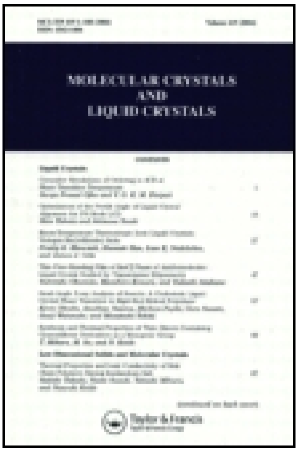

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Charge Transfer States in Polyacene Crystals

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CHARGE TRANSFER STATES IN POLYACENE CRYSTALS

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Abstract The role of charge transfer states in theoretical interpretation of spectroscopic experiments on polyacene crystals in electric field (photocurrent and electroabsorption) is discussed. A crude estimate suggests that while the low energy part of the photocurrent spectrum is probably dominated by CT states generated by direct optical absorption, at higher energies Frenkel exciton autoionization is likely to prevail. For electroabsorption, the notion of CT state degeneracy as a possible reason of the second derivative contribution is examinded on a simple dimer model.

INTRODUCTION

In standard UV-VIS spectroscopy of polyacene crystals, charge transfer (CT) states are practically unobservable. However, their role is essential for spectroscopic experiments in electric field. There are two main groups of such experiments.

PHOTOCURRENT SPECTRA

The anthracene crystal is normally considered as an archetypic example for this sort of measurements[1-3].

The low energy part of its photocurrent spectrum (up to about 4.3 eV) has been semiquantitatively interpreted based on the notion of direct optical generation of CT states and their subsequent thermal dissociation[4-6]. Although some of the detailed assumptions underlying that model are still open to discussion, the reasonably good reproduction of the dependence of the photocurrent quantum yield and activation energy on the energy of incident photons[6] seems to support the conceptual validity of that approach.

At higher energies, the calculated quantum yield of the generated charge carriers drops down, in conflict with the experimental spectrum[1] which registers a further rise (up to a local maximum at about 4.55 eV, followed by two other maxima at 5.5 eV and 6 eV). Concomitantly, the activation energy stabilizes at about 0.09 eV (for $h\nu \approx 4.5$ eV), to drop to a new constant value of 0.07 eV at about 5.5 eV.

These results indicate that a new mechanism may become operative at about 4.5 eV. We suggest (following the early papers on the topic[7-8]) that autoionization of S_3 Frenkel excitons is likely to contribute in that energy range.

The recent results[6] suggest that the bottom of the conduction band in anthracene is located at about 4.4 eV. All states whose energies are higher, are immersed in the continuum of quasi-free electron states, possibly accompanied by vibrational excitations.

An estimate of the decay rate of a discrete Frenkel state into the quasi-free electron continuum may be obtained from the Fermi Golden Rule. Suppose that the crystal is a three dimensional cube with N^3 molecules and that the width of the conduction band is Δ. Then, a rough estimate of the density of states in the band is

$$\rho(E) = N^3/\Delta \qquad (1).$$

The coupling between the Frenkel state and the continuum is mediated by exciton dissociation integrals $\langle A^*B|H|A^+B^-\rangle$ and $\langle A^*B|H|A^-B^+\rangle$. In the nearest neighbour approximation the coupling of the discrete state to the band states assumes the form

$$V(l,m,n) = V\,[\delta_{l,0}\,\delta_{m,0}\,(\delta_{n,1}+\delta_{n,-1})+\delta_{m,0}\,\delta_{n,0}\,(\delta_{l,1}+\delta_{l,-1})+ \delta_{l,0}\,\delta_{n,0}\,(\delta_{m,1}+\delta_{m,-1})] \qquad (2),$$

where l,m,n are the crystallographic indices representing the position of the band electron, and V is the exciton dissociation integral.

The Fourier transformation of Eq.(2) and subsequent substitution in the Fermi Golden Rule yields

$$k = 16\pi/\hbar\; V^2\,(\cos\kappa_x + \cos\kappa_y + \cos\kappa_z)^2/\Delta \qquad (3)$$

for the sought decay rate (including an additional factor of 2 to account for the two ionization channels, corresponding to the two types of dissociation integrals defined above). κ_x , κ_y and κ_z stand for the components of the wave vector of the electron in the conduction band state which is degenerate with the autoionizing Frenkel level.

