



Theoretical models for electro-absorption spectroscopy

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Abstract

Interpretation of the physical mechanisms that are crucial for the understanding of theoretical approaches used to reproduce the electro-absorption (EA) spectra of organic molecular crystals is built step by step from the simplest case of an individual molecule, through a model dimer, then a crystal, and finally a film viewed as a disordered assembly of microscopically well ordered crystallites. The two-state model is used throughout to gain qualitative insight into the discussed effects. As an illustrative example, the calculations performed for sexithiophene where all the discussed effects are operative, are briefly discussed.

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1. Introduction

From the point of view of applications in (opto)electronics, organic materials are presently known to offer some technological advantages. Apart from the low cost, the most obvious potential benefits are to be achieved when the organic systems are prepared in the form of films, always to some extent disordered, but relatively flexible mechanically (when compared to single crystals) and relatively easy to prepare.

However, the ease of their preparation is not paralleled by the ease of theoretical description. Even for a relatively simple system microscopic quantum mechanical description is a challenge, making the use of model approaches and approximate computational methods unavoidable. The

disorder is an additional complication; the calculations have to be repeated for a number of cases representing a statistical ensemble, and the results averaged.

The outcome is not always easy to rationalize in intuitive terms, especially in the contexts where many different factors combine to yield the observed phenomena. This is the case for instance in electro-absorption (EA) spectroscopy; the derivative nature of the corresponding spectra tends to expose some subtler features of the systems under investigation and to highlight their complexity.

Although in any individual case the EA signal may be theoretically reproduced only by relatively involved calculations, the experience collected over a number of cases allows one to earmark some physical mechanisms as particularly important for qualitative understanding of the spectra. In this paper, their simple description will be discussed for model systems of increasing degree of complexity.

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Generally, the approach will be based on the quantum mechanical two-state model. An isolated molecule interacting with external electric field will be considered as the simplest case of its application. Subsequently, we will proceed to the dimer. Its Hamiltonian will be constructed in a basis set suggested by intuitive considerations. The solutions will be discussed for several special situations: When the off-diagonal overlap-dependent charge-transfer coupling vanishes, when it is present but there is no external electric field, and finally when both interactions are present, but the latter is weak. In this last case only qualitative analysis will be given, without detailed numerical results. The analysis will be focused on the consequences for absorption and EA spectroscopy. Next, the analogies and differences between physical mechanisms operative in the dimer and in a molecular crystal will be qualitatively discussed. Finally, the peculiarities of a polycrystalline sample will be shown and illustrated for the case of sexithiophene.

2. Isolated molecule

Let us consider a model molecule with closed-shell ground state $|0\rangle$ and only one excited state $|1\rangle$. The corresponding zero-field energies are $H_{11} = E_0$ and $H_{22} = E_1$. Both states are assumed to be non-degenerate. We also assume that the transition to the excited state is dipole-allowed, i.e., that the off-diagonal matrix $\langle 0|\mu|1\rangle$ does not vanish. In this case, the absorption spectrum consists of a single band centred at $E = E_1 - E_0$. In reality, the band would be accompanied by some vibrational satellites (Franck–Condon progression), but for the time being this issue is disregarded.

An external electric field, presumably weak, couples the two states through the corresponding matrix element $H_{12} = \langle 0|\mu \cdot \mathbf{F}|1\rangle = \mu_{01} \cdot \mathbf{F}$ of the Hamiltonian, assumed to be small. The eigenenergies in the electric field are

$$E_{\pm} = \frac{1}{2} \left[(H_{11} + H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2} \right] \\ = \left[\frac{1}{2}(E_0 + E_1) \pm \sqrt{E^2 + 4(\mu_{01} \cdot \mathbf{F})^2} \right]. \quad (1)$$

The corresponding field-induced shifts may be expressed in terms of polarizability, defined as the second derivative $\partial^2 E_{\pm} / \partial F^2$ of energy with respect to the electric field strength.

As the perturbation pushes the zero-field states apart, the perturbing field stabilizes the ground state (positive polarizability), while the excited state is predicted to be destabilized (negative polarizability). This latter result is evidently an artefact of the model (as recently illustrated for *J*-aggregates [1]): in reality, the polarizability of the molecule in an excited state usually exceeds that in the ground state. This is due to the field-mediated coupling of the excited state to *excited states of higher energy*: As in the molecules with closed-shell ground state the energy gap between this state and the lowest excited state is much larger than the separations between different excited states, in real cases the ensuing downward shift of the excited state exceeds the upward shift due to the interaction with the ground state. This effect is compounded by the large density of excited states: all the states located on energy scale higher than the state in hand contribute to the downward shift. Also the unbound continuum gives its (substantial) share; as a result, even the polarizability of highly excited states usually exceeds that of the ground state.

Consequently, external electric field *reduces* the excitation energy by

$$\Delta E = \frac{1}{2} \Delta p F^2, \quad (2)$$

where Δp is the polarizability increase between the ground and excited electronic state of the molecule.

As the shift is small, the resulting field-induced change $\Delta\alpha$ of the extinction coefficient may be expanded in a power series with respect to ΔE ; normally only the leading linear term is retained. Accordingly, the change, directly measurable as the EA signal, follows the first derivative of the absorption shape, and, as follows from Eq. (2), is quadratic in electric field strength. The derivative shape of the signal has an important consequence: The intensity of a given state in absorption does not translate directly into the size of its contribution to the EA spectrum, and even a quite intense

absorption band, if very broad, may give rise to marginal electro-absorption.

