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Theoretical Estimates of Charge Transfer State Energies in Sexithiophene*

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The example of sexithiophene is used to illustrate some problems related to theoretical interpretation of electro-absorption spectra. Two different theoretical approaches are combined to calculate the energies of localized ionic pairs (charge-transfer states) in the sexithiophene crystal. In the lack of the corresponding experimental data, the ionization potential and electron affinity of the molecule are obtained from quantum chemical DFT-type calculations. The electrostatic energies in the crystal are provided by the microelectrostatic Fourier-transform approach. The probable accuracy of the results is estimated by testing their sensitivity to changes in the input data. Some related theoretical problems that have to be addressed in the future are pointed out.

Keywords: sexithiophene; CT states; ionization potential; electron affinity; DFT calculations; microelectrostatic calculations

1. INTRODUCTION

Owing to their actual use as photocopier grains and to their potential applications in molecular electronics and optoelectronics, the interest in organic crystals and aggregates is still growing. In this context, the location and properties of charge transfer (CT) states of these systems are of primary importance. In view of their low absorption intensity (at least in one-component organic condensed phase), the CT states must be probed by other experimental techniques, electro-absorption (EA) spectroscopy being the tool of choice. However, the traditional analysis of the EA spectrum by resolution into a set of first- and second-derivative signals [1,2] often proves to be interpretationally misleading [3,4,5,6]; it turns out

* Dedicated to the Memory of Professor Edgar A. Silinsh

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that detailed calculations of crystal eigenstates are necessary to provide in-depth understanding of the relevant physics. In such calculations, based on the configuration-interaction process, the (delocalized) eigenstates are expressed as linear combinations of localized charge configurations.

The necessary input data entail the energies of localized charge pairs. These are usually estimated from the Mulliken formula

$$E^{CT}(R) = I - A - 2P + C(R)$$

where I and A denote the ionization potential and electron affinity of the engaged molecules, 2P is the crystal polarization energy due to a pair of infinitely distant charges, $C(R) = \Delta P(R) - e^2/R$ represents the screened electrostatic interaction between the two charges, with $\Delta P(R)$ standing for the change of the polarization energy when the charges are brought to the finite distance R.

Both the last term, often approximated by the screened Coulomb potential, and the polarization energy P can be evaluated by microelectrostatic calculations, either within the SCPF metod introduced by Silinsh [7] or by the alternative Fourier-transform approach [8,9,10].

The calculations of CT state energies usually rely on experimental input data. In typical cases as polyacenes [4,11,12] the microelectrostatic calculations were based on prior knowledge of the experimental dielectric tensor of the crystal [8]; the ionization potential and electron affinity were also taken from experiment.

Nowadays, interest is focused on less common compounds for which this kind of experimental information is often inaccessible. In that case, the calculations by necessity have to be based on a less complete set of input data. For instance, only the mean dielectric constant of the crystal is known and a more or less educated guess must be made to assume some anisotropy of the dielectric tensor. The I and A values may be calculated by quantum chemical methods, but their accuracy is often insufficient for the purpose and judicious adjustments are necessary. Altogether, it is often possible to achieve reasonable results, but the task is far from trivial.

In the present article this point will be illustrated on the example of the sexithiophene crystal which, in addition to the interest it evokes in its own right, has often been viewed as a model system for elucidating the physics of polythiophenes.

2. QUANTUM-CHEMICAL CALCULATIONS

Based on recent experience in our group [13], we selected the methodology of density functional theory (DFT) as the most promising one for getting reliable

values of the ionization potential and electron affinity of the sexithiophene molecule. As we hope that the systematic errors may be detected and possibly reduced by studying a set of homologues, for reference we have done the calculations for a series of polyacenes where the experimental data are available as a standard. We have applied several alternative approaches: the DFT method with local potential (Vosko, Wilk and Nusair 1980 correlation functional[14]: VWN), local potential with a subsequent nonlocal energy correction (Becke 1988 exchange functional[15] with the gradient-corrected 1986 Perdew correlation functional[16]: BP) and with two different hybrid potentials (Becke's one-parameter hybrid functional[17] using the Lee, Yang and Parr non-local correlation functional [18,19]: B1LYP, and Becke's three-parameter functional [20], with the non-local correlation provided by the Perdew 1991 expression [21,22,23,24,25]: B3PW91), all in the 6–31G* basis set. The calculations were performed using the Gaussian-98 program [26]. The ionization potential and the electron affinity was calculated as a difference between the total energy of the corresponding ion and of the neutral molecule. We discuss here the results obtained for optimized geometries (adiabatic values); vertical values were also calculated but are not addressed here.

