, Chem. Phys. **171**, 397 (1993).

[37] P. Petelenz, in *Organic Nanostructures: Science and Applications*, Proceedings of the International School of Physics "Enrico Fermi," Course CXLIX, Bologna, Italy, edited by V. M. Agranovich and G. C. La Rocca (Società Italiana di Fisica, Bologna, Italy, 2002), p. 1.