Transition dipole moments of charge transfer excitations in one-component molecular crystals

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ABSTRACT

Owing to the peculiar structure of oligothiophene crystals, their low-energy *b*-polarized spectra are dominated by the contributions from charge transfer states almost free from Frenkel state admixtures, offering a unique opportunity for in-depth studies of the former. Here, a simple model, rooted in the Mulliken theory of charge transfer transitions, is proposed to estimate the relevant transition dipole moments. For sexithiophene, the resultant estimate agrees with the value used in the recent detailed theoretical reproduction of the absorption and electroabsorption spectra, and is found to be consistent with other input parameters. The approach presented here is readily applicable for other one-component molecular crystals, providing a simple method to estimate the intrinsic transition dipoles of charge transfer configurations.

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1. Introduction

Owing to the (potential and actual) applications of organic molecular crystals in optoelectronics, theoretical description of these systems is being revisited nowadays with new goals in mind. In the new context, the charge-transfer (CT) excitations, characterized by a finite distance between the electron and the hole, come into focus, constituting a bridge between the intramolecular (Frenkel) excitons, which (being endowed with large transition intensities) couple the system to the radiation field, and the unbound electron–hole pairs where the two charge carriers are separated by a distance large enough to make their interaction negligible, which couple the system to the electric field and charge carrier reservoirs.

The recently rediscovered crucial role of CT states for Frenkel exciton energetics in oligoacenes [1] is one of the facets of this new perspective. As noticed about twenty years ago [2], the interaction with the CT states, mediated by electron- and hole-transfer integrals, substantially affects the dispersion of Frenkel states (to the extent of changing the sequence of Davydov components). This was originally reported for tetracene and pentacene [2], to be experimentally confirmed (in the latter case) a few years back [3]. While the original finding was based on a very simplistic model [2], somewhat extended later [4], the present computational results

obtained for tetracene [1] are rooted in full-fledged first-principles theory, leaving no doubt regarding their validity.

However, this recent development is focused specifically on the properties of the eigenstates of Frenkel origin, with the CT manifold acting merely as a perturber of the energy levels naturally defined by the resonance interaction between the molecules. In this way, the CT states are probed only indirectly, with their own spectral contributions tentatively ignored. Admittedly, in oligoacene absorption they are certainly very weak, probably diffuse and masked by the vibronic replicas of the Frenkel state, which makes their observation practically impossible. They are accessible to electroabsorption (EA) spectroscopy, but for the time being an updated reproduction of the corresponding experimental data has been relegated to future work [1].

Meanwhile, a complete approach which allows one to treat the electroabsorption [5] and absorption spectra [5,6] within the same consistent framework has been proposed and applied for the sexithiophene crystal (6T) [7]. Owing to the peculiar lattice geometry, in oligothiophenes the *b*-polarized Frenkel absorption is negligible in the range corresponding to charge transfer excitons whose contribution is therefore not masked [6,8]. By the same token, the *b*-polarized transition dipole moment borrowed by the CT states from the Frenkel states is marginal, in contrast to the situation in oligoacenes.

In consequence, for 6T and other oligothiophenes there is an energy range where the intensity of *b*-polarized absorption is entirely due to the intrinsic transition dipole moment carried by the CT configurations, which evidently is not negligible and, being the sole

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contributor, is becoming important in this new context. However, it is rather an elusive quantity. Its estimates for other systems were crude, and its actual value for oligothiophenes has never been theoretically estimated. This is the objective of the present paper.

In the pioneering theoretical papers on CT excitons [9–11], the intrinsic CT absorption was consistently disregarded. It was noticed at that time that the eigenstates of CT origin are bound to borrow some transition moment from Frenkel excitons, owing to the coupling mediated by charge transfer integrals (in this context called dissociation integrals), but the contribution from the intrinsic CT transition dipole was not invoked. The fact that this latter contribution, although admittedly small, might in principle be comparable to the former, was to become apparent only later, when the first attempt was made to predict the intensities of anthracene electroabsorption features, based on a model explicitly including the off-diagonal couplings within the CT manifold (as well as with Frenkel states) and accounting for the translational symmetry of the crystal [12]. Based on a crude numerical estimate [13], the intrinsic contribution (on the order of a few hundredths of eÅ) was later included in the successful simulation of the experimental EA spectra of oligoacenes [4], and was subsequently adopted in papers that followed. The approach was inherently simplistic; among other inherent shortcomings, the underlying approximations forced the predicted CT transition dipole to be directed along the line joining the centers of the molecules involved in charge transfer, i.e. to be strictly parallel to the permanent (diagonal) dipole moment of the corresponding CT state.

