Polarized Absorption Spectra of Single Crystals of Tetrathiafulvalenium Salts

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The polarized absorption spectra over the range, 5000—37000 cm^{-1}, were observed on the single crystals of the highly-conductive, mixed-valence tetrathiafulvalenium salts, (TTF)Br$_{0.71}$, (TTF)I$_{0.71}$, and (TTF)(SCN)$_{0.57}$, by using a microspectrophotometer. The spectra of these crystals were very similar to each other. The observed spectra were successfully interpreted in terms of the localized model, considering the charge transfer transitions between TTF species and the local excitations associated with the intramolecular transitions of the molecule and ion of TTF. The spectrum of the (TTF)(ClO$_4$) crystal were also studied to aid the interpretations of the spectra of the mixed-valence TTF salts.

The crystal of the charge-transfer salt of tetrathiafulvalene (TTF) with tetracyano-*p*-quinodimethane (TCNQ) is composed of the segregated stacks of TTF and TCNQ. A variety of evidences[1-8] indicate that an incomplete charge transfer is taking place between TTF and TCNQ in this salt, so that the TTF and TCNQ stacks are of mixed-valence characters. In the case of (TTF)(TCNQ), both the TTF and TCNQ stacks are contributing to the metal-like behaviors displayed by this salt.[9,10] This situation causes considerable complexities in analysing the physical properties of (TTF)-(TCNQ).[7,8,11-13] There are a group of the mixed-valence TTF salts which display high electrical conductivities almost comparable to (TTF)(TCNQ). These are (TTF)Br$_{0.71-0.76}$,[14] (TTF)I$_{0.71}$,[14-16] (TTF)-(SCN)$_{0.54-0.58}$[16-18] and (TTF)(SeCN)$_{0.54-0.58}$.[16,17] These mixed-valence TTF salts are almost isomorphous with each other,[16-22] having nearly the same one-dimensional stack of TTF, and the metal-like electrical conductivities as well as other physical properties of these salts, are primarily determined by the nature of the mixed-valence TTF stack. Thus these salts can be regarded as the suitable model compounds for the purpose to study the electronic behaviors of the mixed-valence, one-dimentional TTF stack.

The electrical and magnetical properties of the TTF salts mentioned above have been studied by several authors.[14-18,23,24] As regards their optical properties, the observations of reflection spectra were reported on (TTF)Br$_{0.76}$,[22,25] (TTF)I$_{0.71}$[26] and (TTF)(SeCN)$_{0.54}$,[17] but no direct observation of the absorption spectra of single crystals have been hitherto reported.

In the present work, we have studied the polarized absorption spectra of small single crystals of (TTF)Br$_{0.71}$, (TTF)I$_{0.71}$ and (TTF)(SCN)$_{0.57}$, over the range of 5000—37000 cm^{-1} (0.6—4.5 eV), by use of a microspectrophotometer. For the sake of comparison, we have also studied the absorption spectrum of (TTF)-(ClO$_4$).

Experimental

TTF was synthesized by the method reported by Melby *et al.*,[27] recrystallized from the cyclohexane solution, and finally purified by repeating sublimation in vacuum. The mixed-valence halides, (TTF)Br$_{0.71}$ and (TTF)I$_{0.71}$, were prepared by the procedures described in our previous paper.[24,28] (TTF)(ClO$_4$) was prepared by the method reported by Hünig *et al.*[29] (TTF)(SCN)$_{0.57}$[18] was kindly provided by Dr. H. Kobayashi of Toho University.

The polarized absorption spectra of single crystals were measured at room temperature by means of a microspectrophotometer, Olympus MS-A-IV. In order to observe absorption spectrum, it is necessary to obtain a crystal of the size and thickness suitable for the measurement of absorption spectrum by the microspectrophotometer. We dissolved each salt in the deairated dry hot acetonitrile, dropped a small amount of the hot solution on a quartz plate, and allowed for the solvent to evaporate leaving small crystals of the salt on the quartz plate. We examined the crystals thus formed on the quartz plate, by a polarization microscope to select out a suitable crystal. The crystal habit was also checked by the observation under the polarization microscope. The sizes of the crystals used in the present study of absorption spectra were less than 1 μm in thickness, 5—20 μm in width and 20—50 μm in length.

