Electronic Spectra of $(DBTTF)_3 \cdot SnBr_6$ Complex

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The polarized reflection spectra of $(DBTTF)_3 \cdot SnBr_6$ complex have been measured and the absorption spectra have been determined by the simulation of the observed reflection spectra. The 4000 cm^{-1} band polarized parallel to the stacking axis has been assigned to the charge resonance(CR) band. The theoretical analysis of the electronic structure of $(DBTTF)_3 \cdot SnBr_6$ complex has been made for the explanation of the energy and absorption intensity of the CR band.

Organic charge transfer radical salts of the electron donor TTF (tetrathiafulvalene) and the electron acceptor such as TCNQ (tetracyano-*p*-quinodimethane) display the high electrical conductivties.[1,2] These organic conductors show the special feature of their crystal structures. That is, electrons and holes are delocalized along segregated stacks of the cation donor and anion acceptor free radicals. Therefore, the presence of donor and acceptor stacks causes considerable complexities of solid state properties of organic conductors and there has been a considerable interest in the studies on their highly anisotropic electrical, optical, and magnetic properties. The optical properties of such pseudo-one-dimensional materials were analyzed by Hubbard Hamiltonian as was shown in our earlier paper on TCNQ complexes.[3] On the other hand, after the high conductivity was observed using a four-probe method in single crystals of TTF-TCNQ, many donors and acceptors were synthesized and the preparation of organic metal was intended. Dibenzotetrathiafulvalene (DBTTF) is one of them and the direct oxidation of DBTTF by halogens and metal halides were reported to yield complexes such as $(DBTTF)_2 \cdot I_3$,[4] $(DBTTF)_8 \cdot (SnCl_6)_3$,[5] and $(DBTTF)_3 \cdot SnBr_6$.[5]

In this paper, we report the polarized reflection spectra of $(DBTTF)_3 \cdot SnBr_6$ complex and the theoretical analysis of the new electronic structure found in the $(DBTTF)_3 \cdot SnBr_6$ system.

Experimental

DBTTF was prepared by Nakayama's method[6] and the crystal of $(DBTTF)_3 \cdot SnBr_6$ complex was prepared by the diffusion of DBTTF and $SnBr_4$ molecules in acetonitrile solution. Reflection spectra at the normal incidence were measured over a range of 4000—25000 cm^{-1} with a reflection microspectrophotometer made in our laboratory and all computations were carried out on a FACOM-M382 computer at the NAGOYA university computation center.

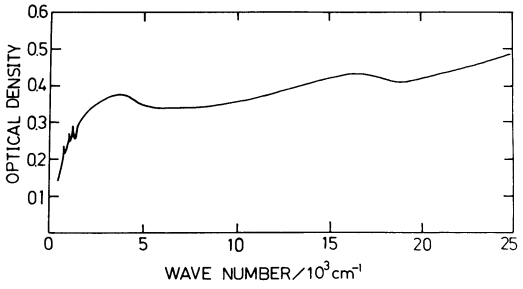

Fig. 1. Absorption spectrum of $DBTTF_3 \cdot SnBr_6$ complex in KBr disk.

Results and Discussion

The absorption spectrum of $(DBTTF)_3 \cdot SnBr_6$ complex in KBr disk is depicted in Fig. 1. The first band is located in the region of 4000 cm^{-1} and the threshold of this band overlaps with a few vibrational bands. The second band is observed at 15000 cm^{-1}.

$(DBTTF)_3 \cdot SnBr_6$ complex forms orthorhombic crystals of space group Pnn2 having two complexes in a unit cell. Projection onto the (100) plane is shown in Fig. 2.[7] The characteristic of the structure of the complex shows the stacking layer of the anion ($SnBr_6^-$) and the molecule DBTTF. Each layer elongates along the direction of the crystalline axis c, and the period along the layers consists of 1 and 3 units of $SnBr_6^-$ and DBTTF, respectively. For the molecule of DBTTF, the center of molecule is located along the direction of two-fold axis and the molecular plane is perpendicular to the stacking axis. Two of DBTTF molecules (molecules 1 and 2) overlaps each other completely, but one of them (molecule 3) has the configuration twisted for the other two molecules.