Somewhat later, the issue got revisited for a different system (perylenetetracarboxylic anhydride, PTCDA) using a more sophisticated methodology. Within a more realistic model at the semiempirical ZINDO level, Hoffmann [14–16] found the direction of the CT transition dipole to deviate from the axis joining the centers of the two molecules and used his conclusions to extract the effective value of the corresponding transition dipole moment by fitting the experimental absorption spectra [14–16]. In passing, he insightfully alluded to the description of CT states proposed by Mulliken for donor–acceptor complexes [14] and extensively referred to in the literature.

Here we will explore his idea, applying the Mulliken approach in a new context. It will enable us to relate the CT transition dipole moment to other input parameters (for which more accurate estimates are available) used in the successful theoretical reproduction of the sexithiophene absorption and electroabsorption spectra [7]. Our study is focused on the lowest (nearest neighbor) CT configuration, crucial for b-polarized oligothiophene spectra where interference from other states is practically negligible, which makes this particular state perfectly suited for testing the intensity scale.

2. Model

Typically, theoretical description of excitons in molecular crystals operates within the subspace of electronic excited states, essentially ignoring their coupling to the ground state of the system. This is one of the crucial advantages of the exciton concept, enormously reducing the formal and computational burden. Were the approach formulated in the basis of Hartree–Fock states of the crystal as a whole, by virtue of the Brillouin theorem it would also be a nearly perfect approximation. Yet, in order to avoid major complications, it is in fact normally couched in terms of *molecular* states, *crystal* eigenstates being the sought result.

In the molecular basis, there is no general reason for the non-diagonal matrix elements of the intermolecular interaction operator between the ground and excited states to vanish. In energy terms, their neglect is entirely justified, since the relevant energy

separation is large as a rule so that the resultant shifts are marginal. However, the mixing between the ground state and the excited states has also an effect on absorption intensities, which for some weak transitions may be significant. This is the case for charge transfer states, as illustrated by the following argument, rooted in the Mulliken model [17].

Let us consider a pair AB of centrosymmetric molecules which we tentatively assume to be different (this limitation will be relaxed later). As a first approximation, the environment (e.g. the rest of the crystal in which the model dimer is embedded) is not explicitly included in the model, but its electrostatic effect is implicitly accounted for in the effective diagonal energies of the relevant CT states.

Suppose that molecule A has a low ionization potential and low electron affinity, while molecule B has a high ionization potential and large electron affinity. Then the energy gap between the A^+B^- and A^-B^+ CT states is large and each of them may be treated separately. We will focus on the first configuration.

The unperturbed wavefunction of the pair $|A^+B^-\rangle_0$ is built from the molecular orbitals of the isolated moieties (presumably orthogonalized). When the distance between A and B is finite, but not too small, the matrix element of the pair Hamiltonian $V = {}_0\langle AB|H|A^+B^-\rangle_0$ does not vanish, yet it is (by assumption) much smaller than the energy gap $\Delta = E_{CT} - E_g$ between the CT state and the ground state of the pair. In that case, the intermolecular interaction may be considered as a perturbation and (correct to first order) the eigenstates of the pair may be approximated as

$$|A^+B^-\rangle = |A^+B^-\rangle_0 + \frac{V}{\Delta}|AB\rangle_0, \tag{1a}$$

$$|AB\rangle = |AB\rangle_0 - \frac{V}{\Delta}|A^+B^-\rangle_0. \tag{1b}$$

The transition dipole moment from the perturbed ground state to the perturbed CT state is then given by

$$\begin{aligned}
\langle AB|\mathbf{M}|A^+B^-\rangle &= \left(1 - \frac{V^2}{\Delta^2}\right){}_0\langle AB|\mathbf{M}|A^+B^-\rangle_0 \\
&+ \frac{V}{\Delta}{}_0\langle A^+B^-|\mathbf{M}|A^+B^-\rangle_0 + \frac{V}{\Delta}{}_0\langle AB|\mathbf{M}|AB\rangle_0.
\end{aligned} \tag{2}$$

