

would not change in qualitative appearance and would never take on values of less than 1.0. For example, a reduced mass ratio of $\mu_D/\mu_H=1.5$ would give an isotopic ratio curve Q_2 with a value of $(1.5)^{2/3}=1.31$ for no barrier height, $(1.5)^{1/2}=1.22$ for a very large barrier, and 1.10 for the minimum.

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Interaction of Electrons and Holes in a Molecular Crystal*

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A classical electrostatic model is used to compute the energy of an anthracene crystal containing an electron and a hole, each localized on specific sites. The calculation is carried out for a large number of sites and gives the effective potential hypersurface of interaction of the charges. The model includes real, finite charge distributions and anisotropic polarizabilities and is carried out to terms in induced-dipole-induced-dipole interactions, which are quite significant. The energy of the charge-transfer state is estimated as 3.84 eV, 0.39 eV above the experimental value. The model gives the energy of two infinitely separated charges as 5.77 eV, 1.85 eV above the reported threshold for intrinsic photoconduction. The energy of (dressed) charge-charge interaction is non-Coulombic for charges in different a , b planes, but is Coulombic if both charges lie in the same a , b plane, in which case the computed effective dielectric constant in the a , b plane is 1.25.

I. INTRODUCTION

Charges in crystals of organic molecules such as anthracene are moderately well localized on individual sites, in several senses. The mobilities of both electrons and holes are low,¹⁻⁵ and their mean free paths are comparable to the nearest-neighbor spacing.^{5,6} The states corresponding to electrons and holes near each other are much more like ion pairs than like Wannier excitons or hydrogen atoms, and are properly called charge-transfer states.

We have attempted to describe the set of states of anthracene corresponding to one electron and one hole, each localized, for the most part, on its own molecules, and each with its own electric field generating a polarization field. This article describes the static problem, in which we have calculated the energy of the crystal for a large set of relative positions of the two charges. At one limit is the configuration in which the positive and negative charges are on nearest-

neighbor molecules. This corresponds to the charge-transfer state first discussed by Lyons⁷ and located at 3.45 eV in the energy spectrum of anthracene by Pope and Burgos.⁸ At the other extreme is the conducting state corresponding to infinite separation of the two charges and their polarization clouds, assigned to the region 3.9–4.5 eV by various experiments.⁹⁻¹² The threshold is probably at 3.92 eV, and the maximum in the curve of intrinsic photocurrent, as a function of light energy, is probably at 4.46 eV. Between these two extremes are all the localized states corresponding to location of the two opposite charges on molecules having finite separation greater than that of nearest neighbors.

By comparing the energies for a sufficient number of such localized states, we generate an effective potential surface for the interaction of the two "dressed" charges, i.e., the two charges and their polarization clouds. The bands associated with these dressed charges are very narrow—even narrower than the spacing of

molecular vibrations. Hence, even though the stationary states of the dressed charges are strictly vibronic-band-like, the localized picture is quite sufficient to construct the effective potential. Delocalization would not affect the conclusions because the bands are much narrower than the energy differences associated with even the smallest changes in electron-hole separation, at least for separations up to about 50 Å (10 lattice parameters). Our static model can also be interpreted as a derivation of the effective potential of interaction of two polarons in a molecular crystal.

We shall see that the static potential itself gives considerable insight into the manner in which an electron and a hole interact in a molecular crystal. In particular, we find that when both charges are in the same (a, b) plane, their interaction is well described by Coulomb's law, even up to nearest-neighbor interactions, whereas interactions between charges in different (a, b) planes involve a barrier in the effective potential which is high enough to prevent the opposite charges from moving toward each other along any c -like direction. In a following publication, we shall use the static effective potential to describe the dynamic problem of electron-hole (or polaron-polaron) scattering and recombination.

II. THE CALCULATION

The method of calculation is an extension of that first used by Lyons⁷ and then extended by Berry, Jortner, Mackie, Pysh, and Rice.¹³ Based on the oriented gas model of a molecular crystal, the method involves the hypothetical removal of an electron from one molecule, its attachment to another molecule, and then establishment of all the other energetic adjustments including the Coulomb attraction of the two charged molecules and the various polarization and higher multipole interactions. The present work was originally prompted by the realization that the terms in the multipole interaction series for this model are small only *after* the term representing induced-dipole-induced-dipole interaction, and that this term is comparable in size to the sum of all the lower terms. This is due, in essence, to the fact that the polarization and Coulomb terms nearly compensate for the work required to produce the two charges.

