JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

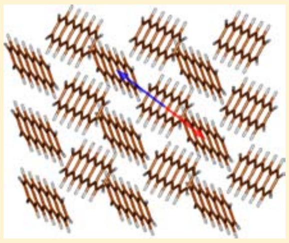
pubs.acs.org/JACS

Is Dipole Moment a Valid Descriptor of Excited State's Charge-Transfer Character?

Piotr Petelenz* and Barbara Pac

K.Gumiński Department of Theoretical Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland

ABSTRACT: In the ongoing discussion on excited states of the pentacene crystal, dipole moment values have been recently invoked to gauge the CT admixture to excited states of Frenkel parentage in a model cluster. In the present paper, a simple dimer model is used to show that, in general, the dipole moment is not a valid measure of the CT contribution. This finding eliminates some apparent disagreement between the computational results published by different research groups. The implications of our results and other related aspects of cluster-type quantum chemistry calculations are discussed in the context of the standing literature dispute concerning the mechanism of singlet fission in the pentacene crystal, notably the role of charge transfer contributions vs the involvement of an excimer-like doubly excited intermediate (D state).



1. INTRODUCTION

According to common wisdom resident in the field for decades, the lowest electronically excited state of a typical one-component organic crystal consisting of centrosymmetric molecules was traditionally expected to have intramolecular (Frenkel) character.[1,2] Over the years, this view has undergone gradual revision, especially for crystals where the constituent molecules are large,[3,4] and recently has been vigorously challenged for the specific case of pentacene.[5,6]

Based on the seminal Merrifield's paper,[7] the early theoretical literature on the subject suggested some charge transfer (CT) admixture to the lowest excited state of oligoacenes.[8,9] Subsequent papers[10] highlighted the crucial role of the CT contribution for the energetics of the Davydov components in higher oligoacenes (confirmed recently by quantitative calculations[11]), and the Frenkel-CT mixing was corroborated by successful theoretical reproduction of the experimental electro-absorption (EA) spectra of these crystals,[12,13] rooted in a reasonably realistic model treatment approximating the many-electron Hamiltonian to first order in nearest-neighbor intermolecular overlap integrals.[14]

During the past decade, the CT admixture was independently supported by EELS measurements of the Knupfer group.[15−17] Meanwhile, various theoretical approaches were applied to calculate the electronic excited states of the pentacene crystal,[5,6,17,18] including very sophisticated ones, based on many-body perturbation theory. The conclusions from most of them consistently confirmed a prominent CT contribution to the lowest pentacene excited state, and some even pronounced this contribution dominant.[6]

The paper by Zimmerman et al.[19] advocating an almost purely Frenkel character of the lowest pentacene excited state is the only exception in this regard. Account taken of its conceptual importance, the issue is not to be dismissed offhand, and the controversy should be resolved in some way. Here we will argue that the conflicting computational results may be reconciled with the same physical reality, the apparent contradiction being due partly to semantic and methodological factors.

A part of the discord results from the fact that the methodology presented by Zimmerman et al.[19] is also exceptional, the argument being based on the calculated dipole moment of a model pentacene cluster. Our present objective is to apply the simplest conceivable generic model to investigate the relationship between this quantity and the actual CT contribution. Our conclusions will have some ramifications concerning the validity of other tenets of ref 19.

2. DIPOLE MOMENT AS A MEASURE OF CT ADMIXTURE

In their quest to rationalize the experimentally observed singlet exciton fission in the pentacene crystal, Zimmerman et al.[19] reported the results of DFT/TDDFT calculations of relatively large pentacene clusters (a tetramer and a decamer). As a measure of the CT admixture to the electronic eigenstates of their model system, they adopted the calculated values of the dipole moment.

Taken literally, this approach is highly questionable. The (centrosymmetric) structure of the pentacene crystal does not support eigenstates with nonzero dipole moment. Even its charge transfer excitons must contain equal contributions of the configurations with reversed charges,[20] so that ultimately their net (diagonal, permanent) dipole moment vanishes (Figure 1). In fact, these excitons would be more aptly referred to as "charge-resonance states", invoked in the literature in a somewhat different context.[21]

The calculated nonvanishing dipole moments[19] are an artifact of the model: in contrast to the crystal as a whole, the cluster for which the calculations were carried out is not centrosymmetric. In consequence, the obtained dipole moments reflect primarily the deviation of the adopted model from

Received: July 18, 2013
Published: October 18, 2013

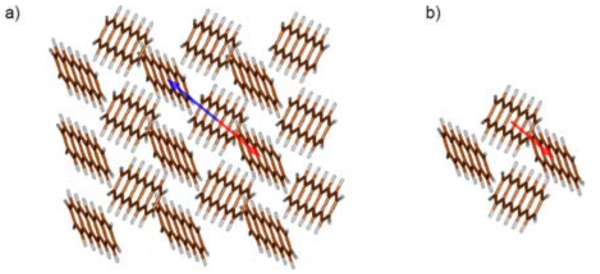


Figure 1. Charge transfer states in pentacene. (a) Crystal, the dipole moments of symmetry-equivalent CT configurations (arrows) cancel each other. (b) Cluster extracted from the crystal, the shown dipole moment (red arrow) is not counterbalanced because the corresponding symmetry-equivalent molecule is not contained in the cluster.

the actual symmetry of the simulated lattice and in the crystal context are simply nonphysical.

