Polarized Absorption Spectra of Single Crystals of Ion Radical Salts. II. K(TCNQ) and $Cs_2(TCNQ)_3$

Shoji HIROMA, Haruo KURODA, and Hideo AKAMATU

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

(Received June 2, 1970)

Polarized absorption spectra in the 10—40 kK region were observed on single crystals of the ion radical salts of tetracyano-*p*-quinodimethane (TCNQ), potassium·(TCNQ) and cesium$_2$·(TCNQ)$_3$. The crystal spectra are shown to be markedly different from the solution spectra of the monomer and dimer of TCNQ ion. It is shown that the 7.8 kK band of K(TCNQ) and the 11.1 kK band of $Cs_2(TCNQ)_3$ are charge-transfer bands associated with the transfer of an electron from a $TCNQ^-$ ion to the neighboring $TCNQ^-$ ion. The first-order and second-order effects were calculated on the local-excitation bands in order to explain the general feature of the observed spectra.

In a previous paper,[1] we reported the polarized absorption spectra of ionic solids composed of the radical anion of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and the radical cation of a π-electron donor such as *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD). We showed that the crystal spectra are composed of the local-excitation (LE) bands associated with the transition of each component ion, and the charge-transfer (CT) band associated with the transfer of an electron from an anion to the adjacent cation. In these crystals, the cation and anion are stacked face-to-face on each other to form a molecular column developed along one of the crystal axes, and there is a relatively strong charge-transfer interaction between them. There is another kind of TCNQ salt, composed of the TCNQ radical anion and a closed-shell cation, in which the closely packed molecular column is formed by the stacking of the TCNQ anion, not by the alternate stacking of the anion and cation. In this case, the charge-transfer interaction is expected to occur primarily between the neighboring TCNQ anions, which should have bearing on the electrical and magnetical properties of the TCNQ salts.

Recently, the absorption spectra of the crystalline powder obtained by use of the diffuse reflection method have been reported by Iida[2] on several TCNQ salts of this kind. He described some characteristic features distinguishing the spectra of the TCNQ salts of high electrical conductivity from those of the TCNQ salts of low conductivity, and pointed out that the latter resembles in several respects the absorption spectrum of the TCNQ ion dimer. However, care should be taken in comparing the crystal spectra with the spectrum of the ion dimer, since, in the crystal, the interaction by the TCNQ ions other than the nearest-neighbor ones might influence the absorption spectrum.

In the present study, we have observed the polarized absorption spectra of single crystals of two TCNQ salts, K(TCNQ) and $Cs_2(TCNQ)_3$, and carried out some theoretical considerations on the exciton states in these salts.

Experimental

We measured the polarized absorption spectra of the 9—40 kK region at room temperature by using single crystals of microscopic size with an apparatus modified from a commercial microspectrophotometer, Olympus MSP-A-IV. The details of the appratus have been described elsewhere.[3]

The TCNQ salts were prepared according to the procedures reported by Melby *et al.*[4] We recrystallized the powders of the salts to obtain very small single crystals suitable for the measurement of spectrum. The recrystallized powder occacionally contains a small amount of the crystal of free TCNQ, but is easily distinguishable from salt crystals by the crystal habits and optical properties.

We observed also the absorption spectrum of crystalline powder by means of the liquid-paraffin-mull method. The spectra thus obtained were used only for the purpose of examining the location of an absorption maximum in the low energy part outside the applicable region of our microspectrophotometer.

Experimental Results

(1) Spectrum of K(TCNQ). A preliminary analysis of crystal structure has been done by Anderson

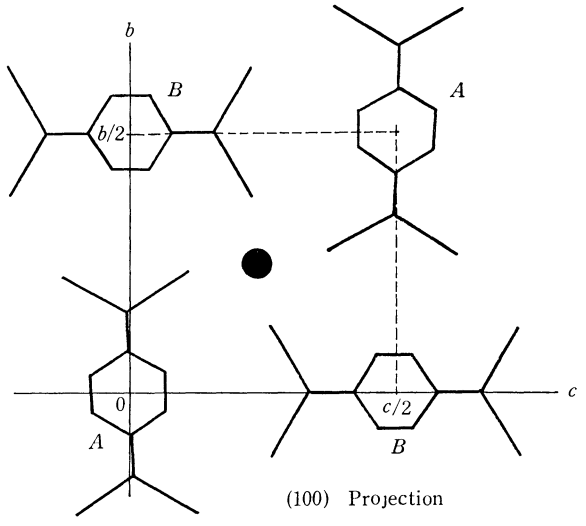

Fig. 1. Model of the crystal structure of K(TCNQ), after Anderson *et al*: ● indicates K^+ ion. $TCNQ^-$ are stacked along the *a*-axis. Two different groups of $TCNQ^-$ sites are indicated as *A* and *B*.

1) H. Kuroda, S. Hiroma, and H. Akamatu, This Bulletin, **41**, 2855 (1968).

2) Y. Iida, *ibid.*, **42**, 71, 673 (1969).

3) H. Kuroda, T. Kunii, S. Hiroma, and H. Akamatu, *J. Mol. Spectrosc.*, **22**, 60 (1967).

4) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).

and Fritchie,[5] who reported that the K(TCNQ) crystal is monoclinic of $P2_1/n$ space group, with the lattice constants; $a=7.10$ Å, $b=18.80$ Å, $c=17.88$ Å and $\beta=94°54'$. The unit cell contains eight formula units. Of the eight TCNQ ions, four are mutually transferable by the symmetry operation of $P2_1/n$ space group, and the other four are mutually transferable among themselves. We shall call the former TCNQ sites *A*-site, and the latter *B*-site (see Fig. 1).

We observed the *a*- and *b*-axis polarized spectra from the direction normal to the developed face (001). The spectra are shown in Fig. 2, and the wave number of peak and the polarization ratio are given in Table 1.

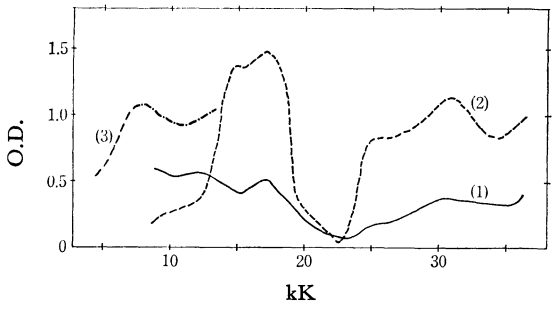

Fig. 2. Crystal absorption spectra of K(TCNQ): (1) *a*-spectrum, (2) *b*-spectrum, (3) spectrum of powder sample.

Table 1. Wave numbers of the absorption peaks and polarization ratios of crystal spectra of K(TCNQ)
(wave numbers in kK)

Band in crystal		I_a/I_b
$\tilde{\nu}_a$	$\tilde{\nu}_b$	
7.8		>2.5
12.5	15.0	0.43
17.3	17.3	0.36
25.0	25.0	0.17
30.8	30.8	0.33

For the sake of comparison, the absorption spectrum of the acetonitrile solution of K(TCNQ) and the spectrum of the dimer of TCNQ anion formed in aqueous solution are shown in Fig. 3. It should be noted that the crystal spectra differ markedly from the spectra of both the monomer and the dimer. The former are extended into a lower-energy region well outside the absorption limit of the latter, while the absorption bands of the crystal in the visible and ultraviolet region are located at appreciably higher energy in comparison with the monomer and dimer. A marked difference is also found in the band shape.

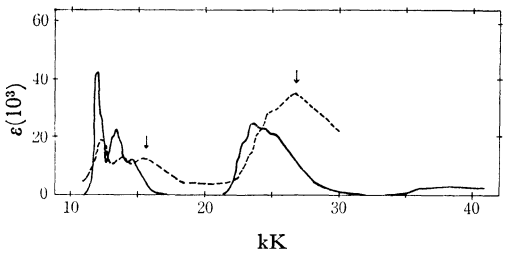

Fig. 3. Solution absorption spectrum of K(TCNQ): ——monomer in acetonitrile, ---- dimer in water (The absorption peaks of the dimer band are indicated by arrows.).

From the spectrum of the powder, we found that the absorption maximum of the low-energy band is located at about 7.8 kK. The polarization ratio, I_a/I_b, is 2.5 at 10 kK, and increases with the decrease of wave number. Thus we can consider that the 7.8 kK band is strongly polarized in the *a*-axis direction, along which $TCNQ^-$ ions are stacked face-to-face on each other. The polarization indicates that the 7.8 kK band is an absorption band associated with the charge-transfer (CT) between $TCNQ^-$ ions. Polarization is quite different in the case of the absorption bands found in the 15—40 kK region. It seems most reasonable to assign them to ones mainly associated with the transition of $TCNQ^-$ ion, which we will call the local-excitation (LE) bands. The bands in the 15—20 kK region appear to be due to the lowest transition of $TCNQ^-$ ion, and those in the 25—35 kK region to the second one.

However, for making a definite interpretation of the observed results, we need to make a theoretical consideration as regards the energy of the CT band, and the crystal shift and factor group splitting of each LE band. This will be discussed in the later part of this paper.

(2) Spectrum of $Cs_2(TCNQ)_3$. In this salt, formally, two electrons are shared among three molecules of TCNQ. The crystal structure has been determined by Fritchie and Arther.[6] According to them, the crystal is monoclinic belonging to $P2_1/c$ space group, with the lattice constants; $a=7.34$ Å, $b=10.40$ Å, $c=21.98$ Å, and $\beta=97.18°$. Two formula units are contained in a unit cell. The projection of the crystal structure from the direction normal to the (001) plane is schematically shown in Fig. 4. It has been concluded from the observed bond lengths that the TCNQ site at the center of symmetry is occupied by a neutral molecule, and is sandwiched by two TCNQ ions

