BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1439—1440 (1969)

A Band Model of the Charge-Transfer Complexes

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(Received July 13, 1968)

The purpose of this note is to propose a theoretical model to explain the high electrical conductivities of some charge-transfer complexes. The complexes of aromatic hydrocarbons with iodine are found to show low resistivities when the mole ratio deviates from 1 : 1, while those of the 1 : 1 complexes are high.[1] For example, the resistivity of the pyrene-iodine (1 : 2) complex is 75 ohm-cm at room temperature[2] and the coronene-iodine (1 : 1) complex has a resistivity of about 10^8 ohm-cm.[3] For a complex in which the ionization energy of the donor is much larger than the electron affinity of the acceptor, the ground state is mainly expressed as a non-bonding structure and the band gap may be presumed to be large. Since the ionization energy of pyrene is nearly equal to that of coronene,[1] the reason for the low resistivity of the pyrene-iodine complex must be discussed.

Since no data are available on the crystal structure of the 1 : 2 complexes, the linear chain indicated in Fig. 1 is assumed[4] in order to calculate the energy bands for the simplest case. In Fig. 1, D is a donor molecule and A is an acceptor molecule. In this arrangement two acceptors (A_1 and A_2) in a unit cell are assumed to occupy equivalent sites. Assuming that the one-electron Hamiltonian, H, has properly been chosen for the linear chain, we define the Bloch orbitals, $\phi_D(\boldsymbol{k})$, $\phi_{A_1}(\boldsymbol{k})$, and $\phi_{A_1}(\boldsymbol{k})$, as follows:

$$\phi_D(\boldsymbol{k}) = \sum_j \exp(i\boldsymbol{k}\boldsymbol{R}_{jD}) \quad \chi_D(r - \boldsymbol{R}_{jD}), \tag{1}$$

$$\phi_{A_1}(\boldsymbol{k}) = \sum_j \exp(i\boldsymbol{k}\boldsymbol{R}_{jA_1}) \quad \chi_A(r - \boldsymbol{R}_{jA_1}), \tag{2}$$

$$\phi_{A_2}(\boldsymbol{k}) = \sum_j \exp(i\boldsymbol{k}\boldsymbol{R}_{jA_2}) \quad \chi_A(r - \boldsymbol{R}_{jA_2}). \tag{3}$$

Here $\boldsymbol{R}_{jD}$, $\boldsymbol{R}_{jA1}$, and $\boldsymbol{R}_{jA2}$ are the coordinates of the molecules D, A_1, and A_2 respectively in the jth cell, and $\boldsymbol{k}$ is the wave vector of an electron. χ_D is the wave function for the highest occupied level of the donor, and χ_A is that for the lowest unoccupied level of the acceptor.

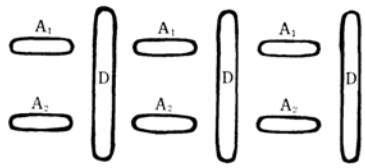

Fig. 1. Assumed structure of 1 : 2 complex. D is a donor and A is an acceptor.

It can be seen from the symmetry that the state:

$$\phi_A^- = 2^{-1/2}(\phi_{A_1} - \phi_{A_2})$$

does not combine with ϕ_D and that it is, therefore, the eigen-state. The corresponding energy, $E^{(-)}(\boldsymbol{k})$, is nearly independent of the wave vector, $\boldsymbol{k}$, since the overlap of χ_A in different cells may be neglected. The other eigen-states are obtained by taking linear combinations of ϕ_D and

$$\phi_A^+ = 2^{-1/2}(\phi_{A_1} + \phi_{A_2})$$

The energies are determined by:

$$\begin{vmatrix} H_D - E, & H_1 \\ H_1^*, & H_A - E \end{vmatrix} = 0, \tag{4}$$

where, for simplicity, the overlap integral is neglected and where:

$$H_D = \int \phi_D^* H \phi_D d\tau, \tag{5}$$

$$H_A = \int \phi_A^{+*} H \phi_A^+ d\tau, \tag{6}$$

$$H_1 = \int \phi_D^* H \phi_A^+ d\tau. \tag{7}$$

If $(H_A - H_D)^2 \gg 4|H_1|^2$, the ground state energy, $E_0(\boldsymbol{k})$, and the excited state energy, $E^{(+)}(\boldsymbol{k})$, may be written as:

$$E_0(\boldsymbol{k}) = H_D - \Delta E, \tag{8}$$

$$E^{(+)}(\boldsymbol{k}) = H_A + \Delta E, \tag{9}$$

where: $$\Delta E = |H_1|^2/(H_A - H_D). \tag{10}$$

These energies are shown in Fig. 2, where $E^{(-)}(\boldsymbol{k})$ and the magnitudes of the integrals (5), (6), and (7) are chosen arbitrarily. The band $E_0(\boldsymbol{k})$ is filled with electrons, since there are two electrons

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2) J. Kommandeur and F. R. Hall, *J. Chem. Phys.*, **34**, 129 (1961).

3) M. M. Labes, R. Sehr and M. Bose, Internat. Conf. Semicond. Phys., Prague (1960), p. 850.

4) T. Uchida and H. Akamatu, This Bulletin, **34**, 1015 (1961).

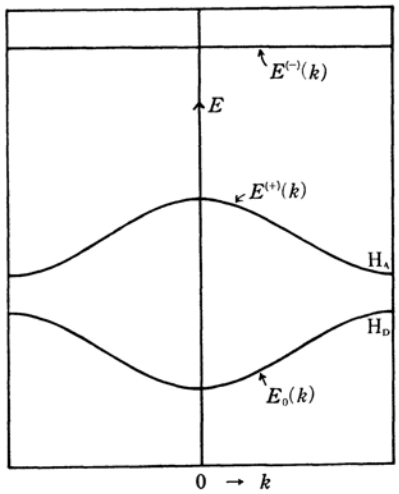

Fig. 2. Band structure of a linear 1 : 2 complex.

per molecule; hence, the smallest band gap is equal to $H_A - H_D$ at the zone boundary.

ΔE represents the part of the binding energy due to the electron transfer from D to A. This charge-transfer energy, ΔE, depends on the distance, R_A, between A_1 and A_2 through H_A. If the magnitude of $|H_1|^2$ does not decrease with R_A, R_A becomes shorter than the van der Waals distance between the two acceptors in order to lower the energy of the state $\phi_A{}^+$; H_A. Therefore, the binding energy of the lattice is expected to increase with a decrease in R_A, although the repulsive force between A_1 and A_2 causes some energy loss. Therefore, the band gap, $H_A - H_D$, may be small even if the difference between the donor ionization energy and the electron affinity of the acceptor is large. The difference between coronene and pyrene may lie in the difference between their highest occupied states, χ_D. Presumably, the χ_D of coronene spreads on a large molecular plane, so a decrease in R_A results in the reduction of the overlapping of ϕ_D and $\phi_A{}^+$.