The polarized reflection spectra shown in Fig. 3 indicate that the 4000 cm^{-1} band observed in the c axis spectrum can be assigned to the band having the transition moment parallel to the intermolecular direction and the 15000 cm^{-1} band is due to the intramolecular transition of DBTTF cation radical.[8] Whole behavior of the observed reflection spectra is similar to that of $(DBTTF)_8 \cdot (SnCl_6)_3$ crystal except for the reflectivity value of 4000 cm^{-1} band ($R \simeq 80\%$).[9]

The reflectivity R can be expressed by the following

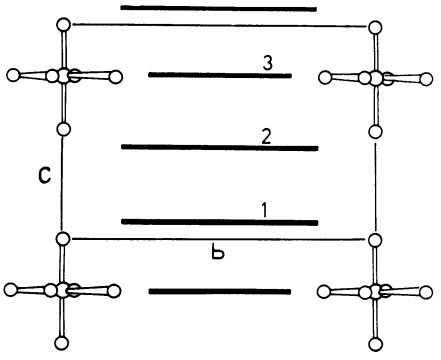

Fig. 2. Projection onto the (100) plane of the crystal of $DBTTF_3 \cdot SnBr_6$ complex.[7]

equations,[10]

$$R = \frac{1 + |\varepsilon| - \sqrt{2(|\varepsilon| + \varepsilon_1)}}{1 + |\varepsilon| + \sqrt{2(|\varepsilon| + \varepsilon_2)}}, \quad (1)$$

and

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega) = \varepsilon_{core} + \sum_j \frac{\Omega_j^2}{\omega_j^2 - \omega^2 - i\,\omega\,\gamma_j}, \quad (2)$$

where $|\varepsilon| = \sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2}$. The parameters Ω_j, ω_j, and γ_j can be determined by the best fit of the calculated reflection values to the observed spectra. The obtained parameters are shown in Table 1 and the best fit curves are plotted in Fig. 3 for comparison with the experimental curves. The absorption coefficient $\alpha(\omega)$ based on these parameters can be obtained by the next equations.[11]

$$\alpha(\omega) = \frac{4\pi}{c\,n(\omega)}\omega\,\varepsilon_2(\omega), \quad (3)$$

and

$$n(\omega)^2 = \frac{1}{2}[\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} + \varepsilon_1(\omega)]. \quad (4)$$

The obtained absorption spectra are described in Fig. 4

Table 1. Dielectric parameters of the Lorentz fits of reflectivity data for $(DBTTF)_3 \cdot SnBr_6$

	//c spectrum	⊥c spectrum	
ε_{core}	2.94	3.10	
Ω_j/cm^{-1}	8700	9000	18500
ω_j/cm^{-1}	3800	15800	28000
γ_j/cm^{-1}	1910	4900	20000

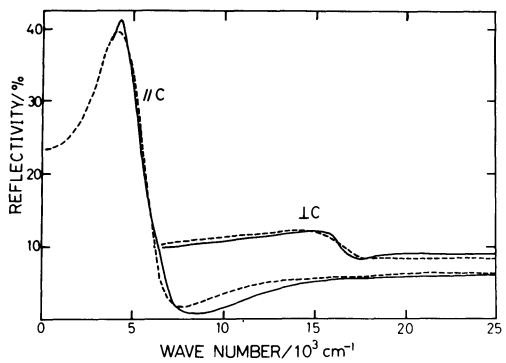

Fig. 3. Observed and calculated reflection spectra of the crystal of $DBTTF_3 \cdot SnBr_6$ complex (——: observed, ----: calculated).

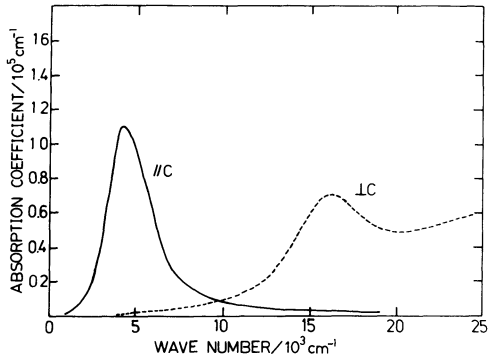

Fig. 4. Calculated absorption spectra of the crystal of $DBTTF_3 \cdot SnBr_6$ complex.

