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Causes of Carrier Trapping Asymmetry in Aromatic Hydrocarbon Crystals

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Mechanisms by which the same physical defect could produce different trap depths for electrons and holes are investigated semi-quantitatively for a model comprising one molecule and one ion. Charge-quadrupole interactions must be included in addition to the polarization energy. The unsymmetrical molecular environment gives rise to a reaction field which polarizes the anion and cation by different amounts, causing electron traps to be possibly 5% deeper than hole traps. The extent of lattice relaxation is governed by the different repulsive potentials of the anion and cation, which are estimated from INDO calculations on naphthalene. Shallow hole traps could be twice as deep as electron traps, with smaller relative changes for deeper traps. These results are compatible with experimental information on trapping asymmetry.

1 INTRODUCTION

Physical trapping of charge carriers in molecular crystals is understood to occur because the polarization energy due to a carrier localized near an imperfect region of the crystal differs from that in the perfect lattice.^{1,2} The depths of such traps and their distribution in energy can be calculated theoretically from the molecular polarizability and the structure of the crystal defect. The structure may be described by some empirical model for the relaxation about the defect,^{1–3} or by calculations of the relaxation using appropriate intermolecular potentials.^{4,5} Trap depths calculated in this way have been the same for electrons and holes, since they depended only on the magnitude of the carrier charge, and on no other property of the localized molecular ion formed by the trapped charge.

Trapping of charge carriers, and of excitons, is greatly influenced by the conditions under which the crystals were grown^{6,7} and by subsequent handling,^{8,9} so that caution is needed in comparing experimental results on

trapping in different crystals. This problem has been circumvented by studying carrier trapping in the same anthracene single crystals before and after mechanical deformation.^{10,11} The results showed that the deformation introduced only electron traps. This implies either that the same physical defect produces traps of very different depths for electrons and holes, contrary to the theoretical predictions, or else that the deformation allowed better access to electron-accepting chemical impurities like oxygen. The latter explanation was preferred.¹⁰

More recent work avoiding mechanical deformation has provided separate information about hole and electron traps in anthracene by thermal and optical detrapping measurements.¹²⁻¹⁴ Injecting electrodes have been used to populate hole or electron traps independently prior to thermally-stimulated conductivity (TSC) measurements,^{12,13} which showed hole trap depths of 0.75, 0.85 and 0.95 eV and electron trap depths of 0.75 and 0.85 eV. Photon-stimulated conductivity (PSC) measurements¹⁴ on crystals from different sources invariably showed hole traps at 0.81 eV and electron traps at 0.9 eV; these energies are obtained directly, whereas the TSC energies are deduced from the temperatures of glow-curve maxima. The TSC and PSC methods have been compared by Sworakowski,¹⁵ who notes that the PSC method would probably fail to detect traps shallower than about 0.75 eV, and presents isothermal decay current (IDC) results indicating a trap at 0.77 eV for injected holes.

These various experiments show clearly that in anthracene electrons and holes experience different sets of trap depths. It also seems clear that these traps are associated with physical rather than chemical defects, as indicated by the variation of TSC peak heights for different crystals grown by the same method and the dependence of peak height on deformation,¹³ as well as by the constancy of trap depth for each carrier in crystals grown by different methods.¹⁴ This conclusion accords with the much greater incidence of physical compared with chemical defects in ultra-high-purity anthracene crystals.¹⁶ It should, however, be noted that the physical defects could be produced by the inclusion of chemically distinct species (such as molecules of any inert atmosphere used during crystal growth) which do not themselves trap the carriers.¹⁶ Since the original polarization energy theory of carrier trapping at physical defects predicted symmetrical trapping of electrons and holes, it is of interest to know whether any extension of the theory could lead to the asymmetry indicated by the experiments.

This paper investigates two sources of asymmetry: the reaction field due to the unsymmetrical environment of a molecular ion at a defect, and the different repulsive potential between a neutral molecule and its anion or cation. Calculations of trap depths for realistic models of defects in crystals are very complicated.⁵ Accordingly, here only semi-quantitative results are

obtained, for a model system comprising one molecular ion and one neutral molecule.