3. Dimer

In the dimer AB where the two identical molecules are related by a symmetry operation, the locally excited states $|A^*B\rangle$ and $|AB^*\rangle$ (hereafter referred to as Frenkel excitons) are replaced by their (symmetry-adapted) in-phase and out-of-phase linear combinations $|F\pm\rangle = 2^{-1/2}(|A^*B\rangle \pm |AB^*\rangle)$, analogous to the Davydov (factor-group) components in a molecular crystal. Each molecular excited state gives rise to two eigenstates, in the first approximation split by the off-diagonal matrix element M of the intermolecular interaction operator V , often referred to as the exciton-resonance

$$E^{\text{CT}} = I - A - C, \quad (4)$$

where I and A denote the ionization potential and electron affinity of the molecule, and C is the energy of the Coulombic interaction between the two ions.

Owing to the intermolecular interaction and overlap, the off-diagonal matrix elements of the dimer Hamiltonian $D_e = \langle A^*B|V|A^+B^- \rangle$ and $D_h = \langle A^*B|V|A^-B^+ \rangle$, usually referred to as the dissociation integrals or charge-transfer integrals, do not vanish. Consequently, neither the intramolecular nor the intermolecular excitations introduced above are eigenstates of the dimer Hamiltonian. However, the excitations introduced above may be used as a convenient basis to express the actual eigenstates. In the Hilbert space they span, the dimer Hamiltonian reads

$$\begin{bmatrix} E - \frac{1}{2}\Delta pF^2 & M & D_e & D_h \\ M & E - \frac{1}{2}\Delta pF^2 & D_h & D_e \\ D_e & D_h & E^{\text{CT}} - \frac{1}{2}\Delta pF^2 - \mathbf{m} \cdot \mathbf{F} & W \\ D_h & D_e & W & E^{\text{CT}} - \frac{1}{2}\Delta pF^2 + \mathbf{m} \cdot \mathbf{F} \end{bmatrix}, \quad (5)$$

integral and commonly represented as the interaction between the transition dipoles μ_A , μ_B of the two molecules:

$$M = \frac{\mu_A \cdot \mu_B}{R^3} - 3 \frac{(\mu_A \cdot \mathbf{R})(\mu_B \cdot \mathbf{R})}{R^5}. \quad (3)$$

In order to improve the above approximation, it has to be taken into account that in addition to the intramolecular excitations (where an electron is promoted from a binding to an antibinding orbital of the *same molecule*), the dimer has a manifold of excitations of a different nature, where an electron is transferred from one monomer to the other (symbolically denoted as $|A^+B^- \rangle$, $|A^-B^+ \rangle$). They may be thought of as consisting of an extra electron located at one molecule (forming an anion), and of a hole located at the other molecule (forming a cation). These excitations are referred to as charge transfer (CT) states, and their approximate energies are given as

where the interaction with external electric field F is included from the outset for future reference, and $W = \langle A^+B^-|H|A^-B^+ \rangle$. The dipole moment $\mathbf{m} = \langle A^+B^-|\mu|A^-B^+ \rangle$ of the CT states, equal to the product of the transferred (unit) charge e and the intermolecular distance, is assumed parallel to the direction of the electric field \mathbf{F} .

This Hamiltonian embodies a limited configuration interaction (CI) scheme. In general, it has to be diagonalized numerically; we will discuss in more detail the model situations where analytical solutions are readily available.

3.1. $D_e = D_h = 0$

If the dissociation integrals are neglected altogether, the Frenkel states are decoupled from the CT states. In the Frenkel manifold, the Davydov components discussed above are the eigenstates. In the electric field, both of them shift by the same amount, exactly equal to that predicted for the

corresponding molecular state. In effect, their contribution to the electro-absorption spectrum consists of two first-derivative signals, spaced by $2M$.

As follows from Eq. (5), the CT states are also subject to the spectral shift governed by the polarizability change (which is usually of the same order as for the intramolecular excitations, and will be assumed equal for the sake of simplicity). However, this contribution is dominated by another one, mediated by the dipole moment. The shape of the signal depends on the value of the matrix element W governing the exchange of the charge between the two ions (polarity flip). Being of the second order in the intermolecular overlap integrals, it is normally quite small. If it is negligible, the ‘local’ CT states described above are the eigenstates of the system. According to the direction of their dipole moments, one of the zero-field states shifts to lower, and the other to higher energies, giving rise, respectively, to a first-derivative EA signal and an ‘inverted’ first-derivative EA signal (where the negative lobe precedes the positive lobe in energy scale).

However, the splitting of the two signals, equal to $2mF$, is usually much smaller than the spectral width of the corresponding absorption band, so that the two first derivatives fuse into one second-derivative shape. This shape is considered typical for charge-transfer transitions.

