

Analysis of the "charge resonance" transition in anthracene dimer anion

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The experimentally observed "charge resonance" transition of anthracene dimer anion is explained in terms of the resonance interaction of the lowest unoccupied orbitals of neighboring anthracene molecules. The distortion energies of the anthracene molecule and anion are shown to make an important contribution to the excitation energy. The numerical estimate of the resonance integral, based on the experimental absorption energy of the dimer anion, is shown to be related to that which is appropriate for a calculation of electron mobility in crystalline anthracene.

I. INTRODUCTION

Shida and Iwata¹ have studied the electronic absorption spectra of γ -irradiated solutions of dianthracene in a low-temperature (77 °K) matrix of methyltetrahydrofuran (MTHF). Dianthracene is a composite molecule made up of two anthracene molecules in a sandwich configuration, with σ bonds connecting the equivalent 9 and 10 positions of each molecule. Shida and Iwata bleached dilute γ -irradiated solutions of dianthracene and observed the resulting optical absorption spectrum to be very nearly a superposition of the spectra of the isolated anthracene molecule and anthracene anion. In addition, a broad absorption occurring between about 5000 and 10 000 cm^{-1} (~ 0.6 – 1.2 eV) with a peak at 6000 cm^{-1} (0.72 eV) was observed. Since the absorption in this region was unlike the doublet that would have been observed for dianthracene anion, and because the rest of the spectrum showed peaks which could be assigned to anthracene molecules and anions, Shida and Iwata explained the absorption commencing at 5000 cm^{-1} in terms of a "charge resonance" transition of a weakly interacting anthracene dimer anion involving an anthracene molecule and anion which are no longer held together by σ bonds. The dimer anion results from the reaction of mobile electrons (formed by bleaching at 520 nm) with the σ -bonded dianthracene anion. According to Shida and Iwata, the charge resonance (CR) absorption involves as upper and lower states the symmetric and anti-symmetric dimer anion wave functions, which are constructed from the ground-state molecule (ϕ_0) and anion (ψ_0) wave functions at sites 1 and 2:

$$\Phi_{00}^* = 1/\sqrt{2}(\phi_0^1 \psi_0^2 \pm \psi_0^1 \phi_0^2). \quad (1)$$

Shida and Iwata calculated the intensities and positions of peaks in the spectrum of the dimer anion using the self-consistent-field molecular orbitals (SCF-MO's) of anthracene molecule as basis orbitals, assuming the short and long symmetry axes of the two molecules to be parallel, and estimating the intermolecular distance to be 3.4 Å or about twice the van der Waals' radius of a typical π system. They predict that the charge resonance absorption will occur at about 4000 cm^{-1} , compared to the experimentally observed energy of 5000 to 10 000 cm^{-1} .

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In Sec. II, we show how the CR energy can be more reasonably accounted for in terms of the resonance energy of the lowest unoccupied molecular orbitals (LUMO's) on the neighboring anthracenes as well as in terms of the geometrical distortion energies of the planar anion and nonplanar molecule. This distortion energy, which shall be shown to make an important contribution to the CR energy, was not accounted for in the calculation of Shida and Iwata, who assumed planar geometries for both molecules in the dimer.

II. ANALYSIS OF THE CHARGE RESONANCE ENERGY ΔE_{CR}

In the following, we consider the CR transition to involve dimer states which can be described in terms of products of a ground-state anthracene molecule wave function $\psi_{1,2}^0(\mathbf{r}, Q)$ and a ground-state anthracene anion wave function $\psi_{1,2}^-(\mathbf{r}, Q)$. The subscripts refer to sites 1 and 2, which are assumed to be 3.4 Å apart. To consider the energy of the vertical CR transition, we must keep in mind that the equilibrium geometry, denoted by the internal coordinates Q , is not necessarily the same for the anion as for the molecule. Let the geometry which minimizes the energy of the molecule be represented by Q_p (planar), and that which minimizes the energy of the anion be given by Q_n (nonplanar). We consider the zeroth-order ground state to consist of a planar molecule at site 1 and a nonplanar anion at site 2:

$$\Psi_g^{(0)} = \psi_1^0(\mathbf{r}, Q_p) \psi_2^-(\mathbf{r}, Q_n). \quad (2)$$

The zeroth-order excited state is composed of a planar anion at site 1 and a nonplanar molecule at site 2:

$$\Psi_e^{(0)} = \psi_1^-(\mathbf{r}, Q_p) \psi_2^0(\mathbf{r}, Q_n). \quad (3)$$

If these two states are allowed to interact, the perturbed ground- and excited-state energies are obtained by diagonalizing the configuration interaction (CI) matrix \underline{H} ,

$$\underline{H} = \begin{bmatrix} \langle \Psi_g^{(0)} | H | \Psi_g^{(0)} \rangle & \langle \Psi_g^{(0)} | H | \Psi_e^{(0)} \rangle \\ \langle \Psi_e^{(0)} | H | \Psi_g^{(0)} \rangle & \langle \Psi_e^{(0)} | H | \Psi_e^{(0)} \rangle \end{bmatrix}. \quad (4)$$

