# Electronic States of the Crystals of TCNE Complexes with Hexamethylbenzene, Acenaphthene, and Dibenzofuran

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(Received May 2, 1977)

The polarized reflection spectra were measured on crystals of tetracyanoethylene and its charge-transfer complexes, and the absolute intensity of the absorption parallel to the crystalline axes has been obtained by the Kramers-Kronig transformation. The charge-transfer degree and the stabilization energy in the ground state were estimated for each complex by analyzing the charge-transfer bands in the crystalline state. In the TCNE–hexamethylbenzene(HMB), acenaphthene, and dibenzofuran complexes, the charge-transfer degrees are 9.05, 12.3, and 4.95% respectively in the ground state.

Tetracyanoethylene, TCNE, is a strong electron acceptor. The formation of charge-transfer complexes with a variety of aromatics in dichloromethane solutions has been studied by Merrifield and Phillips.[1)] These complexes are characterized by an intense electronic absorption in the visible or near-ultraviolet region that can be attributed to neither component of the complex alone, but to a new molecular species, the complex itself. Mulliken[2)] has developed a theory of the intermolecular charge-transfer (CT) interaction which has been applied successfully to the interpretation of the absorption bands characteristic of molecular complexes. Aihara, Tsuda, and Inokuchi[3)] examined the gas-phase spectra of these CT complexes and discussed how an increase in solvent polarity results in a shift of the CT band to a higher-energy region.

The infrared spectra of the complexes showed new bands which appeared on the complex formation,[4,5,16)] and the resonance-enhanced Raman band was concluded to be due to the direct participation of the lowest CT state of the complex in the intermediate states of Raman scattering.[6–9)]

Some of the molecular complexes of tetracyanoethylene can be obtained as crystalline solids, which often exhibit characteristic absorption bands analogous to the CT bands of the molecular complexes in solution. Kuroda *et al.*[10,11)] revealed the presence of marked dichroism in these characteristic bands; the absorption is stronger as the light is polarized parallel to the alternate stack of donor and acceptor molecules, in agreement with the theoretical prediction for a CT transition. Furthermore, the CT interaction between donor and acceptor molecules has been applied to the interpretation of the mechanism of the electrical condition in these crystals of TCNE complexes.[12)]

However, no study has been reported hitherto on the correlation of the electronic states of these complexes with the absolute absorption intensity of the CT band. In the present paper, the author shows the crystal absorption spectra obtained by the K-K transformation of the reflection spectra of TCNE complexes with HMB, acenaphthene, and dibenzofuran and gives information about the electronic states of the complexes.

## Experimental

The single crystals of TCNE complexes with HMB, acenaphthene, and dibenzofuran were grown by sublimation in bottles. These crystals have the crystal habits shown in Fig. 1.

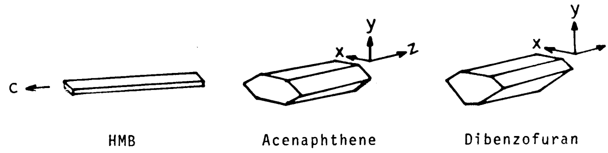

Fig. 1. The crystal habits of TCNE–HMB, acenaphthene, and dibenzofuran.

The reflection spectra at the normal incidence have been measured over the range of 10000—40000 cm$^{-1}$ with a reflection spectrophotometer made in our laboratory, while the absorption spectra have been obtained by the Kramers-Kronig transformation. The oscillator strength along the $\alpha$ axis of the crystal may be evaluated by using the following equation:

$$f^{\alpha} = 4.32\times10^{-9}\int n_{\alpha}(\sigma)\varepsilon_{\alpha}(\sigma)\mathrm{d}\sigma,$$

where the integration is calculated over the whole band, $\sigma$ is the wave number, and $n_\alpha$ and $\varepsilon_\alpha$ are the $\alpha$ components of the refractive index and the molar extinction coefficient. The oscillator strenghts for the three orthogonal axes in the crystal should be compared with that in solution:

$$f^{x}+f^{y}+f^{z} = 3f^{\text{solution}}.$$

## Theoretical

The basic theory of the CT complex was given by Mulliken[2)]; and the energy diagrams are shown in Fig. 2.