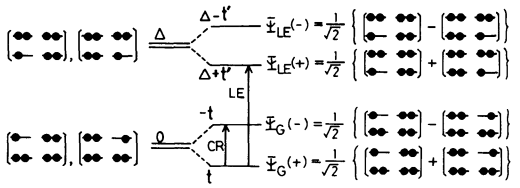

Fig. 5. Energy diagram of $DBTTF_3 \cdot SnBr_6$ complex.

and the oscillator strength f of the 4000 cm^{-1} band is estimated to be 0.3 by using the equation

$$f = \frac{m_e}{2\pi^2 Ne^2}\int \omega \cdot \varepsilon_2(\omega)\,d\omega, \quad (5)$$

where N is the number density ($2.49 \times 10^{21}\,cm^{-3}$) of $DBTTF \cdot SnBr_6$ complex in the crystal and m_e the electron mass. In order to explain the absorption intensity of the 4000 cm^{-1} band, $(DBTTF)_3 \cdot SnBr_6$ complex is proposed to have the electronic structure shown in Fig. 5. That is, the π-electron can transfer between the molecules 1 and 2 in the unit cell, although it can not move between the molecules 1 and 3, or 2 and 3. This model can be supported by the feature of the molecular overlap as is noted in the earlier paragraph. Accordingly, the DBTTF cation radical is either of the molecules 1 and 2.[7] Then, the ground configuration functions of $(DBTTF)_3 \cdot SnBr_6$ complex can be written as follows,

$$\Psi_{G,1} = a_{1,m}|HF>, \quad (6)$$

and

$$\Psi_{G,2} = a_{2,m}|HF>. \quad (7)$$

Here, $|HF>$ means the Hartree-Fock wavefunction of the neutral trimer $(DBTTF)_3$. $a_{1,m}$ and $a_{2,m}$ are the annihilation operators of the highest occupied molecular orbital ($\phi_{1,m}$ and $\phi_{2,m}$) of the molecules 1 and 2, respectively. On the other hand, the locally excited configurations of the cation radical can be expressed in the following equations,

$$\Psi_{LE,1} = a_{1,m-1}|HF>, \quad (8)$$

and

$$\Psi_{LE,2} = a_{2,m-1}|HF>, \quad (9)$$

where $a_{1,m-1}$ and $a_{2,m-1}$ are the annihilation operators of the next highest occupied orbitals ($\phi_{1,m-1}$ and $\phi_{2,m-1}$).

The wave functions and the energies of the ground state $\psi_G(+)$ and the lowest excited state $\psi_G(-)$ are given as the solution of the modified Hubbard Hamiltonian[3] in the next equations,

$$E_G(+) = t_{m,m},\ \Psi_G(+) = \frac{1}{\sqrt{2}}\{\Psi_{G,1} + \Psi_{G,2}\}, \quad (10)$$

$$E_G(-) = -t_{m,m},\ \Psi_G(-) = \frac{1}{\sqrt{2}}\{\Psi_{G,1} - \Psi_{G,2}\}, \quad (11)$$

where $t_{m,m}$ is the transfer integral between $\phi_{1,m}$ and $\phi_{2,m}$. The transition moment between $\psi_G(+)$ and $\psi_G(-)$ is given as follows,

$$<\Psi_G(+)|\mathbf{M}|\Psi_G(-)> = \frac{1}{2}\{<\phi_{1,m}|e\boldsymbol{r}|\phi_{1,m}> - <\phi_{2,m}|e\boldsymbol{r}|\phi_{2,m}>\} = \frac{e}{2}\boldsymbol{R}_{12}. \quad (12)$$

Here, $\boldsymbol{R}_{12}$ is the difference between the position vectors of the center of the molecules 1 and 2 and $\boldsymbol{R}_{12}=3.58$ A.[7] Then, the theoretical oscillator strength f^{theor} can be estimated as follows,

$$f^{theor} = 3 \times 1.085 \times 10^{11} E_{CR} |\boldsymbol{R}_{12}|^2/4 \simeq 0.4, \quad (13)$$

where $E_{CR}=2t_{m,m}$ is the transition energy in cm^{-1} ($\simeq 4000\,cm^{-1}$). The calculated value ($f^{theor}\simeq 0.4$) can be comparable with the observed one ($f\simeq 0.3$). Therefore, the $4000\,cm^{-1}$ band can be called the charge resonance band (CR) corresponding to the transition from the state $\psi_G(+)$ to the state $\psi_G(-)$ as is depicted in Fig. 5. $(DBTTF)_3 \cdot SnBr_6$ complex is the first example of the one-dimensional complex having such electronic structure which is different from the dimer, alternant and island types shown in our earlier paper.[3]

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