Intermolecular Charge-Transfer Spectra. I. Halogen-Aromatic Complexes

Hideo MURAKAMI

(Received February 17, 1953)

Introduction

Recently, Mulliken developed the theory of intermolecular charge-transfer spectra[1,2]. According to him, the concept of intermolecular charge-transfer spectra gives a reasonable explanation for many cases, such as halogen-aromatic complexes, organic molecular compounds, hydrated anions, etc. In the present paper, we shall study the characteristic absorption bands (λ_{max}: 2,800 Å$\sim$3,300 Å, ϵ_c: 7,000$\sim$14,000) of halogen-aromatic complexes, especially the dependence of the absorption intensity on the structure of aromatic components. In the case of methyl derivatives of benzene, experimental results indicate that the true molar extinction coefficient ϵ_c decreases with introducing methyl groups into an aromatic component. On the contrary, the above-mentioned theory indicates the increase of ϵ_c for the same condition as above, and Mulliken himself admits the difficulty of this contradiction. The chief object of the present paper is to solve this puzzle.

When halogen derivatives of benzene are used as aromatic components, the observed values of ϵ_c are mysterious. The reasonable interpretation for these results will also be given.

Absolute Intensity

In the case of hydrated anions, Rabinowitch introduced the idea of electron transfer spectra to explain the characteristic strong absorption band[3]. He attributed it to such an electron transfer from anion to water molecule as follows.

$$X^-\cdot(\mathrm{H_2O}) \xrightarrow{h\nu} X\cdot(\mathrm{H_2O})^-$$

As was emphasized by Rabinowitch, the absorption intensity which corresponded to the above process was very large ($\epsilon\sim$10,000).

It is obvious that anion X^- and molecule H_2O are chemically saturated. Therefore, we cannot expect the usual valence bond between them. Then the distance R between them may be approximately given by addition of their respective van der Waals radius. Consequently, R becomes relatively large compared with the usual covalent bond distances. This situation indicates the small overlapping between orbital functions of two components. Taking this fact into account, the above-described large absorption intensity is somewhat surprising.

Recently, Mulliken gave the quantum mechanical formalism to the idea of electron transfer spectra (in Mulliken's nomenclature, intermolecular charge-transfer spectra), and showed that large absorption intensity was understandable even when the intermolecular distance R was relatively large.

Now, we summarize the essence of Mulliken's theory in the suitable form for the present study. In complex A·B, A and B represents the acceptor and donor respectively. Then, two sorts of wave functions, ψ_0 and ψ_1, are defined. Firstly, ψ_0 is a "no-bond" wave function with respect to covalent bonding, that is

$$\psi_0=\psi(\mathrm{A\cdot B}) \qquad (1)$$

Secondly, ψ_1 is a "dative" wave function corresponding to the transfer of an electron from B to A accompanied by the establishment of a weak covalent bond, that is

$$\psi_1=\psi(\mathrm{A^-{-}B^+}) \qquad (2)$$

Using these wave functions, the wave function of the ground state N of any complex A·B is approximated by

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1) R. S. Mulliken, *J. Am. Chem. Soc.* **72**, 600 (1950).
2) R. S. Mulliken, *J. Am. Chem. Soc.* **74**, 811 (1952).
3) E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

$$\psi_N = a\psi_0 + b\psi_1 \tag{3}$$

In loose complexes, the relation $a^2 \gg b^2$ is expected. Further, we can expect that the overlap integral

$$S = \int \psi_0 \psi_1 dv \tag{4}$$

is very small*, and neglect it in the following rough approximation.

From Eq. (3), the energy of the ground state is given by the lower root of the seqular equation

$$\begin{vmatrix} W_0 - W & H_{01} \\ H_{01} & W_1 - W \end{vmatrix} = 0 \tag{5}$$

where

$$W_0 = \int \psi_0 \boldsymbol{H} \psi_0 dv \ , \qquad W_1 = \int \psi_1 \boldsymbol{H} \psi_1 dv$$

$$H_{01} = \int \psi_0 \boldsymbol{H} \psi_1 dv \tag{6}$$

$\boldsymbol{H}$ is the exact Hamiltonian operator for the entire system. The solution of Eq. (5) is given as

$$\begin{aligned} W = & (W_1 + W_0)/2 \\ & \pm [(W_1 - W_0)^2 + 4H_{01}{}^2]^{\frac{1}{2}}/2 \end{aligned} \tag{7}$$