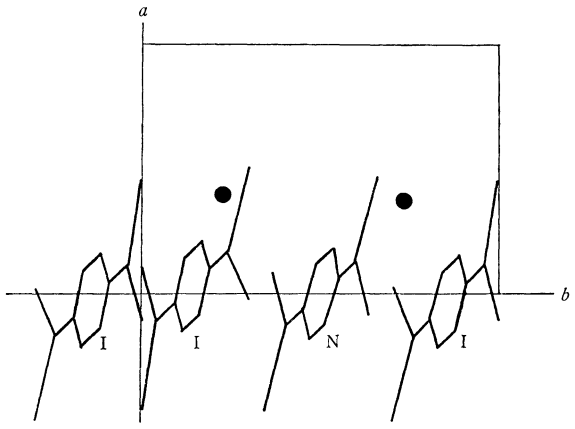

Fig. 4. Stacking of TCNQ ions and molecules in the $Cs_2(TCNQ)_3$ Crystal. (I: ion, N: neutral, ●: Cs)

5) G. R. Anderson and C. J. Fritchie, Jr., 2nd National Meeting of the Society of Applied Spectroscopy, San Diego (1963), Paper 111.

6) C. J. Fritchie, Jr., and P. Arther, Jr., *Acta Crystallogr.*, **21**, 139 (1966).

mutually transferable by the inversion operation.[6]

We observed the *a*-axis and *b*-axis spectra on the (001) plane. The observed spectra are shown in Fig. 5, and the wave numbers and polarization ratios of absorption bands are listed in Table 2.

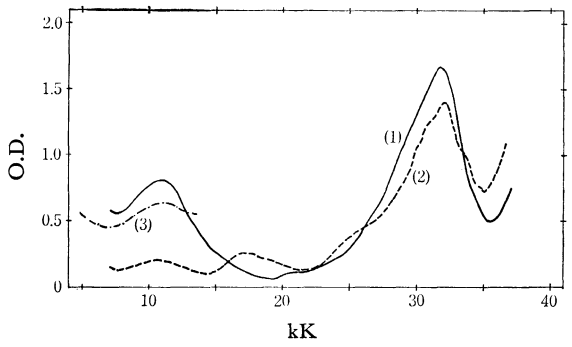

Fig. 5. Crystal absorption spectra of $Cs_2(TCNQ)_3$: (1) *b*-spectrum, (2) *a*-spectrum, (3) spectrum of powder sample.

Table 2. Wave numbers of the absorption peaks and polarization ratios of crystal spectra of $Cs_2(TCNQ)_3$
(wave numbers in kK)

$\bar{\nu}_a$	$\bar{\nu}_b$	I_a/I_b
11.1	11.1	0.25
17.3	~21.5	~2.1
25.0	—	*a*-axis polarized
32.3	31.9	0.84

The 11 kK band is strongly polarized in the *a*-axis direction, and other bands exhibit a different polarization. This suggests that the 11 kK band is the CT band whereas others are the LE bands associated either with the transitions of $TCNQ^-$ ion or with those of TCNQ° molecule. However, the relative intensities of the LE bands are markedly different from the ones expected from the oscillator strengths of transitions of the free component according to the oriented-gas model (Table 4). It should be noted also that the crystal spectra exhibit no strong absorption band at the wavelength corresponding to the second absorption band of $TCNQ^-$ ion and the first band of TCNQ° molecule, both of which are at about 25 kK in the solution spectra. Instead, we found one strong absorption band at about 32 kK in the *a*-axis spectrum as well as in the *b*-axis spectrum.

The large difference between the crystal spectra and the spectra of the components makes it hard to give any simple interpretation of the observed spectra. Thus it is particularly interesting in this case to estimate the crystal shift, factor group splitting, and crystal induced mixing.

The absorption spectrum of the crystalline powder shows that there is no absorption maximum from 5 kK to 10 kK, but the absorption increases with the decrease of wave number in the region below 7 kK, suggesting the presence of another low-energy absorption band. This seems to be associated with the charge transfer between an ion and a molecule of TCNQ.

Discussions

(1) Transitions of the Molecule and Anion of TCNQ. Before discussing the exciton states of salt crystals, we will first consider the transitions of TCNQ molecule and its anion. Although their π-electron states have been theoretically studied by Lowitz[7] by means of the semiempirical self-consistent-field molecular orbital (SCF-MO) method, his results are not satisfactory for the analysis of crystal spectra. Recently, the SCF-MO calculation has been carried out in our laboratory on the molecule and anion of TCNQ using the variable-β,γ modification[8] of Pariser-Parr-Pople method carefully choosing semiempirical parameters.[9] Two different procedures were used: [Method I], all β terms are included and are estimated by using Katagiri-Sandorfy's formula[10] for β; [Method II], only the nearest-neighbor β terms are included, which are estimated by using Nishimoto-Forster's formula.[8] In both cases, the configuration interaction (CI) calculation was carried out by taking into account the lower forty singly-excited configurations. The Longuet-Higgins and Pople method[11] was applied in the case of the anion.

The singlet-singlet transitions of TCNQ predicted by this calculation are shown in Fig. 6, together with the observed results. We find that the theoretical predictions are in satisfactory agreement with the observations. Thus the first and second transitions of TCNQ are assigned to $^1B_{1u}\leftarrow{}^1A_{1g}$ (*long-axis* polarized) and $^1B_{2u}\leftarrow{}^1A_{1g}$ (*short-axis* polarized), respectively. In the case of the anion, the agreement with the observation is found to be better in Method I than in Method II, as seen in Fig. 7.

