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Exciton Trap Depths in Orientationally Disordered Anthracene Crystals

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Results of calculations of exciton trap depths in orientationally disordered anthracene crystals are presented. It is found that a single line of misoriented molecules is insufficient to form a trap, but that more extended disordered regions can lead to significant trap depths when the geometry is favourable.

1. INTRODUCTION

In a recent paper, Craig, Ogilvie and Reynolds[1] made estimates of the extent of orientational disorder in anthracene crystals using energy calculations based on atom–atom potentials. They postulate a simple form of imperfection in which molecules may adopt one of the two orientations observed in the perfect crystal, the disorder arising because the regular pattern is disturbed. They estimate that lines of misorientated molecules are associated with vacancies and dislocations and quote series of 10–100 molecules along direction [010] as an example.

The same workers also find that their calculations suggest three alternative crystal structures close in energy to the observed $P2_1/a$ form which may be labelled by the space group to which they belong: $P2_1/c$, $P2_1/n$ and $P\bar{1}$. Each structure involves the same molecular orientations as in $P2_1/a$ but with different relative arrangements.

In this way, two extreme possibilities have been distinguished for orientational disorder: a single line of misoriented molecules and an extended region with one of the alternative crystal structures.

The study of photodimerisation in anthracene has led to the idea that the chemical reaction takes place in the region of an extended defect in the crystal. The initial photon absorption is to an excited state which is delocalised over the perfect crystal $P2_1/a$ structure. Photochemical reaction takes place at a specific site so that there must be a transition from a delocalized to a localized state before the reaction can take place. Fluorescence from impurity molecules is a competing process and this too necessitates a transition from a delocalized to a localized state. The dynamics of this have been discussed[2] and transition rates estimated which are consistent with experimental fluorescence lifetimes.

A genuine localized state must lie outside the exciton band of delocalized states and is lower in energy in the processes mentioned here. A measure of this is given by the trap depth which is the difference between the energy of the localized state and that of the bottom of the exciton band. It is the object of this paper to calculate trap depths for excitons associated with regions of orientational disorder in crystalline anthracene.

In Section 2, an expression for the trap depth is developed in terms of the matrix elements appearing in exciton theory. A central role is played by the site shift term and the form of this is discussed in detail in Section 3. Finally, the results of calculations of trap depths are presented in section 4 and their implications discussed.

2. EXCITON THEORY AND TRAP DEPTHS

The transition energy from the ground to an exciton state may be written in the simplified form

$$E_{\mathbf{k}} = \Delta\varepsilon + D + I_{\mathbf{k}} \tag{2.1}$$

The energy is partially specified by a wave vector **k** reflecting the translational symmetry of the perfect lattice. $\Delta\varepsilon$ is the gas phase transition energy from the ground state to the corresponding free molecule excited state. D is the formal shift energy term representing the change in the one molecule transition due to the presence of the other crystal molecules. In the case of a molecular crystal, it may be described as the difference between the van der Waals energy for a reference excited state molecule interacting with the surrounding ground state molecules and the same reference ground state molecule with surrounding ground state molecules. It is of central importance in this paper and its form is given in more detail later. $I_{\mathbf{k}}$ is a term describing the effect on the energy of the migration of the excitation from molecule to molecule. The whole set of $E_{\mathbf{k}}$ forms a bounded continuum, the exciton band.

A localized level of the system leading to a trap lies in the gap between the exciton band and the ground state of the crystal. For an impurity molecule, this is easily achieved since the free molecule transition energies are different from the host and can lead to a state lying in the gap. Vibrational levels based on the trap are in resonance with the exciton band and radiationless transitions into the localized system are relatively facile.

Localized levels associated with displaced host molecules cannot arise in this way. The site shift term D is strictly defined separately for each molecule and its value depends on the environment of that molecule. In the perfect crystal region the environment of each molecule is the same so that only a single D term appears in the energy expression Eq. (2.1). In a defect region, however, different values of D arise. If the change in D from the perfect crystal value is sufficiently great to clear the exciton band width, then a localized host molecule state and hence a trap may occur. The trap depth may thus be approximately written

$$\sigma = D' - D - I_{\mathrm{m}} = \Delta D - I_{\mathrm{m}} \tag{2.2}$$

I_{m} is the resonance term for the bottom level of the band and D' is the shift term for the displaced molecule (or a suitable average value for the molecules in an extended defect). ΔD is the change in the D term from the perfect crystal structure.

