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EVALUATION OF INTERMOLECULAR CHARGE TRANSFER INTEGRAL BY MOLECULAR OVERLAP CALCULATION

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Abstract Charge transfer molecular complexes are classified into four groups according to their electronic and crystalline structures. The physical characteristics of these crystals are considered from an unified viewpoint of transfer integral. The magnitude of the integral is estimated by calculating molecular overlap integral with Mulliken's approximation. The calculated values are compared with the experimental values, which are determined for various crystals by different technique.

INTRODUCTION

Since last century chemists have considered the molecular complex as being formed by a special intermolecular force or a residual valence. Quantum mechanical interpretation on this force has been developed since Mulliken's important contribution to the charge transfer theory.[1] Herbstein[2] reviewed chemical, spectral and crystalline structural studies of donor acceptor complexes up to 1970. After the discovery of conducting organic charge transfer complexes such as TTF·TCNQ[3], a variety of new types of conducting crystals have been prepared and their properties have been investigated extensively. During the development of various studies on organic donor acceptor complexes, Mulliken's charge transfer concept gave theoretical guide-

lines and deeper understanding of chemical and physical processes of the complexes.

Among several important features of his theory, some concepts are essential for characterization of the donor acceptor interaction. Mulliken's charge transfer integral has been defined as

$$t_{DA} = \int \phi_D^* \, H \, \phi_A \, dv \tag{1}$$

where ϕ_D and ϕ_A are relevant MO of the donor and the acceptor. The t integral is calculated as proportional to the overlap integral by using the well-known Mulliken-Wolfsberg-Helmholz formula[4], which is described by

$$t_{ij} = KS_{ij} \left(\frac{W_i + W_j}{2} \right) \tag{2}$$

where W_i and W_j are the orbital energies of relevant MO, ϕ_i and ϕ_j, K is proportional constant and the overlap integral S_{ij} is calculated as

$$S_{ij} = \int \phi_i^* \, \phi_j \, dv \quad . \tag{3}$$

The constant K is estimated as being in the range of $K = 1.0 - 2.0$ in semi-empirical MO theory. In this paper the overlap integrals are calculated between the donor and the acceptor orbitals, and the correlation is examined between the calculated S values and experimentally estimated t values. The t integral is important in various phenomena because it determines extent of charge resonance interaction. The magnitude of t is estimated with each crystal by different method. The estimated values are correlated with S by the use of Eq.(2) as is shown in the Table. If the K values determined are within reasonable range the present treatment may be justified to predict strength of intermolecular charge transfer interaction.

CLASSIFICATION OF MOLECULAR COMPLEXES

Crystals of Donor-Acceptor Molecular Complexes

Mixed Stack		Segregated Stack	
neutral	ionic	mixed valence	ionic
D A	D^+A^-	$D^{\delta+}A^{\delta-}$	D^+A^-
A D A D A D	A^- D^+ A^- D^+ A^- D^+	D A D^+ A^- D A D^+ A^- D A D^+ A^-	D^+ A^- D^+ A^- D^+ A^- D^+ A^- D^+ A^- D^+ A^-
insulating diamag.	insulating paramag.	conducting paramag.	insulating para/diamag.

Charge transfer complexes are classified into four groups as shown above based on their electronic and crystalline structures.

(1) Neutral Mixed Stack Traditional weak molecular complexes are composed of the donor and the acceptor mixed stack, and they are stabilized by the charge transfer force. The ground and the excited states wavefunctions of the complex are described by

$$\begin{aligned} \Psi_G &= a\,\Phi_0(\mathrm{D{\cdot}A}) + b\,\Phi_{CT}(\mathrm{D^+A^-}) \\ \Psi_E &= -b\,\Phi_0(\mathrm{D{\cdot}A}) + a\,\Phi_{CT}(\mathrm{D^+A^-}) \end{aligned} \qquad a \gg b \tag{4}$$

and the coefficient b is given by a perturbation theory as

$$b = t / (I_p - E_A - C) \tag{5}$$

or more exactly by solving secular equation. The CT band intensity is greatly dependent on b [5], therefore by using