We can safely assign the first absorption band of the anion observed at 12.0 kK to $^2B_{3u}\leftarrow{}^2B_{2g}$ (*long-axis* polarized) predicted at 9.8 kK by Method I and at 11.2 kK by Method II. According to the calculation, the second absorption band should be considered to be the superposition of two transitions, $^2A_u\leftarrow{}^2B_{2g}$ (*short-axis* polarized) and $^2B_{3u}\leftarrow{}^2B_{2g}$ (*long-axis* polarized). The band shape suggests that this absorption band is composed of a weak component (23.5 kK) and a strong component (25.4 kK). We will assign the former to $^2A_u\leftarrow{}^2B_{2g'}$ and the latter to $^2B_{3u}\leftarrow{}^2B_{2g}$. The next absorption band is probably due to $^2A_u\leftarrow{}^2B_{2g}$ although there is a large discrepancy between the predicted and observed energies. In the later part, we will denote the 12.0, 23.5, 25.4, and 35.7 kK transitions respectively as R, S, U, and S'.

(2) Charge Transfer between TCNQ Anions. In the TCNQ salts studied here, the overlap of the π-orbitals between $TCNQ^-$ ions stacked on each other is large enough to give a fairly strong CT band. The energy

7) D. A. Lowitz, *J. Chem. Phys.*, **46**, 4698 (1967).
8) K. Nishimoto and L. S. Forster, *Theoret. Chim. Acta*, **3**, 407 (1965); **4**, 155 (1966).
9) The details of this calculation will be reported separately.
10) S. Katagiri and C. Sandorfy, *Theoret. Chim. Acta*, **4**, 203 (1966).
11) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc.* (London), **A68**, 591 (1955).

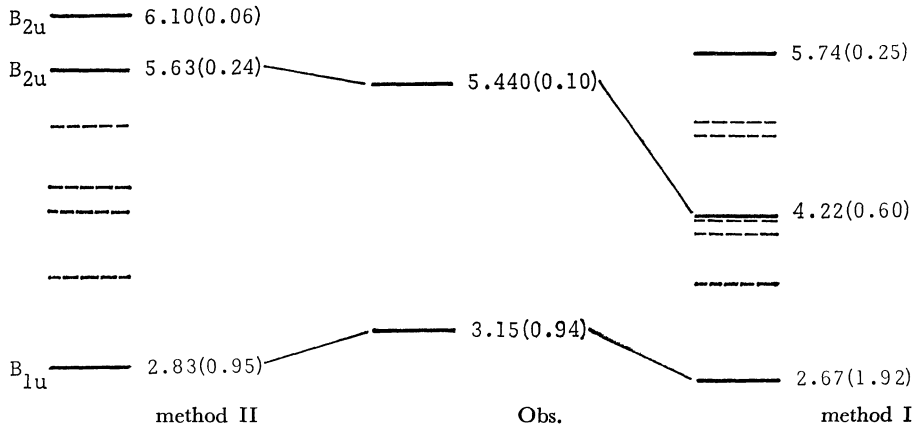

Fig. 6. Singlet excited levels of TCNQ molecule: (—— allowed, ---- forbidden). Excitation energies are given in eV. Oscillator strengths are shown in parentheses.

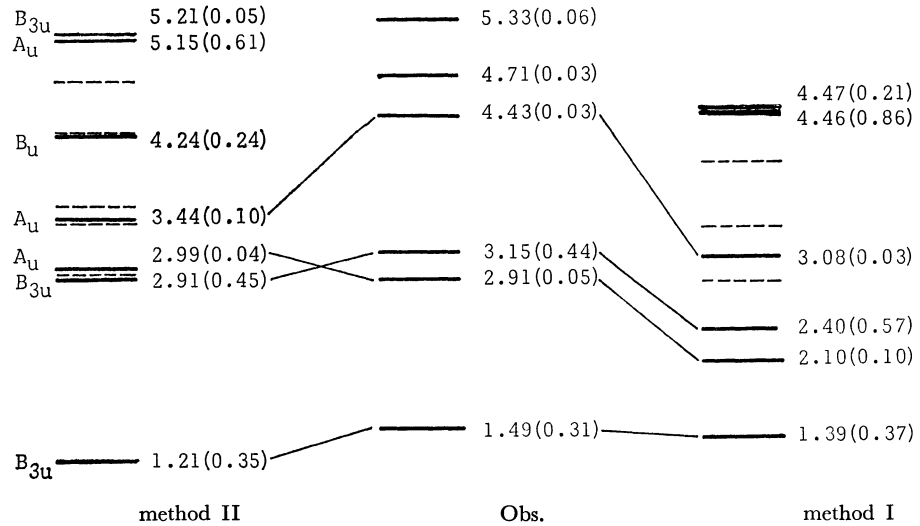

Fig. 7. Excited levels of TCNQ ions. (—— allowed, ---- forbidden). Symmetry of the ground state is B_{2g}. Excitation energies are given in eV. Oscillator strengths are shown in parentheses.