To simplify the calculation, zero overlap of wave functions on different sites is assumed. In this approximation, the H_{11} matrix element is just the sum of the ground-state equilibrium energies of an undistorted

anion and molecule:

$$\langle \Psi_e^{(0)} | H | \Psi_e^{(0)} \rangle \equiv H_{11} = E^-(Q_n) + E^0(Q_p). \quad (5)$$

The H_{22} element is the sum of the energies of a distorted (nonplanar) molecule and a distorted (planar) anion:

$$\langle \Psi_e^{(0)} | H | \Psi_e^{(0)} \rangle \equiv H_{22} = E^-(Q_p) + E^0(Q_n). \quad (6)$$

The off-diagonal terms H_{12} connect anion and molecule wave functions on the same site. To simplify these terms, we suggest an explicit form for the anion and molecule wave functions in terms of Slater determinants of self-consistent molecular orbitals ϕ_i . The wave function for the anion is derived from the Slater determinant for the molecule by adding an electron to the anthracene LUMO ϕ_i^L . Writing the lowest and highest occupied MO's of anthracene molecule as ϕ^1 and ϕ^H , respectively, the ground-state Slater determinant for an anthracene molecule is written as

$$\psi_i^0(r, Q_i) = | \phi_i^1 \alpha \phi_i^1 \beta \cdots \phi_i^H \alpha \phi_i^H \beta |, \quad (7)$$

where the subscript $i = 1, 2$ refers again to the two sites

in the dimer, and α and β are spin functions. The anion wave function is then

$$\psi_i^-(r, Q_i) = | \phi_i^1 \alpha \phi_i^1 \beta \cdots \phi_i^H \alpha \phi_i^H \beta \phi_i^L \alpha |. \quad (8)$$

Next, the Hamiltonian is written in terms of one-electron operators h_i and two electron operators V_{ij} ;

$$H = \sum_{i=1}^{4H+1} h_i + \sum_{i < j=1}^{4H+1} V_{ij}. \quad (9)$$

h_i is just the kinetic energy plus nuclear attraction operator, which is summed over all $4H+1$ electrons on both sites:

$$h_i = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} - \sum_{\beta} \frac{Z_{\beta}}{r_{i\beta}}. \quad (10)$$

The subscripts α and β have been used to distinguish the nuclei at sites 1 and 2. The two-electron operator is the electron-electron repulsion, $V_{ij} = 1/|\mathbf{r}_i - \mathbf{r}_j|$. Using Eqs. (7) and (8) to write the product wave functions $\psi_e^{(0)}$ and ψ_i^0 , we can use the well-known Slater-Condon rules to simplify the matrix element H_{12} :

$$\begin{aligned} H_{12} &= \langle \Psi_e^{(0)} | H | \Psi_e^{(0)} \rangle = \langle \psi_1^0 \psi_2^0 | H | \psi_1^- \psi_2^0 \rangle = \left\langle \cdots \phi_1^H \alpha \phi_1^H \beta \phi_2^H \alpha \phi_2^H \beta \phi_2^L \alpha \left| \sum_i h_i + \sum_{i < j} V_{ij} \right| \cdots \phi_1^H \alpha \phi_1^H \beta \phi_2^H \alpha \phi_2^H \beta \phi_1^L \alpha \right\rangle \\ &= \left\langle \phi_2^L \left| -\frac{1}{2} \nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} - \sum_{\beta} \frac{Z_{\beta}}{r_{i\beta}} \right| \phi_1^L \right\rangle + \sum_{i=1,2} \sum_{k=1}^H \langle \phi_2^L | 2J_i^k - K_i^k | \phi_1^L \rangle \end{aligned} \quad (11)$$

where J_i^k and K_i^k are the usual Coulomb and exchange operators. H_{12} can be expressed as a simple matrix element involving the two LUMO's ϕ_1^L and ϕ_2^L by considering an effective electron-neutral molecule potential at either site in terms of the sum of the nuclear attraction plus Coulomb and exchange interactions

$$V_1^{\text{eff}} = - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{k=1}^H [2J_1^k - K_1^k], \quad (12a)$$

$$V_2^{\text{eff}} = - \sum_{\beta} \frac{Z_{\beta}}{r_{i\beta}} + \sum_{k=1}^H [2J_2^k - K_2^k]. \quad (12b)$$

The final form for the off-diagonal matrix element is thus

$$H_{12} = \langle \phi_2^L | -\frac{1}{2} \nabla^2 + V_1^{\text{eff}} + V_2^{\text{eff}} | \phi_1^L \rangle, \quad (13)$$

which is the usual resonance integral involving two orbitals separated by 3.4 Å. Recall that, in principle, one of the orbitals must be appropriate to a nonplanar anion geometry and the other to a planar anion geometry.