Table 1. Calculated Overlap Integrals and

		Complexes	S	Interplanar Distance(A)
Mixed Stacks	Neutral	Naph.TCNE	0.0345	3.30
		Pery.TCNE	0.0127	3.19
		Pyre·TCNE	0.0161 0.0273	3.32
		DANT·TCNQ	0.0320	3.35
	Ionic	M_2P·$TCNQF_4$	0.0186	3.36
		TMPD·TCNQ	0.0305	3.30
		TMPD·CA	0.0472	3.28
		OMTTF·DBTCNQ	0.0039 0.0232	3.61
Segregated Stacks	Mixed Valence	$(TTF)_7I_5$	0.0264	3.57
		$TTF(SCN)_{0.57}$	0.0278	3.61
		$(Fluora)_2PF_6$	0.0600	3.34
		$(Pery)_2(PF_6)_{1.1}$	0.0308	3.38
		TTF·TCNQ		
		TTF	0.0068	3.47
		TCNQ	0.0269	3.17
		DBTTF·$TCNQCl_2$		
		DBTTF	0.0048	3.51
		$TCNQCl_2$	0.0132	3.42
	Ionic	HMTTF·$TCNQF_4$		
		HMTTF	0.0015	3.61
		$TCNQF_4$	0.0234	3.29
		TMTTF·HCBD		
		TMTTF	0.0016	3.61
		HCBD	0.0082	3.43
		K·TCNQ	0.0301	3.22
		TMPD·I	0.0010	3.38
		DMDBTTF·BF_4	0.0418	3.36

Estimated Transfer Integrals

Distance between centers (A)	$(W_i + W_j)/2$ (eV)	t (eV)	K	ref.
3.61	5.50	0.255	1.34	11
4.12	4.95	0.151	2.41	11
3.99	5.15 5.59	0.148 0.229	1.78 1.50	11
3.90	4.84	0.195	1.26	12
5.87	4.95	0.104	1.13	6
3.86	4.81	0.176	1.19	13
3.28	4.67	0.267	1.21	14
3.73	4.80 5.40	0.033 0.210	1.76 1.67	15
3.55	7.76	0.275	1.34	16
3.61	7.76	0.335	1.55	16
3.34	8.16	0.562	1.15	17
4.29	7.78	0.275	1.15	18
3.82	7.76	0.10	1.89	19
3.82	2.88	0.10	1.29	
3.76	7.96	0.085	2.21	20
3.76	3.21	0.085	2.01	
4.07	7.99	0.079	6.54	21
4.07	3.15	0.098	1.33	
4.02	7.20			22
4.02	3.30			
3.54	2.88	0.271	3.13	23
5.92	8.00	0.081	10.1	7
3.36	8.00	0.253	0.76	24

these relations t integrals may be estimated.

(2) Ionic Mixed Crystal When the electron affinity of the acceptor is large and the ionization potential of the donor is small, nearly a full charge transfer occurs in the ground state and the ground state wavefunction may be given by Ψ_E of Eq.(4). The back CT band may be found in the electronic spectra and the intensity may be analyzed by a similar method. The paramagnetic susceptibilities are found with this type crystals[6]. The linear array of the spin system may be stabilized by the back CT interaction, and the magnetic stabilization energy will be given by

$$J = 2t^2/U \tag{6}$$

Here U is on-site Coulomb energy which may be approximated by the energy of the back CT band. The magnetic susceptibility shows either temperature dependent activation process represented by linear Ising or dimer type singlet-triplet states[7] or by linear Heisenberg model described by Bonner-Fisher formula.[8]

(3) Mixed Valence Segregated Stack Most conducting organic crystals are classified into this category and they show quasi-metallic optical spectra in the infrared and near-infrared region. From the plasma edge of the reflectance, ω_p, the width of the one-dimensional energy band is estimated and t is given by

$$t = \frac{\hbar\,\omega_p^2}{16\,N\,e^2d^2\sin\frac{\pi\rho}{2}}, \tag{7}$$

where d is the lattice spacing, N is the number of site in the unit volume, and ρ is a band-filling factor. The t values are estimated for this group of crystals by Eq.(7).

(4) Ionic Crystal With Segregated Column Very strong donor and acceptor forms segregated stacks in spite of strong Coulomb repulsion between the same charges. It means that the charge resonance interaction of the radicals between the unfilled MO is fairly strong to stabilize the stacked columns. The charge resonance absorption band may be found strongly when the overlap is significant. The paramagnetic susceptibility may be described by either linear Heisenberg or Ising models or singlet-triplet dimer type. The calculated overlap integrals are correlated with values of transfer integrals estimated by several ways, and the agreement is rather poor for this class of crystals.

CALCULATION OF OVERLAP INTEGRALS. The molecular orbitals of the donor and the acceptor are calculated by P-P-P method using appropriate parameters. For the calculation of the overlap integrals between the ϕ_D and ϕ_A, the HF SCF AO developed by Clementi[9] was used with multi zeta functions. The use of HF SCF AO may be important for the calculation of intermolecular interaction.[10] The results shown in the Table indicated that t is reasonably correlated with the overlap integrals. Therefore reasonable assesment of the transfer integral may be possible by the MO calculation and it will be useful to find the mechanism of the charge transfer interaction in many complex systems.

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