The energy of the crystal in a particular generalized charge-transfer state J with the charges localized on any two specified molecules (one on the molecule at the origin and one on molecule J), can presumably be written

$$E_J = I - A + C_J + W_J, \quad (1)$$

where I is the ionization potential of anthracene,¹⁴ 7.4 eV, A is its electron affinity,¹⁵ 0.55 eV, and C_J is the Coulomb attraction between the two molecules,

$$C_J = - \sum_{k,l} \rho(\mathbf{r}_{0k}) \rho(\mathbf{r}_{Jl}) |\mathbf{r}_{0k} - \mathbf{r}_{Jl}|^{-1},$$

where $\rho(\mathbf{r}_{1i})$ is the charge density on carbon atom i of molecule I and the sum is taken over all the carbon atoms of molecules O and J . We have neglected charge density on the hydrogen atoms and assumed that ρ_{1i} could be given by the square of the corresponding coefficient of the highest normally filled (or lowest normally empty) Hückel orbital.

The quantity W is comprised of three terms: The energies associated with the induction of dipoles in the neutral host molecules, with the polarization of one ion by the field of the other and with the interaction of the induced dipoles with each other. The first two of these terms had been included in a previous treatment¹³ of the nearest-neighbor charge-transfer state. The inclusion of the last term and the extension of the calculation beyond just the nearest-neighbor charge-transfer state, are the principal new components in the present work.

The first term in W was computed, in our treatment, as

$$W_1 = -\frac{1}{2} \sum_i \mathbf{E}_i \cdot \alpha \cdot \mathbf{E}_i,$$

where \mathbf{E}_i is the net field at molecule i due to the two ions, and α is the polarizability tensor of anthracene.¹⁶ (The tensor had been approximated heretofore as a scalar.) The components of this tensor were taken as 35.8, 25.5, and 13.9 Å³. The truncated sum appears to be within about 0.1 eV or less of its limit when about 7000 neutral molecules are included. Roughly, this means that the polarization cloud of an ionized molecule extends about 12 molecules in every direction from that ion, in our model. It also means that when the two ions are separated by less than about 24 molecules their polarization clouds interpenetrate, in the sense that the field polarizing a neutral molecule contains contributions from both ions.

We approximated the second term W_2 of W by assuming that the polarizability tensors of the positive and negative ions of anthracene are the same as that of the neutral molecule. Hence the two contributions to W_2 are also of the form $-\frac{1}{2} \mathbf{E} \cdot \alpha \cdot \mathbf{E}$, but here, the field at the positive ion is only that due to the negative ion, and conversely.

The term W_3 representing the induced-dipole-induced-dipole interaction required summing all the pair interactions of about 500 dipoles around each charge. Each member of the sum comprising W_3 has the form

$$W_{KL} = (\mathbf{u}_K \cdot \mathbf{u}_L / r_{KL}^3) - [3(\mathbf{r}_{KL} \cdot \mathbf{u}_K)(\mathbf{r}_{KL} \cdot \mathbf{u}_L) / r_{KL}^5];$$

the dipole moments were computed from the sum of the fields of the two ionic molecules at O and J , as in the other terms of W_J .

III. RESULTS

A. Energies

The results of the calculation are collected in Table I, and are shown graphically in Fig. 1. The location of

TABLE I. Energy of the anthracene crystal containing one charge on the molecule at the origin and an equal but opposite charge located on another molecule. Locations (lattice indices) of the second molecule are given in Column 1. Energies (in electron volts) are given in Column 2; the zero of energy is the neutral crystal in its ground state. Distances between the origin and the center of the other charged molecule are given in Column 3.