Yet, an alternative point of view might potentially be advocated. The deviation of the model cluster from central symmetry might be viewed as a probe with which to gauge the sensitivity of the eigenstates of Frenkel parentage to external perturbation. It is conceivable that the dipole moment induced by external field might reflect the CT contribution to the eigenstate in hand, and in that case the conclusions of Zimmerman et al.[19] could be defendable.

3. MODEL

Our present aim is to investigate the effect of external perturbation on a generic model that would be as simple as possible and yet would contain some ingredients essential for the behavior of the crystal.

The symmetry-breaking perturbation will be mimicked by uniform electric field. As the response of the crystal is to a good approximation reducible to the interplay between pairs of states coupled by the field,[22] the above requirements are satisfied by a fictitious dimer AB, parametrized in such a way as to imitate exciton energetics at the center of the Brillouin zone at zero electric field. The moieties of the dimer are by assumption centrosymmetric and are assumed to be related by an abstract symmetry operation (which may be tentatively identified with the center of symmetry). If needed, the two molecules may be thought of as representing two sublattices of the crystal, but the flexibility of the dimer model allows one to encompass a variety of other cases as well.

The necessary minimum basis set is spanned by two Frenkel configurations $|A^*B\rangle$, $|AB^*\rangle$ with the excitation (*) located at either of the two moieties and by two CT configurations $|A^+B^-\rangle$, $|A^-B^+\rangle$; the corresponding wave functions are assumed to be orthonormal. The two CT configurations are related by charge reversal and endowed with the dipole moments $\boldsymbol{\mu} = e\langle A^+B^-|\mathbf{r}|A^+B^-\rangle = -e\langle A^-B^+|\mathbf{r}|A^-B^+\rangle$ ($\mathbf{r}$ standing for the radius vector and e for the elementary charge), by assumption (anti)parallel to the electric field $\mathbf{F}$. Being significantly smaller,[12,13,23] the terms quadratic in electric field strength, proportional to molecular polarizability, are consistently neglected. The Frenkel states are split by twice the value of the resonance integral $M = \langle A^*B|H|AB^*\rangle$ (if the two molecules represent different sublattices, this is the familiar Davydov splitting). The quanitity $2W$ is the counterpart of this splitting in the CT manifold; it simulates the effect of the coupling of the $|A^+B^-\rangle$, $|A^-B^+\rangle$ states to the CT states engaging other crystal molecules, not included explicitly in the present model, and here is introduced as a phenomenological parameter. For the CT analogues of Davydov components, this coupling is mediated by electron and hole transfer between translationally equivalent molecules (cf. refs 24 and 25), and its order of magnitude is set by the values of the appropriate CT integrals.

In the following, Δ stands for the separation between the diagonal energies of Frenkel and CT configurations prior to their mixing. The two manifolds are coupled by the exciton-dissociation integrals $D_e = \langle A^*B|H|A^+B^-\rangle$ and $D_h = \langle A^*B|H|A^-B^+\rangle$, describing electron and hole transfer, respectively. For practical reasons, the zero of energy is set at the diagonal energy of an excited pentacene moiety.

Then the model Hamiltonian assumes the following matrix form[26]where $D_\pm = D_e \pm D_h$.

$$\begin{array}{c|cccc|} & A^*B & AB^* & A^+B^- & A^-B^+ \\ \hline A^*B & 0 & M & D_e & D_h \\ AB^* & M & 0 & D_h & D_e \\ A^+B^- & D_e & D_h & \Delta - \boldsymbol{\mu}\mathbf{F} & W \\ A^-B^+ & D_h & D_e & W & \Delta + \boldsymbol{\mu}\mathbf{F} \end{array}$$

$$\rightarrow \begin{array}{c|cccc|} & F^+ & F^- & CT^+ & CT^- \\ \hline F^+ & M & 0 & D_+ & 0 \\ F^- & 0 & -M & 0 & D_- \\ CT^+ & D_+ & 0 & \Delta + W & \boldsymbol{\mu}\mathbf{F} \\ CT^- & 0 & D_- & \boldsymbol{\mu}\mathbf{F} & \Delta - W \end{array} \qquad (1)$$

The Hamiltonian is readily transformed to the symmetry-adapted basis

$$|F^+\rangle = \frac{1}{\sqrt{2}}(|A^*B\rangle + |AB^*\rangle) \qquad (2a)$$

$$|F^-\rangle = \frac{1}{\sqrt{2}}(|A^*B\rangle - |AB^*\rangle) \qquad (2b)$$

$$|CT^+\rangle = \frac{1}{\sqrt{2}}(|A^+B^-\rangle + |A^-B^+\rangle) \qquad (2c)$$

$$|CT^-\rangle = \frac{1}{\sqrt{2}}(|A^+B^-\rangle - |A^-B^+\rangle) \qquad (2d)$$

as shown in eq 1.