for transferring one electron from a $TCNQ^-$ ion to the neighboring $TCNQ^-$ ion to form a pair consisting of TCNQ° and $TCNQ^{2-}$ can be given by

$$\Delta E_{CT} = I - A - C \qquad (1)$$

where I and A are respectively the ionization potential and electron affinity of the $TCNQ^-$ ion, and C the Coulomb energy term. As can be easily seen, the difference, $I-A$, must be equal to the energy of the repulsion between the two electrons in the highest occupied orbital of the $TCNQ^{2-}$, which can be estimated from the molecular orbital by using the semiempirical values of the one-center and two-center repulsion integrals.[12] We obtained 3.9 eV for $I-A$. By considering the energy cycle of the charge-transfer process, we can show that the term C is approximately equal to the repulsion between the two $TCNQ^-$ ions in question. We estimated it by using the charge distribution obtained from the calculated molecular orbitals of $TCNQ^-$, and obtained the value of 3.0 eV for $Cs_2(TCNQ)_3$. It is almost the same also for K(TCNQ). Thus ΔE_{CT} is predicted to be 0.9 eV. We can therefore, expect the CT band to appear at about 7.2 kK. This is in agreement with the observed location of the CT band of K(TCNQ). In the case of $Cs_2(TCNQ)_3$, a CT band is found at 11 kK, which is considerably large as compared with the predicted values. It should be noted, however, that the actual location of the CT band will naturally be affected by the interactions with other CT states as well as by those with LE states.

In the crystal of $Cs_2(TCNQ)_3$, there can be another type of CT band, namely that associated with the transfer of an electron from $TCNQ^-$ to the adjacent TCNQ°. In this case, the value of $(I-A)$ in Eq. (1) becomes zero, and the term C must be very small. Therefore, this CT band should appear at a lower wave number, possibly in the infrared region. We will attribute the absorption below 5 kK to this CT band. A similar low-energy CT band can be expected to appear generally in the case of TCNQ salts which contain a neutral TCNQ molecule.

(3) Local Excitation Bands. Since the LE bands of the crystal spectra are markedly different from the

12) We have taken here the values of one-center repulsion integral, $\gamma_{\mu\mu}$, as 11.13, 10.09 and 11.52 respectively for carbon in the aromatic ring and carbon and nitrogen in C≡N group. The two-center repulsion integral $\gamma_{\mu\nu}$ was estimated by using the Nishimoto-Mataga method, *viz.*,

$$\gamma_{\mu\nu} = \frac{14.3897}{a_{\mu\nu} + R_{\mu\nu}}, \quad a_{\mu\nu} = 2\frac{14.3897}{\gamma_{\mu\mu} + \gamma_{\nu\nu}}$$

spectra of the free components, we will estimate the crystal shift and splitting of the LE bands by the calculation method within the usual approximation of the exciton theory of molecular crystal.[13,14] We will describe the zero-th order wavefunction of an exciton state, associated with the fth excited state of $TCNQ^-$ ion by the following equation neglecting the part associated with other components.

$$\Phi_r^f = \frac{1}{\sqrt{Nh}} \sum_{m=1}^{N} \sum_{\alpha=1}^{h} B_\alpha^r \phi_{m\alpha}^f \tag{2}$$

herewith

$$\psi_{m\alpha}^f = \phi_{m\alpha}^f \prod_{n\beta \neq m\alpha}{}' \phi_{n\beta}^\circ$$

where $\phi_{m\alpha}^f$ and $\phi_{m\alpha}^\circ$ are the wavefunctions of the fth excited state and the ground state of the $TCNQ^-$ ion at the αth site of the mth unit cell, respectively and B_α^r is the numerical factor characteristic of the rth representation of the symmetry group of the crystal.

In the first order approximation, the exciton level relative to the ground state is given as

$$\Delta E_r^f = \varepsilon^f + D^f + \sum_{n\beta \neq m\alpha} B_\alpha^r B_\beta^r I_{m\alpha,n\beta}^f \tag{3}$$

where ε^f is the transition energy of the free ion (or molecule), and D^f, $I_{m\alpha,n\beta}^f$ are defined as follows:

$$D^f = \sum_{n\beta \neq m\alpha} \{\langle \phi_{m\alpha}^f \phi_{n\beta}^\circ | V | \phi_{m\alpha}^f \phi_{n\beta}^\circ \rangle - \langle \phi_{m\alpha}^\circ \phi_{n\beta}^\circ | V | \phi_{m\alpha}^\circ \phi_{n\beta}^\circ \rangle\} \tag{4}$$

$$I_{m\alpha,n\beta}^f = \langle \phi_{m\alpha}^f \phi_{n\beta}^\circ | V | \phi_{m\alpha}^\circ \phi_{n\beta}^f \rangle \tag{5}$$

