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Reflection Spectra of the Crystalline Electron Donor-Acceptor Complexes of TCNQ

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The polarized reflection spectra were measured on the crystals of TCNQ complexes with phenothiazine, anthracene, pyrene, acenaphthene, carbazole, hexamethylbenzene and 1,10-phenanthroline. The crystalline absorption spectra have been obtained by the *K-K* transformation of the reflection spectra. The charge transfer degree and the stabilization energy in the ground state were estimated for each complex by analysing the CT bands in the solid state.

1 EXPERIMENTAL

The observed oscillator strength along the α axis of the crystal can be evaluated by using the following equation:

$$f^{\alpha} = 4.32 \times 10^{-9} \int n_{\alpha}(\sigma)\varepsilon_{\alpha}(\sigma)\, d\sigma$$

where σ is the wavenumber, n_{α} and ε_{α} are the α components of the refractive index and the molar extinction coefficient.

2 THEORETICAL

The analysis of the electronic states of the CT complexes was discussed by Tanaka[1] and is briefly summarized here.

TCNQ complexes form the configuration of ADA type in the crystal. Then, the ground state can be described by a wavefunction:

$$\Psi_0 \simeq \Phi(\mathrm{ADA}) + \sum b_i\{\Phi_i(\mathrm{AD^+A^-}) + \Phi_i(\mathrm{A^-D^+A})\}/\sqrt{2}$$

The charge transfer degree and the stabilization energy in the ground state are given as $\sum b_i^2$ and $\Delta E = \sum b_i^2 E_{\mathrm{CT}}^i$. 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 strength is defined as follows:

$$f_i = 3 \times 1.085 \times 10^{11} E_{\mathrm{CT}}^i b_i^2 |R_{\mathrm{AD}}|^2$$

Accordingly, by comparison between the experimental and theoretical oscillator strengths, we can obtain the magnitude values of b_i^2 and give the information about the electronic states of the CT complexes.

The coefficient b_i can be correlated to the so-called transfer integral $t_{\mathrm{A}k,\mathrm{D}l}$ as follows:

$$\begin{aligned} b_i &= \sqrt{2}\langle\Phi(\mathrm{ADA})|H|\Phi_i(\mathrm{AD^+A^-})\rangle/E_{\mathrm{CT}}^i \\ &\equiv 2t_{\mathrm{A}k,\mathrm{D}l}/E_{\mathrm{CT}}^i \\ t_{\mathrm{A}k,\mathrm{D}l} &\simeq -KS_{\mathrm{A}k,\mathrm{D}l} \quad (K = 15\,\mathrm{eV}) \end{aligned}$$

Therefore, the comparison between the observed and calculated values of b_i^2 makes it possible to assign the character of the CT band.

3 RESULTS AND DISCUSSION

The complex of TCNQ-phenothiazine crystallizes in the form of needles elongated along the a axis and the space group is C2/c.[2] TCNQ and phenothiazine molecules are stacked alternately in infinite columns parallel to the a axis and the mode of overlapping is shown in Figure 1. The reflection spectra are observed for the polarized light parallel and perpendicular to the a axis on the (010) face and the absorption spectra are obtained by the K-K transformation, as is shown in Figure 2.

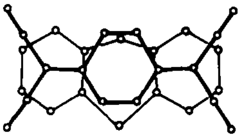

FIGURE 1 The molecular overlap of the TCNQ-phenothiazine complex.