When the perturbation $\boldsymbol{\mu}\mathbf{F}$ is absent, in the new representation the Hamiltonian splits into two commuting parts

$$\begin{bmatrix} M & D_+ \\ D_+ & \Delta + W \end{bmatrix} \begin{bmatrix} -M & D_- \\ D_- & \Delta - W \end{bmatrix} \qquad (3)$$

readily diagonalized analytically to yield the eigenvectors

$$|\psi_+\rangle = \cos\frac{\vartheta_+}{2}|F^+\rangle + \sin\frac{\vartheta_+}{2}|CT^+\rangle \qquad (4a)$$

$$|\varphi_+\rangle = -\sin\frac{\vartheta_+}{2}|F^+\rangle + \cos\frac{\vartheta_+}{2}|CT^+\rangle \qquad (4b)$$

$$|\psi_-\rangle = \cos\frac{\vartheta_-}{2}|F^-\rangle + \sin\frac{\vartheta_-}{2}|CT^-\rangle \qquad (4c)$$

$$|\varphi_-\rangle = -\sin\frac{\vartheta_-}{2}|\mathrm{F}^-\rangle + \cos\frac{\vartheta_-}{2}|\mathrm{CT}^-\rangle \tag{4d}$$

with

$$\tan\vartheta_+ = \frac{2D_+}{M - \Delta - W} \qquad \tan\vartheta_- = \frac{2D_-}{-M - \Delta + W} \tag{5a,b}$$

and the eigenvalues

$$E_{F_+} = \frac{1}{2}(M + \Delta + W) - \frac{1}{2}\sqrt{(M - \Delta - W)^2 + 4D_+^{\,2}} \tag{6a}$$

$$E_{\mathrm{CT}_+} = \frac{1}{2}(M + \Delta + W) + \frac{1}{2}\sqrt{(M - \Delta - W)^2 + 4D_+^{\,2}} \tag{6b}$$

$$E_{F_-} = \frac{1}{2}(-M + \Delta - W) - \frac{1}{2}\sqrt{(-M - \Delta + W)^2 + 4D_-^{\,2}} \tag{6c}$$

$$E_{\mathrm{CT}_-} = \frac{1}{2}(-M + \Delta - W) + \frac{1}{2}\sqrt{(-M - \Delta + W)^2 + 4D_-^{\,2}} \tag{6d}$$

A simple derivation demonstrates that for all the eigenstates (irrespective of their origin, Frenkel or CT), the expectation values of the dipole moment vanish. Yet, when the symmetry-breaking perturbation $H' = \boldsymbol{\mu}\mathbf{F}$ is included, it mediates cross-coupling between the eigenstates belonging to the (+) and (−) manifolds, engaging the matrix elements off-diagonal in the basis of zero-field eigenstates. As a result, *all* of the new (finite-field) eigenstates do possess some dipole moment. In the following the electric field is assumed to be weak, enabling one to use perturbation theory.

4. FIELD-PERTURBED EIGENSTATES AND THEIR DESCRIPTORS

Subsequently, we are seeking a set of descriptors that would characterize the perturbed eigenstates of Frenkel parentage and could be directly related to the results of ref 19.

We will focus our attention on the Frenkel (+) state, presumably the lowest-energetic one. Correct to the first order in the perturbation, its wave function $|\psi_+'\rangle$ reads

$$|\psi_+'\rangle = |\psi_+\rangle + \frac{H_{\mathrm{FF}}'}{E_{F^+} - E_{F^-}}|\psi_-\rangle + \frac{H_{+\mathrm{FCT}-}'}{E_{F^+} - E_{\mathrm{CT}^-}}|\varphi_-\rangle \tag{7}$$

where

$$H_{\mathrm{FF}}' = \boldsymbol{\mu}\mathbf{F}\,\sin(\vartheta_+/2)\sin(\vartheta_-/2) \tag{8a}$$

$$H_{+\mathrm{FCT}-}' = \boldsymbol{\mu}\mathbf{F}\,\sin(\vartheta_+/2)\cos(\vartheta_-/2) \tag{8b}$$

Given this wave function and the resultant (field-induced) dipole moment in the perturbed Frenkel (+) state

$$\begin{aligned}\langle\psi_+'|\vec{\mu}|\psi_+'\rangle &= 2\boldsymbol{\mu}^2\mathbf{F}\left(\frac{\sin^2(\vartheta_+/2)\sin^2(\vartheta_-/2)}{E_{F^+} - E_{F^-}}\right.\\ &\qquad \left. + \frac{\sin^2(\vartheta_+/2)\cos^2(\vartheta_-/2)}{E_{F^+} - E_{\mathrm{CT}^-}}\right)\\ &= \boldsymbol{\mu}m_0\end{aligned} \tag{9}$$

as potentially valuable descriptors we will use (1) the ratio m_0 of this dipole moment to the dipole moment $\boldsymbol{\mu}$ of an individual CT configuration (in other words, the dimensionless equivalent of the above dipole moment, expressed in the units of the dipole moment of a CT configuration) and (2) the ratio m of this dipole moment to the dipole moment of the perturbed eigenstate of CT parentage

$$\begin{aligned}m = &\left(\frac{\sin^2(\vartheta_+/2)\sin^2(\vartheta_-/2)}{E_{F^+} - E_{F^-}} + \frac{\sin^2(\vartheta_+/2)\cos^2(\vartheta_-/2)}{E_{F^+} - E_{\mathrm{CT}^-}}\right)\\ &\Big/\left(\frac{\cos^2(\vartheta_+/2)\sin^2(\vartheta_-/2)}{E_{\mathrm{CT}^+} - E_{F^-}} + \frac{\cos^2(\vartheta_+/2)\cos^2(\vartheta_-/2)}{E_{\mathrm{CT}^+} - E_{\mathrm{CT}^-}}\right)\end{aligned} \tag{10}$$

[eq 10 pertains to the eigenstate of CT parentage belonging to the (−) manifold, coupled to the Frenkel (+) state under consideration; the corresponding expression for the (CT^+) eigenstate yields numerically similar results and for this reason need not be treated separately].

The above descriptors are to be correlated with the admixture of CT configurations in the eigenfunction of the Frenkel (+) eigenstate

$$\rho = \sin^2(\vartheta_+/2) \tag{11}$$

This admixture is only marginally affected by the (weak) electric field (which was checked numerically), so that there is no need to differentiate between the perturbed and unperturbed eigenstate.