3. THE SITE SHIFT TERM

The site shift term D introduced briefly in Section 2 should when expressed more fully contain a reference to the particular molecule under consideration. In this way, for a molecule n and an excited state labelled by r

$$D_n^r = \sum_{m \neq n} (W_{nm}^{r0} - W_{nm}^{00}) \tag{3.1}$$

W_{nm}^{r0} represents the van der Waals interaction energy between molecule n in excited stage r and molecule m in its ground state. Correspondingly W_{nm}^{00} is the interaction energy for both molecules in the ground state. The van der Waals interaction in general contains terms of several kinds but it is here the difference between two such expressions which is of interest. Following previous work[3] attention is confined to the dipole–dipole term of the dispersion interaction. In this way, W_{nm}^{r0} becomes

$$W_{nm}^{r0} = - \sum_{s \neq r} \sum_{t \neq 0} (\mu_n^{rs} \mu_m^{0t})^2 (I_{nm}^{rs0t})^2 (E^{sr} + E^{t0})^{-1} \tag{3.2}$$

with a corresponding expression for W_{nm}^{00}. μ_n^{rs} is the magnitude of the dipole moment for a transition from state r to s in molecule n. E^{rs} is the free molecule transition energy in the sense $E^s - E^r$. I_{nm}^{rs0t} is the term describing the dependence on the separation and mutual orientation of the two transition dipoles.

$$I_{nm}^{rs0t} = R_{nm}^{-3}\{(\hat{\boldsymbol{\mu}}_n^{rs} \cdot \hat{\boldsymbol{\mu}}_m^{0t}) - 3(\hat{\boldsymbol{\mu}}_n^{rs} \cdot \hat{\mathbf{R}}_{nm})(\hat{\boldsymbol{\mu}}_m^{0t} \cdot \hat{\mathbf{R}}_{nm})\} \tag{3.3}$$

R_{nm} is the distance between the centres of molecules n and m. $\hat{\mu}_n^{rs}$ is the unit vector along the direction of the transition dipole moment and $\hat{\mathbf{R}}_{nm}$ the unit vector along the line joining n to m. In anthracene, the transition dipole moment may only lie along one of the three symmetry axes of the molecule. The sums appearing in Eq. (3.2) may thus be divided according to the dipole directions involved. A convenient procedure, following Craig and Dissado,[4] is to replace each of the geometrically classified sums by a single term. The interaction may then be described in terms of a small number of average energies and transition dipole moments. In this way Eq. (3.2) becomes

$$W_{nm}^{r0} = -\sum_{ab} d_a^2\, d_b^2 (I_{nm}^{ab})^2 (E_a^r + E_b^0)^{-1} \tag{3.4}$$

a and b are summed over the three dipole directions in molecules n and m respectively, which are sufficient to specify the geometrical factor I_{nm}^{ab}. d_a is the transition dipole moment for direction a, assumed to have the same value for transitions from ground and excited state. E_a^r is the single energy term assumed for transitions along a from state r. The values of the parameters used here are summarized in Table I and are taken from Craig and Dissado.[4] L is the longer, and M the shorter in–plane symmetry axis and N normal to the plane.

The shift term D_n^r may thus be calculated using the expressions developed in this section for perfect and defect regions provided the structures are known.

TABLE I

Values of parameters used in site shift calculations for anthracene

Axis a	L	M	N
Square of transition dipole $d_a^2/10^{-18}$ m^2	0.0753	0.0798	0.0479
Ground state average energy E_a^0/cm^{-1}	42,270	59,800	59,800
Excited state average energy E_a^r/cm^{-1}	25,104	48,628	59,800

4. RESULTS AND DISCUSSION

In this section, the results of calculations for traps in orientationally disordered regions of the crystal are reported. According to Eq. (2.2), the trap depth σ is given by the difference in shift terms ΔD between a molecule in the defect and a molecule in the perfect crystal minus I_m the resonance term for the bottom level of the exciton band. The calculation of ΔD has been discussed in detail in Section 3. I_m is not known exactly but may be approximated as half the Davydov splitting of the origin electronic band. Using the experimental data of Lacey and Lyons[5] I_m is given the value 190 cm^{-1}.