2 POLARIZATION ENERGY

2.1 Simple model

We consider an ion of charge q at a distance r from a neutral molecule of isotropic polarizability α . In the simplest treatment, the polarization energy is $-\frac{1}{2}\alpha E^2$, where E is the field produced at the molecule by the ion. Since E is $q/4\pi\epsilon_0 r^2$, the energy is

$$W_0 = -\frac{1}{2}\beta Q^2/r^4, \quad (1)$$

where $\beta = \alpha/4\pi\epsilon_0$ and $Q^2 = q^2/4\pi\epsilon_0$. In the crystal, there are also contributions to the polarization energy from the interactions between the dipoles induced by the ion. These contributions amount to typically a quarter of the ion-dipole energy, but are relatively insensitive to crystal perfection, and so are usually neglected.¹ Since they produce no difference between electron and hole polarization energies, they may also be ignored for present purposes.

This model represents the perfect crystal for $r = r_0$. In the imperfect crystal, the lattice deformation around a defect brings molecules closer together,^{4,5} and so we make the model represent this situation by taking $r = r_0 - \delta r$. Then to first order in the fractional displacement $\delta r/r_0$ the trap depth is

$$\Delta_0 = 2\beta Q^2 \delta r/r_0^5. \quad (2)$$

For anthracene, the mean polarizability β has been estimated¹⁷ as $25 \times 10^{-30} \text{ m}^3$, and the shortest intermolecular distance is $r_0 \simeq 5 \times 10^{-10} \text{ m}$. Then for $\delta r/r_0 = 0.1$, the trap depth Δ_0 is 0.18 eV; in the crystal, this is increased by the extra neighbours.

2.2 Charge-quadrupole interaction

Before considering how the polarization energy could differ for holes and electrons, we note that polarization energy is not the only contribution to the trap depth. Benzene, naphthalene and anthracene have no dipole moments, but they do have permanent quadrupole moments. These give rise to an energy of interaction with the carrier which is distance-dependent and hence changes at a defect.

The energy of a charge q on the axis of a quadrupole of strength Θ at a distance r is¹⁸

$$W_Q = -6q\Theta/4\pi\epsilon_0 r^3, \quad (3)$$

giving rise to a trap depth

$$\Delta_Q = (18q\Theta/4\pi\epsilon_0)\delta r/r_0^4. \quad (4)$$

For naphthalene Θ has been estimated¹⁹ to be some 50% larger than the value measured²⁰ for benzene, $1 \times 10^{-39} \text{ C m}^2$. Then with $\delta r/r_0 = 0.1$ and $r_0 = 5 \times 10^{-10} \text{ m}$ again, Δ_Q is found to be 0.21 eV. Like Δ_0 , this would be increased by the extra neighbours in the crystal, but the increase would probably be smaller than for Δ_0 , because for some neighbours the charge will lie off the quadrupole axis and hence give a contribution smaller than (4). Polarization energies alone have tended to give trap depths smaller than those observed experimentally.⁵ Since charge-quadrupole contributions may be of comparable size, their omission could account for the difference. However, no asymmetry between electrons and holes is introduced by Δ_Q .

2.3 Reaction field

In a perfect aromatic hydrocarbon crystal, the dipoles induced either side of an ion produce no net field at the ion, by symmetry. However, in an imperfect crystal, the ion is in an unsymmetrical environment and may experience a net reaction field. This situation is represented (in an exaggerated fashion) by the present model. When there is a reaction field, the polarization energy depends on the polarizability α' of the ion, and so will differ for holes and electrons. For our model, eq. 3.138 of Ref. 18 gives

$$W_R = -\frac{1}{2}\beta Q^2/r^4(1 - 4\beta\beta'/r^6), \quad (5)$$

where $\beta' = \alpha'/4\pi\epsilon_0$. To first order in $\delta r/r_0$ and $\beta\beta'/r_0^6$, the trap depth becomes

$$\Delta_R = (2\beta Q^2/r_0^4)(\delta r/r_0 + \beta\beta'/r_0^6). \quad (6)$$

Including the reaction field thus increases the trap depth, and since the anion should be more polarizable than the cation, the electron trap should be the deeper. However, for $\beta' = \beta$ the reaction field contributes only some 2% of the total trap depth, so that even in the extreme case of β' being for the anion twice β and for the cation half β the trap depths would differ by only 3%, electron traps being slightly deeper.