5. CALCULATIONS

If at least one of the dipole moment ratios, m_0 or m, could be correlated with the CT contribution ρ to the wave function given by eq 7, one might be able to directly infer about the CT admixture from the value (calculated or experimental) of the dipole moment in the field-perturbed Frenkel-type eigenstate. Unfortunately, it is evident at the first glance that m_0 and m are not universally determined by the CT admixture alone but in addition are influenced by other independent parameters of the model. In other words, a specific preset CT admixture may potentially lead to various values of the dipole moment depending on other input data, and for different sets of input data, the same CT admixture ρ may yield various dipole moments.

Intuitively, one would expect some universal proportionality relation between the Frenkel state dipole moment and the CT admixture. According to eqs 9 and 10, this simplistic expectation is in general false. Yet, it is in principle conceivable that the parameter-dependent deviations from proportionality could actually be negligible; the fundamental question is how significant they would be for physically realistic parameter sets. This will be tested by numerical calculations.

The tests are designed to simulate within the dimer model the physical situation described in considerable detail by the cluster models of Yamagata et al.[11] and of Zimmerman et al.,[19] and the parameters are chosen accordingly. As in the latter paper vibronic effects are not included, in our basic set of data we do not include them either. In order, though, to check their influence on our conclusions, we have also carried out the same series of calculations with the off-diagonal matrix elements of the Hamiltonian reduced by the respective vibrational overlap integrals, and registered no qualitative change.

Accordingly, in the basic parameter set, the dissociation integrals D_e and D_h are assumed equal to those explicitly evaluated in ref 11. All other input parameters (Δ, M, W) are viewed as variable, with the constraints imposed by the energetics of the model tetramer of Zimmerman et al.[19] Specifically, we require that the calculated Davydov-like splitting between the (+) and (−) Frenkel-type eigenstates be on the order of several hundredths of an electronvolt (0.02−0.12 eV) and that the gap between the eigenstates of Frenkel and CT parentage be enclosed in the interval 0.2−0.4 eV, roughly approaching the values reported in ref 19. As Zimmerman et al. present the energies of four eigenstates of Frenkel and four of CT parentage, there is some ambiguity in selecting the two reference states for each class. To circumvent the potential consequences of this ambiguity, we decided to encompass all reasonable combinations of reference states by deliberately adopting wide margins of tolerance for the energy gaps.

It should be reminded marginally that the crystal Davydov splitting (DS), critically depending on the number of neighbors in the lattice, is not adequately reproduced by calculations performed for small clusters (ref 27, *vide infra*). In the present context, this is not relevant, since we are merely generating a collection of parameter sets that are vaguely reminiscent of the actual situation in pentacene, the general objective consisting of probing a reasonably large sector of the parameter space without straying overly from the description of the system of our primary interest. This approach is justified by the fact that it is not our point to favor one specific result over another, while practically all the relevant calculations reported in the literature are in some respect subject to controversies.

The dipole moment of the CT configuration is assumed to be 5 Å long, based on the approximate nearest-neighbor distance in the sexithiophene lattice.

The electric field invoked in this paper is consistently set at 50 kV/cm, which is a typical value used, for example, in electroabsorption measurements, and is small enough to legitimize application of perturbation theory. This enables us to draw some conclusions from the analytic formulas, instead of relying exclusively on numerical results. Moreover, the saturation effects inevitable for stronger fields would further obfuscate the conclusions.

6. RESULTS

In this paper, the electric field is meant to mimic the symmetry-breaking perturbation resulting from the noncentrosymmetric geometry of a model cluster. As the dipole moment for all zero-field solutions [eqs 4a−4d] vanishes, its substantial values in the cluster eigenstates of CT origin, such as those reported in ref 19, yield little information about the corresponding CT exciton levels in the actual crystal, merely showing that the local symmetry in the model cluster is distorted to a pretty large extent, failing to reflect the situation in the unperturbed system. In view of eq 9, the same applies to the Frenkel exciton dipole moment m_0; being proportional to the perturbation (which is an artifact of the cluster model), in itself it is not informative at all.

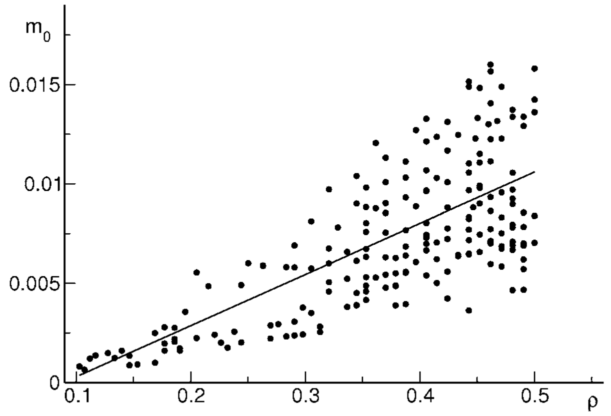


Figure 2. The dimensionless dimer dipole moment m_0 in the lower eigenstate of Frenkel parentage (expressed in the units of the dipole moment $\boldsymbol{\mu}$ of a CT configuration), as a function of the CT admixture ρ.