Results and Discussion

(TTF)(ClO$_4$), a Simple Cation Radical Salt. (TTF)(ClO$_4$) is expected to be a salt composed of (TTF)$^+$ and (ClO$_4$)$^-$. Fig. 1 shows the infrared spectra of (TTF)(ClO$_4$) and (TTF)(DDQ),[30] measured by the Nujol-mull method. The infrared spectrum of (TTF)-(DDQ) shows all absorption bands characteristic of (DDQ)$^-$, which appear in the infrared spectrum of Li$^+$(DDQ)$^-$,[31] and exhibits no band attributable to DDQ molecule. Thus, (TTF)(DDQ) can be concluded to be a salt composed of (TTF)$^+$ and (DDQ)$^-$. We can attribute all of the residual bands in the infrared spectrum of (TTF)(DDQ) to those arising from (TTF)$^+$. When the infrared spectrum of (TTF)(ClO$_4$) is compared with that of (TTF)(DDQ), we can see that all bands in the former spectrum correspond to the ones which have been attributed to (TTF)$^+$ in the latter case, there being no band attributable to TTF molecule. This fact proves that (TTF)(ClO$_4$) is indeed the salt composed of (TTF)$^+$ and (ClO$_4$)$^-$.

From the Weissenberg photographs, it was found that the crystal of (TTF)(ClO$_4$) is orthorhombic, with the space group Pbca(D_{2h}^{15}), the approximate lattice constants being $a=16.7$, $b=20.6$, and $c=12.8$ Å. It crystallizes from the acetonitrile solution as thin crystals elongated along the a-axis with the developed face (001). We measured the polarized absorption spectra

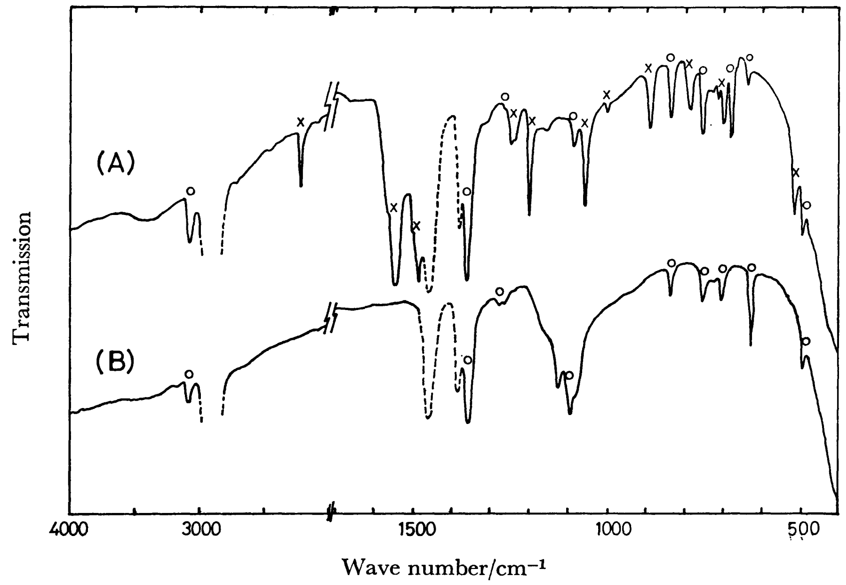

Fig. 1. Infrared spectra of TTF–DDQ(A) and TTF–ClO$_4$(B). The bands due to (TTF)$^+$ are indicated with a open circle and those due to (DDQ)$^-$ with a cross. The dashed line represent the absorption by Nujol.