For anthracene, $V \approx 0.05$ eV[9], $\Delta \approx 0.25$ eV[10]. Both the bandwidth and the dissociation integrals have to be reduced by polarization effects (about -30%[11]) and vibrational overlap factors. This latter factor, estimated from the photoionization spectrum is about 0.65; effectively, Δ=0.11 eV.

Hence, the conduction band extends from 4.4 eV to 4.51 eV, so that the S_3 state at 4.63 eV is out of it. However, the first vibronic replica of the band (with vibrational excitation on the presumably stationary hole) extends from 4.57 eV to 4.68 eV, and the S_3 state is embedded in this continuum.

Consequently, the effective dissociation integral relevant to autoionization should be reduced according to the formula

$$\tilde{V} = \langle A^*B|H|A^+B^-\rangle = V\,(\chi_0^{A^*}|\chi_1^{A^+})\,(\chi_0^{B}|\chi_0^{B^-}) \qquad (4),$$

(where (|) denotes integration over vibrational coordinates), and by additional 30% on account of polarization. A simple estimate from the photoelectron and absorption spectra yields $(\chi_0^{A^*}|\chi_1^{A^+})^2$=0.04.

In order to estimate the wave vector dependent part of Eq.(3), we assume for the dispersion curve the shape appropriate for a one dimensional crystal

$$E(k) = E_0 + \Delta/2 \cos \kappa_x \qquad (5),$$

Given the band gap E^G=4.4 eV[6], it is straightforward to find that the discrete state at 4.63 eV is degenerate with the band state for which $\cos \kappa_x = 0.09$. Assuming that the band structure is the same for κ_y and κ_z, and that the decay channels to the κ_x, κ_y and κ_z manifolds are independent, one gets from Eq.(4) $k \simeq 7\times10^{11}$ s^{-1}.

The decay rate of the S_3 state in solution[12] is $k_{rel} \simeq 10^{14}$ s^{-1}. Assuming the same value for the crystal, one gets $\phi = k/(k_{rel}+k) = 0.007$ for the yield of created geminate pairs. It agrees very well with the experimental value, which is between 10^{-3} and 10^{-2} [1,3].

There is essentially no reason to prevent the autoionization process from generating a state where the created cation or anion would be excited. Based on the excitation energies of the ions, the corresponding autoionization channels are expected to open at 5.5-5.6 eV and 6.0-6.2 eV. (It should be noted that in view of the low electron affinity of anthracene, the excited states of the anion would not be bound in the gas phase; in the crystal they are stabilized by intermolecular forces).

In analogy to the situation encountered at about 4.4 eV, there should exist a manifold of bound (finite radius) CT levels just below the threshold energy for each new autoionization channel. They would be shifted by 1.1-1.2 eV and 1.5-1.7 eV with respect to those observed by Sebastian et al.[13]. The lowest ones should appear at about 4.6-4.7 eV. The background in the absorption spectrum, starting to rise smoothly from that energy might be a manifestation of their existence.

They should contribute to the photocurrent; although Frenkel exciton autoionization is expected to be the dominant mechanism of charge generation in that energy range, it is reasonable to suppose that the cumulation of the contributions due to direct excitation of the CT levels and to autoionization should in each case produce a maximum in the charge carrier quantum yield, just as it does in the vicinity of the lowest autoionization threshold (4.4 eV).

The experimental photocurrent quantum yield[1] registers maxima at about 5.5 eV and 6 eV, i.e. at the onsets of the new continua - in very good agreement with this interpretation. In each case, a peak in the absorption spectrum indicates the presence of an intense Frenkel state nearby, likely to autoionize into the new continuum, and lending intensity to the CT states. The fact that the maxima in the photocurrent appear at slightly lower energies than their counterparts in absorption might support this qualitative picture.

By and large, it seems that the near threshold (3.8-4.3 eV) photocurrent of anthracene is due to directly generated CT states, while at higher energies the autoionization mechanism probably prevails.