Nonetheless, as shown in Figure 2, the span of m_0 values calculated for a more or less random collection of input parameter sets (*vide supra*) does lead to a conclusion, be it an indirect one. Although the trend line of the $m_0(\rho)$ plot seems to support the intuitive qualitative expectation that the larger the CT admixture the larger the induced dipole moment, practical usefulness of this observation is next to none in view of the enormous scatter of the data points, especially in the important region of strong mixing between the Frenkel and CT configurations: the CT admixture approaching 50% may yield a commensurately large dipole moment (0.36 D) in the perturbed Frenkel eigenstate but does not contradict a value that is almost three times smaller. Effectively, while *large* dipole moment is admittedly compatible only with a large CT contribution ρ to the eigenstate of Frenkel parentage, *small* dipole moments, in contrast, may occur for *small as well as for large* CT admixtures. The conclusion is that the minuscule dipole moments reported in ref 19 for Frenkel states are no indication of the extent of Frenkel−CT mixing; effectively, they have no diagnostic value.

Figure 3 shows another descriptor, namely, the relative value m of the Frenkel exciton dipole moment in the cluster (i.e., perturbed by the field), taken with respect to the dipole moment of the corresponding CT-type eigenstate. In the figure, the $m(\rho)$ trend line is almost horizontal, showing that, on the average, the field-induced dipole moment lent by the CT state to the eigenstate of Frenkel parentage is no indicator of the CT state admixture contained in this latter eigenstate. Depending on the specific set of parameters (all compatible with the energetics of the cluster of ref 19), the same value of m can be reconciled with drastically different CT admixtures ρ. For instance, the ratio m on the order of 0.13−0.17 obtained from the calculations of Zimmerman et al. (Table 1 of ref 19) may correspond to the CT contribution ρ of about 25%, but 50% is equally possible. This situation is not altered when the length (absolute value) of the dipole moment is considered instead of the actual vector: although the trend line is no longer horizontal, the range of CT admixtures compatible with small m values is as wide as previously.

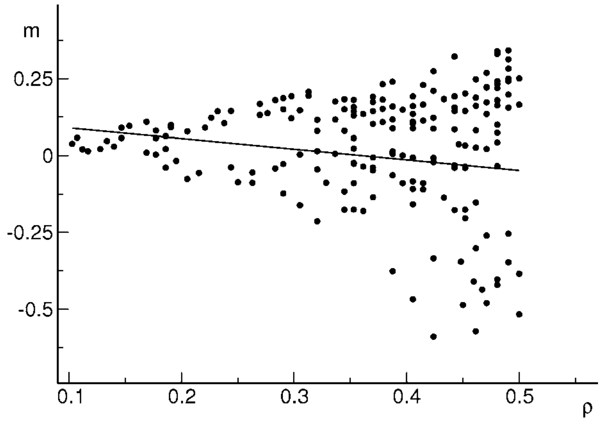


Figure 3. The ratio m of the dimer dipole moment in the lower eigenstate of Frenkel parentage to the dipole moment of the perturbed eigenstate of CT parentage, as a function of the CT admixture ρ.

The varying sign of the relative dipole moment m in Figure 3 may at the first glance look puzzling if not downright counterintuitive. As the dipole moment (vanishing in the absence of the perturbation) is induced by the electric field, one might expect it to minimize the system's energy, that is, to be generally directed downfield, which in reality (cf. Figure 3) does not seem to be necessarily the case.

This behavior is readily rationalized by observing that the changing sign of m is due to the denominator in eq 10, which represents the induced dipole moment of the (−) eigenstate of CT origin. The ultimate cause of the field-induced shifts is the off-diagonal $\boldsymbol{\mu}\mathbf{F}$ term in the symmetry-adapted form of the Hamiltonian matrix given by eq 1, which couples the (CT^+) and (CT^-) zero-field eigenstates, shifting them apart. Then, inevitably, the lower of the states gets stabilized and the upper destabilized. According to eqs 6b and 6d, their zero-field energies depend on model parameters. If for a specific parameter set the (CT^-) state happens to be the lower one, it does get stabilized by the field; otherwise the effect is reversed. This observation once again highlights the fact that in the absence of the symmetry-breaking field the dipole moments of both CT-type eigenstates exactly vanish; when the perturbation is introduced, in the lower eigenstate the downfield charge configuration becomes dominant.

In summary, Figures 2 and 3 demonstrate that neither the *absolute* nor the *relative* value of the Frenkel state dipole moment *in the cluster* (i.e., perturbed by the model field) is a valid measure of the CT admixture *in the crystal* (i.e., prior to the perturbation). In effect, the small dipole moments of the cluster eigenstates that follow from the calculations of ref 19 are *not* a valid argument against the CT admixture of about 50% suggested in ref 11. Conversely, assuming that the latter is correct, the dipole moments published by Zimmerman et al. are no proof that their results are wrong. Simply, the two pieces of information are not related in any straightforward way, and there is no contradiction between them.

7. DISCUSSION

Addressing the specific question posed in the title of this paper, it seems that dipole moment *is not* a valid descriptor of the CT admixture contained in an eigenstate of Frenkel provenance. This conclusion is expected to be valid *a fortiori* for more sophisticated models, dependent on a larger number of parameters; it does not matter whether the parameters are introduced from external sources or generated automatically within a complex quantum chemistry program.

In the specific context of existing literature on pentacene, the above results eliminate the apparent disagreement between the dipole moments resulting from the DFT calculations reported in ref 19 for a model cluster and the CT admixture to the lowest Frenkel state obtained from the phenomenologically parametrized cluster approach of ref 11. There is no simple dependence relating the two quantities to each other.