In case of loose complex, we can expect the relation

$$1 \gg 4H_{01}{}^2/(W_1 - W_0)^2 \tag{8}$$

Taking this relation into account, we expand the second term of the right hand side of Eq. (7), then

$$\left.\begin{aligned} W_N &\simeq W_0 - H_{01}{}^2/(W_1 - W_0) \\ W_E &\simeq W_1 + H_{01}{}^2/(W_1 - W_0) \end{aligned}\right\} \tag{9}$$

where W_N and W_E represents the energy of normal and excited state respectively. These are familiar second-order perturbation equations, and correspond to Mulliken's equations in which the overlap integrals S are taken as zero. The wave function ψ_E which belongs to the eigenvalue W_E takes the following formula

$$\psi_E = a\psi_1 - b\psi_0 \tag{10}$$

The ratio of the coefficients a and b is easily given as follows,

$$\pm \rho = b/a \simeq -H_{01}/(W_1 - W_0) \tag{11}$$

Using Eqs. (3) and (10), the dipole moment μ_{EN} of transition ($\psi_E \rightarrow \psi_N$) is given as

$$\begin{aligned} \mu_{EN} &= -e\int \psi_E \vec{r}\, \psi_N dv \\ &\simeq eab(\vec{r}_B - \vec{r}_A) \end{aligned} \tag{12}$$

where $\vec{r}_B$ and $\vec{r}_A$ represents the radius vector from origin of arbitrary coordinate to the center of two components B and A, respectively. So long as the wave functions ψ_N and ψ_E are normalized, the condition $a^2 \gg b^2$ requires that a is very near to unity and b is relatively small compared with unity. Under such a condition, the dipole moment μ_{EN} is very sensitive to the value of b and, according to Mulliken, a relatively small value of b is sufficient to explain the observed large absorption intensity. At the present stage, however, the reliable and exact determination of the value of b has not been established yet.

Relative Intensity (Analysis of Experimental Results)

In 1938, Aickin, Bayliss and Rees studied the absorption spectra of bromine in solution and observed the new intense absorption bands in the neighbourhood of 2950 Å in case of aromatic solvents[4]. They interpreted these bands, however, as bromine bands which were enormously enhanced by the solvent effect. Later, Benesi and Hildebrand investigated the absorption spectra of iodine in aromatic solvents[5]. The intense absorption bands which were analogous to those of bromine solutions were observed. Moreover, they found that the extinction coefficient of these bands was directly proportional to the iodine concentration using aromatic solvents. This fact indicates the existence of the equilibrium as follows,

$$I_2 + Ar \rightleftharpoons I_2 \cdot Ar$$

where Ar denotes the aromatic hydrocarbon, and $I_2 \cdot Ar$ denotes the iodine-aromatic complex.

They considered that the above-mentioned intense absorption bands in the near ultraviolet region were due to only the presence of the complex $I_2 \cdot Ar$, and determined the

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* The exact determination of the value of S is somewhat difficult. In case of iodine-benzene complex, Mulliken considered that the upper limit of S is the order of 0.1~0.2. According to our estimate, however, the overlap integral between π-orbital of benzene and σ-orbital of iodine do not exceed 0.02 so long as we assume the usual Slater type functions and the same model of complex as that of Mulliken.

[4] R. G. Aickin, N. S. Bayliss and A. L. G. Rees, *Proc. Roy. Soc.* (London), **A169**, 234 (1933).

[5] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

true molar extinction coefficient ϵ_c of complex by taking into account the equilibrium constant for the above reaction. The results are given in Table 1. Keefer and Andrews performed the same experiment using chlorine, bromine and iodine monochloride instead of iodine and obtained the interesting results as shown in Table 1 and 2[7,8]. From these results, we can extract some noticeable relations as follows:

Table 1

Experimental Values of λ_{max} and ϵ_c

Aromatic Component	I_2-Aromatic Complexes		Cl_2-Aromatic Complexes	
	λ_{max} (A)	ϵ_c	λ_{max} (A)	ϵ_c
Benzene	2970	15400		9090
m-Xylene				6340
Mesitylene	3330	9300		

Table 2

Experimental Values of λ_{max} and ϵ_c

Aromatic Component	Br_2-Aromatic Complexes		ICl-Aromatic Complexes	
	λ_{max} (A)	ϵ_c	λ_{max} (A)	ϵ_c
Benzene	2920	13400	2870	9900
Toluene	3010	10500	2940	9050
t-Butylbenzene			2900	8470
o-Xylene	3130	8200	3030	7720
m-Xylene	3120	10100	3010	9000
p-Xylene	3060	7300	2950	7200
Chlorobenzene	2860	7300	2870	5650
Bromobenzene	2880	7600	2890	5750
Iodobenzene	3100	17000		

a) When toluene or *t*-butylbenzene is used as aromatic component instead of benzene, the true molar extinction coefficient ϵ_c derceases to some extent.