We proceed now to solve for the energy in the approximation $\langle \Psi_e^{(0)} | \Psi_e^{(0)} \rangle = 0$:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} = 0. \quad (14)$$

The difference between the two roots of Eq. (14) is the charge resonance excitation energy ΔE_{CR} and is given by

$$\begin{aligned} \Delta E_{\text{CR}} &= [(H_{22} - H_{11})^2 + 4H_{12}^2]^{1/2} = \{ [E^0(Q_n) - E^0(Q_p) \\ &+ E^-(Q_p) - E^-(Q_n)]^2 + 4H_{12}^2 \}^{1/2}. \end{aligned} \quad (15)$$

The term $E^-(Q_p) - E^-(Q_n)$ is the anion distortion energy and is equal to the experimentally available difference between the adiabatic and vertical electron affinities of anthracene molecule,

$$E_{\text{dis}}^- \equiv E^-(Q_p) - E^-(Q_n) = EA_{\text{ad}} - EA_{\text{vert}}. \quad (16)$$

Using values of EA_{ad} and EA_{vert} from Ref. 2, the anion distortion energy is estimated to be about 0.10 to 0.17 eV. Similarly, the neutral molecule distortion energy, $E_{\text{dis}}^0 = E^0(Q_n) - E^0(Q_p)$, ought to be equal to the difference in the vertical and adiabatic ionization potentials (I.P.'s) of anthracene anion. Since these I.P.'s are not readily available in the literature, the approximation $E_{\text{dis}}^0 = E_{\text{dis}}^-$ will be made. If it is true that the frequency of the vibrational mode responsible for the distortion of the anion is unchanged upon ionization, then this assumption will be valid. With the estimate $E_{\text{dis}}^- \approx E_{\text{dis}}^0 \approx 0.17$ eV, we proceed to estimate the magnitude of H_{12} needed to account for the observed energy (~ 0.72 eV) at the peak of the CR absorption (the maximum in the absorption is appropriate because of our considerations of a vertical transition from a nonplanar anion):

$$0.72 \text{ eV} = [4(0.17)^2 + 4H_{12}^2]^{1/2}, \quad (17)$$

which implies $|H_{12}| \sim 0.32$ eV, or about 2700 cm^{-1} . (Using the lower limit of $E_{\text{dis}}^- = 0.1$ eV results in $H_{12} \sim 0.35$ eV). It is interesting to note that this is very close to the CR energy predicted by Shida and Iwata on the basis of an SCF calculation in which both anthra-

enes were restricted to be planar. This is, of course, not surprising since the distortion energies were neglected in Ref. 1, which results in ΔE_{CR} arising entirely from H_{12} .

The value of 0.32 eV for the resonance integral must be viewed as only a crude estimate because of the approximations made. Although it is quite close to the value of the resonance integral computed using quantum chemical methods by Shida and Iwata, we decided to attempt a third (independent) estimate of H_{12} . In Sec. III, we support the above interpretation of the dimer anion excitation energy by calculating H_{12} in an independent, but rather approximate, manner making use of techniques introduced by Katz *et al.*³ in their study of the motion of excess electrons (and holes) in anthracene crystal.

III. RESONANCE INTEGRAL FROM AN ELECTRON MOBILITY STUDY

Katz *et al.*³ have computed resonance integrals in connection with a calculation of the mobility of excess electrons in crystalline anthracene. Their Hamiltonian is a one-electron operator consisting of the kinetic energy and the sum over lattice sites of the electron-neutral molecule potential. The resonance integral e_n connecting anthracene LUMO's on molecules separated by a lattice vector \mathbf{R}_n is, in the notation of Ref. 3,

$$e_n = \langle \phi(\mathbf{r}) | -\frac{1}{2}\nabla_{\mathbf{r}}^2 + \sum_i V(\mathbf{r} - \mathbf{R}_i) | \phi(\mathbf{r} - \mathbf{R}_n) \rangle \quad (18)$$

The $\phi(\mathbf{r})$ were taken as linear combinations of carbon atom $2p_z$ basis functions, using expansion coefficients from a Hückel calculation. The effects of anion distortion are not included, thus all of the $\phi(\mathbf{r} - \mathbf{R}_n)$ are appropriate to the planar geometry of neutral anthracene. Katz *et al.* also made the assumptions that each $\phi(\mathbf{r} - \mathbf{R}_n)$ is an eigenfunction of the particular one-electron Hamiltonian involving an electron moving in the potential of the neutral molecule at \mathbf{R}_n , $-\frac{1}{2}\nabla_{\mathbf{r}}^2 + V(\mathbf{r} - \mathbf{R}_n)$ and that the overlap of LUMO's on different lattice sites is zero. With these approximations and the neglect of three-center integrals (that is, those involving a potential and two LUMO wave functions on three different lattice sites), the above resonance integral is reduced to

$$e_n \approx \langle \phi(\mathbf{r}) | V(\mathbf{r} - \mathbf{R}_n) | \phi(\mathbf{r} - \mathbf{R}_n) \rangle. \quad (19)$$