When W is no longer negligible, it is convenient to introduce the symmetry-adapted basis functions $|\text{CT}\pm\rangle = 2^{-1/2}(|A^+B^- \rangle \pm |A^-B^+ \rangle)$. In this basis set, the Hamiltonian assumes the form

$$\begin{bmatrix} E^{\text{CT}} - \frac{1}{2}\Delta pF^2 - W & \mathbf{m} \cdot \mathbf{F} \\ \mathbf{m} \cdot \mathbf{F} & E^{\text{CT}} - \frac{1}{2}\Delta pF^2 + W \end{bmatrix}. \quad (6)$$

It should be noted that in the symmetry-adapted basis the dipole moment operator is off-diagonal ($\langle \text{CT} + |\mu| \text{CT} - \rangle = \langle A^+B^- | \mu | A^-B^+ \rangle \neq 0$), and the eigenvalue problem is exactly equivalent to that previously discussed in Section 2. The eigenenergies are again given by Eq. (1). The external electric field shifts the two eigenstates of CT origin apart, again giving rise to a pair of first-derivative signals (one simple, one inverted). The predicted EA signal now depends on the spectral

width of the corresponding absorption bands. If the width is larger than the splitting between the eigenstates, the two first derivatives combine into a second derivative, and a typical CT signal is recovered. In the opposite limit, when W is much larger than the spectral width, the simple first derivative signal due to the lower eigenstate is well separated from the inverted signal of the upper eigenstate, and both should be discernible in the EA spectrum as individual contributions. (In some dimer geometries other signal shapes may also emerge owing to field-mediated intensity transfer from one symmetry-adapted component to the other. This complication will not be discussed here.)

The sensitivity of the CT states to electric field is normally much larger than that of the Frenkel states. Firstly, as W is usually small, the interaction mediated by the field couples the zero-field states that are degenerate or nearly degenerate. Secondly, the length of the dipole moment involved is of the order of intermolecular rather than intramolecular distances. On the other hand, the intensity of optical absorption to the CT states is usually small, being limited by intermolecular overlap. In consequence, the CT absorption, often buried under intense vibronic satellites of intramolecular excitations, is rarely detectable, while the corresponding EA signal is comparable to that of Frenkel states, since the large shifts of the CT states in electric field compensate their small absorption intensity. There is a corollary to this observation: In any individual case, there may be no simple relationship between the absorption spectrum (dominated by intramolecular excitations) and the electro-absorption spectrum (where both the Frenkel and the CT states prominently contribute).

3.2. $D_e \neq 0$, $D_h \neq 0$, $F = 0$

In the absence of external electric field, the Hamiltonian is block-diagonalized by transformation to the symmetry-adapted Frenkel and CT basis set of the previous subsection. Both 2×2 Hamiltonians that result are readily diagonalized as in Section 2 to yield the eigenenergies

$$\begin{aligned}
 E_{1,2}^- &= \frac{1}{2} \left[(E - M + E^{\text{CT}} - W) \pm \sqrt{(E - M - E^{\text{CT}} + W)^2 + 4D_-^2} \right], \\
 E_{1,2}^+ &= \frac{1}{2} \left[(E + M + E^{\text{CT}} + W) \pm \sqrt{(E + M - E^{\text{CT}} - W)^2 + 4D_+^2} \right].
 \end{aligned}
 \tag{7}$$

The off-diagonal coupling $D_{\pm} = D_h \pm D_e$ always stabilizes the lower state (E_1) and destabilizes the upper state (E_2), thereby increasing the gap between the Frenkel and CT excitons. It should be noted that the states of different parity (+ or -) generally undergo different shifts. This behaviour has two concurrent reasons: Firstly, the off-diagonal matrix elements (D_+) and D_-) are usually different. Secondly, the energy separation between the coupled states also differs because of the difference in the energies of the two Davydov components, containing the Frenkel exciton resonance integral M with opposite signs. The influence of the different signs of W is usually marginal, as W is small.

The eigenvectors have now a mixed Frenkel-CT character. The degree of mixing depends on the difference between the diagonal energies of the basis configurations of different origin prior to their mixing. Quite often the starting states are amply spaced, and the CT integrals that couple them are much smaller than their separation. Consequently, the eigenstates may be reasonably well characterized by their provenance, either Frenkel or CT; the admixture from the other manifold is in that case relatively small.

Even if this is the case, the mixing has profound conceptual consequences.

On the one hand, the states of CT parentage now acquire some Frenkel character. As the intrinsic transition moments from the ground state carried by the CT configurations is small, being linear in intermolecular overlap integrals, even a modest admixture of the (potentially intense) Frenkel states considerably increases their absorption intensity. It also changes the polarization of the corresponding optical transitions, which may considerably affect the shape of the EA signal for some specific orientations.

On the other hand, the CT states share with the Frenkel states some of their high sensitivity to electric field.

3.3. $D_e \neq 0$, $D_h \neq 0$, $F \neq 0$

In the basis of zero-field eigenstates discussed in the preceding subsection, the polarizability-dependent part of the interaction with electric field remains diagonal. As previously, for each state it gives rise to a first-derivative EA signal, centred at the maximum of the corresponding absorption band. For the intense Frenkel states, this is a significant contribution. For the CT states it remains marginal, since in spite of the intensity borrowing from the Frenkel states, the absorption intensity of the eigenstates of CT parentage is still small.

The other term $\mathbf{m} \cdot \mathbf{F}$ contributing to the interaction with external electric field is mediated by the dipole moment operator. As mentioned in Section 3.1, the latter is off-diagonal in the symmetry-adapted basis. Being a vector, it couples those of the eigenstates (derived above) of the zero-field Hamiltonian that have different parity, and pushes them apart. In this way, the eigenstates deriving from $|\text{CT}+\rangle$ are coupled to $|\text{CT}-\rangle$ and $|\text{F}-\rangle$, while those deriving from $|\text{CT}-\rangle$ are coupled to $|\text{CT}+\rangle$ and $|\text{F}+\rangle$.