In the AD type, the ground state is partly ionic and

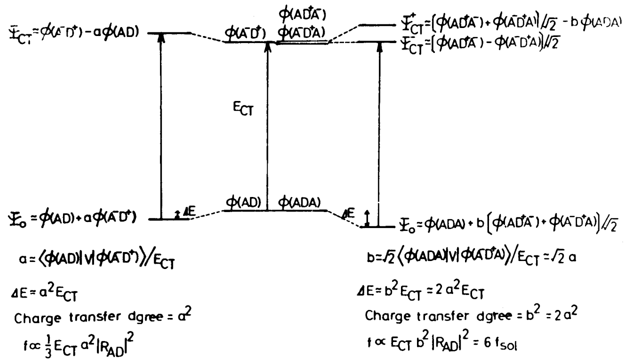

Fig. 2. The energy diagrams of the charge-transfer complexes.

may be described by a wavefunction

$$\Psi_0 \simeq \phi(\mathrm{AD}) + \sum_i a_i\phi_i(\mathrm{A^-D^+}) ,$$

where $\phi(\mathrm{AD})$ represents a non-bonding, and $\phi_i(\mathrm{A^-D^+})$ the $i$-th CT wavefunction involving the transfer of an electron from D to A. Then, the charge-transfer degree and the stabilization energy are given as $\sum_i a_i^2$ and $\Delta E = \sum_i a_i^2 E_{\mathrm{CT}}{}^i$. For the $i$-th charge-transfer excited state, we can write the wavefunction, $\Psi_{\mathrm{CT}}{}^i$ given by

$$\Psi_{\mathrm{CT}}{}^i \simeq \phi_i(\mathrm{A^-D^+}) - a_i\phi(\mathrm{AD}).$$

This is responsible for the characteristic color of the complex and the oscillator strengths in the solution and crystal are given as follows:

$$f_i(\mathrm{AD})^{\mathrm{solution}} = 1.085\times10^{11}E_{\mathrm{CT}}{}^i a_i{}^2|R_{\mathrm{AD}}|^2 ,$$

$$f_i(\mathrm{AD})^{\mathrm{crystal}} = 3f_i(\mathrm{AD})^{\mathrm{solution}} ,$$

where $R_{\mathrm{AD}}$ is the vector between the acceptor and donor molecules in the unit of cm and $E_{\mathrm{CT}}{}^i$ the excitation energy in cm$^{-1}$.

In the ADA type, the ground state can also be described by a wavefunction

$$\Psi_0 \simeq \phi(\mathrm{ADA}) + \sum_i b_i\{\phi_i(\mathrm{AD^+A^-}) + \phi_i(\mathrm{A^-D^+A})\}/\sqrt{2} ,$$

where $\phi(\mathrm{ADA})$ represents a non-bonding, and $\phi_i(\mathrm{AD^+\text{-}A^-})$ and $\phi_i(\mathrm{A^-D^+A})$ the $i$-th CT wavefunctions. Then, the charge-transfer degree and the stabilization energy in the ground state are given as $\sum_i b_i^2$ and $\Delta E = \sum_i b_i^2 \cdot E_{\mathrm{CT}}{}^i$. Therefore, it should be noted that they are twice as much as those in the AD type. The wavefunction, $\Psi_{\mathrm{CT}}{}^i(-)$, for the optically allowed $i$-th excited state is given by

$$\Psi_{\mathrm{CT}}{}^i(-) \simeq \{\phi_i(\mathrm{AD^+A^-}) - \phi_i(\mathrm{A^-D^+A})\}/\sqrt{2} ,$$

and the oscillator strengths in the solution and crystal are as follows:

$$f_i(\mathrm{ADA})^{\mathrm{solution}} = 1.085\times10^{11}E_{\mathrm{CT}}{}^i b_i{}^2|R_{\mathrm{AD}}|^2,$$

$$f_i(\mathrm{ADA})^{\mathrm{crystal}} = 3f_i(\mathrm{ADA})^{\mathrm{solution}}.$$