At first glance, none of the applied approaches seems to be obviously superior to others. As expected, the errors tend to increase with the size of the molecule, although there are some deviations from this rule in individual cases.

Starting from naphthalene, the VWN and BP functionals consistently underestimate the ionization potential, the errors gradually increasing to 0.23 eV and 0.46 eV, respectively, for pentacene. On the other hand, the electron affinity is consistently overestimated (for pentacene by 0.51 eV and 0.33 eV, respectively). In effect, the errors tend to cumulate when the difference of the two quantities is calculated, as required by Eq.(1). Owing to this instability, there is a serious risk that the total discrepancy (of about 0.75 eV for pentacene) may uncontrollably explode for more complex systems.

The ionization potentials are even more remarkably underestimated by the hybrid density functionals (for pentacene by 0.64 eV within the B3PW91 scheme and 0.91 eV within the B1LYP scheme). However, these functionals also consistently underestimate the electron affinity (by 0.12 eV and 0.43 eV, respectively), so that considerable error compensation occurs when the difference I-A is calculated. Assuming that this conclusion remains valid for non-hydrocarbon systems, the hybrid potentials offer a good chance of avoiding uncontrollable error accumulation in the CT state energies, and therefore may be considered more appropriate for this particular application. This agrees with the results of De Proft and Geerlings concerning the related problem of calculating the hardness parameters of atoms and small molecules [27].

Fig. 1 shows the dependence of the calculated difference I-A on the number of benzene rings in the polyacene series. It is readily seen that for benzene all versions of the DFT approach generally overestimate the calculated quantity, the discrepancy being larger (of the order of 0.8 eV) for the hybrid potentials. On the other hand, for large systems (which is the range of main interest) the B3PW91 and B1LYP schemes are more successful than the VWN and BP schemes, although even the hybrid potentials still consistently yield lower values than experiment. For the largest molecule studied, i.e. for pentacene, the experimental result is underestimated by about 0.5 eV and the observed trend suggests that for polyacenes with a still larger number of rings the discrepancy should gradually increase. Based on extrapolation one may expect that for hexacene (six benzene rings) the hybrid potentials would underestimate the difference I-A by some 0.6 eV.

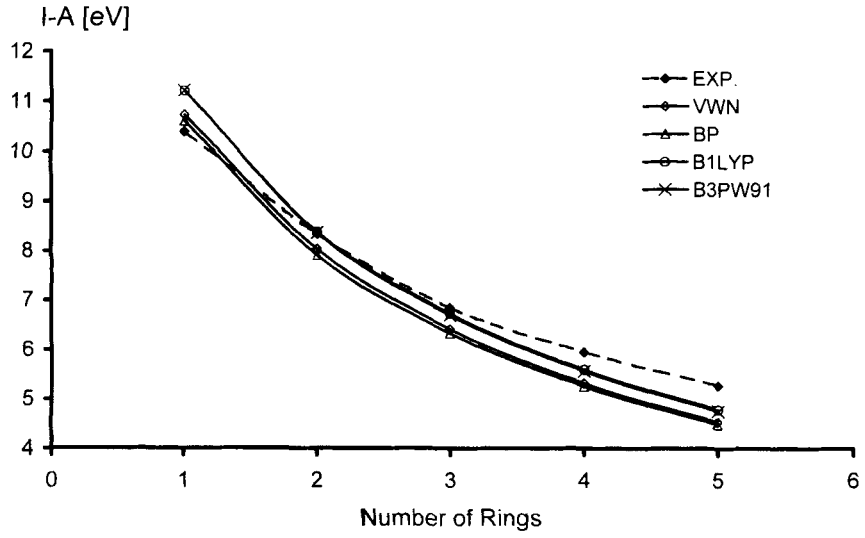

FIGURE 1 Dependence of the difference I-A on the number of rings in the polyacene series (experimental and calculated by different versions of the DFT approach)