In the unsymmetrical environment at a defect, the quadrupole on the neutral molecule can induce a dipole on the ion. This gives a polarization energy like Eq. (5) but with Q replaced by an effective charge Q_e given by

$$Q_e^2 = (q + 12\beta'\Theta/r^5)^2/4\pi\epsilon_0. \quad (7)$$

For the parameter values used previously and $\beta' = \beta$, the new term constitutes about 10% of q . Differences in β' for anion and cation now have a more substantial effect on Δ_R : if β' for the anion is 10% greater than β and

β' for the cation is 10% less than β , the trap depths differ by 5%, the electron traps again being the deeper. Hence there is still no substantial difference for plausible β' values, and in the crystal the difference would be even smaller because not all quadrupoles will be oriented so as to give the maximum contribution represented by (7).

3 LATTICE RELAXATION

3.1 Origin

To date, calculations of physical trap depths have mostly been based on the estimated or calculated molecular arrangement at a defect in the neutral crystal. However, it has also been realized^{4,5} that the polarization produced by a charge carrier at a defect gives rise to additional forces on the surrounding molecules, causing the lattice to relax. The relaxation occurs in such a way as to reduce the energy by increasing the magnitude of the polarization energy, thus increasing trap depths by an amount⁵ of the order of 0.1 eV.

The amount of relaxation depends on the intermolecular forces. For aromatic hydrocarbon crystals, the lattice energies can be well reproduced by a set of pairwise atom-atom potentials; quadrupolar interactions are generally small.¹⁹ It is also found that a sizeable part of the lattice energy and nearly all its dependence on the molecular orientations are determined by repulsions between the peripheral hydrogen atoms.^{21,22} The repulsion is commonly described by the empirical potential $B \exp(-Cr)$, which is also a reasonable approximation to calculated exchange energies.²³ If the polarization energy W_0 of Eq. (8) is written as $-K/r^4$ and the attractive potential is ignored for simplicity, the separation between a molecule and an ion after relaxation satisfies

$$r'^5 \exp(-Cr') = 4K/BC, \quad (8)$$

where only one repulsive interaction is considered. This separation is to be compared with that in the neutral crystal, which for an attractive potential $-A/r^6$ satisfies

$$r^7 \exp(-Cr) = 6A/BC. \quad (9)$$

Now for present purposes what matters is not so much the amount of relaxation as the extent to which it depends on the carrier trapped, and so we concentrate on Eq. (8). In general, the interaction of a hydrogen atom on a neutral molecule with one on an anion will differ from that with one on a cation, and because of the exponential in Eq. (8) relatively modest changes in C could cause significant changes in r' . In real aromatic hydrocarbon

crystals, the relaxation could be even more sensitive to changes in C because of their effect on the orientation of the molecules, with their markedly anisotropic polarizability. From Eq. (8), the dependence of r' on C is given by

$$d \ln r' / d \ln C = (Cr' - 1)/(5 - Cr'). \quad (10)$$

Different authors have used significantly different values of C for hydrogen-hydrogen repulsions,²⁴⁻²⁶ but a value of $4 \times 10^{10} \text{ m}^{-1}$ would be typical. The closest pairs of hydrogen atoms in aromatic hydrocarbon crystals are some $2.5 \times 10^{-10} \text{ m}$ apart,²⁷⁻²⁹ so that the right-hand side of Eq. (10) is about -2 . A fractional change in C from anion to cation thus produces about twice as large a fractional change in r' , in the opposite sense.

3.2 Ion-molecule repulsions

We now estimate how much the repulsive exponent in the interaction of hydrogen atoms on neutral molecules changes when one molecule becomes an ion. The repulsion arises from the overlap of charge clouds, and is often taken as proportional to the square of the appropriate overlap integral, with results similar to those obtained with the exponential form already discussed.^{21,22} Since the hydrogen $1s$ orbital is exponential, it seems plausible to take the repulsive exponent as proportional to the sum of the orbital exponents for the interacting hydrogen atoms in an LCAO MO description of the molecule and its ion.

For molecules as large as the aromatic hydrocarbons, the orbital exponents are usually fixed in MO calculations. However, for small molecules it is found that the optimum hydrogen exponent is linearly correlated with the electronic population of the atom.³⁰ Analysis of the results shows that for a gross atom population P the exponent can be estimated from

$$\zeta(P) = 1.85 - 0.70 P, \quad (11)$$

where atomic units are implied. The populations in question are those calculated with the optimized exponents, and are thus still not directly accessible for aromatic hydrocarbons. Fortunately it transpires that these populations are well predicted for the small molecules by the semi-empirical INDO method.³¹ INDO calculations are feasible for the aromatic hydrocarbons, and hence can provide populations from which we may estimate the optimized exponents, assuming that Eq. (11) remains valid.