In typical electro-absorption experiments the electric field is weak, so that the dominant effect is due to the coupling between the states that are relatively closely spaced. In typical cases the zero-field splitting of the two states of CT provenance ($|\text{CT}+\rangle$ and $|\text{CT}-\rangle$) is smaller than the separation of these states from the Frenkel states, so it is their interaction that has to be considered in the first place. When compared to the situation where the CT integrals were neglected (*vide supra*), the main change (apart from the Frenkel state admixture which increases the absorption intensity) is in the gap between the two zero-field eigenstates, due to the difference in the shifts of the $|\text{CT}+\rangle$ and $|\text{CT}-\rangle$ resulting from their coupling to the Frenkel states. This difference may considerably exceed the original splitting $2W$ between the two

symmetry-adapted states of CT origin. If it also happens to exceed the spectral width of the corresponding absorption bands, the pair of first-derivative signals which were expected to fuse into a second-derivative shape as long as the coupling with the Frenkel states was neglected, now may readily split into two separate first-derivative contributions (one simple, one inverted). While in the classic phenomenological analysis of electro-absorption spectra the former situation would be considered the normal one, in reality the latter is equally likely.

As the zero-field eigenstates of Frenkel origin have now some CT admixture, a part of the off-diagonal dipole moment of the symmetry-adapted CT states spills into the Frenkel manifold. It couples $|F+\rangle$ to $|CT-\rangle$ and $|F-\rangle$ to $|CT+\rangle$. The coupling is weaker than that between the two zero-field eigenstates of CT origin on two accounts: Firstly, only a fraction of the original CT dipole moment is transferred to the Frenkel states, and secondly the energy gap between the Frenkel and CT states is usually larger than the splitting between $|CT+\rangle$ and $|CT-\rangle$. Nevertheless, it is a significant contribution, since originally there was *no* matrix element of the dipole moment operator that would couple the Frenkel states to any other excitations (the transition dipole moment μ_{01} , governing the optical absorption, provides the coupling to the *ground state*, which is much more distant).

As usually, the off-diagonal perturbation $\mathbf{m} \cdot \mathbf{F}$ pushes the coupled states apart. Consequently, if the Frenkel state is located below the CT state, it is stabilized; if it is located above the CT state, it is destabilized. Direct derivation shows that this shift is quadratic in electric field, so it may be interpreted in terms of an additional contribution to the polarizability, in the former case positive and in the latter case negative. The energy of the lowest intramolecular excitation is usually lower than that of the lowest CT state; hence the polarizability of the lowest Frenkel state is increased due to the coupling with the CT manifold. This contribution to polarizability, sometimes referred to as ‘intermolecular’ or ‘non-local’, is substantial: It may exceed several times the intramolecular polarizability discussed in Section 2 (which is the case e.g. in polyacenes [2]).

By the same token, the above analysis predicts a *decrease* of the polarizability in higher Frenkel states with respect to its molecular value. To date, no direct experimental evidence of this effect seems to have been observed.

The cases that have been considered so far are idealized: The energy gap between the Frenkel and CT states is assumed to be large with respect not only to the energy of the interaction with the electric field, but also to the spectral width of individual absorption bands. This allows one to separate the EA contributions from different states. In real situations this is not always the case. In general, the EA signals from individual states may be impossible to resolve and the various effects discussed above may combine. Especially interesting results are expected when the resonance splitting of the Frenkel state considerably exceeds the energy gap between the intramolecular excitation and the CT manifold, which is then enclosed between the two Davydov components and affects each of them in a different way.

4. Single crystal versus polycrystalline sample

From the conceptual point of view, in most respects the difference between the dimer and the crystal is quantitative rather than qualitative. There are many molecules, but owing to the translational symmetry the Hamiltonian is separable into commuting contributions corresponding to the different values of crystal momentum \mathbf{k} from the first Brillouin zone. Due to the $\mathbf{k} \cong 0$ selection rule, only the states at the centre of the zone are of spectroscopic interest.

The number of physically distinct Frenkel states is equal to the number of molecules in the unit cell. The situation is slightly more complex for the CT states.

In the first place, the two charges need not be located at the nearest neighbour molecules; essentially, the hole may reside at any molecule of the crystal, and the electron at any other molecule. These different CT states may be characterized by the relative crystallographic position of the electron with respect to the hole (for simplicity located at the centre of coordinates); accordingly, there are

families of CT states with different distance between the two charges. The large-radius CT states are crucial for the photocurrent [3–5], but their contribution to the absorption and electro-absorption spectra is marginal: Both the intrinsic transition dipole moment carried by the CT states and the CT integrals that govern the intensity borrowing from the Frenkel manifold are roughly proportional to the intermolecular overlap integrals, and these decrease exponentially with intermolecular distance. In effect, only the CT states engaging nearby molecules are spectroscopically relevant.