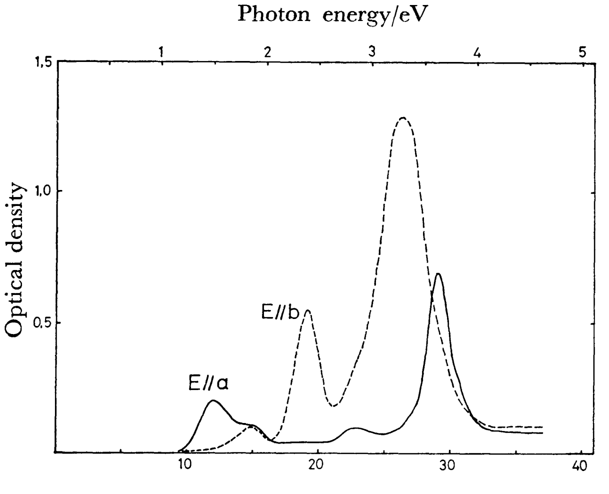

Fig. 2. Polarized absorption spectra observed on the (001) plane of a single crystal of (TTF)(ClO$_4$).

on the (001) plane of (TTF)(ClO$_4$) crystal, with the light polarizations, parallel to a- and b-axes respectively, and obtained the spectra shown in Fig. 2.

In the region below 17×10^3 cm^{-1}, the a-axis spectrum exhibits an absorption maxium at 12.0×10^3 cm^{-1} with a shoulder at about 15×10^3 cm^{-1}, while the b-axis spectrum shows a maxium at 15.0×10^3 cm^{-1}. Seemingly there are two absorption bands; the one is at 12.0×10^3 cm^{-1}, completely polarized in the a-axis direction, and the other is at 15.0×10^3 cm^{-1} with a transition moment in the direction inbetween the a- and b-axes. In these regions, we can not expect any local-excitation (LE) band associated with an intramolecular transition of (TTF)$^+$. Thus the observed absorption bands must be the ones arising from the charge transfer between (TTF)$^+$ ions. The fact that the first CT band (at 12.0×10^3 cm^{-1}) is completely polarized in the a-axis direction, indicates that (TTF)$^+$ ions are stacked on each other along the a-axis. The origin of the second CT band (at 15.0×10^3 cm^{-1}) is not clear. Presumably, there are two different types of the overlap between the neighboring (TTF)$^+$ ions in the crystal, and the first CT band arises from the one with the closest overlap and the second CT band arises from the other type of overlap.

TABLE 1. WAVE NUMBERS AND RELATIVE INTENSITIES (given in the parentheses)$^{a)}$ OF LOCAL EXCITATION BANDS OF (TTF)$^+$(ClO$_4$)$^-$ AND THOSE OF THE SOLUTION SPECTRUM OF THE (TTF)$^+$ ION

Transition	Transition in (TTF)$^+$				(TTF)$^+$(ClO$_4$)$^-$	
	(calcd)$^{b)}$			(exp.)$^{c)}$		
	Assignment	Polarization	$\tilde{\nu}$(10^3 cm^{-1})	$\tilde{\nu}$(10^3 cm^{-1})	$\tilde{\nu}$(10^3 cm^{-1})	Polarization
LE$_1$	$b_{1u}\leftarrow b_{2g}$	x	16.8 (0.48$^{d)}$)	17.3 (0.27$^{e)}$)	19.2 (0.28$^{f)}$)	b-axis
LE$_2$	$b_{3g}\leftarrow b_{1u}$	y	17.8 (0.21)	20.3 (sh.)	22.8 (0.03)	(a-axis)
LE$_3$	$b_{2g}\leftarrow b_{1u}$	x	19.5 (1.00)	23.0 (1.00)	26.4 (1.00)	b-axis
LE$_4$	$b_{1u}\leftarrow b_{3g}$	y	23.7 (0.52)	29.6 (0.32)	29.1 (0.34)	(a-axis)

a) Relative to the intensity of the LE$_3$ band. b) See Ref. 32. The x-axis is chosen for the long axis of molecule. c) See Ref. 29. d) Relative oscillator strengths. e) Relative absorption coefficients. f) Relative peak heights (correspond to absorption coefficients).