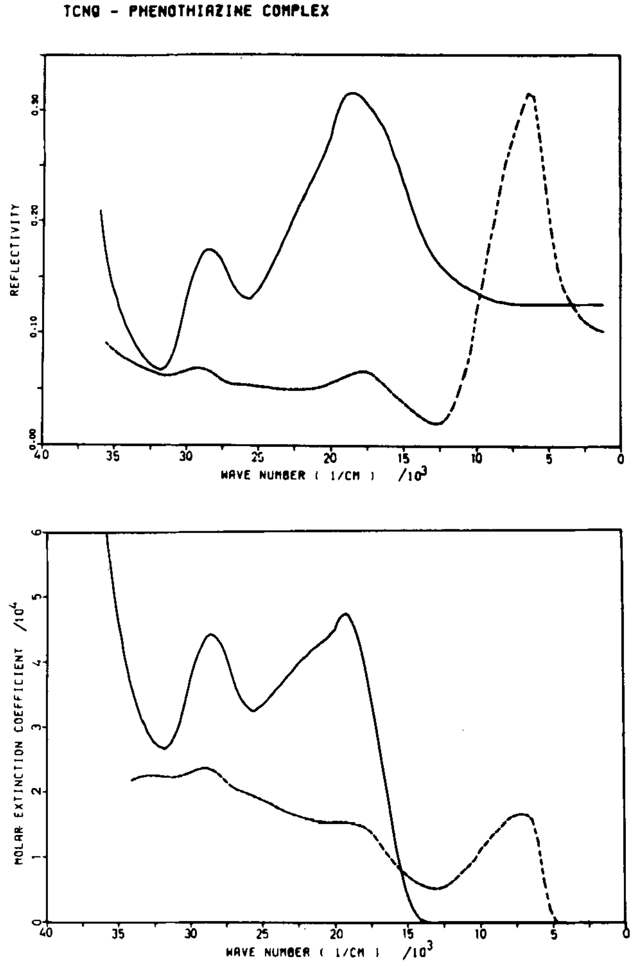

FIGURE 2 The reflection and absorption spectra of the crystal of TCNQ-phenothiazine complex (the dashed line shows the a axis spectrum and the solid line the $a_{\perp}$ axis spectrum).

The 6200 cm^{-1} band is exclusively polarized along the a axis and can be assigned to the CT transition from the highest occupied orbital of the phenothiazine molecule to the lowest unoccupied orbital of the TCNQ molecule. The oscillator strength of this band is 0.549, and the observed charge-transfer degree (19.2%) is in good agreement with the calculated value of 17.0%, as is shown in Table I. The 18500 cm^{-1} and 29000 cm^{-1} bands are strongly polarized along the $a_{\perp}$ axis. The inclination of the long axis of the molecule with respect to the stacking a axis is 75° on the (010) face, and the long axis transitions of the TCNQ and phenothiazine molecules

TABLE I

The CT transition energies (E_{CT} in 10^3 cm^{-1}), the charge transfer degrees (b_i^2 in %) and the stabilization energies (ΔE in K cal) in the ground state of the crystals of TCNQ complexes

						Obsd.			Calcd.		
Donors	E_{CT}	I_p(eV)	C(eV)	P(eV)	I_c(eV)	f_i	R_{AD}(A)	b_i^2	$S_{Ak.Dl}$	b_i^2	ΔE
Phenothiazine	7.1	7.14	2.36	1.10	4.36	0.549	3.52	19.2	0.0121	17.0	3.89
Anthracene	12.8	7.4	2.32	0.69	5.6	0.189	3.50	3.7	0	0.0	1.34
	21.4					0.583	3.50	6.8	0.0190	4.6	4.16
(total)								(10.5)		(4.6)	(5.50)
Pyrene	13.2	7.55	2.28	0.83	5.8	0.212	3.57	3.9	0.0072	1.7	1.46
	19.5					0.091	3.57	1.1	0.0051 0.0039	0.4 0.2	0.61
(total)								(5.0)		(2.3)	(2.07)
Acenaphthene	14.3	7.66	2.36	0.73		0.271	3.37	5.1	0.0123	4.3	2.04
Carbazole	14.6		2.40			0.637	3.34	12.0	0.0246	16.6	5.00
Hexamethylbenzene	16.0	7.85	2.30	0.77		0.765	4.28	8.0	0.0163	6.1	3.66
o-Phenanthroline	20.5		2.34			0.407	3.41	5.2	0.0078	0.8	3.06

should be more intensely observed in the $a_\perp$ axis spectrum. Therefore, the 18500 cm^{-1} band may be regarded as due to the long-axis transition of the TCNQ molecule,[3] and the 29000 cm^{-1} band as due to the long-axis transition of the phenothiazine molecule.

The polarized reflection spectra were also measured on the crystals of TCNQ complexes with anthracene, pyrene, acenaphthene, carbazole, hexamethylbenzene, and 1,10-phenanthroline and the charge-transfer degrees of these TCNQ complexes were calculated. Those of the TCNQ-carbazole, anthracene and hexamethylbenzene complexes are 12.0%, 10.5% and 8.0%, while those values for TCNQ-1,10-phenanthroline, acenaphthene and pyrene are about 5%. The charge-transfer degrees of these TCNQ complexes are given in Table I together with the stabilization energies in the ground state.

The energy of the CT transition, E_{CT}, is given approximately by the equation

$$E_{\mathrm{CT}} = I_p - E_A - C - P$$

where I_p is the ionization potential of the donor; E_A, the electron affinity of the acceptor; C, the coulombic interaction between donor and acceptor molecules, and P, the polarization energy. The Coulomb energy, C, can be estimated by the use of the Nishimoto–Mataga approximation and the electron affinity, E_A, of the TCNQ molecule was determined to be 2.80 eV by Klots, Compton and Raaen.[4] Then, the polarization energy, P, can be deduced as is shown in Table I. It should be noted that the crystal of the TCNQ-phenothiazine complex has a large polarization energy ($P = 1.10$ eV) although those of the other complexes are 0.7–0.8 eV.

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