ELECTRONIC SPECTRA AND ELECTRON-TRANSFER INTERACTION BETWEEN ELECTRON DONOR AND ACCEPTOR

S. NAGAKURA

*The Institute for Solid State Physics,
The University of Tokyo, Japan*

The concept of intramolecular charge-transfer absorption band was developed by the present author and Tanaka¹, and also by Longuet-Higgins and Murrell², by analogy with Mulliken's theory for intermolecular cases³. A dominant characteristic of this concept is that systems where electron donating and accepting groups are combined with each other directly, or through a bridge of conjugated double bonds, generally show additional absorption bands characteristic of the interaction between electron donor (D) and acceptor (A). In other words, it may be said that absorption bands of this kind appear additionally as the result of the contribution of so-called charge-transfer (abbreviated hereafter as CT) structures A^--D^+ to the resonance hybrid. This is schematically shown in *Figure 1*. In this figure, $E_G(\psi_G)$ and $E_{CT}(\psi_{CT})$ represent the energies (wave functions) of the ground (or no-bond) and CT configurations, respectively. As the result of interaction between these two configurations, we can obtain the two energy levels W_0 and W_1 , the transition between them corresponding to the CT band.

Figure 1. Schematic explanation of the interaction between ground (no-bond) and CT configurations

Therefore, the appearance of charge-transfer (CT) bands may be regarded as evidence for the existence of electron transfer interaction between D and A. In reality the situation generally becomes more complicated, since locally excited configurations, which contain electron excitation within each component, take part in the configuration interaction. This situation is shown in *Figure 2*. In some cases, the CT configuration and the locally

Figure 2. Configuration interaction among ground, CT and locally excited configurations

excited configuration mix with each other to such an extent that the CT band and the local excitation band cannot strictly be classified. Then we need careful analysis of absorption spectra from both theoretical and experimental points of view to identify CT bands.

During the past few years, we have carried out various investigations on the nature of intra- and intermolecular CT absorption bands from both the theoretical and experimental points of view. In addition to the usual near ultraviolet absorption measurements of solutions or gases, polarized ultraviolet absorption measurements of single molecular crystals and vacuum ultraviolet absorption spectroscopy were used as principal experimental tools. Here the author will report on some important results mainly concerning intramolecular cases.

First of all, let us take acetic acid as a simple example of systems composed of D and A. Since in this case the electron donating group (OH) is directly connected with the electron accepting group (C=O), we may expect the appearance of intramolecular CT absorption. So far, however, only a weak band due to the $n \rightarrow \pi^*$ transition has been observed at 200 m μ with acetic acid. Under these circumstances, Tsubomura and Kaya in our laboratory measured the vacuum ultraviolet absorption spectrum of gaseous acetic acid and found a fairly strong absorption band ($\epsilon \approx 4000$) at 160 m μ . The result is shown in *Figure 3*, where the absorption spectrum of ethyl acetate is also shown for the purpose of comparison. In order to clarify the

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nature of this band, energy levels and wave functions of acetic acid were evaluated by considering the interaction between the three electron configurations given in *Figure 4*. This figure shows also the wave functions of the

Figure 3. Vacuum ultraviolet spectra of acetic acid and ethyl acetate in gaseous state

$$E_G = 0 \quad E_{LE} = 7.92 \text{ eV}$$

$$E_{CT} = I_O - A_{C=O} - (0.5472)^2 [CC|OO] - (0.8370)^2 [OO|OO]$$

$$= 6.63 \text{ eV}$$

$$H_{G,CT} = 1.184 \beta_{CO} \quad H_{LE,CT} = -0.547 \beta_{CO}$$

$$H_{G,LE} = 0$$

Figure 4. Electron configurations of acetic acid

π electron orbitals of the C=O group used in the present study, which were obtained by Kon⁴. Of these configurations, the ground configuration was taken as the standard for the energy calculation. Then the energy of the locally (C=O) excited configuration (E_{LE}) can be assigned as 7.918 eV from the position of the $\pi \rightarrow \pi^*$ transition band in formaldehyde. Furthermore, the energy of the CT configuration can be evaluated by the following equation:

$$E_{CT} = I_D - A_{C=O} - (0.5472)^2[CC|OO] - (0.8370)^2[OO|OO]$$

Here I_D and $A_{C=O}$ are the ionization potential of DH and the electron affinity of AH, respectively^{1b}. The former was taken from the data published by Watanabe⁵, and the latter was regarded as an experimental parameter and assumed to be -1.20 eV for a series of carbonyl compounds. $[CC|OO]$ and $[OO|OO]$ are two-centre coulomb integrals and were evaluated following the method of Pariser and Parr⁶. Off-diagonal elements ($H_{G,CT}$, $H_{G,LE}$, $H_{LE,CT}$) necessary for the calculation of configurational interaction were obtained with the aid of the formulation by Pople⁷ and by Longuet-Higgins and Murrell².

Thus, the π -electron energy levels of acetic acid were finally evaluated as -1.156 , 6.572 , and 9.132 eV. The result given in Figure 5 and Table 1 shows that the system is stabilized by 26.7 kcal/mole from the electron-transfer interaction between the OH and C=O groups. By subtracting the compression energy from this stabilization energy, we can evaluate the so-called resonance energy of acetic acid to be 16 kcal/mole in good agreement with

Figure 5. Energy levels and wave functions of acetic acid

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Table 1. Energy states and wave function of acetic acid

Energy (eV)	Wave function
$W_2 = 9.132$	$\underline{\Psi}_2 = 0.210\psi_G - 0.731\psi_{C=O} - 0.649\psi_{CT}$
$W_1 = 6.572$	$\underline{\Psi}_1 = 0.301\psi_G + 0.680\psi_{C=O} - 0.669\psi_{CT}$
$W_0 = -1.156$	$\underline{\Psi}_0 = 0.930\psi_G - 0.055\psi_{C=O} + 0.363\psi_{CT}$

the value estimated from the thermal data. The transition energy between the ground level (W_0) and the lowest excited level (W_1) was calculated to be 7.73 eV. It is obvious that this transition corresponds to the 160 m μ band (7.72 eV). The present calculation shows that in the upper state of this transition, the CT and locally (C=O) excited configurations mix in almost equal proportion and, therefore, that the 160 m μ band has the characteristics of both a CT band and a shifted band of the 155 m μ band belonging to the C=O group.

Similar calculations were made with formamide^{1b}, acrolein^{1b}, thioacetamide^{1c}, thiourea^{1c}, tropone⁸, nitramide⁹ and ethyl nitrate⁹. In the case of formamide, theoretical consideration of which was made by taking three configurations into account as shown in Figure 6, two excited levels W_1 and W_2 were obtained (see Figure 7). $W_0 \rightarrow W_1$ and $W_0 \rightarrow W_2$ transitions apparently correspond to the observed 172 and 135 m μ bands, respectively. As is easily seen from the wave functions of the W_0 and W_1 levels, the $W_0 \rightarrow W_1$ transition band has the character of a CT band. That is to say, the CT band and the local excitation band are more clearly identified in formamide

$$E_{CT}^F = I_D - A_{C=O} - (0.5472)^2 [CC | NN] - (0.8370)^2 [OO | NN]$$

$$H_{G, CT}^F = 1.184\beta_{CN}$$

$$H_{CT, C=O}^F = -0.5472\beta_{CN}$$

$$H_{G, C=O}^F = H_{G, C=O}^A, C=O = H_{G, C=C}^A, C=C=O$$

$$H_{G, CT}^A = 1.184\beta_{CC}/2$$

$$\left. \begin{aligned} \phi_{C=O}^f &= 0.5472x_C + 0.8370x_O \\ \phi_{C=O}^v &= 0.8370x_C - 0.5472x_O \end{aligned} \right\}$$