In the region above 17×10^3 cm^{-1}, both the a-axis and b-axis spectra show two absorption bands. The wave numbers and relative intensities of these bands are listed in Table 1. The absorption spectrum of the $(TTF)^+$ ion in the solution shows four absorption bands in the corresponding region, the maxima of which are located at 17.3×10^3, 23.0×10^3, and 29.6×10^3 cm^{-1}, respectively.[29] According to the semi-empirical limited-CIS-CF-MO calculation,[32] the lowest four allowed transitions of $(TTF)^+$ are associated respectively with the following electronic excitations between π-orbitals, $b_{1u}\leftarrow b_{2g}$ (x polarized), $b_{3g}\leftarrow b_{1u}$ (y polarized), $b_{2g}\leftarrow b_{1u}$ (x polarized) and $b_{1u}\leftarrow b_{3g}$ (y polarized), where x and y stand for the long and short axes of the ion, respectively. The predicted energies and oscillartor strengths of these transitions well correspond to the four absorption bands observed in the solution spectrum, as shown in Table 1. By comparing the spectra of $(TTF)(ClO_4)$ with the solution spectrum of $(TTF)^+$, we can conclude that the 19.2×10^3 and 26.4×10^3 cm^{-1} bands of the b-axis spectrum are the local-excitation (LE) bands associated with the 17.3×10^3 and 23.0×10^3 cm^{-1} transitions of $(TTF)^+$. Note that the intensity ratio of the above two bands are in good agreement with the intensity ratio of the corresponding bands in the solution spectrum. We will call the 19.2×10^3 and 26.4×10^3 cm^{-1} bands of $(TTF)(ClO_4)$ as LE_1 and LE_3, respectively.

The 29.1×10^3 cm^{-1} band in the a-axis spectrum is likely to be the LE band associated with the 29.6×10^3 cm^{-1} transition of $(TTF)^+$. Since the LE band associated with the 20.3×10^3 cm^{-1} transition of $(TTF)^+$ should appear in the spectrum of $(TTF)(ClO_4)$ in the region of 20—24×10^3 cm^{-1} with the same polarization as the above LE band, we can attribute the weak absorption band at 22.8×10^3 cm^{-1} in the a-axis spectrum, to this LE band. The intensity ratio of the two absorption bands of the a-axis spectrum is consistent with this interpretation. We will call the 20.3×10^3 and 29.1×10^3 cm^{-1} bands of $(TTF)(ClO_4)$ as LE_2 and LE_4, respectively.

The LE_1, LE_2, and LE_3 bands have been shifted to higher energy by about 2×10^3 cm^{-1} as compared with the corresponding absorption bands of the solution spectrum of $(TTF)^+$. This is just the magnitude of the shift that is often found in the crystal where the intermolecular charge-transfer interaction is taking place between the constituent radical ions. According to the above interpretation of the observed spectra, the LE bands associated with the long-axis polarized transitions of $(TTF)^+$ appear only in the b-axis spectrum, showing that they have no components of the transition moments in the a-axis direction. This fact implies that the long axis of $(TTF)^+$ is in the bc plane of the $(TTF)(ClO_4)$ crystal.

Mixed-valence TTF Salts. The TTF sublattices of $(TTF)Br_{0.71}$,[19] $(TTF)I_{0.71}$,[20,21] and $(TTF)(SCN)_{0.57}$[18] are very similar to each other as illustrated in Table 2, where the unit cell of $(TTF)(SCN)_{0.57}$ has been transformed from a tetragonal simple lattice to a C-centered lattice in order to facilitate the comparison with the halides. In all of the three salts, TTF molecules (or ions) are stacked along the c-axis with an eclipsed overlap, making their molecular planes almost perpendicular to the c-axis (see Fig. 3). All three salts crystallize from the hot acetonitrile solutions as crystals elongated along the a-axis with the developed face (100). The absorption spectra were measured on the (100) planes of these crystals with the light polarizations, parallel to the b- and c-axis respectively. The observed spectra are

TABLE 2. TTF SUBLATTICES OF $(TTF)Br_{0.71}$, $(TTF)I_{0.71}$, AND $(TTF)(SCN)_{0.57}$

	a(Å)	b(Å)	c(Å)	β(deg)
$(TTF)Br_{0.71}$[a]	15.62	15.63	3.57	91.2
$(TTF)I_{0.71}$[b]	16.01	16.04	3.55	91.3
$(TTF)(SCN)_{0.57}$[c]	15.77	15.77	3.61	90.0

a) See Ref. 19. b) See Refs. 20 and 21. c) See Ref. 18. The tetragonal unit cell is changed to a C-centered unit cell.

