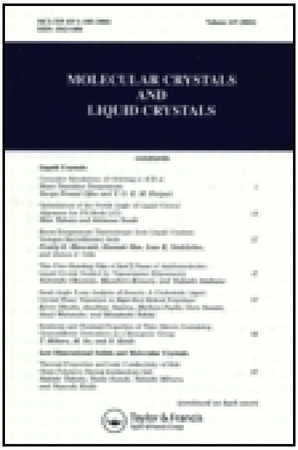

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Charge Transfer States in Polyacene Crystals - Direct and Indirect Manifestations of Their Existence

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CHARGE TRANSFER STATES IN POLYACENE CRYSTALS - DIRECT AND INDIRECT MANIFESTATIONS OF THEIR EXISTENCE

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Abstract Direct (photocurrent) and indirect (Frenkel exciton spectra) manifestations of the existence of charge transfer states in polyacene crystals are analyzed. The new calculations suggest that the photocurrent spectrum of anthracene may be consistently rationalized without resorting to different band gaps for electrical and optical phenomena. The indirect CT effects in the local states of doped naphthalene crystals are semiquantitatively interpreted in terms of a two-dimensional cluster model.

From the point of view of many possible applications of organic materials (e.g. in molecular electronics), the understanding of their photocurrent characteristics may be of critical importance. This motivates the interest in charge transfer states, which are the precursors of quasi-free charge carriers.

The anthracene crystal is the only organic system for which a semiquantitative interpretation of the photocurrent spectrum has ever been attempted[1]. The interpretation[1] was based on the notion of charge transfer (CT) states created by direct optical absorption and dissociating thermally according to the Onsager mechanism. In order to reproduce the wavelength dependence of the photocurrent quantum yield $\phi^0(h\nu)$ and activation energy $E_a(h\nu)$, a semi-empirical theory rooted in the one-dimensional Merrifield model[2] was proposed. Three adjustable parameters were introduced: the total intensity I_{CT} of optical absorption to the CT states, the constant Λ governing the decrease of absorption intensity with the distance between the electron and the hole (radius of the CT state), and the width Δ of an individual CT band. While independent arguments derivable from the Merrifield model[2] allowed to set some limits on the former two values, there were no obvious constraints on the value of Δ (=0.03 eV in the final fit). The band gap E^G=4.18 eV was estimated from the experimental $E_a(h\nu)$ plot by extrapolation to zero activation energy. The uniqueness of the final fit was not verified at that time.

The subsequent measurement of the electroabsorption spectrum of the anthracene crystal[3] produced different values of the band gap and of the width. The discrepancy between the value of the ("optical") band gap obtained from electroabsorption experiments (4.4 eV), and the ("electrical") value on which the interpretation of the photocurrent spectrum had been based (4.18 eV), was attributed to lattice relaxation[4,5], which in that case appeared to be unreasonably large[5]. This started a long standing controversy in the literature.

Our new results demonstrate that the original fit of the photocurrent spectrum[1] may not only be equalled, but even improved (without increasing the number of adjustable parameters) if the "optical" value of the band gap (4.4 eV) is used, provided that the width is also changed (Δ=0.06 eV).

The calculations[6] are based on a model similar to that used previously[1], with a slight modification in the way the CT state energies and absorption intensities are generated. Our present approach takes into account the anisotropy of the crystal by adopting realistic geometry (monoclinic structure), assuming the dielectric constant to depend on crystal direction (with the interpolation suggested previously for large electron-hole distances[7]) and relating the intensity decrease constants Λ_i for different crystal directions to the values of the corresponding charge transfer integrals (known from calculations of other authors[8]). The empirical parameter that replaces the parameter Λ of ref.1 is the overall scaling factor common for all crystal directions. However, the details of crystal structure and its anisotropy turn out to have only secondary effect on the results, so that ultimately the difference in the quality of the fit has to be attributed mainly to the different values of the adjustable parameters.

The new parameter values are closer to those that emerged from the microscopic model[1], and therefore are more credible physically. The reproduction of the photocurrent characteristics is better than that obtained previously. It is also more consistent, since the results reproduce the $\phi^0(h\nu)$ and $E_a(h\nu)$ dependences from the same set of experimental data[9], which was not the case previously.

The present results demonstrate that, contrary to previous contentions, the electrical band gap of 4.4 eV (rather than 4.1-4.2 eV) is entirely compatible with the observed photocurrent spectrum. It is the procedure of determining the band gap from the wavelength dependence of the photocurrent activation energy which is suspect. This suggests that the distinction between the "electrical" and "optical" band gap is probably unnecessary.

