Intermolecular Charge-Transfer Spectra. IV. Electronic Structure of Molecular Complexes

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As was mentioned in the previous paper¹⁾, the observed molar extinction coefficient ϵ_c of intermolecular charge-transfer spectra decreases by a considerable amount with the increase of donor character of B-component (or that of acceptor character of A-component) in spite of the appreciable decrease of the factor (W_1-W_0). In order to solve this apparent contradiction and caculate the absorption intensity f_{EN} or ϵ_c, it was pointed out that one should take the following factors into account:

1) Electron density distribution in the molecular orbitals which are essential to the intermolecular charge-transfer spectra.

2) The degree of extension of each atomic orbital.

For example, as was stated in the previous paper, it is easy to show that these two factors make the value of resonance integral $|H_{01}|$ and consequently that of ϵ_c smaller for the substituted benzene complex than that for benzene complex. Somewhat later, Kuboyama and Nagakura also suggested the smaller value of resonance integral for naphthalene complex than for benzene complex in order to explain their own experimental results concerning heat of formation²⁾. It is obvious that this suggestion can be included in the afore-mentioned statement 1) as special case.

In the present paper, the previous idea will be shown in the more concrete and quantitative form. Moreover, the predicted relative value of ϵ_c will be compared with some of the experimental results.

General Theory

In the third paper of this series¹⁾, the simple relation between resonance energy and absorption intensity is given as follows:

$$H_{01}^2/(W_1-W_0)\simeq(3h^2/8\pi^2 m)f_{EN}/(\gamma_B-\gamma_A)^2 \qquad (1)$$

where f_{EN} is the oscillator strength of intermolecular charge-transfer spectra and $(\gamma_B-\gamma_A)$ is the distance between the respective electronic center of B- and A-component. The left hand side of the above equation represents the resonance energy between two hypothetical electronic structures $\Psi_0=\Psi(A\cdot B)$ and $\Psi_1=\Psi(A^- - B^+)$.

Since the resonance intergral H_{01} and the overlap integral S is given respectively by

$$H_{01}=(\Psi_0\,|\,\boldsymbol{H}\,|\,\Psi_1),\quad S=(\Psi_0\,\Psi_1),$$

it is reasonable to postulate the approximate

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1) H. Murakami, This Bulletin, 27, 268 (1954).

2) A. Kuboyama and S. Nagakura, *J. Chem. Soc. Japan*, 75, 1082 (1954).

proportionality between them; that is*,

$$H_{01} \simeq const.\, S \qquad (2)$$

Now it is desirable to introduce the simple molecular orbitals ϕ_A and ϕ_B which are essential to the resonance interaction or the intermolecular charge-transfer spectra. According to Mulliken[3], the charge-transfer process involves essentially the jump of one electron in a molecular orbital ϕ_B of the B-component into a previously unoccupied molecular orbital ϕ_A of the A-component, and there exists the relation

$$S \simeq 2^{1/2} S_{AB}/(1+S_{AB}^2)^{1/2} \simeq 2^{1/2} S_{AB} \qquad (3)$$

where

$$S_{AB} = (\phi_A | \phi_B).$$

In order to estimate the overlap integral S_{AB}, one should consider that the overlapping part of ϕ_A and ϕ_B in actual molecular complex is rather localized and consequently ϕ_A and ϕ_B can be devided into two parts, respectively, as follows:

$$\begin{aligned} \phi_A &= \phi_\alpha + \phi_{\alpha'} \\ \phi_B &= \phi_\beta + \phi_{\beta'} \end{aligned} \qquad (4)$$

where ϕ_α and ϕ_β is the partial molecular orbital of A- and B-component, respectively, which are overlapping with each other for a given relative configuration. Accordingly, $\phi_{\alpha'}$ and $\phi_{\beta'}$ is defined as the remaining part of them, respectively, which are not overlapping with each other. Under such a definition as above, S_{AB} is given by

$$S_{AB} = (\phi_\alpha | \phi_\beta) \qquad (5)$$

In order to develop the calculation, we introduce the following simplifing approximation:

$$\begin{aligned} \phi_\alpha &= \sum_i^l C_i^{(\alpha)} \phi_i^{(\alpha)} \simeq C_l^{(\alpha)} \sum_i^l \phi_i^{(\alpha)} \\ \phi_\beta &= \sum_j^m C_j^{(\beta)} \phi_j^{(\beta)} \simeq C_m^{(\beta)} \sum_j^m \phi_j^{(\beta)} \end{aligned} \qquad (6)$$

where $\phi_i^{(\alpha)}$ and $\phi_i^{(\beta)}$ is the constitutent atomic orbital in the partial molecular orbital ϕ_α and ϕ_β respectively. In Eq. (6), the mean effective coefficient $C_l^{(\alpha)}$ and $C_m^{(\beta)}$ is defined respectively by

$$\begin{aligned} [C_l^{(\alpha)}]^2 &= \sum_i^l [C_i^{(\alpha)}]^2 / l \\ [C_m^{(\beta)}]^2 &= \sum_j^m [C_j^{(\beta)}]^2 / m \end{aligned} \qquad (7)$$