Position of negative charge (positive charge at 0, 0, 0)	Total energy of crystal (eV)	Distance between positive and negative charges (Å)	Position of negative charge (positive charge at 0, 0, 0)	Total energy of crystal (eV)	Distance between positive and negative charges (Å)
0, 2, 0	4.03312	6.036	1, 1, 1	4.77056	9.883
0, 4, 0	4.69381	12.072	2, 2, 2	5.68290	19.766
0, 6, 0	5.02401	18.108	3, 3, 3	5.80947	29.649
0, 8, 0	5.26665	24.144	4, 4, 4	5.73383	39.532
0, 10, 0	5.37521	30.180	$\bar{2}$, 0, 1	5.27556	17.511
2, 0, 0	4.37886	8.561	$\bar{4}$, 0, 2	5.58716	35.023
4, 0, 0	4.97536	17.122	$\bar{6}$, 0, 3	5.58292	52.534
6, 0, 0	5.28535	25.683	$\bar{8}$, 0, 4	5.56247	70.045
8, 0, 0	5.44146	34.244	$\bar{10}$, 0, 5	5.55571	87.556
10, 0, 0	5.50024	42.805	$\bar{1}$, 1, 1	5.16681	14.367
12, 0, 0	5.54806	51.366	$\bar{2}$, 2, 2	5.62400	28.734
14, 0, 0	5.56805	59.927	$\bar{3}$, 3, 3	5.67452	43.101
16, 0, 0	5.58002	68.488	$\bar{4}$, 4, 4	5.57201	57.469
1, 1, 0	3.83735	5.238	0, $\bar{2}$, 1	5.03952	12.690
	nearest neighbor		0, $\bar{4}$, 2	5.64125	25.381
2, 2, 0	4.45881	10.476	0, $\bar{6}$, 3	5.67278	38.071
3, 3, 0	4.84997	15.714	0, $\bar{8}$, 4	5.60993	50.762
4, 4, 0	5.10904	20.952	0, $\bar{10}$, 5	5.56460	63.452
6, 6, 0	5.39139	31.428	1, $\bar{1}$, 1 ^a	4.77056	9.883
8, 8, 0	5.49138	41.904	2, $\bar{2}$, 2	5.67995	19.766
0, 0, 1	4.93668	11.163	3, $\bar{3}$, 3 ^a	5.80947	29.649
0, 0, 2	5.68571	22.326	4, $\bar{4}$, 4	5.73384	39.532
0, 0, 3	5.71827	33.489	$\bar{1}$, $\bar{1}$, 1 ^a	5.16681	14.367
0, 0, 4	5.66077	44.652	$\bar{2}$, $\bar{2}$, 2	5.62425	28.734
0, 0, 5	5.62013	55.815	$\bar{3}$, $\bar{3}$, 3 ^a	5.67452	43.101
2, 0, 1	4.70005	9.443	$\bar{4}$, $\bar{4}$, 4	5.52666	57.469
4, 0, 2	5.57495	18.885	1, $\bar{1}$, 0 ^a	3.83735	5.238
6, 0, 3	5.76496	28.328	2, $\bar{2}$, 0	4.51722	10.476
8, 0, 4	5.74549	37.770	3, $\bar{3}$, 0 ^a	4.84997	15.714
10, 0, 5	5.69235	47.213	4, $\bar{4}$, 0	5.12408	20.952
0, 2, 1	5.06670	12.690	6, $\bar{6}$, 0	5.39773	31.428
0, 4, 2	5.64219	25.381	2, $\bar{2}$, 2 ^b	5.62421	28.734
0, 6, 3	5.67274	38.071	∞	5.77188	∞
0, 8, 4	5.61012	50.762			
0, 10, 5	5.56452	63.452			

^a Derived by symmetry and does not represent a separate calculation.