V being the perturbing potential due to the intermolecular interaction. The off-diagonal matrix element of the second-order calculation is given as

$$H_r^{fg} = \Delta^{fg} + \sum_{n\beta \neq m\alpha} B_\alpha^r B_\beta^r \Gamma_{m\alpha,n\beta}^{fg} \tag{6}$$

where

$$\Delta^{fg} = \sum_{n\beta} \langle \phi_{m\alpha}^f \phi_{n\beta}^\circ | V | \phi_{m\alpha}^g \phi_{n\beta}^\circ \rangle \tag{7}$$

$$\Gamma_{m\alpha,n\beta}^{fg} = \frac{1}{2} \left\{ \langle \phi_{m\alpha}^f \phi_{n\beta}^\circ | V | \phi_{m\alpha}^\circ \phi_{n\beta}^g \rangle + \langle \phi_{m\alpha}^g \phi_{n\beta}^\circ | V | \phi_{m\alpha}^\circ \phi_{n\beta}^f \rangle \right\} \tag{8}$$

Although the equations described above are the same as ones usually given in the exciton theory of molecular crystal, we have to take into account several aspects characteristic of the TCNQ salts in carrying out the numerical calculation. First, we should note that it is the electrostatic interaction between ions that gives the largest contribution to D^f, and, second, we are not allowed to use the dipole-dipole approximation for evaluating $I_{m\alpha,n\beta}^f$ and $\Gamma_{m\alpha,n\beta}^{fg}$ when two TCNQ ions or molecules are in direct contact with each other.

We estimated D^f by the following formula taking the point charge approximation.

$$D^f = \sum_\mu \sum_q \sum_\nu (\rho_{p\mu}^f \rho_{q\nu}^\circ - \rho_{p\mu}^\circ \rho_{q\nu}^\circ)(e^2/R_{p\mu,q\nu}) \tag{9}$$

where $\rho_{p\mu}^f$ and $\rho_{p\mu}^\circ$ are the charge density at the μth atom of the pth ion in the fth excited state and the ground state, respectively, and the summation over q is to include also the cations. We used the charge density of an atom in the $TCNQ^-$ ion estimated from the molecular orbitals. In the evaluation of $I_{m\alpha,n\beta}^f$ we used the following equation when the distance between the $m\alpha$ and $n\beta$ sites was within 10 Å, but used the dipole-dipole approximation when the distance was larger than 10 Å.

$$I_{p,q}^f = a_{i,j}^2 \sum_\mu \sum_\nu c_{i\mu} c_{j\mu} c_{i\nu} c_{j\nu} (e^2/R_{p\mu,q\nu}) \tag{10}$$

we have assumed here that the fth excited state is associated with the excitation of an electron from the ith molecular orbital to the jth molecular orbital; $a_{i,j}$ is the numerial factor equal to 1 or $\sqrt{2}$ depending on the type of orbitals concerned, and $c_{i\mu}$ is the coefficient in the ith molecular orbital. Similarly, when the gth excited state is associated with the excitation from the kth orbital to the lth orbital, $\Gamma_{m\alpha,n\beta}^{fg}$ was evaluated by the following equation for a distance up to 10 Å, and by the dipole-dipole approximation for a larger distance.

$$\Gamma_{p,q}^{fg} = a_{ij} a_{kl} \sum_\mu \sum_\nu c_{i\mu} c_{j\mu} c_{k\nu} c_{l\nu} (e^2/R_{p\mu,q\nu}) \tag{11}$$

The Δ^{fg} term is negligible unless $i=k$ or $j=l$. If $i=k$, it can be estimated by

$$\Delta^{fg} = b_{ij,k} \sum_\mu \sum_q \sum_\nu \rho_{p\mu}^{ij} \rho_{q\nu}^\circ (e^2/R_{p\mu,q\nu}) \tag{12}$$

where $b_{ij,k}$ is a numerical factor characteristic of the types of orbitals with respect to the fth and gth excitation, $\rho_{p\mu}^{ij}$ is a quantity defined as $\rho_{p\mu}^{ij} = c_{i\mu} c_{j\mu}$, and the summation over q is to include the cations.

(a) K(TCNQ): When we label the $TCNQ^-$ ions at A-sites as 1, 1′, 2, and 2′ so that 1 and 1′, or 2 and 2′ are in direct contact with each other, and the $TCNQ^-$ ions at B-sites as 3, 3′, 4, and 4′ in a similar way, the zero-th order wavefunctions are described as follows:

$$\Phi_A^\pm = \frac{1}{\sqrt{4N}} \sum_{m=1}^{N} \{(\psi_{m1} - \psi_{m1'}) \pm (\psi_{m2} - \psi_{m2'})\} \tag{13}$$

$$\Phi_B^\pm = \frac{1}{\sqrt{4N}} \sum_{m=1}^{N} \{(\psi_{m3} - \psi_{m3'}) \pm (\psi_{m4} - \psi_{m4'})\} \tag{14}$$

Φ_A^+ and Φ_B^+ belong to A_u representation, and Φ_A^- and Φ_B^- belong to B_u representation of C_{2h} symmetry group. Since the exact atomic coordinates were not reported by Anderson and Fritchie,[5] we carried out numerical calculation using the approximate coordinates we estimated from the data given in their report.