The above restriction eliminates most of the CT states from the scope of our present interest, but even the remaining ones are quite numerous. A CT state engages *two* molecules: Given the position of the hole, the electron may be located at any of the surrounding molecules, also those that belong to the adjacent unit cells. Consequently, the number of relevant CT states that have to be included in the minimal basis set spanning the Hilbert space of low-energy crystal excitations exceeds, as a rule, the number of Davydov components of the Frenkel state.

In order to illustrate this point, let us consider the anthracene crystal, which is monoclinic and its unit cell contains two molecules related by a screw axis and a glide plane. Suppose that the hole is located at the first of the two molecules of the central unit cell, i.e. at the position (0,0,0). Then all of the four CT states with the electron located at $(\pm 1/2, \pm 1/2, 0)$ are equally feasible and have to be treated on equal footing. They are characterized by the same electron–hole distance (hence their diagonal energies are the same), and are transformable into each other by the symmetry operations of the crystal space group. Yet, only *one* of these states engages the second molecule from the same unit cell; in the other three states molecules from different unit cells are involved. Likewise, the hole could have been located at the second sublattice [position $(1/2, 1/2, 0)$], again giving rise to four symmetry-equivalent (but physically distinct) CT configurations.

When the eigenstates of the crystal are sought along the lines sketched for a dimer in the preceding section, all of the *eight* CT configurations

described above have to be consistently included; this is to be compared with the total of *two* Davydov components of the Frenkel state. In actual calculations for anthracene and similar crystals, also the $(0, \pm 1, 0)$ CT configurations have to be taken into account, since their diagonal energies are close to those of the $(\pm 1/2, \pm 1/2, 0)$ configurations; there are altogether four such states, as the hole may be located at either of the two sublattices, and the electron may reside on either side of the hole. This produces the total number of 12 CT configurations of spectroscopic relevance [6].

In contrast to the dimer case where the local CT configurations were coupled only by the charge-flip integral W (quadratic in intermolecular overlap integrals), which determined the (marginal) splitting between the zero-field symmetry-adapted states of Eq. (6), the corresponding symmetry-adapted configurations of the crystal are split by the electron (J_e) and hole (J_h) transfer integrals that are linear in intermolecular overlaps. The reason for this behaviour may again be illustrated on the anthracene case. As has already been mentioned, the local CT states with the hole at the centre of coordinates and the electron at $(1/2, 1/2, 0)$ and at $(1/2, -1/2, 0)$, respectively, are symmetry-equivalent in the crystal symmetry group, and hence their diagonal energies are equal. Consequently, as usually in degenerate manifolds, the splitting between the levels corresponding to their symmetry-adapted combinations must be linear in the perturbation that couples the local states. At the same time, the $(1/2, 1/2, 0)$ and $(1/2, -1/2, 0)$ may be turned into one another by moving *one* electron from one molecule to the other, hence the corresponding transfer integral depends on the *first* power of the intermolecular overlap integral. It follows that so does the splitting of the appropriate energy levels. A similar argument holds for the local CT configurations coupled by the hole-transfer integral, and the resultant splittings are governed by the sum and the difference of the electron and hole transfer integrals [7]; these are much larger than the charge-flip integral W , operative in the dimer.

This has two consequences: Firstly, in the presence of the terms linear in intermolecular

overlaps those that are quadratic may normally be safely neglected. Secondly, the splitting between the different symmetry-adapted CT configurations prior to their mixing with the Frenkel states is considerably larger. Accordingly, while in a dimer observation of discernible first-derivative EA signals from individual eigenstates of CT parentage was a remote possibility and a fused second-derivative signal was usually to be expected, in the crystal the CT states may readily produce the EA spectra of either shape, or a combination thereof. The latter is the case in polyacenes [6]. In fullerene, owing to the high symmetry of the lattice, the effects of the coupling mediated by the electron and hole transfer integrals for different crystal directions cumulate to split one of the levels of CT origin as far as 0.2–0.3 eV off the other states, giving rise to a well pronounced first-derivative EA signal [8].

In view of the short range of the off-diagonal CT interactions due to exponential dependence of the CT integrals on intermolecular distance, the actual spatial extent of the crystal affects only the diagonal energies of the CT configurations, via the electrostatic energy contribution (polarization and quadrupole interactions). The latter rapidly converges with increasing distance, so that practically only the CT states of the surface layer are substantially influenced by crystal boundaries [9,10].

This behaviour has to be contrasted with that of the Frenkel states. In the crystal, the actual splittings in this manifold (prior to the mixing with the CT states) are governed by the so-called lattice sums, containing the exciton-resonance integrals for all the surrounding molecules of a given sublattice, weighted by a phase factor dependent on crystal momentum \mathbf{k} ,

$$M(\mathbf{k}) = \sum_l M(\mathbf{R}_l) \exp(i\mathbf{k} \cdot \mathbf{R}_l). \quad (8)$$

The individual contributions to the lattice sums depend on the intermolecular distance as R^{-3} (dipole–dipole interaction), whereas the number of molecules at a given distance increases as R^2 . Therefore, the net contribution corresponding to a given distance decreases as R^{-1} , giving rise to a series that is only conditionally convergent. In effect, even infinitely distant molecules give a finite

contribution to the sum, and the result depends on the boundary conditions, specifically on the assumed shape of the crystal.