In the present approximation, S_{AB} is given as follows,

$$S_{AB} \simeq C_l^{(\alpha)} C_m^{(\beta)} S_{\alpha\beta} \qquad (8)$$

where

$$S_{\alpha\beta} = \Big(\sum_i^l \phi_i^{(\alpha)} \Big| \sum_j^m \phi_j^{(\beta)} \Big).$$

The combination of Eq. (8) with Eqs. (1), (2) and (3) provides us with the formula

$$\begin{aligned} [C_l^{(\alpha)}]^2 [C_m^{(\beta)}]^2 S_{\alpha\beta}^2 / (W_1 - W_0) \\ \simeq const.\, f_{EN}/(\gamma_B - \gamma_A)^2 \end{aligned} \qquad (9)$$

If the rather insensitive terms $(W_1 - W_0)$ and $(\gamma_B - \gamma_A)^2$ are ignored, Eq. (9) reduces to a very simple relation

$$[C_l^{(\alpha)}]^2 [C_m^{(\beta)}]^2 S_{\alpha\beta}^2 \simeq const.\, f_{EN}. \qquad (9a)$$

Remembering the well known formula

$$f_{EN} \simeq 4.32 \times 10^{-9} \epsilon_c \Delta\nu$$

and assuming the approximate constancy of the half width $\Delta\nu$ of the absorption band, Eq. (9a) is rewritten in the form

$$[C_l^{(\alpha)}]^2 [C_m^{(\beta)}]^2 S_{\alpha\beta}^2 \simeq const.\, \epsilon_c \qquad (9b)$$

where ϵ_c is the molar extinction coefficient of the intermolecular charge-transfer spectra. Thus, the evaluation of the relative value of ϵ_c is reduced to the electron density calculation of the molecular orbitals which are essential to the intermolecular charge-transfer spectra.

Application to Some Examples

In Eq. (9b), the numerical values of $S_{\alpha\beta}^2$ and *const.* are not known. Consequently, the theoretical prediction is limited in the relative value of ϵ_c for various complexes in which A- or B-component is the same. In the present paper, we consider the former case and define the relative value k of ϵ_c as follows:

$$k = \frac{\epsilon_c \text{ of } (A \cdot Ar)}{\epsilon_c \text{ of } (A \cdot Bz)}$$

where A represents the common A-component, and Ar, Bz respectively represents any aromatic molecule and benzene as B-component.

In case of quinhydrone-type molecular complexes, it is reasonable to assume the most compact relative configuration between two components in which the ring portion of each component is facing and contacting with the other and the substituted groups in both components are also facing with each other so long as such a configuration is allowed (see the discussion in the preceding paper[1]). Since the spatial extension of $2p$-atomic orbital of oxygen or nitrogen is considerably smaller than that of carbon, we can expect very small overlap integrals between substituted groups even in the above-described

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* In the following, the numerical value and the physical dimension of *const.* should be considered for the respective case and it is not necessary to be equal throughout the every cases.

[3] R. S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952).

configuration and can neglect them. Consequently, ϕ_B corresponds to the appropriate linear combination of $2p\pi$-atomic orbitals of ring carbon and does not contain the atomic orbitals in the substituted groups. When B-component is benzene, there exists the relation

$$\phi_B=\phi_\beta, \quad \sum_j^6[C_j^{(\beta)}]^2=1$$

as special case.

Moreover, it is reasonable to assume that $S_{\alpha\beta}$ is approximately the same regardless of the molecular size of B-component since the electronically interacting area is the same throughout the molecular complexes considered so long as the A-component is common.

TABLE I

OBSERVED AND CALCULATED VALUES OF THE RATIO k OF MOLAR EXTINCTION COEFFICIENT ϵ_c IN VARIOUS MOLECULAR COMPLEXES

A-Component	B-Component	ϵ_c	$k_{obs.}$	$k_{calc.}$	Reference
p-Quinone	Benzene	(2800)[a]	1.00	1.00	(1)
	Phenol	1200	0.43	0.66[b]	(2)
	Hydroquinone	890	0.32	0.32	(2)
Maleic anhydride	Benzene	3140	1.00	1.00	(1)
	Styrene	1940	0.62	0.50	(1)
	Dimethylaniline	1590	0.51	0.66[b]	(1)
Iodine	Benzene	16400	1.00	1.00	(3)
	Dibenzyl	11200	0.68	1.00	(3)
	Bromobenzene	10400	0.63	0.66[b]	(3)
	Styrene	7350	0.45	0.50	(3)
	Stilbene	7140	0.44	0.31	(3)
	Naphthalene	7640	0.47	0.50	(3)

a) Extrapolated value (not so exact)

b) Estimated from Fig. 5 in reference 5) assuming the equal electron density at 1- and 4-positions. (Assumed values of parameter are $a\simeq0.6$, $b=1.0$. Of course, these values may differ more or less for the different compounds and consequently the predicted values of k may also deviate from the listed value 0.66.)