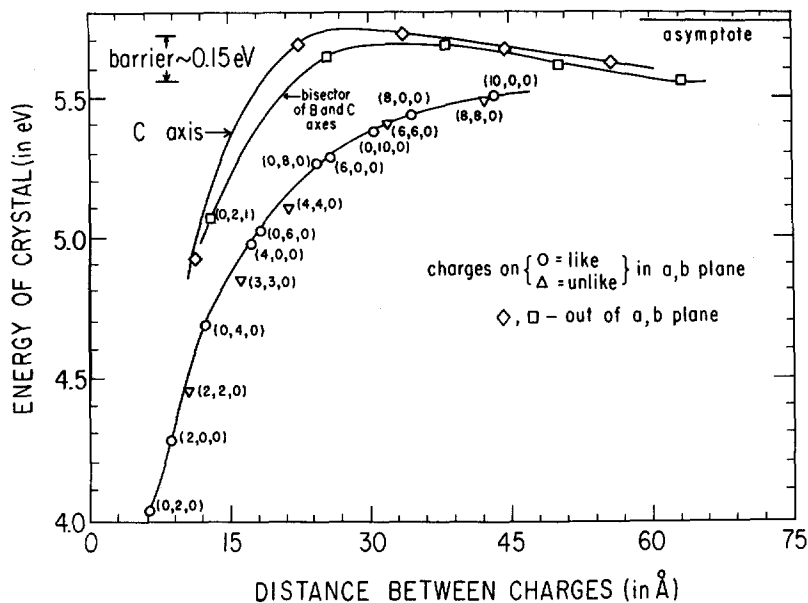
^b Result used to check symmetry arguments.

the positive ion is at the origin, and of the negative, at the site indicated by the indices in the first column of the table. For reference, the a dimension of the unit cell is 8.56 Å, the b dimension is 6.02 Å and is perpendicular to the a direction, and the c dimension is 11.9 Å, and the c vector is inclined to the a vector, forming an angle of 124°41'. The two molecules defining the unit cell have centers separated by 5.238 Å.

Two features of the results should be noted; both are abundantly clear in Fig. 1. First, the energy of

the crystal, when both ions are in the same a - b plane, lies on a single Coulombic curve. Even the nearest-neighbor interaction, not shown on the curve, deviates only slightly from the curve. Second, and in contrast to the interactions of ions in the same a - b plane, the crystal energy does not follow a Coulomb curve if the two ions lie in different a - b planes, nor do all the interactions even follow the same curve. In fact, the crystal energy, or the effective potential energy of interaction between the ions, shows a local maximum

FIG. 1. Energy of the anthracene crystal containing two opposite charges localized on specific molecules, as a function of the distance separating the molecules. The lowest curve is drawn for both charges in the same a, b plane. The two upper curves, showing maxima in the region of 27 Å, connect energies for locations along two directions out of the a, b plane: along the c axis (upper curve) and along the bisector of the angle between the b and c axes. Coordinates of the second molecule are given for some of the points.



when the ions are separated by an interval of 25–40 Å. This maximum constitutes an effective barrier about 0.15 eV high in the interaction potential. This barrier is high and thick enough that we can infer that, at ordinary temperatures, it must inhibit recombination of electrons and holes when they approach each other from a long distance in different a - b planes.

From the shapes of the curves in Fig. 1, one sees that the attractive potential is greater in a negative sense than thermal energy when the ions are about 50 Å apart or less, if they are in the same a - b plane. Hence, if the ions migrate by hopping, they are effectively trapped in their mutual field whenever they encounter each other in a circle of radius 50 Å in one a - b plane. However, a pair of ions approaching each other in different a - b planes may be expected to repel each other when they reach a separation of order 35–40 Å, and possibly even to be trapped in their mutual field, so that they maintain a separation between about 35 and 80 Å. This is only a rough picture based on the assumption that the charges on polarons come to thermal equilibrium with the lattice each time they move. A subsequent treatment will deal with the dynamical problem of polaron-polaron recombination.

B. Dielectric Constant

That the interaction energy of two ions in the same a - b plane is Coulombic is strikingly clear in Fig. 2. Here, we have plotted $r_{OJ}E$ as a function of r_{OJ} ; if the curve of Fig. 1 is indeed Coulombic, then

$$r_{OJ}E(r_{OJ}) = -e^2\epsilon^{-1} + r_{OJ}E(\infty).$$

The points do clearly fall on the same line, with a slope of 5.75 eV, the energy which our model gives for the energy of the anthracene crystal with two

infinitely separated, oppositely charged molecules, relative to the energy of the ground state of the crystal. Moreover the intercept of -11.5 corresponds to a dielectric constant in the a - b plane of 1.25.