Nevertheless, the Ewald method [11] or alternatively the de Wette–Schacher planewise summation method [12] allow one to calculate the lattice sums. At crystal momentum approaching zero, they turn out to depend on its direction [13–15]; evidently, even the residual effect of the oscillating phase factor in Eq. (8) is crucial for the actual value of the sums. It follows that at $\mathbf{k} \cong 0$ the energies of the Frenkel states exhibit non-analytic behaviour, depending on the direction in the Brillouin zone. For each Davydov component, two limiting cases may be discerned, namely when \mathbf{k} is perpendicular and when \mathbf{k} is parallel to the transition dipole moment, corresponding to the transverse and longitudinal exciton, respectively; the energy of the latter is higher.

Owing to the non-analytic term in Frenkel exciton energy at $\mathbf{k} \cong 0$, the energies of the corresponding optical transitions depend on the direction of incident radiation, so that the observed absorption spectrum depends on crystal orientation. This dependence is substantial only for intense transitions where the length of the transition dipole moment is comparable with the lattice period, as e.g. in sexithiophene. In a polycrystalline sample, the crystallites differently oriented with respect to the incident photons absorb at different energies, giving rise to spectral broadening. For sexithiophene, this effect was successfully modelled both at the phenomenological [16,17] and microscopic [18,19] level.

When compared to the dimer case, the above picture and the cited calculations [16–19] correspond to the first model situation of the preceding section where the coupling between the Frenkel and CT states is disregarded ($D_c = D_h = 0$). In reality, the two manifolds are coupled by the Frenkel exciton dissociation integrals. The actual eigenstates of the crystal (which subsequently interact with incident radiation to give the spectra) are mixtures of the two types of excitations. In order to calculate them, the crystal Hamiltonian has to be constructed in the Hilbert space spanned by the Frenkel states and all the relevant CT states discussed above, then Fourier-transformed to

crystal momentum representation, and its $\mathbf{k} = 0$ block diagonalized; the latter almost always must be done numerically.

For the sake of the present analysis where only qualitative insight into the properties of the solutions is needed, this tedious process may be avoided. It is sufficient to note that the off-diagonal interaction mediated by the dissociation integrals pushes the two manifolds apart, and that their eventual shifts depend on the energy separation of the initial states prior to their mixing. Then it is evident that the directional dependence of Frenkel state energies will also affect the eigenstates of CT parentage, although for them the effect is expected to be weaker, since it is indirect.

As the EA contributions from the CT states are usually large, this conclusion is crucial for the understanding of the electro-absorption spectra. The EA signal of the CT states is bound to exhibit directional dependence [20], as absorption intensity depends on the orientation of the transition dipole moment with respect to incident radiation, while the scalar product of the permanent dipole moment with the strength of the external electric field governs the level shift. Yet, these factors influence only the intensity of individual EA features; the argument presented above demonstrates that (in strongly absorbing crystals) also their energies may be affected [21].

In a polycrystalline sample different crystallites are differently oriented with respect to incident radiation. Morphological data give some information about the incidence of various orientations, which may be modelled statistically. The spectrum is a superposition of the spectra of individual crystallites, so it is bound to differ from that of a single crystal. The differences may be substantial for intense transitions, since in that case the non-analytic contributions to exciton energy are large.

5. Vibronic coupling

In the above considerations, the vibrational degrees of freedom have been entirely disregarded. In reality, the geometry of most molecules changes upon electronic excitation or ionization, which

generates a coupling of the electronic states to molecular vibrations.

The gist of the problem is best discussed for a dimer [22–24]; generalization for a larger number of molecules is mathematically complicated and often intractable numerically, but conceptually straightforward.

The behaviour of the system in hand is governed by the ratio of the vibronic deformation energy to the splitting between the electronic levels (gauged e.g. by the Davydov splitting in a molecular crystal). Simple solutions are obtainable when this ratio is either very small or very large, which corresponds to the limits of weak vibronic (or strong intermolecular) coupling, and of strong vibronic (weak intermolecular) coupling, respectively.

In the limiting case of weak vibronic coupling [22], each electronic transition is accompanied by the satellites whose positions are shifted by $\nu = 1, 2, 3$ etc. vibrational quanta, and the intensities are well approximated by the Poisson distribution, characterized by the value of the displacement parameter (related to the so-called Huang–Rhys factor). The corresponding EA signals, obtained as the difference between absorption spectra calculated at non-zero and at zero electric field, are shifted and weighted in a similar way.

In the opposite limit of strong vibronic coupling [6,22], the vibrational excitation is bound to the electronic excitation and perfectly follows it in its motion from one molecule to another. The off-diagonal elements of the Hamiltonian matrix (M, W, D, J) are scaled by the vibrational overlap integrals. In effect, there is a different effective Hamiltonian for each value of the vibrational quantum number ν . The eigenstates have to be obtained by diagonalization to yield the energies and intensities of the optical transitions; the EA spectrum is again obtained as the difference between the appropriate absorption spectra.

In realistic situations, the coupling to vibrations is intermediate and the electronic excitation may drag a cloud of virtual vibrational excitations on nearby molecules [25]. In the crystal, unbound states with vibrational excitation moving independently from the electronic excitation, also occur and can be optically probed [25]. The

intermediate cases may be theoretically investigated only by tedious numerical diagonalization of the vibronic Hamiltonian. This is feasible for a model one-dimensional crystal [25] or (if the CT states are ignored) for relatively small aggregates [26], but for the complex structure of an actual crystal has never been successfully treated.