As the moieties are centrosymmetric, the last integral vanishes. If the molecules are embedded in a crystal, their distance R_{AB} is usually very large by molecular standards, and so is the permanent (diagonal) dipole moment of the CT configuration ${}_0\langle A^+B^-|\mathbf{M}|A^+B^-\rangle_0$. Hence, on the right-hand side the second term is expected to dominate. It is worth noting that its direction coincides with that of the permanent dipole moment of the charge transfer configuration in hand. As noticed by Hoffmann [14–16], the leading contributions to the integral in the first right-hand side term come from the regions where the orbitals of the two moieties strongly overlap; in general, these regions are not oriented in any special manner with respect to the radius vector joining the centers of the molecules, which results in deviations of the CT transition dipole from the direction of the corresponding permanent dipole moment. The deviations are not expected to be very large, but are not necessarily negligible.

The same line of reasoning may be applied for the configuration with reversed charges $|A^-B^+\rangle$. If the two moieties are identical, the unperturbed energies of the two configurations are the same. However, an elementary estimate shows that the splitting in the CT manifold, induced by the interaction with the ground state, is marginal ($\sim 10^{-3}$ eV) and may be safely neglected in comparison with other interactions, as long as the CT excitation energy and the CT integral V are of the order of those encountered in typical one-component molecular crystals (such as oligoacenes or oligothiophenes).

In effect, there is no need to invoke explicitly the coupling of the exciton subspace with the ground state, provided that the intrinsic transition dipole of CT configurations is identified with that of Eq. (2). The total value from Eq. (2) is usually quite small compared to typical transition dipole moments of Frenkel states. Although only a fraction of the latter is lent to the eigenstates of CT origin (the lending being mediated by exciton dissociation integrals), it suffices to account for most of the observed CT state intensity; at least in oligoacenes, the intrinsic CT transition dipoles were apparently a mere correction [18]. However, with present perspective their original a priori estimates [12,13] seem to have been too low, so that this statement should be taken with a grain of salt. As no single-crystal electroabsorption spectra were available for those systems, confrontation with experiment was then possible only for film samples, which precluded more stringent tests based on the different polarization of Frenkel and CT transition dipoles, whereas some potential discrepancies might have been absorbed in the values of dissociation integrals, known only approximately.

The situation is different in oligothiophenes. For 6T the b-polarized electroabsorption spectrum is available and the absence of Frenkel b-polarized contribution to optical absorption of the eigenstates of CT parentage exposes the intrinsic CT contribution, allowing one to test its estimate almost quantitatively. Here, we are taking advantage of this opportunity.

3. Dependence on intermolecular overlap

Some of the input parameters needed to estimate the transition dipole moment of Eq. (2) are ready to hand. The permanent dipole moment of a CT configuration is determined by the positions of the two molecules in the lattice and may be obtained from the known crystal structure. The energy gap Δ may be identified with the diagonal energy of the corresponding CT configuration prior to its mixing with other CT and Frenkel states, described by exciton theory such as that presented e.g. in Ref. [7] (it might alternatively be approximated by the energy of the resultant eigenstate of CT parentage, owing to the modest size of the splittings induced in this manifold by the interactions within exciton subspace).

The order of magnitude of the matrix element $_0\langle AB|\mathbf{M}|A^+B^-\rangle_0$, as well as that of the charge transfer integral $V = {}_0\langle AB|H|A^+B^-\rangle_0$, is limited by intermolecular overlap. In the following, we will use an approximate approach to focus on this dependence. Reduced to orbital basis, both integrals of interest engage the HOMO of molecule A and the LUMO of molecule B. These can be easily found using a standard quantum chemistry program package.

According to Tanaka [19], a rough estimate of the CT integral is given by

$$V = KS, \tag{3}$$

where $S = \langle A^{HOMO}|B^{LUMO}\rangle$ is the overlap integral between the HOMO of the electron-donating molecule A and the LUMO of the electron-accepting molecule B.