b) When xylene or mesitylene are used instead of benzene, ϵ_c decreases further except in the case of *m*-xylene. In the case of *m*-xylene complex, ϵ_c is almost the same as in toluene complex.

c) When chlorobenzene or brombenzene is used, ϵ_c is small and the same order of *o*-or *p*-xylene. In case of iodobenzene complex, howeuer, ϵ, is larger than that of benzene complex.

d) Now, we compare ϵ_c of Br_2-complex with those of corresponding ICl-complexes. (See Table 2). To extract the interesting regularity, we define the ratio *k* of ϵ_c as follows.

$$k_1 = \frac{\epsilon_c \text{ of } Br_2\text{-substituted benzene complex}}{\epsilon_c \text{ of } Br_2\text{-benzen complex}}$$

$$k_2 = \frac{\epsilon_c \text{ of ICl-substituted benzene complex}}{\epsilon_c \text{ of ICl-benzene complex}}$$

The values of k_1 and k_2 for various aromatic components are easily calculated using ϵ_c in Table 2, and shown in Table 3. Then, it is obvious that in any case the relation

$$k_2 > k_1$$

exists without exception.

Table 3

Comparison of k_1 and k_2

Aromatic Component	k_1	k_2
Benzene	1.00	1.00
Toluene	0.78	0.91
o-Xylene	0.61	0.78
m-Xylene	0.75	0.91
p-Xylene	0.54	0.73
Chlorobenzene	0.54	0.57
Bromobenzene	0.57	0.59

The main object of this paper is to explain the above-mentioned relations a), b), c) and d) considering the relative configuration of two components from the statistical point of view.

As is described in a) and b), true molar extinction coefficient ϵ_c decreases with introducing metyl groups into the aromatic components. According to Mulliken's theory, the reverse is predicted. As shown in Table 4, the ionization potential of an aromatic molecule decreases with introducing methyl groups[8]. This makes the value of $(W_1 - W_0)$ smaller, and according to Eq. (11), the value of $\rho = b/a$ larger. Consequently, Eq. (12) predicts the increase of dipole moment μ_{EN}, that is, the increase of absorption intensity. At first sight, the contradiction of experimental and theoretical results seems very difficult to solve. We can show, however, that the harmony between them is obtainable by the examination of a model.

Table 4

Lowest Ionization Potential (in ev)[8]

Aliphatic Compound	I. P.	Aromatic Compound	I. P.
Methane	13.1	Benzene	9.24
Ethane	11.6	Toluene	8.92
Propane	11.3	*t*-Butylbenzene	8.5*
Methyl Chloride	11.25	*o*-Xylene	8.3*
Ethyl Chloride	10.89	*m*-Xylene	8.3*
Methyl Bromide	11.17	*p*-Xylene	8.3*

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[6] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **72**, 4677, 5170 (1950).

[7] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **73**, 462 (1951).

[8] W. C. Price, *Chem. Rev.*, **41**, 257 (1947).

Ethyl Bromide	10.92 10.24a)	Chlorobenzene	9.42b)
Methyl Iodide	9.49	Bromobenzene	9.41b)
Ethyl Iodide	9.34 9.295a)	Iodobenzene	9.10b)

* These value have been estimated by consideration of spectroscopic features other than Rydlberg series, and probably less accurate.

a) W. C. Price, *J. Chem. Phys.*, **3**, 365 (1935).

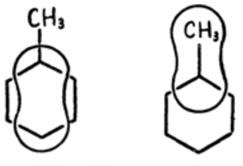
b) J. D. Morrison and H. J. C. Nicholson, *J. Chem. Pys.*, **20**, 1021 (1952).

Relative Intensity (Statistical Consideration)

For the relative configuration of two components in the complex, Mulliken assumed the model, in which iodine or bromine molecule rests on the benzene molecule with its axis parallel to the plane of the benzene and its center on the sixfold axis of the benzene. It is obvious that this model is the most compact one, and stable on account of van der Waals interaction. Moreover, according to Mulliken's opinion, the resonance energy $-H_{01}^2/(W_1-W_0)$ between ψ_0 and ψ_1 in the ground state is larger in this model than in the other. (See Eq. (9)). Then, it is an interesting and important problem to compare the magnitude of van der Waals interaction energy with that of resonance stabilizing energy.