The exciton levels predicted by the second-order calculations are summarized in Table 3. Each transition of $TCNQ^-$ ion gives four exciton levels, two A_u and two B_u states. Each of them is associated mainly with either one of the wavefunctions given by Eqs. (13) and (14). We will denote the levels associated with

13) A. S. Davydov, "Theory of Molecular Excitons," McGraw-Hill, New York (1962).

14) D. P. Craig and S. H. Walmsley, "Physics and Chemistry of the Organic Solid State," Vol. 1, ed. by M. M. Labes, D. Fox, and A. Weissberger, Wiley, New York (1963), p. 585.

15) The same formula can be used for the exciton state associated with the TCNQ molecule in $Cs_2(TCNQ)_3$, if we replace $\phi_{m\alpha}^f$, $\phi_{m\alpha}^\circ$ with the corresponding wavefunction of the molecule.

Φ_A^+, Φ_A^-, Φ_B^+, and Φ_B^- as $A_u(A)$, $B_u(A)$, $A_u(B)$, and $B_u(B)$, respectively. It should be noted that the energies are almost equal between the $A_u(A)$ and $B_u(B)$ states and between the $B_u(A)$ and $A_u(B)$ states. This means that there will be little difference between the *b*-axis and *a*-axis spectra as regards the locations of LE bands. This is in agreement with the observation except for the difference between the $A_u(A)$ and $B_u(B)$ components of the R-band. The observed shifts of the transitions of $TCNQ^-$ ion are also well predicted by the present calculation.

TABLE 3. EXCITON LEVELS OF K(TCNQ) CRYSTAL PREDICTED BY THE SECOND ORDER CALCULATION[a)]
(in kK)

Band	Solution (obs.)	$A_u(\Psi_A)$	$A_u(\Psi_B)$	$B_u(\Psi_A)$	$B_u(\Psi_B)$
R	12.0	14.98	15.59	15.61	15.00
S	23.5	23.88	24.22	24.23	23.87
U	25.4	28.16	29.70	29.70	28.28
S′	35.7	36.01	35.84	35.84	36.04

a) A_u: *b*-axis polarized component.
B_u: *a*-axis polarized component.

A considerable discrepancy is found between prediction and observation in the case of the R-band. In the *b*-axis spectrum, we find peaks at 15.0 and 17.3 kK, which should correspond to the $A_u(A)$ and $B_u(B)$ components of the R-band predicted respectively at 15.0 and 15.6 kK. The 17.3 kK peak can be found also in the *a*-axis spectrum, but a peak does not appear at 15.0 kK. Instead, it is found at 12.5 kK. The wave number difference between this peak and the 17.3 kK one is very much larger than the predicted splitting between the $B_u(B)$ and $B_u(A)$ components of the R-band, the latter value being only 0.6 kK. However, it is difficult to find the origin of this peak other than the $B_u(B)$ component of the R-band. We can not attribute it to the second CT band, because the energy difference between the half-filled molecular orbital and the next filled orbital exceeds 2 eV, so that the second CT band is expected to appear at about 24 kK. Therefore, we will tentatively assign the 12.5 kK band to the $B_u(B)$ component of R-band. This discrepancy between prediction and observation could be associated with the interaction between the CT and LE exciton states.

(b) $C_{S2}(TCNQ)_3$: As already mentioned, the unit cell contains four sites of $TCNQ^-$ ion and two sites of TCNQ° molecule. We will label the former sites 1, 1′, 2, and 2′, and the latter 3 and 4, so that the ions at sites 1 and 1′ are mutually transferable by inversion with respect to site 3. The zero-th order wave functions of the optically allowed states are then described as follows. For the exciton states associated with $TCNQ^-$ ion, we have

$$\Phi_{\mathrm{I}}^{\pm} = \frac{1}{\sqrt{4N}} \sum_{m=1}^{N} \{(\psi_{m1} - \psi_{m1'}) \pm (\psi_{m2} - \psi_{m2'})\} \qquad (15)$$

and, for those associated with TCNQ° molecule,

$$\Phi_{\mathrm{II}}^{\pm} = \frac{1}{\sqrt{2N}} \sum_{m=1}^{N} (\psi_{m3} \pm \psi_{m4}) \qquad (16)$$

We carried out the first-order and second-order calculations taking into account the lower four transitions of $TCNQ^-$ ion, *i. e.* R, S, U, and S′ transitions, and the lowest transition of TCNQ° molecule. We will denote the last one as the *N* transition. The results of the calculations are illustrated in Fig. 8, where the absorption bands predicted for the *a*-axis and *b*-axis spectra are shown as vertical lines with a length proportional to the predicted oscillator strength.