The constant K, obviously depending on the level of approximation used to evaluate the overlap integral, should be adjusted to the specific basis set applied here. Based on the Mulliken approximation, the scaling factor K for the HOMO–LUMO integral is approximated as the mean of those appropriate for the HOMO–HOMO (K_h) and LUMO–LUMO (K_e) cases, which are bound to differ significantly. The requisite electron and hole transfer integrals $J_e = \langle A^-B|H|AB^-\rangle = \langle A^{LUMO}B|H|AB^{LUMO}\rangle$ and $J_h = \langle A^+B|H|AB^+\rangle = \langle A^{HOMO}B|H|AB^{HOMO}\rangle$ are available as a reference, having been evaluated in the past from a tight-binding fit to the results of band structure calculations in a large plane-wave basis set [7,20].

The estimate of the HOMO–LUMO matrix element needs to be corrected in one respect. As noted earlier, the perturbation approach leading to Eq. (2) is strictly valid in an orthogonal basis set. To compensate for the fact that the basis functions used in Eqs. (1b), (2) are not orthogonalized, we follow the standard practice [21] of replacing V in the actual estimates by the effective value

$$V_{eff} = V - \frac{1}{2}S\Delta. \tag{4}$$

The other needed ingredient, i.e. the off-diagonal matrix element of the dipole moment [the first term on the right-hand side of Eq. (2)] is approximated according to Mulliken [17]

$$_0\langle AB|\mathbf{M}|A^+B^-\rangle_0 = \sqrt{2}e(\mathbf{R}_A - \mathbf{R}_0)S, \tag{5}$$

where e is the electron charge, $\mathbf{R}_A$ is the radius vector of the center of moiety A, and $\mathbf{R}_0$ is the radius vector of the center of gravity of the transition density between the two states, for the sake of simplicity tentatively identified with the midpoint between the geometric centers of the two molecules, which yields $\mathbf{R}_A - \mathbf{R}_0 = \frac{1}{2}\mathbf{R}_{AB}$. (Admittedly, this approximation is inherently unable to capture the small contribution perpendicular to $\mathbf{R}_{AB}$).

Summarizing, the effective intrinsic transition dipole moment carried by a CT configuration in the exciton subspace is directed approximately along the axis joining the centers of the molecules involved in charge transfer and (neglecting second order corrections) is reasonably approximated by

$$\langle AB|\mathbf{M}|A^+B^-\rangle = 2^{-\frac{1}{2}}eS\left(1 - \frac{V_{eff}^2}{\Delta^2}\right)\mathbf{R}_{AB} - e\mathbf{R}_{AB}\frac{V_{eff}}{\Delta}$$

$$= eS\mathbf{R}_{AB}\left[\left(1 - \frac{V_{eff}^2}{\Delta^2}\right)2^{-\frac{1}{2}} - \frac{K}{\Delta} + \frac{1}{2}\right]$$

$$\cong eS\mathbf{R}_{AB}\left[\left(\frac{1+\sqrt{2}}{2}\right) - \frac{K}{\Delta}\right]. \tag{6}$$

Evidently, it is limited (linearly) by the intermolecular overlap integral, which depends (roughly exponentially) on the intermolecular distance. As noted above, the same applies to the CT integrals J_e and J_h relevant for the coupling of CT excitons with Frenkel excitons, mediating intensity transfer between these states. Accordingly, inclusion of the transition moment carried by the CT configurations is indispensable for internal consistency of the exciton approach such as that of Ref. [7].

4. Transition dipoles in crystal lattice

It follows from Eq. (6) that (apart from special relative orientations of the moieties where equality results e.g. from point symmetry) the transition dipoles to the two conceivable CT configurations $|A^+B^-\rangle$ and $|A^-B^+\rangle$, engaging the same pair of molecules, may differ even in length. This is a direct consequence of the fact that the corresponding transition moments are proportional to different overlap integrals $\langle A^{HOMO}|B^{LUMO}\rangle$ and $\langle A^{LUMO}|B^{HOMO}\rangle$. It should be noted in passing that the same statement is valid for the corresponding Hamiltonian matrix elements V ($\langle A^{HOMO}|H|B^{LUMO}\rangle$ and $\langle A^{LUMO}|H|B^{HOMO}\rangle$) approximated by Eq. (3), in contrast to the standard electron

$$J_e = \langle A^{LUMO}|H|B^{LUMO}\rangle = \langle B^{LUMO}|H|A^{LUMO}\rangle$$

and hole

$$J_h = \langle A^{HOMO}|H|B^{HOMO}\rangle = \langle B^{HOMO}|H|A^{HOMO}\rangle$$