Experimentally, Cromwell and Scott measured the heat of formation of iodine-benzene complex.[9] Their results indicate that ΔH is approximately -1.4 Kcal./mol. This value is smaller than the energy in weak hydrogen bond and is the order of magnitude which is understandable as mere van der Waals interaction energy. Further, Ham, Rees and Walsh found out that the infrared spectra of saturated solution of iodine in the purified mesitylene was indistinguishable from that of mesitylene[10]. These results probably indicate that the main interaction is the van der Waals type, and the resonance type (in Mulliken's nomenclature, charge-transfer force) is smaller compared with the former.

If the van der Waals type is predominant and the resonance type is negligible compared with the former, Mulliken's idealized model needs some revision for halogen-substituted benzene complexes. For example, when the aromatic component is monosubstituted benzene, we can consider the two configurations (α) and (β) in Fig. 1, and can expect almost the same stability for them considering van der Waals type interaction. Then it occurs that (α) and (β) type complexes exist in solution with almost equal statistical weight.

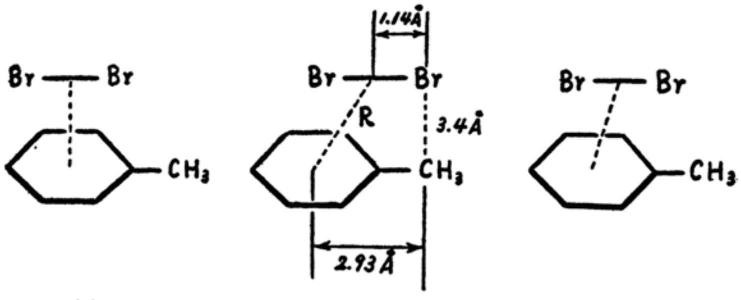


(α) Fig. 1 (β)

In case of model (β), the overlapping between π-orbital of aromatic component and σ-orbital of halogen component is decreased considerably, and the distance between centers of two components is slightly lengthened. These situations make the value of H_{01} smaller and of (W_1-W_0) slightly larger. Remembering Eqs. (11) and (12), we can expect the decrease of coefficient b, and then of dipole moment μ_{EN}.

In the experimental determination of ϵ_c, it was assumed that all the complexes had the same absorption intensity. As is shown before, however, this assumption is not a reasonable one, and the experimental values are nothing but the statistical mean for complexes (such as models (α) and (β)) which have their own various absorption intensities.

a) **Bromine-Toluene Complex.**—As idealized model, we consider the two relative configurations (α) and (β) which are shown in Fig. 2.



(α) (β) (γ)

Fig. 2

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

[10] N. S. Ham, A. L. G. Rees and A. Walsh, *J. Chem. Phys.*, **20**, 1336 (1952).

In model (α), all conditions are equal to that of an idealized model for bromine benzene complex which has been postulated by Mulliken, except the decrease of ionization potentical of aromatic component by amount of 0.32 ev. (See Table 4). Since the decrease of ionization potential causes the decrease of (W_1-W_0) by almost the same amount, it is expected that the wavelength $\lambda_{\max}$ at maximum absorption of toluene complex shifts towards the longer side. Taking $\lambda_{\max}=2920$ Å. of benzene complex as origin, the decrease of (W_1-W_0) by amount of 0.32 ev. predicts $\lambda_{\max}=3160$ Å. for model (α) of bromine-toluene complex. This is longer than the experimental value 3010 Å. As is easily shown, the absorption intensity of bromine-toluene complex in model (α) is almost the same as that of bromine-benzene complex, that is, $\epsilon_c{}^{(\alpha)}\sim 13400$. (See Table 2).

In model (β), the intermolecular distance R which combines the center of bromine molecule and center of benzene ring is lengthened by the amount of 0.44 Å. This causes the decrease of absolute value of Coulombic energy by the amount of 0.48 ev in excited state. If the effect of polarization is taken into account, this value may become smaller to some extent. The decrease of absolute value of Coulombic energy tends to conpensate the variation of ionization potential and exchange interaction energy. Therefore, we assume that (W_1-W_0) is equal to that of bromine-benzene complex. Then $\lambda_{\max}$ in model (β) is expected to be 2920 Å. (See Table 2). In model (β), as discussed before, the overlapping between π-orbital of benzene ring and σ-orbital of bromine may decrease and this causes the decrease of ϵ_c considerably. The exact calculation of ϵ_c in model (β) is somewhat defficult; then we postulate that the value of ϵ_c in model (β) is the half of that in model (α) as tentative one, that is, $\epsilon_c{}^{(\beta)}\sim 6700$.