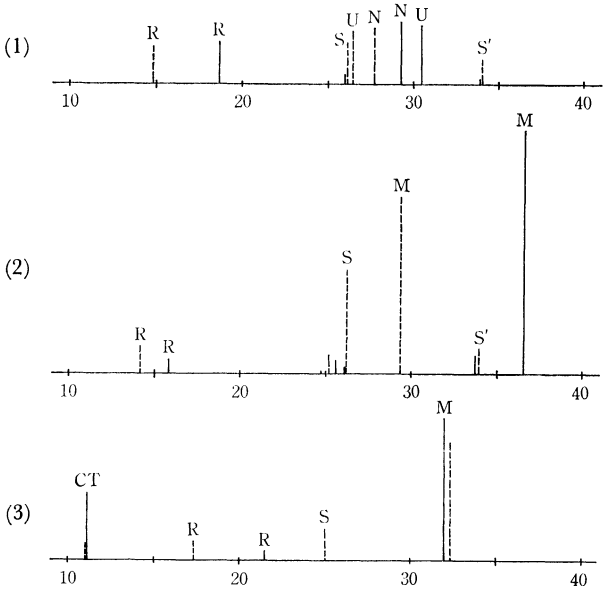

Fig. 8. Results of calculation on the first order and second order effects on the LE bands in $Cs_2(TCNQ)_3$ crystal. (1) Results of the first order calculation, (2) Results of the calculation including the second order effect, (3) Observed spectra. (energy unit in kK)

As shown in Fig. 8, the A_u and B_u components of each intramolecular transition are split appreciably by the first-order effect. The predicted spectra significantly change when the second-order effect is taken into account. Namely, the U- and N-transitions are mixed to give new absorption bands, which are denoted M and M′ in Fig. 8, and the oscillator strength of the R-band is markedly reduced. In Table 4, the oscillator strength of the absorption bands predicted by the second-order calculation are compared with the oriented-gas values. It can be seen that the oscillator strength of the M-band is larger than the sum of the oriented-gas values of the U- and N-bands, the former being about 1.3 times the latter in the *a*-axis spectrum and almost twice in the *b*-axis spectrum. This is mainly caused by the intensity stealing from the R-band.

The observed *a*-axis spectrum seems to be well explained by the present calculation. We will assign the absorption maxima found at 17.3, 25.0, and 32.3 kK to B_u components of R-, S-, and M-bands, respectively. According to the present calculation, the *b*-axis spectrum should exhibit one strong absorption band at 36.5 kK. This is not the case in the observed spectrum. Instead, we find a strong band at 31.9 kK. Within the approximation made in the present study, it seems difficult to find any good explanation for this discrepancy. We observed a very weak shoulder at about 20 kK, which can be assigned to the B_u component of the R-band.

TABLE 4. RESULTS OF CALCULATION ON THE ABSORPTION BANDS OF $Cs_2(TCNQ)_3$ CRYSTAL

Band	Solution spectrum		Crystal spectra								
			Oriented gas value			Calculation (including second order effect)					
	ΔE (kK)	$f^{a)}$	f_a	f_b	f_a/f_b	Band	ΔE_a (kK)	ΔE_b (kK)	f_a	f_b	f_a/f_b
R	12.0	0.63	0.243	0.253	0.96	R	14.23	15.91	0.162	0.076	2.13
S	23.5	0.10	0.250	0.049	5.17	S	26.22	25.65	0.621	0.083	7.48
U	25.4	0.88	0.389	0.354	0.96	M[b)]	25.22	26.26	0.110	0.032	3.44
N	25.4	0.94	0.317	0.368	0.86	M'[b)]	29.32	36.54	0.944	1.441	0.66
S'	35.7	0.06	0.150	0.029	5.17	S'	33.90	33.74	0.146	0.119	1.23

a) Oscillator strengths for $Cs_2(TCNQ)_3$, namely, the value of a band associated with $TCNQ^-$ is taken as twice of the corresponding value of $TCNQ^-$.
b) See text.

Summary and Conclusion

In the present study, we have observed the polarized absorption spectra of single crystals of K(TCNQ) and $Cs_2(TCNQ)_3$, and have shown that the 7.8 kK band of K(TCNQ) and the 11 kK band of $Cs_2(TCNQ)_3$ are the CT bands associated with the transfer of an electron from a $TCNQ^-$ ion to the neighboring $TCNQ^-$ ion. It is also shown that the LE bands observed in the crystal spectra are appreciably shifted from the locations of the corresponding absorption bands in the solution spectra. We have theoretically estimated the first-order and second-order effects on the LE bands of these crystals. In this calculation, we have adopted the method given for the ordinary molecular crystal, composed of neutral molecules, but have taken into account a few aspects associated with the ionic character of these crystals. Although discrepancies between prediction and observation are found in several respects, the general feature of the observed spectra seems to be explainable by the present calculation. From the various conclusions obtained by this study, we wish to point out, first, that the long-range interactions of Coulombic nature provide a large contribution to the crystal shift, and, second, that there is a marked mixing between the transitions of $TCNQ^-$ ion and those of $TCNQ^\circ$ molecule in the case of $Cs_2(TCNQ)_3$. These aspects should always be taken into account when we consider the interpretation of the crystal spectra of TCNQ salts. We have omitted exchange interaction between molecules, mixing between the CT and LE exciton states. This mixing could have a significant effect on the crystal spectra of TCNQ salts. A more sophisticated calculation might be needed to establish a quantitative interpretation of the crystal spectra of TCNQ salts.