It should be also noted that in the specific controversy concerning pentacene, direct comparison is precluded also by the difference in the methodologies applied in the two papers: Zimmerman et al.[19] operate within the Born−Oppenheimer approximation, while the Spano group[11] do not, dealing specifically with vibronic coupling. Other input data being supposedly equal, in order to generate the parameters for the Spano vibronic model, the off-diagonal matrix elements of the Hamiltonian of ref 19 (were they known) would in the first approximation have to be multiplied by the appropriate vibrational overlap integrals.

Another argument invoked by Zimmerman et al. in favor of negligible CT admixture to crystal eigenstates of Frenkel parentage is simply not valid. It is based on the close similarity between the distribution of the electron and hole natural transition orbitals (NTOs) for the S1 state of the model tetramer, both orbitals being delocalized over all molecules of the cluster. However, for the crystal, this similarity would be perfectly normal irrespective of the parentage of the state in hand (*vide infra*). For the tetramer of ref 19, it merely indicates that the nonphysical symmetry breaking (which is an artifact of the model) is not strong enough to make orbital deformation visually noticeable. This point can be illustrated in the following way.

If cluster-type DFT calculations could be performed for an infinite model crystal, for example, anthracene, *every* resultant orbital would have to transform according to a specific irreducible representation of the crystal symmetry group. In the monoclinic anthracene lattice *every two molecules* are related by some symmetry operation, which implies that in any crystal orbital the weights of the orbitals of all constituent molecules would have to be *exactly the same*. This statement applies to LCAO MO as well as Kohn−Sham orbitals, and to *all eigenstates*, irrespective of their Frenkel or CT character. In turn, the symmetry-enforced shape of Kohn−Sham orbitals defines the form of the transition density matrix at the TD DFT level, which then consists of symmetry-determined blocks. Consequently, the diagonalization of this matrix ultimately yields the natural transition orbitals, which are also bound to belong to well-defined irreducible representations of the crystal group, that is, to contain equal contributions from all the molecules. This is valid both for electron and hole NTOs.

The situation is somewhat different for the (triclinic) pentacene, where the two sublattices are not equivalent by symmetry. This, however, changes the situation only to a minor extent. First, the crystal is still centrosymmetric and for this reason does not support eigenstates with nonzero dipole moments. Second, the deviation of the crystal from monoclinicity is small (for CT configurations giving rise to energy differences on the order of hundredths of an electronvolt, resulting from charge−quadrupole interactions[28]), so the actual inequivalence of the two sublattices is marginal.

As the model tetramer of ref 19 has a lower symmetry than the crystal (the crucial issue being the absence of the symmetry center), the cluster orbitals might be distributed in a somewhat different way for the electron and the hole. The fact that (as the authors report) these distributions differ only slightly merely gives credit to the model, indicating that the violation of central symmetry does not distort the underlying physics to an intolerable extent. However, if there were a slight difference, it would be mostly an artifact of the model, incapable of mimicking the symmetry of the crystal, not an indication of actual CT character.

Looking at the problem from the simple LCAO MO perspective, in pentacene both the lowest Frenkel state and the CT states of interest derive from the same pair of orbitals, that is, HOMO and LUMO, and in both kinds of electron configurations the contributions from the molecules involved enter the combination with equal weights. In general, in centrosymmetric systems, the orbital picture is not geared to discriminate between Frenkel and CT states, because an orbital is a one-particle concept. The electron density must be centrosymmetric in both types of states. The difference between the Frenkel and CT states consists in interdependence between electron and hole positions, embodied in the total many-electron wave function, or for example, in the electron−hole correlation function, which for a Frenkel-type configuration has the global maximum at the center of coordinates and for a CT-type configuration at the nearest-neighbor distance. In DFT, for a system where all molecules are related to each other by symmetry operations, for every state the peaks of the correlation function would have equal height for all symmetry-related molecules.

The above analysis couches the estimate of the CT admixture to Frenkel states proposed by Zimmerman et al. in the broader context of other theoretical estimates. However, there still remains the question to what extent the above conclusions pertain to the specific problem raised in the paper by Zimmerman et al.,[19] of which the issue of the CT contribution to the lowest excitation of the pentacene crystal is merely a fragment. Actually, the main value of the paper consists in offering a novel perspective on the process of singlet exciton fission in pentacene. While the hypothesis launched there is tantalizing in its own right and may be correct, also some other arguments used to corroborate it need a thorough scrutiny, the dipole moment issue being only a fragment of a more general picture.

To start with, the size of the model clusters of ref 19 is rather small. It is reasonable to expect that for a sufficiently large cluster the boundary effects should be negligible. The question is how large the cluster would really have to be in order to eliminate them.

The Davydov splitting of the (optically dominant) Frenkel excitons is largely governed by the number of interacting molecules at a given distance from the molecule in hand. Although the (intermediate-range) contribution from more distant molecules is not necessarily negligible, the interaction with the nearest neighbors usually dominates, so the short-range contribution to DS is roughly proportional to their number. As already noted in the past,[27] at least the molecules at the cluster boundary have a reduced number of neighbors, so considerable caution must be exercised to correctly identify those of the monomers that truly represent the crystal bulk. In the model tetramer of ref 19, *no* molecule satisfies this obvious condition, and in the decamer only the two central molecules do. In effect, for most molecular pairs of the cluster, the calculated Davydov splitting is bound to be underestimated by the corresponding factor, with obvious consequences for the exciton stabilization energy. On this view, the reported tendency for exciton localization at the two central molecules is an inevitable consequence of the geometry decreed for the model cluster, and there are no grounds to suppose that it reflects in any way the actual proclivities of the exciton in the crystal; most likely, it is just an artifact of the model with broken translational symmetry. This invalidates the posit that a cluster consisting of two molecules is sufficiently large to yield correct conclusions.