transfer integrals, where the same kind of orbital (either HOMO or LUMO) of both molecules is involved. The integrals J_e and J_h govern the couplings within the exciton subspace, along with the Frenkel

exciton dissociation integrals. For the latter, similar equalities hold approximately:

$$D_e = \langle A^*B|H|A^+B^-\rangle = \langle AB^*|H|A^-B^+\rangle$$

$$D_h = \langle A^*B|H|A^-B^+\rangle = \langle AB^*|H|A^+B^-\rangle$$

as long as the molecular excited state A^*, B^* results from HOMO-to-LUMO promotion and orbital relaxation in the excited state is disregarded. In effect, although for a given pair of molecules the CT states with reversed polarities couple to other states in the exciton subspace by analogous matrix elements, their transition dipole moments from the ground state may in general differ.

For pairs of molecules related by symmetry operations some consequences of the explicit dependence of the transition dipole on overlap integrals, as stipulated by Eq. (6), are nontrivial and may be quite relevant for detailed interpretation of the spectra. There is a natural tendency to identify the sense of the transition dipole moment with the direction of actual charge transfer (which we also did in our earlier papers [2,4,12,18,20]), i.e. with the sense of the permanent dipole moment of the generated CT state. This is not always correct, because the overlap integral S in Eq. (6) may be negative, as illustrated in Fig. 1.

In the figure, a centrosymmetric stack of centrosymmetric molecules is generated by translation (which is the constitutive feature of all crystals); in addition, it is endowed with a center of symmetry (which is very common in molecular crystals). The phases of the orbitals are consistently generated by translation (note that HOMO and LUMO belong to different irreducible representations of the molecule point group). It follows from symmetry that the overlap integrals between the HOMO of the central molecule A and the LUMOs of molecules B and C, respectively, have opposite signs. The senses of the corresponding radius vectors $\mathbf{R}_{AB}$ and $\mathbf{R}_{AC}$ are also mutually opposite; in consequence, according to Eq. (6), the senses of the corresponding transition dipoles $\langle AB|\mathbf{M}|\ A^+B^-\rangle$ and $\langle AC|\mathbf{M}|A^+C^-\rangle$ are *the same*, as shown in the figure. Likewise, the sense is also the same for $\langle AB|\mathbf{M}|A^-B^+\rangle$ and for $\langle AC|\mathbf{M}|A^-C^+\rangle$.

Paradoxically, the sense of the *transition* dipoles of all the CT states considered above is identical, irrespective of the sense of their *permanent* dipole moments, set by the relative arrangement of the two created charges. Of course, this fact influences the selection rules. Contrary to simplistic intuitive expectations, it is the *sum*, not the *difference* of the transition dipoles of the CT states with opposite polarities that does not vanish (in contrast to some expectations in the literature [22–24]).

The significance of the above observations is rather conceptual than practical; in view of their resolution, in most experimental spectra available to date the differences between the predictions based on differently set phases of CT transition dipole moments are probably hidden in the overall width of the spectral bands. On the other hand, in the model studies of Refs. [22–24], correctness of the predictions is restored by the arbitrary setting of the signs of some transfer integrals (unphysical for the systems studied

there, but compensating the effect of the implicit assumptions concerning the relative phases of the transition dipoles).

However, by highlighting the role of the actual shape and nodal structure of the underlying molecular orbitals, the present study shows that parametrization of the models applied at the level of exciton theory may need more insight into the features of the individual molecules forming the crystal and more input from quantum chemistry calculations than practiced hitherto.

5. Numerical estimates

Although this paper is focused on sexithiophene for which a complete set of reference data is available, for comparative purposes we have extended our estimates also for quaterthiophene (4T) where, owing to the smaller size of the molecule, the computations are more reliable. We concentrate our attention on the nearest neighbor CT state (engaging the translationally non-equivalent molecules located in the same plane of tight herringbone packing). The transition dipoles for higher CT excitations are less relevant, being much smaller or not contributing in the critical b polarization; for these reasons they are not suitable for the ultimate test. Nevertheless, for the sake of completeness we also present the results for the CT configurations engaging the translationally equivalent molecules along the c (in 6T) or a (in 4T) direction, where the anomalously large intermolecular LUMO overlap gives rise to large transition dipoles; for all other CT states they are negligibly small.