The results of INDO calculations on naphthalene and its ions are shown in Table I. For comparison, *ab initio* calculations with a minimal Gaussian basis set and fixed exponents give mean populations of 1.07 for the anion and 0.92 for the cation.³² The mean populations in Table I when substituted

TABLE I

Hydrogen atom electron populations in naphthalene and its ions, calculated by the INDO method.

Species	α -H	β -H	Mean
Naphthalene	1.021	1.012	1.016
Anion	1.065	1.065	1.065
Cation	0.977	0.956	0.968

in Eq. (11) give exponents 1.14, 1.10 and 1.17 for naphthalene, anion and cation respectively. The sum of the exponents for the molecule and the anion is thus 1.6% less than for two molecules, and the sum for the molecule and the cation 1.4% more. By the arguments of §3.1, the separation between an anion and a neutral molecule should thus be about 3% larger than that between two neutral molecules, and the separation between a cation and a neutral molecule about 3% smaller. These results are in overall agreement with physical expectations. In the anion the molecular charge cloud expands and repulsion is greater; in the cation the cloud contracts and repulsion is less.

The estimated changes are not large in themselves, but what matters is how large they are compared with the change in going from the perfect to the imperfect crystal. If for illustrative purposes we take $\delta r/r$ as -10% with neutral-molecule repulsions, then for the anion this is decreased to -7% and for the cation increased to -13% . Hence for deformations of this magnitude the hole traps could be twice as deep as the electron traps. For larger deformations, i.e. deeper traps, the effects would be smaller.

4 DISCUSSION

Although the model of a defect used here is highly simplified, it should contain enough realistic features to make the conclusions drawn from it qualitatively applicable to real systems. The conclusions may be summarized as follows. Charge-quadrupole interactions may make substantial contributions to trap depths, but not to differences between electron and hole trap depths. The different polarizabilities of an anion and a cation affect trap depths through the reaction field, but produce only small differences. Somewhat larger differences are produced through quadrupole-induced-dipole interactions. In each case the electron traps become slightly the deeper. The different repulsions between an anion or a cation and a neutral molecule lead to different lattice relaxations on polarization. These could make shallow hole traps twice as deep as the corresponding electron traps, with smaller relative changes in deeper traps.

The largest difference between electron and hole traps makes the hole traps the deeper. This result does not explain the production of electron rather than hole traps by mechanical deformation of anthracene crystals,^{10,11} and the explanation in terms of chemical trapping¹⁰ seems preferable. The prediction that the hole trap associated with a given physical defect is deeper than the corresponding electron trap means that the same total number of traps is distributed over a larger energy range for holes than for electrons. Hole trap densities should therefore be lower than electron trap densities in equivalent regions of energy (i.e. regions associated with the same defects). This conclusion accords with results showing that the trap density around the lowest trapping level in a series of anthracene crystals was lower for holes than for electrons.¹⁶ All the differences between electron and hole trap depths depend on differences between the electronic properties of anion and cation. As the size of the molecule increases, the fractional change in electron density produced by adding or removing one electron decreases, and so the differences decrease. Since the hole traps are predicted to be the deeper, this dependence on molecular size is consistent with observed trends in carrier lifetimes³³: the ratio of the lifetimes of electrons and holes in benzene is over 200, decreasing through biphenyl, naphthalene and anthracene until for pyrene it is unity.

It has been pointed out¹⁶ that deep carrier traps may be produced by incipient dimers associated with certain types of partial dislocations, a suggestion supported by calculations.⁵ The present treatment has not been designed to deal with this situation, which probably needs separate consideration, since calculations³⁴ show that in the anthracene dimer itself quadrupole-quadrupole interactions are much more important than in the crystal. The present estimates also take no account of molecular anisotropy or of the enhanced molecular polarizability in the crystal.³⁵ Nevertheless, it does appear that there could be detectable differences between the depths of at least the shallower electron and hole traps. Previous calculations used molecular parameters, which are bracketed by the ionic ones, and so gave some average trap depth. The present results show that calculations of individual trap depths unfortunately entail a more complicated treatment.

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