In order to reproduce the local exciton energies correctly, the model cluster would have to be much larger, probably exceeding the capacity of presently available computational resources. This observation does not necessarily refute the conclusions based on the dimer model of ref 19, merely exposes its arbitrariness. Possibly a more extended model would lead to the same conclusions, but this has yet to be proven. At any rate, if the underestimated Davydov splitting would be corrected, the energy of the S1 state would be lowered, possibly below the hypothetical D state.

Moreover, the energies of spectroscopically observable Frenkel states (at wave vector $\mathbf{k} = 0$) have a nonanalytic contribution[2] from very distant parts of the crystal, resulting from conditional convergence of the lattice sums. The nonalytic term is entirely absent from the cluster approach. In the specific case of oligoacenes where the lowest electronic transition has a modest oscillator strength, a simple estimate suggests that the corresponding correction should not exceed 0.01−0.02 eV,[22] which is probably negligible compared with other inherent inaccuracies of the approach of ref 19. Nevertheless the correction, when supplemented by the (inevitably neglected) intermediate-range interactions with the crystal molecules not included in the model cluster, might potentially tip the stability balance between S1 and D, which is precarious anyway; this unfavorably affects the credibility of the conclusions.

The finite size of the cluster also influences the energies of the eigenstates of CT origin. A substantial part of the individual diagonal CT configuration energies comes from polarization terms.[27−31] The latter comprise a substantial contribution from nearest neighbors which, by the same token as for the Davydov splitting of Frenkel states, makes the polarization energy estimate from the cluster model substantially smaller than the true value corresponding to the crystal bulk. Also, in order to get the polarization energy right in practical calculations, it is normally necessary to include at least several coordination spheres and then add the contribution from the infinite surrounding crystal.[29−32] This practically precludes quantitative accuracy of CT state energies extracted from the cluster model. As the polarization contribution stabilizes the system, its part inevitably disregarded in cluster calculations (a crude estimate suggesting a discrepancy on the order of a few tenths of an electronvolt) is likely to compensate the inherent error of the DFT method, where (at least for functionals with uncorrected asymptotics) the CT state energies are notoriously too low, and may account for the altogether numerically reasonable overall result of ref 19.

One has to realize, however, that the calculated energies of the excitations attributed by Zimmerman et al. to CT states, taken literally, are incompatible with the experimental electroabsorption (EA) spectrum of pentacene, measured by Weiser and collaborators.[12] The spectrum exhibits a few signals characteristic for CT excitons, among them an unmistakably strong one at 2.12 eV; the second-derivative shape of the latter and the coincidence of its minimum with the position of the corresponding peak in the absorption spectrum clearly point to a modestly split eigenstate of CT parentage. This interpretation is also supported by the relatively low intensity of the absorption band, contrasting with the large amplitude of the pertinent EA signal and indicative of strong sensitivity to electric field, as well as by the consistency of the result with the trend observed for anthracene[13] and tetracene.[12]

A simple way to test the physical relevance of the eigenstates calculated in ref 19 would consist in calculating directly the tetracene and pentacene electro-absorption signals by means of the same approach and to compare them with the experimental spectra. This would be also advisable for other methodologies used to calculate the pentacene excited states.[3−6,11,18,19]

For the time being, the existing evidence[12−14] suggests that the actual CT state energies are considerably lower than those calculated by Zimmerman et al. Nevertheless, the calculated spacing between the levels of Frenkel and CT parentage is in reasonable agreement with experiment[12] and may be construed to support the contention[19] that *real* CT states (crystal eigenstates of CT parentage) are unlikely intermediates in singlet exciton fission, because their energies are too high. However, an analogous contention concerning the involvement of *virtual* CT states as an admixture to the lowest singlet eigenstate (of Frenkel parentage), which gives rise to a superexchange-type bridge, is not justified by the calculations presented there.[19]

First, as we have argued above, the conclusion concerning the allegedly small CT admixture to the lowest singlet state is poorly founded, since the dipole moment is not a valid descriptor of the CT contribution. If this contribution is not negligible, there is no reason to rule out the CT-mediated fission mechanism; in that case, the hypothesis of the D-state as an intermediate is no longer needed. Second, the inherent deficiencies of the (small-) cluster approach underlying the results presented in ref 19 preclude quantitative relevance of the latter, making the applicability of the (ultimately used) dimer model questionable in that context, and rendering the final conclusion concerning the stabilization of the D state with respect to S1 dubious. As this stabilization is a pivotal ingredient of the singlet fission mechanism involving the D-state,[19] the latter is also open to doubt.

It should be noted in passing that the crucial role of the CT admixture to the lowest triplet state for the Davydov splittings in the anthracene and tetracene crystals was demonstrated in the early 1970s by Tiberghien and Delacote.[33,34] The CT contribution is dominant there, despite the fact that the energy gap between a single triplet Frenkel exciton and the CT state is much larger than for a pair of triplets produced by fission, and that all these energy gaps are larger in lower oligoacenes than in pentacene.[3,4] The recent contributions of Berkelbach et al.[35] are consistent with the classic findings[33,34] and provide a convincing description of the fission process.

■ AUTHOR INFORMATION

Corresponding Author

petelenz@chemia.uj.edu.pl

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors express their gratitude to Dr G. Mazur for valuable comments and inestimable assistance with the artwork. The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (Contract No. POIG.02.01.00-12-023/08).