The molecular orbitals of 6T and 4T were obtained from Hartree–Fock calculations in the 6-311G** basis, wherefrom the sought overlap integrals were generated. The stability of the results was confirmed by repeating the runs in shorter basis sets. The reference values of the electron and hole transfer integrals J_e, J_h were ready to hand, evaluated earlier from a tight-binding fit to the results of band structure calculations in a large plane-wave basis set [7,20]. Their scaling according to Eq. (3) provided the respective values of the constants K_e, K_h for electron and hole transfer, listed in Table 1 along with the resultant averaged constants K and other relevant quantities. For the energies of the CT states we took the values used previously to reproduce the electroabsorption spectra [7], which had been found to agree rather well with independent *a priori* estimates. The permanent (diagonal) dipole moment of CT configurations ensues from the known crystal structure.

As mentioned in the preceding section, in a general relative orientation of the molecules A and B (no point symmetry) even the absolute values of the integrals for HOMO-to-LUMO transfer may depend on whether the electron is transferred from A to B or from B to A. This is the case for the nearest neighbors in oligothiophene
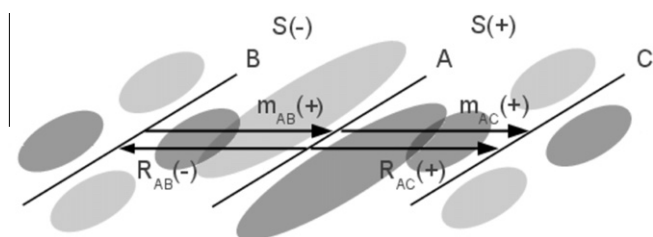

Fig. 1. HOMO–LUMO overlap between translationally equivalent centrosymmetric molecules, and CT transition dipole moment. Different shading tints indicate different sign of the orbital.

Table 1
CT transition dipole moments and relevant input data.

	4T, n.n.[a]	4T, $\|a$	6T, n.n.[a]	6T,$\|c$
J_e, eV	0.040	0.088	0.038	0.09
$S_{HOMO-LUMO}$	0.00330	−0.0258	0.00314	−0.0261
K_e, eV	12.13	−3.41	12.10	−3.45
J_h, eV	−0.017	−0.019	−0.017	−0.01
$S_{HOMO-HOMO}$	−0.00353	0.0030	−0.00324	0.00161
K_h, eV	4.81	−6.33	5.10	−6.21
K, eV	−8.47	−4.87	8.60	−4.83
Δ, eV	3.04	3.24	2.75	2.78
R_{AB}, Å	4.90	6.09	4.95	6.03
$S_{HOMO-LUMO^1}$	0.00666	−0.00594	0.00724	−0.00377
m_1, Å	0.0515	−0.098	0.0688	−0.067
$S_{HOMO-LUMO^2}$	0.00368	0.00548	0.00609	0.00409
m_2, Å	−0.0284	−0.090	−0.0578	−0.073
$|m_{eff}|$, Å	0.042	0.094	0.064	0.070

[a] n.n. = nearest neighbor.

lattices, which generates two sets of transfer integrals V_1, V_2 and transition dipoles m_1, m_2, both collected in Table 1. However, the exciton model underlying the recent theoretical reproduction of the sexithiophene spectra [7] is simplified in this regard, as the pertinent CT transition dipoles are assumed there to be equal. In order to maintain the total intensity balance, we define the effective transition dipole moment (to be compared with that of Ref. [7]) by the relationship $m_{eff}^2 = \frac{1}{2}(m_1^2 + m_2^2)$. By repeating the exciton calculations of Ref. [7] we have checked that differentiation between the two kinds of transition dipoles affects the predicted spectra to a marginal extent.

It is surprising to note that the difference between the transition moments to the CT states of opposite polarities varies so much from one system to the other: while for quaterthiophene there is a disparity of almost a factor of 2, for sexithiophene the two moments differ by a mere 20%. It cannot be ruled out that the effect is genuine, resulting from the difference in orbital structures and lattice geometries of 4T and 6T. In fact, for orbitals with rich nodal structure even minor variations in relative orientation may lead to substantial changes in intermolecular overlap integrals, as we learned in the past for PTCDA and related systems [25]. It is equally possible, though, that the inordinately increased value of the smaller transition moment in 6T is a computational artifact, stemming from uncontrollable mixing in the bloated space of virtual orbitals, rapidly growing with the size of the molecule. The smaller molecular size favors the 4T result as the more reliable one, and the overall close similarity of the two systems (manifested e.g. in the values of electron and hole transfer integrals) might suggest that for sexithiophene a somewhat smaller value of the CT transition dipole would be more credible.