Accordingly, by a comparison between the experimental and theoretical oscillator strengths, we can obtain the magnitude values of $a_i^2$ or $b_i^2$ and get information about the electronic states of the CT complexes. Furthermore, TCNE complexes form configurations of the AD type in the solution and of the ADA type in the crystal. This means that the oscillator strength in the crystal is six times that in the solution:

$$f_i(\mathrm{ADA})^{\mathrm{crystal}} = 6f_i(\mathrm{AD})^{\mathrm{solution}}.$$

## Results

*TCNE.* TCNE forms monoclinic crystals of the P2$_1$/n space group, and there are two centrosymmetric molecules in the unit cell. The polarized absorption spectra can be obtained from the reflection spectra, as is shown in Fig. 3. The long-axis transition band of the molecule has a structure; its origin is located at 36300 cm$^{-1}$, and other vibronic levels appear at 37600, 38800, and 39800 cm$^{-1}$.

*TCNE–HMB Complex.* The TCNE–HMB complex forms triclinic crystals,[13] as is shown in Fig. 1. TCNE and HMB molecules are stacked alternately in columns parallel to the c axis. Both molecular planes are perpendicular to the c axis, and the interplanar separation, $R_{\mathrm{AD}}$, is 3.35 Å. The reflection spectra are observed for the polarizations parallel and perpendicular to the c axis, and the absorption spectra are obtained by the K-K transformation of the reflection spectra, as is shown in Fig. 4.

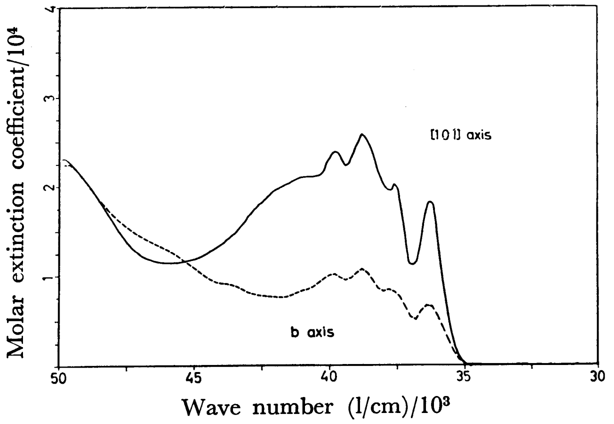

Fig. 3. The absorption spectra of TCNE crystal obtained from the K-K transformation of the reflection spectra.

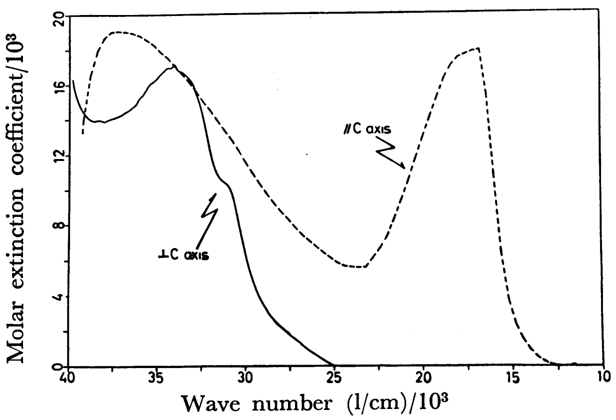

Fig. 4. The absorption spectra of the crystal of TCNE–HMB complex obtained from the K-K transformation of the reflection spectra.