Figure 6. π -Electron configurations of formamide

Figure 7. Energy levels and wave functions of formamide

than in acetic acid. This is because the energy of CT configuration is lower in formamide than in acetic acid and, therefore, the interaction between the CT and locally excited configurations is smaller in the former than in the latter. In this connection, the result with thiourea seems to be interesting. This molecule shows two absorption bands at 236 and 195 $m\mu$ (Figure 8), whose directions of transition moments are determined as shown in Figure 9 from the polarized ultraviolet absorption measurements on the single crystal of the molecule¹⁰. From the combination of the observed direction of transition moment with the theoretical considerations, the 195 $m\mu$ band may safely be assigned as the $W_1 \rightarrow W_4$ transition. In this transition the upper

Figure 8. Ultraviolet absorption spectra of thioacetamide (1) and thiourea (2) in aqueous solution

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Figure 9. The polarized ultraviolet absorption spectrum of thiourea and the projection of the molecules to the (110) plane; arrows show the observed directions of the transition moments

Figure 10. Energy level diagram for thiourea, showing the relation between observed (in parentheses) and calculated transition energies

state W_4 has 100 per cent CT character. This situation occurs from the fact that the configuration H_{CT}^a (anti-symmetric CT configuration) has a different symmetric character from those of the other configurations (see Figure 10). The results on acetic acid, formamide, thioacetamide, and thiourea are collected in Table 2, in which the theoretically predicted directions of transition moments are given and compared with the observed results.

Now let us turn our attention to more complicated molecules. Nitrobenzene is a typical example exhibiting a strong CT band caused by the electron-transfer interaction between the benzene ring (D) and the nitro

Table 2. CT bands of acetic acid, formamide, thioacetamide and thiourea

Molecule	Transition energy (eV)		Contribution of CT configuration (%)		Direction of transition moment	
	obs.	theoret.	ground	upper	obs.	theoret.
$\text{Me}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ (ref. 10)	7.72	7.73	13.2	44.7	—	—
$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$ (ref. 11)	7.19	7.08	20.8	60.2
$\text{Me}-\overset{\text{S}}{\parallel}{\text{C}}-\text{NH}_2$ (ref. 11)	4.75	4.77	17.4	43.3
$\text{H}_2\text{N}-\overset{\text{S}}{\parallel}{\text{C}}-\text{NH}_2$ (ref. 11)	6.36	5.84	24.7	100

group (A). In 1954 the 240 $m\mu$ band of nitrobenzene was first interpreted as an intramolecular CT band by the present author and Tanaka on the basis of the simple LCMO treatment¹. Since that time, several new experimental results have been accumulated concerning the electronic spectrum of nitrobenzene. Labhart in Basle measured the spectrum of nitrobenzene in hexane solution under a strong electric field for the purpose of determining the direction of the transition moment¹². According to the results shown in Figure 11, it is unambiguous that there appear three absorption bands at 330, 280 and 240 $m\mu$, and that they are polarized parallel, perpendicular and parallel to the C—N bond, respectively. Further, the near and vacuum

Figure 11. The absorption spectrum of nitrobenzene measured by Labhart under strong electric field (in hexane solution)

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ultraviolet absorption spectrum of gaseous nitrobenzene was measured in our laboratory with the result given in *Figure 12*. A noticeable fact is that two strong bands appear at 193 and near 170 $m\mu$ in addition to the 240 $m\mu$ band which is well known as the characteristic band of nitrobenzene. From the qualitative point of view, the above-mentioned experimental results strongly support the previous interpretation that the 240 $m\mu$ band is