Fig. 2 shows a similar plot for oligothiophenes. Unfortunately there are no experimental data to refer to. Based on the polyacene analogy, for large molecules the hybrid potentials are expected to be the more reliable ones, and to underestimate the unknown experimental values. It is reasonable to suppose that for sexithiophene the discrepancy should be roughly the same as for hexacene (same number of rings), i.e. of the order of 0.5–0.6 eV. Accordingly, the expected

value of I-A for the sexithiophene molecule is in the 5.0–5.1 eV range, which may be subsequently used for estimating the CT state energies.

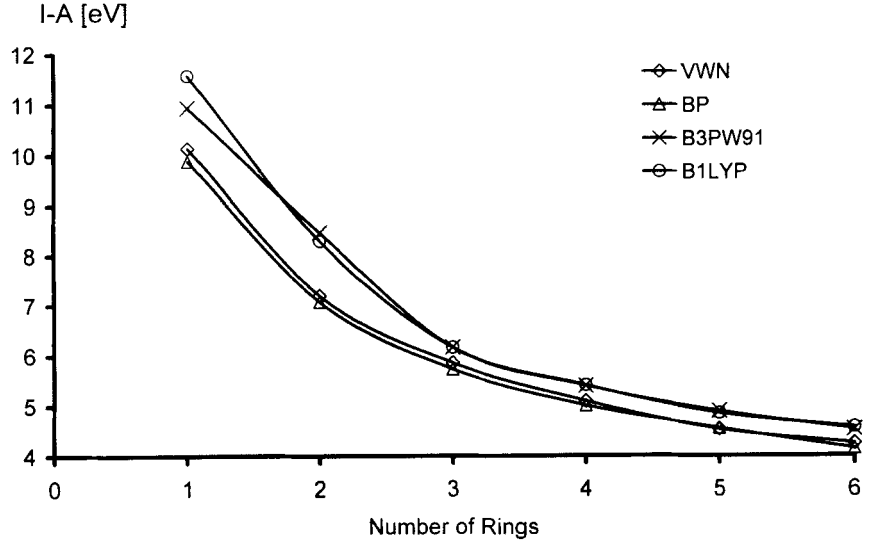

FIGURE 2 Dependence of the difference I-A on the number of rings in the oligothiophene series (calculated by different versions of the DFT approach)

3. MICROELECTROSTATIC CALCULATIONS

The Fourier transform method was described in a series of papers concerning polyacenes [8,9,10]. Its actual implementation used in this article is based on the submolecule approximation, suitable for the highly asymmetric, long molecules of sexithiophene [9,28,29,30]. Each molecule in the crystal unit cell is divided into six submolecules located at the centres of the thiophene rings. If a molecule is ionised, the charge is equally distributed over the six submolecules consituting the ion.

Normally, the effective polarizabilities of the molecules in the crystal are evaluated by fitting the experimental dielectric tensor. Unfortunately, there is no direct experimental evidence concerning its anisotropy in sexithiophene. For this reason, our calculations are based on the experimentally available information regarding the corresponding averaged quantity, while the assumed detailed structure of the tensor and the orientation of its principal axes with respect to crystal axes is based on analogy to the structurally related *p*-terphenyl crystal. This is justified by the results of our recent paper [31] where the sensitivity of the calcu-

lated energies to different choices of the dielectric tensor anisotropy and orientation was found to be marginal, the differences never exceeding several hundredths of an eV.