The experimental value of the dielectric tensor of anthracene is not well established. A mean value of 3.46 was determined from a powder sample by Kronberger and Weiss¹⁷; a value of 1.24 was obtained by Carrelli, Fittipaldi, and Pauculo,¹⁸ with the sample orientation unspecified.

It should be recognized that the present calculations are, in effect, a computational determination of the microscopic dielectric function for an anisotropic species, for essentially all distances. For isotropic species, and for liquid argon in particular,¹⁹ it has proved possible to derive this function and connect it to the Clausius-Mosotti equation. The present calculations indicate that the (tensor) dielectric function of the anthracene crystal is probably a constant, equal to the bulk dielectric constant, in the a, b plane, up to distances as close as next-nearest neighbors. However the other two principal components of the dielectric function are quite definitely not constant and only approach the bulk dielectric constant values when the test point is more than about 50 or 60 Å from the point charge.

IV. DISCUSSION

Two points require some discussion. One is the convergence and accuracy of the expansion we have used to obtain the energy of the crystal. The other is the discrepancy between the energy we obtain for two widely separated charged molecules and the energy of the intrinsic conduction band as determined from experiment.

As to the method of calculation, hand calculations

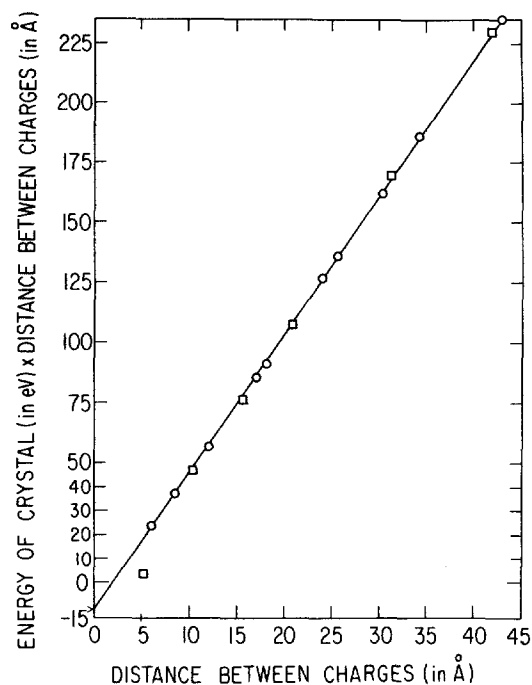


FIG. 2. Energy times distance vs distance of separation for the two opposite charges localized in the anthracene crystal. The slope is 5.75 eV and the intercept, $-11.5 \text{ eV} \cdot \text{Å}$.

and symmetry-based consistency checks were used to check the programs. Convergence, with respect to the number of neutral molecules in the polarization shells, was checked by examining the terms of E individually as the number of molecules was increased. For example, the energy associated with a single ion's inducing dipoles in 7200 neutral molecules is -1.842 eV ; if the number of molecules is increased to 30 656 neutrals, the induction energy drops to -1.914 eV . An estimate of the contribution from the neglected molecules was made with a continuum approximation, for molecules 105 Å or further from the site of the ion. This contributed $\sim -0.013 \text{ eV}$.

In like manner, the energy of interaction of the closest 565 induced dipoles with each other is 1.313 eV . Increasing the number of molecules to 1200 increases the energy of dipole-dipole interaction to 1.369 eV .

Summing the contributions from the various terms of W , we estimate that this kind of convergence error in W , for a single isolated charge, is less than 4%, for any configuration of positive and negative ions. The corresponding convergence error in W , for the case of positive and negative charges on neighboring sites (corresponding to the usual charge resonance state) is less than 1%.

A second sort of convergence problem was also examined; this was the question of the truncated multipole expansion. We have estimated the neglected terms next in order after the ones we included. The contribution of the field of induced dipoles to the

induction field, and therefore to the induction energy, gives a maximum of 0.029 eV for the inductive interaction of the *largest* induced dipole with its nearest neighbor, and other terms are all less than 0.01 eV . The contribution due to interaction of the permanent quadrupoles of the neutrals with the gradients of the fields of the ions is exactly zero.