Now, we bring up the third assumption that models (α) and (β) have almost equal stability and exist in solution with almost equal statistical weight. Then the molar extinction coefficient of bromine-toluene complex is give by

$$\epsilon_c=(\epsilon_c{}^{(\alpha)}+\epsilon_c{}^{(\beta)})/2=10500$$

The observed ϵ_c is just 10500 (See Table 2). On account of the superposition of two bands, the wavelength at absorption maximum becomes to lie in the middle of $\lambda_{\max}$ which are predicted for models (α) and (β), then approximately at about 3040 Å. The observed value is 3010 Å. The same result is obtainable by postulating model (γ) instead of the third assumption. In model (γ), the relative position of bromine to benzene ring is in the middle of models (α) and (β).

b) Bromine-Xylene complexes.—When *o*- or *p*-xylene is used as aromatic component, we can expect the three relative configurations as shown in Fig. 3. Then, as is postulated in bromine-toluene complex, we assume that these configurations have almost the same stability. Using the same values of $\epsilon_c{}^{(\alpha)}$ and $\epsilon_c{}^{(\beta)}$ as those used before, we obtain ϵ_c of bromine-xylene complex as follows.

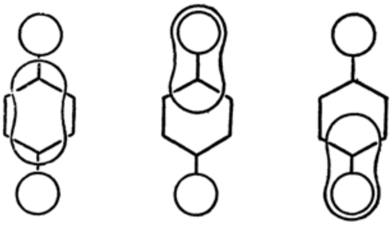

Fig. 3.

$$\epsilon_c=(\epsilon_c{}^{(\alpha)}+2\epsilon_c{}^{(\beta)})/3=8933$$

The observed value is 8200 for *o*-xylene complex, and 7300 for *p*-xylene complex.

In case of *m*-xylene complex, the observed value of ϵ_c is very large, that is 10100. This fact indicates that model (α) is more stable than model (β) and predominant statistically in solution. Consequently, we must consider that the benzene ring in *m*-xylene has a larger van der Waals attraction than that in *o*- or *p*-xylene.

According to experimental results of Platt and Klevens, the intensity of $N\rightarrow V$ type transition of π-electron in *m*-xylene is larger than that in *o*- or *p*-xylene.[11] The experimental total oscillator strength f of this transition is 1.46 for *m*-xylene and 1.22∼1.23 for *o*- or *p*-xylene. According to our tentative estimate, this strong $N\rightarrow V$ type transition contributes considerably to the van der Waals interaction, and the larger f value of *m*-xylene may probably sufficient to explain the required larger van der Wasls attraction of benzene ring in *m*-xylene.

c) Bromine-Halogenobenzene Complexes.—When chlorobenzene or bromobenzene is used as aromatic component the observed ϵ_c is very small, and it has the same order with $\epsilon_c{}^{(\beta)}$ (See Table 2). This requires that model (β) is more stable than model (α), and almost all the complexes exist in the con-

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[11] J. R. Platt and H. B. Klevens, *Chem. Rev.*, **41**, 301 (1947).

figuration of model (β). If we take into account the interaction between large dipole of C—Cl or C—Br bond and the induced dipole in bromine molecule, the above requirement may probably be understandable.

On the contrary, when iodobenzene is used as aromatic component, the observed ϵ_c is very large. In case of iodobenzene, the ionization potential of substituted iodine (9.295 ev.) is almost equal to that of benzene (9.24 ev.) (See Table 4). Then, being different from other cases, π-electrons in substituted iodine can contribute to intermolecular charge-transfer spectra as well as π-electron in benzene ring. Consequently, the magnitude of H_{01} in model (β) may be equal to or larger than that in model (α). This situation may probably explain the observed large ϵ_c.

d) Iodine Monochloride-Aromatic Complexes.—As is shown in Table 3, there exists the relation,

$$k_2 > k_1$$

This relation requires that the stability of model (α) relative to model (β) is larger in ICl-aromatic complexes than in corresponding Br_2-aromatic complexes. This requirement may be understandable considering the interaction between large dipole of ICl and the induced dipole in the benzene ring.

The above discussions all concern the halogen-aromatic complexes. We can expect the validity of the analogous discussions for the other molecular compounds, such as quinhydron type molecular compounds. The detailed study for these cases will be reported later.

Summary

The intermolecular charge-transfer spectra of halogen-aromatic complexes have been studied theoretically. Especially, the dependence of absorption intensity on the structure of aromatic component has been investigated. To solve the discrepancies between experimental results and Mulliken's theoretical predictions, we have introduced the statistical consideration for the relative configurations between two components. Using some reasonable assumptions, we have obtained the satisfactory agreement between theoretical predictions and experimental results, at least qualitatively.

The author wishes to express his sincere thanks to Prof. S. Akabori for his encouragement and interest in the course of this work, and also to Mr. I. Tanaka and Y. Mori for their valuable discussions.

Faculty of Science, Osaka
University, Osaka