The 17000 cm$^{-1}$ band is exclusively polarized along the c axis, which can be assigned to a CT band. The oscillator strength of this band is 0.563, and the charge-transfer degree is 9.05%. The stabilization energy in the ground state is given as 4.40 kcal, as is shown in Table 1. The spectrum polarized perpendicular to the c axis consists of the locally excited band of the TCNE molecule, and the broad band in the region of 30000—37000 cm$^{-1}$ corresponds to the 36000 cm$^{-1}$ band of the TCNE crystal.

*TCNE–Acenaphthene Complex.* The crystal of this complex ($\rho_{\mathrm{obsd}}$=*ca.* 1.3 g/cm$^3$) is a brownish black prism, and its crystal structure is not known. The reflection spectra are observed for the light polarized along the three orthogonal axes (x, y, and z), and the absorption spectra are obtained by the K-K transformation of the reflection spectra, as is shown in Fig. 5.

The z-axis spectrum has three bands— at 14800, 23200, 30000 cm$^{-1}$— which can be assigned to the CT band. The oscillator strengths of these bands are 0.388,

Table 1. The observed transition energy ($E_{CT}$ in $10^3$ cm$^{-1}$) and oscillator strength ($f$) and the calculated charge-transfer degree ($b^2$ in %) and stabilization energy ($\Delta E$ in kcal) in the ground state of TCNE complexes

| TCNE complex | $f$ | $E_{CT}$ | $b^2$ | $\Delta E$ |
|---|---|---|---|---|
| HMB | 0.563 | 17.0 | 9.05 | 4.40 |
| Acenaphthene | 0.388 | 14.8 | 7.17 | 3.03 |
| | 0.238 | 23.2 | 2.80 | 1.86 |
| | 0.250 | 30.0 | 2.28 | 1.96 |
| (Total) | | | 12.3 | 6.85 |
| Dibenzofuran | 0.269 | 21.4 | 3.44 | 2.11 |
| | 0.160 | 29.0 | 1.51 | 1.25 |
| (Total) | | | 4.95 | 3.36 |

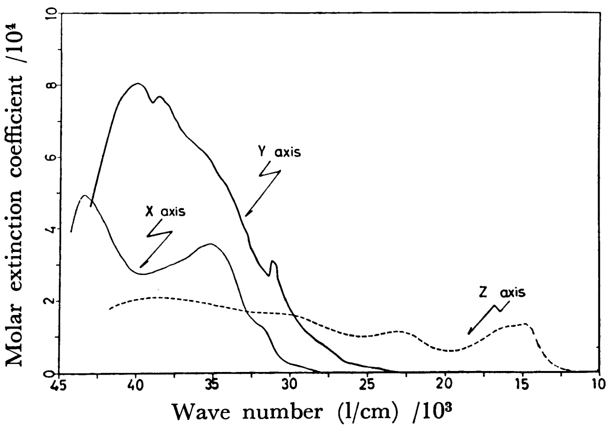

Fig. 5. The absorption spectra of the crystal of TCNE–acenaphthene complex obtained from the K-K transformation of the reflection spectra.

0.238, and 0.250 respectively. Each band contributes to the charge-transfer degree in the ground state, and the total degree becomes 12.3% by using $R_{AD}=3.35$ Å, as is shown in Table 1. The stabilization energy is also given as 6.85 kcal. The y-axis spectrum may consist of the $\alpha$ and $\beta$ bands corresponding to the 30900 and 41800 cm$^{-1}$ bands of the acenaphthene crystal,[14] while the x-axis spectrum consists of the p and $\beta'$ bands corresponding to two bands at 31400 and 45000 cm$^{-1}$ of the acenaphthene crystal and one band at 36000 cm$^{-1}$ of the TCNE crystal.

*TCNE–Dibenzofuran Complex.* The crystal of this complex ($\rho_{obsd}=ca.$ 1.3 g/cm$^3$) is a brownish black prism; its crystal structure is not known. The reflection spectra are observed for the light polarized along the three orthogonal axes (x, y, and z), while the absorption spectra are obtained by the K-K transformation of the reflection spectra, as is shown in Fig. 6.