Hence, the convergence error is probably less than 0.5 eV for the total energy of the crystal containing two widely separated charges, and less than 0.1 eV for the crystal energy when the charges are located on nearest neighbors.

Two possible sources of error are the nonconstancy of the dipole polarizability with field and the quadrupole polarization. Contributions from these phenomena, the so-called hyperpolarizability and the quadrupolar polarizability (response to a field gradient), were estimated from the higher polarizabilities given by Schweig.^{20,21} Both terms are negligible. The largest contribution of either type is the quadrupole polarization of a molecule by a nearest-neighbor ion, and is of order 0.005 eV .

Errors due to electron-phonon (or hole-phonon) coupling can be estimated from the treatment of Gosar and Choi.²² The contribution from variation in polarizability with molecular displacement is $0.03\text{--}0.08 \text{ eV}$. The root-mean-square deviation in the transfer integrals due to lattice vibration is about 0.03 eV , which we take as an estimate of the error from this variation. Hence the total error from electron-phonon coupling is probably less than 0.11 eV .

Having estimated these errors, we come to this conclusion: While the model provides an interesting picture of the potential of interaction of two oppositely charged "dressed" charges and rationalizes the energy of the charge-transfer band in anthracene, the model locates the energy of two infinitely separated charges at a value far higher than one expects from the experimental data. To review, the CT state is found experimentally at 3.45 eV and, from this calculation, at 3.84 eV . The threshold of the intrinsic conduction band is probably at 3.92 eV , whereas, if the state consisting of two infinitely separated charges is to be identified as the bottom of the intrinsic conduction band, the model gives a value of 5.77 eV . The experiments indicate that $(3.92\text{--}3.45) = 0.47 \text{ eV}$ is required to "ionize" the CT state, if the intrinsic conduction band is as just described, while the model gives the figure $(5.77\text{--}3.84) = 1.93 \text{ eV}$. It may be that as much as 0.5 eV of this difference is associated with convergence errors, but certainly, the larger part of the difference has not yet been accounted for.

Two possibilities, neither one included in this treatment, may help to bring experiment and theory closer. First, the measured intrinsic conduction may not involve the state corresponding to our two infinitely separated charges. For example, it could involve a variety of two-charge localized states with the opposite

charges located at finite distances. One thing mitigates against this particular explanation, the low density of charges in the experiments in which the energy of the conduction band was determined. This low-density problem could be resolved if there were some appropriate ordering of the charges in the presence of an external field, but there is no evidence to warrant such an ad hoc assumption. However it is possible to conceive of other ways in which the state responsible for the measured intrinsic conduction differs from our state of separated charges. For example, small amounts of mixing among the wavefunctions for widely separated configurations of the ions could permit conduction to occur in states of large charge separation. This process would presumably be field dependent, at least for low charge densities. In effect, this phenomenon would make the high-energy states of the two-ion system at least a bit more like Wannier exciton states than our localized model allows. In view of the reasonable values the model gives for the energy of the CT state and for the dielectric constant, this viewpoint has some attractions.

The second possibility that has come to our minds as a possible explanation of the apparent discrepancy lies with charge delocalization, from a charged molecule onto neighboring molecules. This phenomenon must occur in real systems, even in a (nonstationary) state in which a charge is formally localized on a single molecule. The delocalization is small, according to the overlap calculations of Glaeser and Berry, and a quantum-mechanical second-order calculation of the effect of this delocalization on the energy, based on diagonalization of a model Hamiltonian, indicates that the quantum mechanical effects can only shift the energy a few hundredths of an electron volt. One further effect, closely related to the mixing phenomenon mentioned in the previous paragraph, would be the calculation of the classical electrostatic interactions with the overlapping charges taken into account. We have not examined this effect. The

calculations reported here are based on the interaction of finite, anisotropic charge distributions with anisotropic polarizabilities. However the assumption was made that the charge distributions are nonoverlapping, so that the distance from the center of one charge distribution to any point within that distribution is always assumed to be less than the distance from the center of the charge distribution to points in other charge distributions. This way, we were able to use the multipole-multipole expansion. Possibly, a more extensive calculation, based on the multipole expansion for overlapping charges, would help resolve the problem.

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