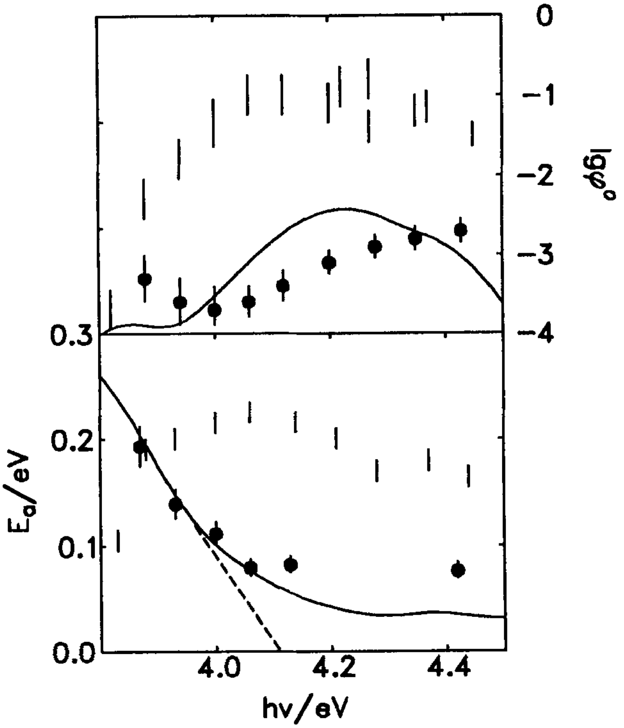

FIGURE 1 Calculated vs experimental photocurrent spectra. Barred dots - ref. 9, bars - ref. 10.

While the relevance of the CT states to the interpretation of electrical phenomena has never been seriously challenged, the indirect role of those states in optical spectroscopy of one component organic crystals has not been recognized until recently. The exciton spectra of typical crystals (like anthracene) are dominated by the Frenkel states. However, the recent results[11,13] suggest that some properties of the Frenkel excitons are governed by the CT interactions. For instance, the Davydov splitting in the lowest excited state of tetracene[11], pentacene and naphthalene[12,13] seems to be largely due to the coupling of this state with the CT manifold. The effects of charge transfer are still more prominent in the pressure dependence of the Davydov splitting in naphthalene and anthracene, which is apparently controlled by the CT contributions[12,13].

New evidence of the indirect influence of the CT states on the Frenkel manifold, mediated by the off-diagonal coupling, is found in the spectra of the doped naphthalene crystals[14-16]. As the exciton resonance integrals in the lowest Frenkel state of the naphthalene crystal are very small, the contribution of charge transfer terms to the interaction between the impurity and the host crystal becomes important. In effect, Charge Transfer Induced Local Frenkel States (CTILFES) are formed[17].

This is demonstrated by the experimentally observed dependence of the energy of the lowest local Frenkel state on the ionization potential of the impurity[14-16].

A semi-quantitative interpretation of this dependence may be obtained within the following simple model of the coupling between the Frenkel and the CT excitons[18]:

The crystal is represented as a rigid two dimensional cluster with two molecules in the unit cell, monoclinic structure and periodic boundary conditions. One of the molecules (substitutional impurity) is different from the others. The lowest electronic excited states of the cluster are superpositions of localized Frenkel excitons and localized nearest neighbour CT states involving the electron and the hole in the (0,±1,0) and (±1/2,±1/2,0) relative positions.

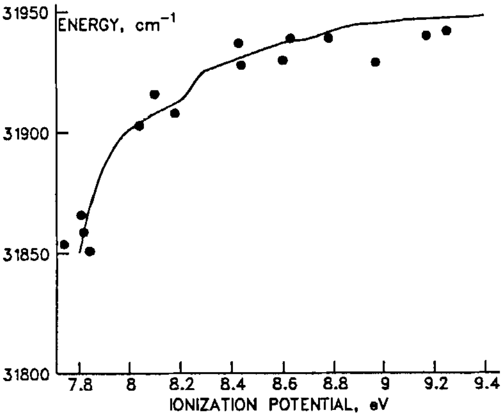

FIGURE 2 The energy of the lowest local state in doped naphthalene crystals vs the ionization potential of the impurity. The points correspond to experimental results.

The Hamiltonian, where only the nearest neighbour interactions are taken into account, is essentially a two dimensional analog of that proposed by Merrifield[2] and subsequently generalized[11,13]. The eigenstates of the system are found by its direct diagonalization.

The typical cluster sizes that can be handled range from 6×7=42 to 10×12=120 molecules. The calculations of other authors (available in the literature) provide reasonable estimates of all the necessary matrix elements, so that the treatment is essentially non-empirical.

The main success of this approach consists in its ability to account for the large stabilization energies of the local states observed for the impurities with low ionization potential, which were impossible to rationalize in terms of earlier models of local excitons.

A direct generalization of the cluster model for an infinite crystal[19] may be applied in the interpretation of electro-absorption spectra. In contrast to the models used previously in that context[19], it accounts correctly for the symmetry of the crystal. Our tentative results suggest a prominent role of the phonon subsystem in electroabsorption spectroscopy of CT states.

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