Figure 12. Ultraviolet absorption spectra of nitrobenzene and nitromesitylene

not a shifted band pertinent to the benzene ring, but is an additional band caused by the electron-transfer interaction between the benzene ring and the nitro group. In order to make a quantitative study of this point, the present author calculated the energy levels and wave functions of nitrobenzene by the same method as described in the case of acetic acid, taking eight electron configurations into account. There are, besides the ground configuration, the two CT configurations and the five locally excited configurations. The two CT configurations are caused by removing an electron from each of the doubly degenerated highest occupied orbitals of the benzene ring to the lowest vacant orbital of the nitro group (see *Figure 13*). Of the five locally excited configurations, four are caused by the electron excitation within the benzene ring and one corresponds to the $\pi \rightarrow \pi^*$ transition (198 $m\mu$ band) of the nitro group. The energy values of these configurations were determined as shown in *Table 3* from the observed wavelength of the peaks of benzene and nitromethane¹³. The π -electron energy levels and wave functions of nitrobenzene, evaluated by considering the configurational interaction among the above-mentioned eight electron configurations, are given in *Figure 14* and *Table 4*. From this theoretical study, the absorption bands

Figure 13. CT configurations of nitrobenzene

Table 3. Energy values of electron configurations of nitrobenzene

Ground configuration	$E_G = 0$
Locally excited configuration	$\left\{ \begin{array}{l} E_{B_{2u}} = 4.71 \text{ eV} \\ E_{B_{1u}} = 5.96 \text{ eV} \\ E_{E_{1u}}^s = 6.74 \text{ eV} \\ E_{E_{1u}}^a = 6.74 \text{ eV} \\ E_{NO_2}^a = 6.24 \text{ eV} \end{array} \right.$
Charge transfer configuration	$\left\{ \begin{array}{l} E_{CT}^s = 4.93 \text{ eV} \\ E_{CT}^a = 5.06 \text{ eV} \end{array} \right.$

Figure 14. Energy level diagrams of nitrobenzene

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Table 4. Energy states and wave functions of nitrobenzene

Energy (eV)	Wave function
$W_7 = 6.9575$	$\overline{\Psi}_7 = -0.0571\psi_G - 0.1994\psi_\beta + 0.9146\psi_\gamma^s + 0.3471\psi_{CT}^s$
$W_6 = 6.9306$	$\overline{\Psi}_6 = 0.0812\psi_\alpha + 0.9458\psi_\gamma^a - 0.3146\psi_{CT}^a$
$W_5 = 6.2400$	$\overline{\Psi}_5 = \psi_{NO_2}$
$W_4 = 6.1658$	$\overline{\Psi}_4 = 0.0594\psi_G + 0.8902\psi_\beta + 0.3191\psi_\gamma^s - 0.3198\psi_{CT}^s$
$W_3 = 5.3433$	$\overline{\Psi}_3 = -0.6419\psi_\alpha + 0.2911\psi_\gamma^a + 0.7094\psi_{CT}^a$
$W_2 = 4.7644$	$\overline{\Psi}_2 = -0.2052\psi_G + 0.4092\psi_\beta - 0.2477\psi_\gamma^s + 0.8539\psi_{CT}^s$
$W_1 = 4.2361$	$\overline{\Psi}_1 = 0.7625\psi_\alpha + 0.1443\psi_\gamma^a + 0.6307\psi_{CT}^a$
$W_0 = -0.2577$	$\overline{\Psi}_0 = 0.9575\psi_G + 0.0202\psi_\beta - 0.0180\psi_\gamma^s + 0.2195\psi_{CT}^s$

observed with nitrobenzene can be interpreted quantitatively as tabulated in Table 5, except for the weak band at 330 m μ which may conceivably be assigned to the $n \rightarrow \pi^*$ transition. The direction of the transition moments for the $W_0 \rightarrow W_1$ and $W_0 \rightarrow W_2$ transitions are predicted theoretically to be perpendicular and parallel to the C—N bond, respectively; the prediction being in good agreement with the experimental result by Labhart.