ELECTROABSORPTION

There is presently no doubt that the high energy part of the electroabsorption spectra of polyacene crystals is dominated by a contribution that follows the second derivative of the absorption spectrum (first order Stark effect) and is due to CT states. Common knowledge attributes the prominence of CT states in the electro-modulated signal to their large permanent dipole moment. Yet, symmetry considerations based on the molecular and lattice structure of those crystals (invariance of the Hamiltonian upon electron-hole exchange) evidently rule out the existence of electronic states with non-zero dipole moment.

Two solutions of this paradox have been proposed. According to one[14], the second derivative electroabsorption signal of CT states is either non-intrinsic or non-bulk, and supposedly results from the energetic inequivalence of the (+-) and (-+) local states in the vicinity of defects, surfaces etc. The other explanation[15] attributes the observed signal to quasi-degeneracy of the crystal eigenstates of CT parentage. If this interpretation is to be adopted, it is necessary to assess how closely the eigenstates would have to be spaced, in order to behave as effectively degenerate in the electric field used in typical experiments. This is our present objective.

It is expedient to study the effect on the simplest, i.e. dimer, model. We assume that there are two excited local CT states ((+-) and (-+)), spaced in energy by Δ in the absence of electric field, and coupled by an effective "exchange" integral V. In the electric field, the energies of the local (basis) states change by $-\frac{1}{2}pF^2 \pm mF\cos\vartheta$, m and F denoting the dipole moment of the (+-) state and the electric field strength, respectively, ϑ standing for the angle between the two vectors, and p being the polarizability in the CT states. In the local basis, the Hamiltonian matrix reads:

$$\begin{bmatrix} -\frac{1}{2}pF^2 - mF\cos\vartheta & , & V \\ V & , & \Delta - \frac{1}{2}pF^2 + mF\cos\vartheta \end{bmatrix} \qquad (6).$$

This matrix can be analytically diagonalized to yield the eigenvalues and eigenvectors at arbitrary field and for arbitrary values of the parameters. The electroabsorption signal is evaluated by subtracting the absorption spectrum at F=0 from that calculated at given F≠0.

For this purpose, each of the eigenstates is represented by a Gaussian, whose width is taken as energy unit. The transition moment μ of the zero-order (+-) and (-+) states is taken as another unit. The intensity of each of those states is assumed to be polarized fractionally (x) along the direction of the permanent dipole moment **m** and fractionally (1-x) perpendicular to it. The former part is the intrinsic transition moment of the CT state, while the latter represents the contribution borrowed from the Frenkel states. The parameter $x \in [0,1]$ governs this polarization ratio. The results are averaged over possible orientations of the dimers by numerical integration over the angle ϑ, assuming that **m**, μ and **F** are coplanar.

The ground state of the dimer is assumed to be neutral and (for the sake of simplicity) to have zero polarizability.

In the bulk of a polyacene crystal Δ=0. With 10^4 V/cm as unit of electric field and the Gaussian width of 0.04 eV[13], $p=3\times10^{-7}$ and $m=10^{-2}$ may be considered as typical values. 2V is the splitting between the eigenstates in zero electric field and imitates the gap between the quasi-degenerate states of CT parentage in the actual crystal. It is the dependence on this parameter which is the main point of this paper.

The details of the calculations and results will be published elsewhere. In general, the calculated electroabsorption signal is a superposition of the contributions that follow the first and the second derivative of the absorption spectrum, and their weights depend on the electric field. For the parametrization described above and up to reasonably strong electric fields ($F=200$), the second derivative contribution evidently dominates when $V\leq 1$.

Hence, it is the width of the CT transitions that sets the scale according to which the CT levels should be classified as quasi-degenerate or not. The tentative results[16] indicate that in polyacene crystals there may be many such levels in an energy interval of the order of the typical width of bands observed in electroabsorption (0.04 eV). This suggests that detailed quantitative interpretation of electroabsorption spectra of these crystals may not be amenable to simple considerations of isolated states or even of isolated pairs of states, but may need a more complete approach where the electric field induced coupling between multiple states would be properly taken into account.

It seems generally that the ultimate understanding of electromodulation spectroscopy of centrosymmetric one-component crystals, although misleadingly simple at the first glance, may require a great deal of new conceptual effort.

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