To relate the above resonance integral to H_{12} of Eq. (13), we note that while the neglect of three-center integrals is indeed valid for the case of an isolated dimer, we should probably not ignore the LUMO-LUMO overlap when the intermolecular distance is only 3.4 Å. We make, therefore, the approximation

$$\langle \phi(\mathbf{r}) | -\frac{1}{2}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}) | \phi(\mathbf{r} - \mathbf{R}_n) \rangle \approx \epsilon_{LUMO} \langle \phi(\mathbf{r}) | \phi(\mathbf{r} - \mathbf{R}_n) \rangle \quad (20)$$

For the dimer anion $|\mathbf{R}_n| = 3.4$ Å and the overlap $\langle \phi(\mathbf{r}) | \phi(\mathbf{r} - \mathbf{R}_n) \rangle$ will be denoted by S . Thus for e_n calculated according to Eq. (19) at $R_n = 3.4$ Å, H_{12} is approximately related to the e_n of Katz *et al.* by means of the relation

$$H_{12} \equiv \langle \phi(\mathbf{r}) | -\nabla_{\mathbf{r}}^2 + V(\mathbf{r}) + V(\mathbf{r} - \mathbf{R}) | \phi(\mathbf{r} - \mathbf{R}) \rangle \approx e_n + \epsilon_{LUMO} S. \quad (21)$$

The equality is not exact because e_n is calculated in Ref. 3 for the undistorted planar geometry.

The electron-molecule potential was taken by Katz *et al.* to be a sum of neutral carbon-atom potentials according to a formula derived by Goepfert-Mayer and Sklar.⁴ Using numerical integration, they computed e_n for all anthracene pairs separated by less than about 15 Å. The largest value of e_n they obtained was ~ -0.026 eV for two anthracene separated by 5.2 Å and having their planes perpendicular. This does not really indicate what order of magnitude to expect for e_n when the molecular planes are parallel and separated by 3.4 Å. Since we are interested in estimating the order of magnitude of H_{12} , we decided to calculate the value of e_n for the dimer orientation arising in our work. To do this, the LUMO was taken as a linear combination, using Hückel coefficients, of carbon atom $2p_z$ Slater orbitals. The orbital exponent, following LeBlanc,⁵ was taken as 3.08 Å⁻¹. (Katz *et al.* have noted that a single Slater-orbital approximation to the wave function underestimates the amplitude at large electron-molecule distance, resulting in values of e_n which are too small.) The potential form of Goepfert-Mayer and Sklar was also used, but all the three-center terms (the term center referring now to atoms rather than molecules) in the expansion of e_n were ignored. Katz *et al.* have shown that neglect of three-center integrals leads to values of e_n which are too small by as much as a factor of 5. Thus the value of e_n that we estimate here for the dimer anion must be considered to be a lower bound, by as much as 500%, to the actual value. Using the closed-form expressions for the two-center integrals given in Ref. 3, we find $e_n \approx -0.04$ eV. In order to use Eq. (21) to find H_{12} , the overlap S was calculated by us and found to be ~ 0.03 , and the orbital energy was approximated by the negative of the electron affinity of anthracene, $\epsilon_{LUMO} \sim -0.6$ eV. Thus our estimate of H_{12} , which is to be compared with the "spectroscopy" estimate of $|H_{12}| = 0.33$ eV given earlier, is

$$H_{12} \approx e_n + \epsilon_{LUMO} S$$

$$H_{12} \approx -0.04 + (-0.6)(0.03) \text{ eV} \approx -0.06 \text{ eV}. \quad (22)$$

In our opinion, it is likely that $0.06 \text{ eV} \leq |H_{12}| \leq 0.30 \text{ eV}$ represents a reasonable energy range for our prediction of H_{12} . Knowing that a more negative value of e_n could have been obtained by using a better carbon atom $2p_z$ function and by computing the three-center integrals, this order of magnitude agreement between the two estimates of H_{12} is rather satisfactory. The fact that there is no gross discrepancy tends to confirm the validity of our interpretation of the charge resonance transition. Perhaps more importantly, the fact that Shida and Iwata compute $|H_{12}| \approx 0.2$ eV by more reliable quantum chemical methods tends to further support our explanation of the nature of the CR transition in the anthracene dimer anion. By including the effects of molecule and anion

distortion energies, we have been able to better explain the energy range of the charge resonance absorption.

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