Our calculations refer to the low-temperature phase of α-sexithiophene. In the crystal, the all-*trans* planar sexithiophene molecules are arranged in close packed, parallel layers showing the herringbone pattern known from the polyacene crystals. The long molecular axis is tilted by about 23° with respect to the normal to the layer, the shortest intermolecular centre-to-centre distance within the layer is less than 5Å, while the interlayer spacing exceeds 22Å. Such a structure implies a pronounced two-dimensional character of the crystal. In particular, charge transfer is expected to occur preferentially along the directions parallel to the layers [32]. The crystal lattice is monoclinic with highly asymmetric unit cell (space group $P2_{1/n}$, a=44.708Å, b=7.851Å, c=6.029Å, β=90.76°) containing four molecules (two pairs from two adjacent layers). The single crystals grown from the vacuum phase have the form of thin flakes (thickness of several μm), with the layers parallel to the platelets surface [32], and are apparently of insufficient size to permit the complete determination of the indicatrix. To the best of our knowledge, the only single crystal refractive index measurement was carried out with the light propagating along the a crystal direction [33]. The refractive index $n_{\parallel}$=1.656 was obtained with light polarized parallel to the optical axis of the crystal (the b direction) while the perpendicular polarization yielded $n_{\perp}$= 1.867. (Unfortunately, the orientation of the indicatrix being undetermined, these values cannot be identified with the principal refractive indices of the αT6 crystal).

TABLE I Single-charge polarization energies and electrostatic stabilization energies (in eV) of charge pairs in the sexithiophene crystal. $\Delta P - e^2/r$ and E^{CT} denote the stabilization energy with respect to the energy of a pair of infinitely distant ions in the crystal and in the gas phase, respectively

		ε = *3.447*	ε = *4.4*
0,1/2,1/2:	P	-0.81	-0.87
	$\Delta P - e^2/r$	-0.58	-0.50
	E^{CT}	-2.20	-2.23
0,0,1:	P	-0.81	-0.87
	$\Delta P - e^2/r$	-0.53	-0.45
	E^{CT}	-2.15	-2.19

Based on some extra information from thin-film experiments [34,35,36], in our preceding paper [31] we took the latter value as the mean refractive index. It corresponds to the macroscopic dielectric constant of 3.447. Since that time, the results of independent direct measurements of the macroscopic dielectric con-

stant have been published [37], producing the value of 4.4. As follows from our present calculations and is shown in Table I, the change of the dielectric constant (with other parameters unchanged) produces only a minor shift of the absolute CT state energies, since the decrease in the electrostatic attraction between the charges is partly compensated by the increase of the stabilization energy of the individual charges.

4. RESULTS

Based on the I-A value from the quantum chemical calculations of section 2 and on the electrostatic stabilization energy from the microelectrostatic calculations of section 3, the predicted energy of the lowest CT configuration in the sexithiophene crystal is in the 2.75–2.85 eV range. This configuration corresponds to a hole located at the centre of coordinates and an electron in the (0,1/2,1/2) crystallographic position. For the CT configurations where the electron is located in the (0,0,1) and (0,1,0) positions the energy is higher by 0.04 eV and 0.18 eV, respectively.

The EA spectrum of the αT6 thin film displays in the 2.7–3.1eV region a complex structure, whose intensity and shape change considerably with temperature. For fullerene crystals, such behaviour was found characteristic of the EA signal from eigenstates of CT parentage [38,39], which is consistent with the original assignment of the sexithiophene EA structure mentioned above to excitons of CT origin [40].

Although such excitons usually contain admixtures of Frenkel character and are delocalized, so that they cannot be directly identified with the localized charge configurations studied in this paper [5,6,42,43], our experience suggests that in typical cases the shifts and splittings caused by the off-diagonal interactions rarely exceed 0.1–0.2 eV [41]. Accordingly, the diagonal energies of localized CT configurations provide a reasonable approximation of the corresponding eigenenergies. On this view, the agreement between the energy range where CT-type excitations are observed by electro-absorption and the predicted energies of localized CT configurations in sexithiophene seems to confirm the validity of the adopted approximations.

We have demonstrated previously [31] that these energies are almost insensitive to the uncertainties regarding the detailed form and orientation of the dielectric tensor of the crystal; owing to compensation effects, they are also barely affected even by relatively substantial changes of the mean dielectric constant. The variation of the results is of the order of 0.05 eV. Therefore, the lack of or inaccuracies

in experimental information concerning this group of input data has a relatively minor effect on the net predictive power of the theoretical approach.