In this situation some caution in the interpretation is imperative, but the overall conclusions are rather reassuring. Even if the sexithiophene result is to be taken at face value, the estimated transition dipole length of 0.064 Å exceeds by some 40% that used to reproduce the absorption and electroabsorption spectra (0.045 Å [7]), which may be viewed as a provisional "experimental" result. This accuracy is perfectly reasonable for an order-of-magnitude estimate. In fact, Eq. (3) is indubitably quite crude, and so is the Mulliken approximation which justifies the relationship between the scaling constants K for the various charge transfer integrals. The inherent errors are probably compounded by the Gaussian basis used in our calculations, poorly suited to reproduce the crucial large-distance tails of atomic orbitals. Then, within the overall limits of the applied approach, the agreement with experiment seems better than fair. If, on the other hand, the large discrepancy between the 4T and 6T cases is indeed a computational artifact, the net value for the latter system should be reduced, so that it would be even closer to the target result.

The transition dipole moment for charge transfer along the lattice period (i.e. between translationally equivalent molecules) is more difficult to compare with experiment, since it contributes only in c polarization (for 6T), dominated by very intense absorption of Frenkel origin. Nonetheless, the value of about 0.07 eÅ obtained here (larger than for the nearest-neighbor CT state, in accordance with the large electron transfer integral and large LUMO overlap) substantially exceeds the previously assumed value of 0.02 eÅ [7], providing extra intensity in the region about 2.8–3.1 eV where some intensity was evidently missing in the simulated profile (cf. Fig. 4 of Ref. [7]). Although this piece of evidence is inconclusive in view of the sensitivity of the c-polarized spectrum to potential discrepancies in reproducing the contributions of Frenkel parentage (which are very likely to result especially from the simplistic description of the background absorption to the exciton-phonon continuum [26]), the general trend is rather encouraging.

6. Discussion

Intrinsic charge transfer absorption of one-component molecular crystals, normally masked by Frenkel transitions and their vibronic replicas, came into limelight in the case of oligothiophenes, where, owing to the peculiar lattice geometry, it dominates the b-polarized spectra. It appears even more prominently in the electroabsorption spectrum, also measured for this particular polarization [5]. Combined, these two spectroscopies offer a considerable body of experimental data calling for theoretical interpretation.

Electroabsorption however, being based on a differential signal, is very sensitive to any shortcomings of the underlying theoretical description; in consequence, it is not yet possible to date to plausibly *predict* EA spectra based on first principles alone. At the present stage, a successful interpretation consists in fitting the experimental spectrum with a set of parameters enclosed within the bounds resulting from inherent inaccuracies of the theoretical methods used for their a priori estimates. So far, the estimate of the transition dipole moments of CT configurations was by far the least reliable, being based primarily on analogies.

This paper, although intended to provide merely order-of-magnitude estimates, represents some progress in this regard. It may be viewed as a consistency test. In the calculations of Ref. [7], where nearly quantitative agreement with experiment was achieved both for the absorption and electroabsorption spectra, the value of the CT state intrinsic transition dipole moment was an independent parameter, a priori known rather vaguely and ultimately adjusted by fitting the spectra.

The main goal of the present work consists in the fact that the value of this elusive quantity is now related to other input parameters used in Ref. [7], and is found to be consistent with them. Admittedly, the approximations that allow one to express the CT transition dipole moment in terms of the electron and hole transfer integrals and CT state energies of Ref. [7] are inherently crude. On this view, the nominal 40% discrepancy between the present estimate for 6T and the value found optimal for reproducing the experimental spectra may be considered surprisingly small. Moreover, the lower value obtained for quaterthiophene is encouraging in suggesting that a part of the discrepancy may be due to error cumulation resulting from the large size of the sexithiophene molecule, and might potentially be eliminated in the future by using a more sophisticated scheme of quantum chemical calculations.

It would be a worthy task which would complete the set of parameters needed to simulate the absorption and electroabsorption spectra of this model system. Other input data being known with better accuracy, this would be an important step on the way to a predicting power comparable to that recently attained for Frenkel states [1].

Acknowledgements

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