The intricacies of vibronic coupling must be necessarily included in the discussion of crystal emission spectra where it may have dramatic consequences [23,27,28]. In absorption these complexities give rise to intensity redistribution [25], but even in some intermediate cases the spectrum obtained in the strong-coupling limit is a reasonable approximation. Actually, in most cases of interest the EA spectrum should be amenable to acceptable reproduction either in one or in the other limit. This holds a fortiori for thin film spectra where the disorder-induced broadening is an important factor.

A technical difficulty arises in the cases where the absorption spectrum is dominated by a very intense Frenkel excitation, which also strongly couples to CT states. Owing to the non-analytic contribution to Frenkel state energy, the electronic splittings may be very large for some crystallite orientations (longitudinal excitons), but for other orientations quite small (transverse excitons). In sexithiophene, the only case for which the film spectrum has been modelled in these circumstances [21], this problem is circumvented by switching between the weak-coupling and strong-coupling limits at a certain threshold value of the Davydov splitting, of the order of the vibronic deformation energy. It seems reasonable to expect that although the values of the transition energies and intensities calculated in this way are not very accurate, the discrepancies should be masked by the averaging over different crystallite orientations, which produces broad spectral features with individual transitions unresolved.

6. Theoretical calculations of EA spectra

The Hamiltonians describing the coupling between the different kinds of Frenkel and CT excitations in any actual crystal are complicated

because of the large number of states involved. Normally, only the lowest Frenkel and CT excitons are taken into account, and only the terms up to the linear order in the (small) intermolecular overlap integrals are retained. The calculations of this kind have been done for anthracene, tetracene, pentacene [6], fullerene [8], perylenetetracarboxylic dianhydride (PTCDA) [29] and sexithiophene [21,30].

Only in this last case the effect of directional dispersion (non-analyticities in exciton energies) has been explicitly taken into account; consequently, only this case exemplifies the whole range of effects described in the preceding sections. Moreover, only for this particular system the EA spectrum of a single crystal is available [31], which offers a more stringent test on the theoretical model than the (commonly available) thin-film spectra. For this reason, sexithiophene will be taken here as an illustrative example.

The specific form of the model Hamiltonian follows directly from crystal structure. In sexithiophene, the four molecules contained in the unit cell are arranged in two closely spaced pairs. The distance between the pairs is much larger, so that the corresponding CT interactions are much weaker and may be safely neglected. In effect, the crystal may be well approximated by the herringbone structure analogous to that encountered in polyacenes.

The parametrization is amply discussed in [30]; here it will be only briefly summarized. Generally, the input parameters were either extracted from literature data based on independent experiments on isolated molecules, or calculated by appropriate quantum chemical/microelectrostatic methods, and in some cases subsequently modified by up to 10–15% (i.e. within the inherent accuracy of these methods) to fit the experimental EA spectrum.

It is a standard practice in this kind of calculations to derive the properties of the crystal or film from the properties of the isolated molecules, which are taken for granted. This may yield the diagonal energies and the transition dipole moments of the Frenkel states, the molecular ionization potential I and electron affinity A . As these values are not always available from independent measurements, it is sometimes necessary to estimate them based on

the results of quantum chemical calculations. The energies and intensities of intramolecular excitations are best calculated by Time-Dependent Density Functional Theory (TD DFT), the difference $I - A$ needed to calculate the CT state energies may be estimated by DFT calculations with some corrections for systematic errors [32].

In the specific case of sexithiophene, the energies and transition moments of the intramolecular excitations were taken from the experimental data available in the literature. In order to get the diagonal Frenkel exciton energies, one has to include also the gas-to-crystal site shift, dominated by dispersion forces and difficult to estimate quantitatively. Consequently, the energy of the lowest excitation of intramolecular origin was adjusted by fitting the position of the corresponding absorption band to that observed experimentally. The diagonal energies actually used in the calculations are 2.52, 2.80, 3.30, 3.63, 4.12 and 4.20 eV for the five intramolecular excitations included in the model.

The energies of the CT states (2.66, 2.75 and 2.83 eV for the three lowest configurations) were based on the value of $I - A = 4.9$ eV (from DFT calculations). The most recent state-of-the-art approach to the calculation of electrostatic stabilization energies explicitly accounts for the field-induced changes of π -electron population at individual atoms of the molecule, and includes the σ -electron contributions to polarizability in an effective way [33,34]. In our calculations for sexithiophene a less sophisticated approach was adopted, using the Fourier Transform (FT) method in submolecule resolution [35]. A similar approach was used to calculate the analytic part of the lattice sums of the resonance integrals describing the transfer of Frenkel excitons.

For calculating the charge transfer integrals we used a tight-binding fit to the results of orbital band structure calculations performed within the DFT approach. The values of the integrals are listed in the original paper [30]. The diagonal dipole moments of the localized CT configurations that form the basis set follow directly from the crystal structure. The corresponding transition moments were assumed to be roughly the same as in polyacenes [6].

The textural disorder in the film was simulated by adopting a Gaussian-type probability function for the angle θ describing the deviation of the long crystal axis from the normal to the substrate [35].

Two vibrational modes were explicitly taken into account: the normal mode ($\omega_1 = 1450 \text{ cm}^{-1}$) which forms the most prominent Franck–Condon progression [36], and a low-frequency mode ($\omega_2 = 340 \text{ cm}^{-1}$, discernible in absorption only at high resolution [37,38]). The corresponding vibronic displacement parameters were estimated from the experimental absorption spectra of matrix-isolated molecules, available in the literature.