On the other hand, the errors inherent to the quantum chemical calculations of section 2 are much larger, in the 0.5 eV range. The calculations for polyacenes suggest that the DFT approach with hybrid potentials systematically underestimates the difference between the ionization potential and electron affinity, giving rise to a uniform shift of all CT levels. It seems that this shift should be comparable for molecules of comparable size. This allows one to adopt a correcting procedure whereby all CT state energies are consistently increased by a constant scaled for a set of molecules for which complete experimental information is available. For sexithiophene this simple expedient turns out to be remarkably successful, reproducing the experimental range of CT state energies observed by electro-absorption correct to about 0.1 eV, i.e. within the accuracy set by the neglect of the off-diagonal CT interactions. In order to achieve a still better accuracy and a better understanding of the sexithiophene EA spectra, these interactions would necessarily have to be included in the theoretical model. The corresponding extensive study is presently underway in our laboratory.

5. DISCUSSION

It would be premature to draw general conclusions based on the single case of sexithiophene, but our results do suggest that the quality of input data affects the electrostatic part of the calculated CT state energies only marginally, and that the ionization potential and electron affinity are the main sources of errors. It seems worthwhile to invest more experimental effort in measuring these quantities.

The main experimental tool that can be used to study the CT states is electro-absorption spectroscopy which is a very sensitive and in effect interpretationally unforgiving technique. In spite of these difficulties, the recently developed models [42,43,44] seem to provide an effective theoretical framework in which to interpret the EA signals, as demonstrated by successful reproduction of the spectra of several crystals [43,44]. However, these models rely on the input data that have to be gathered either from independent experiments or from theoretical calculations.

As a rule, the off-diagonal matrix elements of the Hamiltonians come from this latter source. The methods for calculating the dipole lattice sums, which yield the effective Frenkel exciton transfer integrals, were developed in the seventies and eighties (ref. [45] and references therein). The same essentially applies to charge transfer integrals [46,47,48] although this task is much more difficult because a very realistic representation of atomic orbitals is necessary to correctly reproduce

the long-range behaviour of the wavefunctions, which is of critical relevance. On the other hand, the evaluation of the matrix elements diagonal in the localized basis set has been traditionally based to a large extent on independent experimental information: the effective polarizabilities were normally obtained by fitting the experimental dielectric tensor, while the ionization potential and electron affinity were taken directly from experiment. These data are not accessible for many crystals of interest. Moreover, it is one of the priorities of any theoretical treatment to minimize the necessary input that has to be gathered from experimental data.

So far, the accuracy of quantum chemical calculations of the ionization potential and electron affinity of large molecules was insufficient for interpretation of the EA spectra. The present results suggest that the DFT methodology combined with a judicious correcting scheme might in some cases allow one to approach the necessary level of accuracy, although it would be premature to assess the general validity of this shortcut. Ultimately, it can be considered only as a tentative measure to be used until more accurate quantum chemical methods become accessible for large molecules.

In the future, also the molecular polarizabilities obtained from experimental dielectric data should be replaced by the calculated ones (e.g. from DFT calculations). Apart from the accuracy of the calculated values, this presents another problem: the effective polarizability which correctly reproduces the dielectric tensor is normally some 10% larger than that of an isolated molecule. This difference is easy to rationalize in principle, since the molecule in the crystal is bound to be affected by its neighbours, but the detailed explanation is less obvious. Upon closer scrutiny, in most cases of interest the nonlocal contributions to ground-state polarizability [49,50] turn out to be much smaller, and those due to the shifts of the intramolecular energy levels seem to be too small as well.

Interpretation of an EA spectrum is a complex multi-step process. In the first place, it requires an effective theoretical model of the coupling between the CT and Frenkel excitations of the crystal. Such models have been developed and tested for several systems. Although they need some extensions and extra testing to handle other cases, they provide the necessary conceptual framework for further studies. However, as illustrated here on the example of sexithiophene, the necessary input data are not readily available for less common crystals of interest. In order to fill this gap without resorting to experiments, quantum chemical methods will have to be improved to provide more reliable values of the ionization potentials, electron affinites and molecular polarizabilities. Tentatively, *ad hoc* correcting schemes may be used to approach the needed accuracy. On the solid-state side, the relationship between the polarizabilities of an isolated mole-

cule and that embedded in the crystal is far from clear and deserves more attention in the future.

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