Table 5. Transition energies and other related quantities of nitrobenzene

Transition	Transition energy (eV)		Electron configuration which shows largest contribution to the upper state (%)
	obs.	theoret.	
$W_0 \rightarrow W_1$ ($\perp$)*	4.38	4.49	Local excitation of benzene B_{2u} (58) CT ^s (73)
$W_0 \rightarrow W_2$ ($\parallel$)*	5.16	5.02	
$W_0 \rightarrow W_3$ ($\perp$)*	{ Weak band covered	5.60	CT ^a (50)
$W_0 \rightarrow W_4$ ($\parallel$)*		6.42	Local excitation of benzene B_{1u} (79)
$W_0 \rightarrow W_5$ ($\perp$)*	{ 6.41	6.50	Local excitation of NO ₂ (100)
$W_0 \rightarrow W_6$ ($\perp$)*		7.19	Local excitation of benzene E_{1u} (89)
$W_0 \rightarrow W_7$ ($\parallel$)*		7.21	Local excitation of benzene E_{1u} (84)

In view of the fact that the C—N bond distance of nitrobenzene determined by the X-ray crystal analysis technique is almost equal to the ordinary value and shows no shrinkage due to double bond character¹⁴ (see Figure 15), a question has recently been raised as to the existence of resonance interaction or electron-transfer interaction between the benzene ring and the nitro group within the nitrobenzene molecule¹⁵. However, the above-mentioned experimental and theoretical results, especially the appearance of a strong

CT band at 240 $m\mu$, definitely supports the existence of the electron transfer interaction in the ground state, although according to the present theoretical consideration the contribution of a CT structure to the ground state is only 4.8 per cent (resonance energy = 5.9 kcal/mole), considerably smaller than in the cases of acetic acid, formamide, *etc.* In this connection, it seems to be of much interest to compare the absorption spectrum of nitrobenzene with that of nitromesitylene. In the latter the nitro group is twisted by 66.5° from the plane of the benzene ring owing to the steric hindrance of the methyl groups, and hence the electron transfer interaction is inhibited to a great extent. According to our opinion, the CT band of nitrobenzene may be expected to disappear completely, or to be greatly diminished in intensity, in nitromesitylene. The absorption spectrum of the molecule measured by Kojima and Maruyama in our laboratory is shown in *Figure 12* in comparison with that of nitrobenzene. The result shows that the intensity of the 250 $m\mu$ band of nitromesitylene is only a fifth of that of the corresponding 240 $m\mu$ band of nitrobenzene, and therefore that our opinion on the electron transfer interaction of nitrobenzene is correct. Anyhow it is certain that the problem of the resonance interaction of nitrobenzene is almost completely cleared up by the present study. The question as to the C—N bond distance is thought to be solved by considering some factors other than the double bond character; for example, the weakening of the σ bond in the CT structure, which may be caused by the repulsion between positive charges on both the nitrogen atom and the adjacent carbon atom (see *Figure 15*)¹⁶.

Figure 15. Geometrical configuration of nitrobenzene and π -electron density of the symmetric CT configuration

Similar considerations were applied to benzoic acid, whose polarized ultraviolet absorption was measured by Tanaka in our laboratory¹⁷. The combination of his spectrophotometric result and the X-ray crystal analysis data shown in *Figure 16* leads to the conclusion that the 230 $m\mu$ band of benzoic acid has the direction of transition moment inclined away from the bond connecting the benzene ring and the carboxyl group by 6.5° . This result strongly supports the view that the band is of the CT type, because the

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Figure 16. The polarized ultraviolet absorption of the single crystal of benzoic acid and the orientation of molecules in the unit cell

observed direction is completely coincident with the direction predicted for the CT band.

The conception of CT absorption plays an important rôle in the interpretation of electronic spectra of organic compound ions as well as of neutral

Figure 17. The absorption spectrum of $[\text{C}_6\text{H}_5\text{NO}_2]^- \text{K}^+$

molecules. According to theoretical and experimental studies on the electronic spectra of the nitromethyl¹³, acetylacetonate¹⁸, and nitrobenzene radical anions, these ions clearly show a strong CT band caused by resonance interaction between D and A. As an example, the absorption spectrum of the nitrobenzene ion studied by Ishitani in our laboratory is shown in *Figure 17*. In this figure, the two vertical lines represent the band positions and intensities of the radical ion evaluated theoretically taking sixteen electron configurations. Of these two bands, the longer wavelength one possesses predominantly the character of a CT absorption.

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