The CT bands located at 21400 and 29000 cm$^{-1}$ are observed in the z and y axes spectra. The total oscillator strengths of these two bands are 0.269 and 0.160, and the total charge-transfer degree in the ground state is estimated to be 4.95% by using $R_{AD}=3.35$ Å. The stabilization energy is also calculated to be 3.36 kcal, as is shown in Table 1. The y-axis spectrum may consist of the $\alpha^*$, p, and $\beta'$ bands corresponding to the 33300, 39100, and 46000 cm$^{-1}$ bands of dibenzofuran[15] in addition to two CT bands. The x-axis spectrum may consist of the $\alpha$ and $\beta$ bands corresponding to two bands at 32600 and 42500 cm$^{-1}$ of the dibenzofuran crystal and one band at 36000 cm$^{-1}$ of the TCNE crystal.

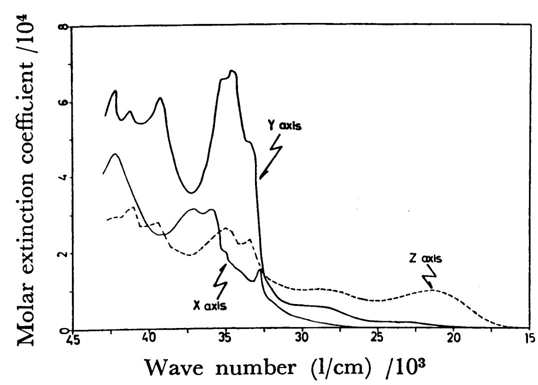

Fig. 6. The absorption spectra of the crystal of TCNE–dibenzofuran complex obtained from the K-K transformation of the reflection spectra.

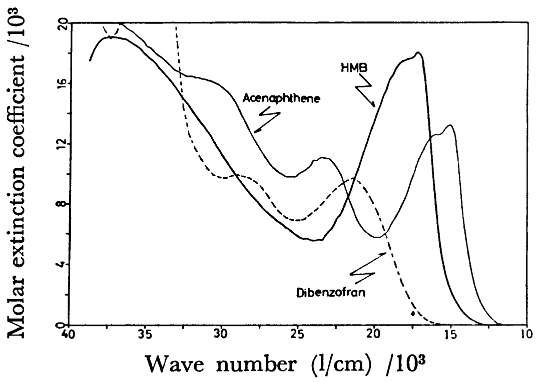

Fig. 7. The absorption spectra characteristic of crystals of TCNE complexes with HMB, acenaphthene, and dibenzofuran.

## Discussion

The absorption bands characteristic of crystals of TCNE complexes are again depicted in Fig. 7. The first CT band of the TCNE complexes with HMB and acenaphthene splits into doublets, the separation of which are 1500—1200 cm$^{-1}$. In the crystal of the TCNE–HMB complex,[13] the TCNE residues are disordered in two perpendicular orientations about the normal plane, with relative occupancies of 3 : 1. Therefore, two independent energy bands can be formed in the crystal as a result of the disorder and observed as a doublet.

Another characteristic of the absorption spectra of the TCNE complexes is the appearance of the second and third CT bands. This phenomenon can be observed with complexes of acenaphthene and dibenzofuran. These bands may be assigned to the CT transition from the highest, second highest, and third highest occupied orbitals of the donor to the lowest vacant orbital of TCNE.

The molar extinction coefficient, $\varepsilon$, and the halfwidth of the TCNE–HMB complex are 4390[1,9] and 5200[8] $cm^{-1}$ in the $CH_2Cl_2$ solution, and the oscillator strength is calculated to be $f^{solution}=0.09$; the value of $6f^{solution}=0.54$ is comparable to that of $f^{crystal}=0.563$ which is shown in Table 1.

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