For the defect systems considered, values will always be given for ΔD, but σ will only be quoted if its value is negative i.e. only if a trap is actually predicted.

In the first set of calculations, one row of molecules is changed in orientation. To simplify the model it is assumed that the misplaced row is infinitely long so that D' refers to an arbitrary molecule in the row. Values are given for rows parallel to the *a*, *b* and *c* unit cell directions with the results

Axis	*a*	*b*	*c*
ΔD/cm^{-1}	−182	−157	−186

It can be seen that no trap is formed for any of these possibilities but that the D term has about the same magnitude as I_m. In this way, the minimum orientational disturbance leads to a shift term which essentially cancels out the band width. A more extended region of disorder might then be expected to lead to a trap in favourable cases.

It is strictly an approximation to calculate trap depths by using only a single molecule type in the defect region. To give an estimate of the rapidity of change, ΔD has been calculated to be 80 cm^{-1} for a molecule adjacent to a misoriented row.

A maximum degree of orientational disturbance can be investigated by referring to the alternative crystal structures suggested by Craig, Ogilvie and Reynolds.[1] ΔD may then be calculated in which D' refers to a molecule in one of these new structures and D to a molecule in the regular $P2_1/a$ crystal. The results are as follows

Structure	$P2_1/c$	$P\bar{1}$	$P2_1/n$
ΔD/cm^{-1}	−532	−480	+248
σ/cm^{-1}	−342	−290	

The implication is that regions in the anthracene crystal having structures close to $P2_1/c$ and $P\bar{1}$ would act as very effective exciton traps whereas $P2_1/n$ would not.

An important feature of the D term calculations in the form presented here is that the change in intermolecular energy on excitation is ascribed solely to changes in dispersion interactions. These are attractive terms varying as R^{-6}. It is therefore important that relaxation should be allowed for in the defect region under consideration, so that the ground state should be in equilibrium within the constraints imposed by the defect conditions. In addition if molecules are much closer than in the minimum structure, the D terms become large and spurious results may be obtained.

TABLE II

Unit cell parameters for four possible crystal structures of anthracene, with molecular positions and orientations

	$P2_1/a$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/nm	0.809	0.860	0.846	0.870
b/nm	0.596	0.586	0.585	0.567
c/nm	2.216	2.203	2.263	2.274
α/deg	90	90	90	88.6
β/deg	123.0	124.4	122.7	122.9
γ/deg	90	90	90	91.9
Molecules with orientation 1	(000) ($00\frac{1}{2}$)	(000) ($\frac{1}{2}00$)	(000) ($\frac{1}{2}0\frac{1}{2}$)	(000) ($00\frac{1}{2}$) ($\frac{1}{2}00$) ($\frac{1}{2}0\frac{1}{2}$)
Molecules with orientation 2	($\frac{1}{2}\frac{1}{2}0$) ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$)	($0\frac{1}{2}\frac{1}{2}$) ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$)	($\frac{1}{2}\frac{1}{2}0$) ($0\frac{1}{2}\frac{1}{2}$)	

The unit cell is chosen to be the same for each structure, except for the effects of relaxation, and is not primitive for any of the examples. Molecules of orientation 1 are transformed to those of orientation 2 by a 180 degree screw rotation about the b axis.

In the work of Craig, Ogilvie and Reynolds,[1] the structures have been relaxed with respect to unit cell dimensions so that the trap depth calculations are satisfactory in this respect. The unit cell parameters are summarized in Table II.

A new polymorphic form of anthracene has been identified[6] when the normal crystal is compressed perpendicular to the (001) plane. It belongs to the space group $P\bar{1}$. Preliminary calculations lead to a ΔD value of $+311\ \mathrm{cm}^{-1}$ relative to $P2_1/a$. If as has been proposed, the normal form of anthracene contains regions of the new polymorph, this suggests that there would not be an associated exciton trap.

Work is in progress to extend the calculations to other defect systems, making allowance for structural relaxation where appropriate.

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