■ REFERENCES

(1) Karl, N., Low Molecular Weight Organic Solids. In *Organic Electronic Materials*; Farchioni, R., Grosso, G., Eds.; Springer: Berlin Heidelberg, 2001; Chapter 6.3.
(2) Schlosser, D. W.; Philpott, M. R. *Chem. Phys.* **1980**, *49*, 181.
(3) Hummer, K.; Ambrosch-Draxl, C. *Phys. Rev. B* **2005**, *71*, No. 081202.
(4) Ambrosch-Draxl, C.; Nabok, D.; Puschnig, P.; Meisenbichler, C. *New J. Phys.* **2009**, *11*, No. 125010.
(5) Sharifzadeh, S.; Biller, A.; Kronik, L.; Neaton, J. B. *Phys. Rev. B* **2012**, *85*, No. 125307.
(6) Cudazzo, P.; Gatti, M.; Rubio, A. *Phys. Rev. B* **2012**, *86*, No. 195307.
(7) Merrifield, R. E. *J. Chem. Phys.* **1961**, *34*, 1835.
(8) Bounds, P. J.; Siebrand, W. *Chem. Phys. Lett.* **1980**, *75*, 414.
(9) Bounds, P. J.; Siebrand, W.; Petelenz, P. *Chem. Phys.* **1981**, *63*, 303.
(10) Petelenz, B.; Petelenz, P.; Shurvell, H. F.; Smith, V. H., Jr. *Chem. Phys.* **1988**, *119*, 25.
(11) Yamagata, H.; Norton, J.; Hontz, E.; Olivier, Y.; Beljonne, D.; Brédas, J.-L.; Silbey, R. J.; Spano, F. C. *J. Chem. Phys.* **2011**, *134*, No. 204703.
(12) Sebastian, L.; Weiser, G.; Bässler, H. *Chem. Phys.* **1981**, *61*, 125.
(13) Sebastian, L.; Weiser, G.; Peter, G.; Bässler, H. *Chem. Phys.* **1983**, *75*, 103.
(14) Petelenz, P.; Slawik, M.; Yokoi, K.; Zgierski, M. Z. *J. Chem. Phys.* **1996**, *105*, 4427.
(15) Knupfer, M.; Berger, H. *Chem. Phys.* **2006**, *325*, 92.
(16) Schuster, R.; Knupfer, M.; Berger, H. *Phys. Rev. Lett.* **2007**, *98*, No. 037402.
(17) Roth, F.; Schuster, R.; König, A.; Knupfer, M.; Berger, H. *J. Chem. Phys.* **2012**, *136*, No. 204708.
(18) Tiago, M. L.; Northrup, J. E.; Louie, S. G. *Phys. Rev. B* **2003**, *67*, No. 115212.
(19) Zimmerman, P. M.; Bell, F.; Casanova, D.; Head-Gordon, M. *J. Am. Chem. Soc.* **2011**, *133*, 19944.
(20) Petelenz, P. In *Proceedings of the International School of Physics "Enrico Fermi"*; Agranovich, V. M., La Rocca, G. C., Eds.; IOS Press: Amsterdam, 2002; Course CXLIX, pp 1−25.
(21) Hochstrasser, R. M. *J. Chem. Phys.* **1962**, *36*, 1099.
(22) Slawik, M.; Petelenz, P. *J. Chem. Phys.* **1999**, *111*, 7576.
(23) Petelenz, P. *Chem. Phys. Lett.* **1993**, *215*, 607.
(24) Munn, R. W.; Petelenz, P.; Siebrand, W. *Chem. Phys.* **1987**, *111*, 209.
(25) Petelenz, P.; Slawik, M. *Chem. Phys.* **1991**, *157*, 169.
(26) Petelenz, P. *Org. Electron.* **2004**, *5*, 115.
(27) Petelenz, P.; Andrzejak, M. *Chem. Phys. Lett.* **2001**, *343*, 139.
(28) Bounds, P. J.; Munn, R. W. *Chem. Phys.* **1979**, *44*, 103.
(29) Eisenstein, I.; Munn, R. W. *Chem. Phys.* **1983**, *77*, 47.
(30) Bounds, P. J.; Siebrand, W.; Eisenstein, I.; Munn, R. W.; Petelenz, P. *Chem. Phys.* **1985**, *95*, 197.
(31) Tsiper, E. V.; Soos, Z. G. *Phys. Rev. B* **2003**, *68*, No. 085301.
(32) Soos, Z. G.; Tsiper, E. V.; Pascal, R. A., Jr. *Chem. Phys. Lett.* **2001**, *342*, 652.
(33) Tiberghien, A.; Delacote, G. *J. Phys. (Paris)* **1970**, *31*, 637.
(34) Tiberghien, A.; Delacote, G. *Chem. Phys. Lett.* **1971**, *8*, 88.
(35) Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R. *J. Chem. Phys.* **2013**, *138*, No. 114102; **2013**, *138*, No. 114103.

(36) Sharifzadeh, S.; Darancet, P.; Kronik, L.; Neaton, J. B. *J. Phys. Chem. Lett.* **2013**, *4*, 2197.
(37) Beljonne, D.; Yamagata, H.; Brédas, J. L.; Spano, F. C.; Olivier, Y. *Phys. Rev. Lett.* **2013**, *110*, 226402.

■ NOTE ADDED IN PROOF

Two other recent articles of crucial relevance have come to our attention after this paper was accepted for publication. They are listed as refs 36 and 37.