(1) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **75**, 3776 (1953).

(2) H. Tsubomura, This Bulletin, **26**, 304 (1953).

(3) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952).

These situations enable us to give a simple expression for k, that is,

$$k=\sum_j^m[C_j^{(\beta)}]^2. \tag{10}$$

This formula is also applicable to the halogen-aromatic complexes since the dimension of the halogen molecule is almost the same as that of the benzene ring.

As was discussed by McConnell et al., there is an excellent correlation between the wavelengths of absorption maximum of intermolecular charge-transfer spectra and the estimated ionization potentials of B-components[4]. Therefore, it is almost certain that the molecular orbital in the B-component which is essential to the intermolecular charge-transfer process is the highest occupied one. Fortunately, the electron density distribution of the highest occupied molecular orbital have been calculated by Fukui et al. for various aromatic compounds in relation to their reactivity as frontier electron theory[5]. From Eq. (10), it is easy to see that k is given by the half of the total electron density in the partial molecular orbital ϕ_β since the complete orbital ϕ_B is filled by two electrons. By using the numerical value of Fukui et al., one can easily predict the approximate value of k for various molecular complexes. Some examples are shown in Table I together with the experimental results. The agreement between predicted and observed values are relatively good at least qualitatively. From the quantitative point of view, however, one should remember the existence of the following situations which prevent the exact comparison:

1) The simplifing assumption such as Eq. (6) is introduced.

2) The insensitive terms $1/(W_1-W_0)$ and $1/(\gamma_B-\gamma_A)^2$ are neglected although in some cases they might not be negligible.

3) In the present consideration, k is defined as the ratio of ϵ_c for convenience, sake although it should be defined as that of f_{EN} from the more exact point of view.

4) The statistical situation on the relative

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[4] McConnell, Ham and Platt, *J. Chem. Phys.*, **21**, 66 (1953).

[5] Fukui, Yonezawa, Nagata and Shingu, *J. Chem. Phys.*, **22**, 1433 (1954).

configuration between two components is neglected.

At any rate, it is almost certain that the interesting behavior of ϵ_c among such molecular complexes as shown in Table I is explainable by the consideration of their electronic structures.

Appendix

In case of iodine-benzene complex, the observed value of oscillator strength ($f_{EN} \simeq 0.38$) is very large. Consequently, Eq. (1) seems to predict the much larger resonance energy than the observed heat of formatian ($\Delta H \simeq 1.4$ Kcal./mol.[6]). This apparent contradiction can be solved by the examination of its electronic structure.

According to Mulliken, the attractive resonance energy in halogen-benzene complex (symmetry C_{2v}) is essentially given by the electronic interaction between antibonding σ-orbital $b_2\sigma_u$ in halogen molecule and the molecular orbital which has the same symmetry b_2 in benzene[3]. Therefore, the electronic interaction between any other pair of orbitals (especially that of π-orbitals) which are occupied by electrons contribute to exchange repulsive interaction. (In the rough approximation, the contribution of excited electronic configurations can be neglected since the degree of contribution of them is expected to be small.)

Now we examine the geometrical situation of each atomic orbital in halogen molecule. As is well known, the electron density distribution of σ-orbital is rather concentrated on the molecular axis, on the contrary, that of π-orbital is extended to the direction which is normal to the molecular axis. Taking this fact into account and assuming the most compact relative configuration, it is quite reasonably expected that the attractive resonance energy is negligibly small even at the region (distance between two components) in which the exchange repulsive energy amounts to considerable value. This situation is expressed in Fig. 1 diagramatically. In this figure, the curve I, II and III represents, respectively, the ponential energy curve of van der Waals type attraction, exchange repulsion and resonance attraction. Comparing the resultant curve (I+II) and (I+II+III), it is easy to see that the contribution of resonance attraction (ΔR) to the total binding energy ($V+\Delta R$) is small enough although the absolute value of resonance energy (R) in equilibrium position is very large. This situation seems to suggest the special importance of the repulsive term in the charge-transfer type interaction.

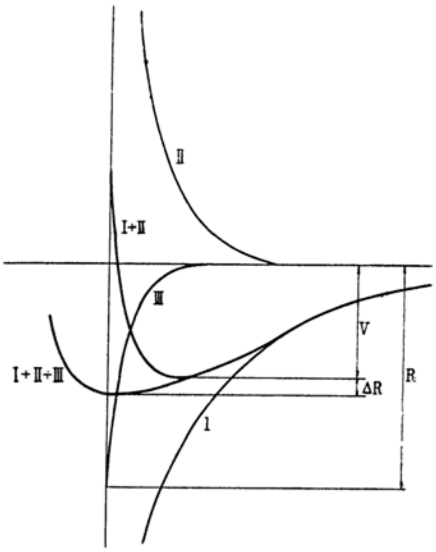

Fig. 1.

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[6] T.M. Cromwell and R.L. Scott, *J. Am. Chem. Soc.*, 72, 3825 (1950).