For the low-frequency vibration, characterized by a small value of vibronic deformation energy, the adiabatic approximation was consistently adopted. For the high-frequency mode the adiabatic (weak vibronic coupling) approach was used for the crystallites where the Davydov splitting exceeded the threshold value of 0.2 eV, while for smaller Davydov splittings the model of strong vibronic coupling was used. The threshold was adjusted by fitting the experimental EA spectrum; it is consistent with the vibronic deformation energy for the high-frequency mode.

The resultant spectra of the single crystal and of the film are shown in Fig. 1, and compared with the experimental ones available in the literature.

The agreement is excellent for the single crystal and good for the film. Qualitatively, the results may be rationalized in the following way.

Owing to the peculiar geometric arrangement of the molecules in the T6 lattice the lower Davydov component (b -polarized, located at about 2.3 eV) of the lowest intramolecular transition of sexithiophene is practically forbidden; it acquires some intensity by vibronic coupling [38], but by far not enough to exhibit a substantial orientation-dependent shift. The corresponding EA signal follows the first derivative of the absorption spectrum (as usual for an isolated Frenkel state).

In contrast, the upper Davydov component (c -polarized) is very intense, so that the non-analytic contribution to its energy is large; in consequence, the energy of this component differs by several thousand wavenumbers for different crystal orientations. For the specific arrangement in which the single crystal spectrum was measured [31] the

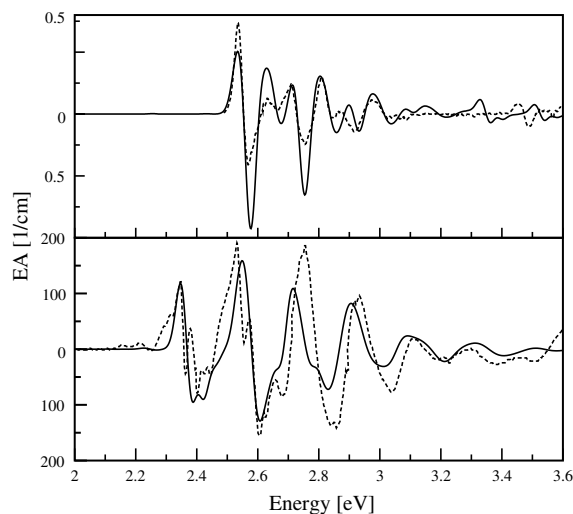


Fig. 1. Calculated and experimental electro-absorption spectra of sexithiophene: upper panel—single crystal (calculated: solid line [29], experimental: broken line [30]); lower panel—thin film (calculated: solid line [21], experimental: broken line [16,17]).

eigenstates of CT parentage are located between the two Davydov components. They dominate the EA spectrum in the 2.6–2.7 eV region; their signal, mostly of second-derivative shape, is due to the field-induced coupling between the different zero-field eigenstates of CT origin, mediated by the CT dipole moment, off-diagonal in this basis set (as in Eq. (6)).

The broad absorption due to the upper Davydov component gives rise to a marginal EA signal, as the corresponding derivative is small. On the other hand, the CT contribution, relatively weak in absorption, is very prominent here, which again was to be expected. The evident difference [16,17] between the spectra of the single crystal [31] and polycrystalline film [16,39] documents the effects of the indirect influence of Frenkel state non-analycities, transmitted to the CT manifold by off-diagonal interactions, as described above.

As in fullerene, one of the eigenstates of CT parentage is split far off the others and gives rise to a first-derivative signal. Being *c*-polarized, it does not contribute to the measured single crystal spectrum [31], but is activated for other crystallite orientations. It is observable in the film spectrum at about 2.4 eV, superimposed on the weak vib-

ronically induced contribution from the lower Davydov component.

The agreement with experiment, achieved both for the single crystal and for the film as a result of the calculations based on a microscopic model, provides a strong confirmation of the applied approach. Moreover, the CT assignment of the states in the 2.6–2.7 eV energy range is supported by independent arguments based on the measurements of the pressure dependence of the absorption spectrum [40].

This assignment is in conflict with the original interpretation [16,17,31] where all the observed transitions were attributed to Frenkel states. This required the ad hoc assumption that an intense Frenkel state gives rise to the second-derivative EA signal, i.e. that the corresponding field-induced shift is proportional to the first power of the off-diagonal matrix element of the dipole moment operator (transition moment). The said assumption is difficult to reconcile with basic premises of quantum theory and is in conflict with the interpretational paradigm consistently used in EA spectroscopy [41,42]. In contrast, the present approach is based on a well defined microscopic Hamiltonian and has already successfully reproduced the EA spectra in a number of cases [6,8,29].

This consistency, lending credence to the method, opens some possibilities of new applications. On the one hand, the orientational dependence of the EA spectra offers a chance to use EA spectroscopy, accompanied by theoretical modeling, as a tool for texture studies. On the other hand, the agreement between the parameters of the model Hamiltonian that successfully reproduce the spectra and those calculated microscopically validates a simplified approach where the microscopic Hamiltonian would be parametrized by direct phenomenological fit of the experimental EA spectrum, which will enable one to apply the same methodology for systems of much larger complexity.

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