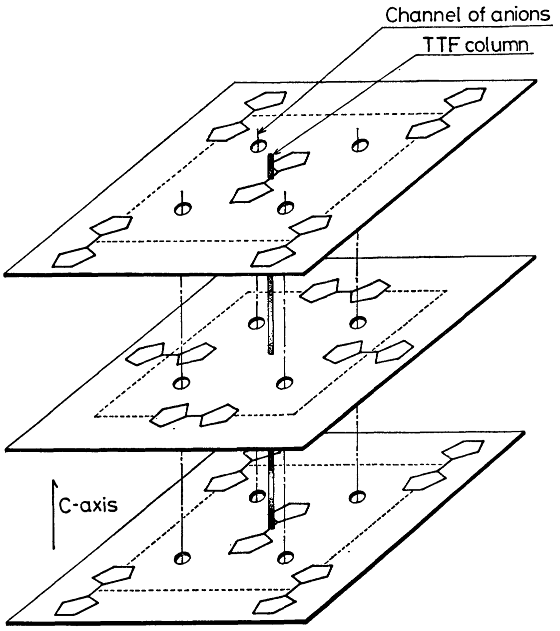

Fig. 3. Schematic picture of the TTF sublattice found for the mixed-valence TTF salts. About eight times enlarged in the c-axis direction.

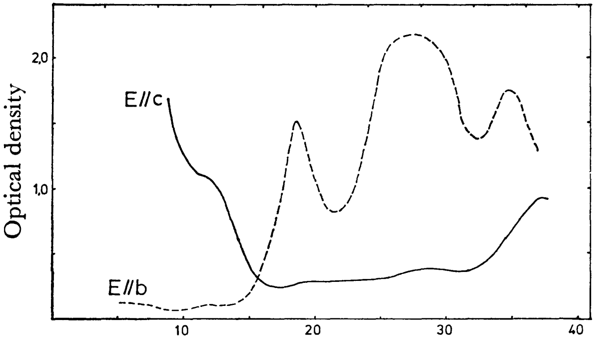

Fig. 4. Polarized absorption spectra observed on the (100) plane of a single crystal of $(TTF)\ Br_{0.71}$.

TABLE 3. WAVE NUMBERS OF ABSORPTION BANDS IN THE SPECTRA OF THE MIXED-VALENCE TTF SALTS

Transition character	c-axis spectra $\tilde{\nu}(10^3\ \mathrm{cm}^{-1})$			b-axis spectra $\tilde{\nu}(10^3\ \mathrm{cm}^{-1})$			Intramolecular transitions[a]	
	Bromide	Iodide	Thiocyanate	Bromide	Iodide	Thiocyanate	TTF^+	TTF^0
CT band								
$(TTF)^+(TTF)^0 \rightarrow (TTF)^0(TTF)^+$	<9.0	<7.5	<8.0					
$(TTF)^+(TTF)^+ \rightarrow (TTF)^0(TTF)^{2+}$	12.5	12.4	11.0					
LE band								
$(TTF)^+$ LE_1				18.5	18.4	17.6	17.3(5030) 20.3(sh)	
LE_3+LE_4				27.5	27.0	27.7	23.0(18600) 29.6(5970)	22.4(263) 28.0(sh)
$(TTF)^0$				34.9	33.0	34.5		32.5(12200)
Unknown	≈37	≈35	≈37					

a) See Ref. 29. Absorption coefficient is given in the parenthesis.

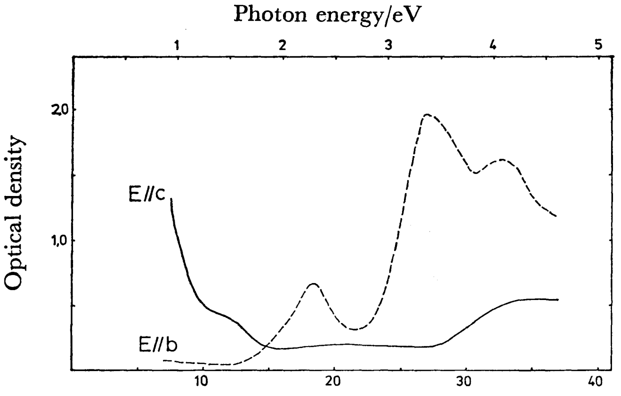

Fig. 5. Polarized absorption spectra observed on the (100) plane of a single crystal of $(TTF)I_{0.71}$.

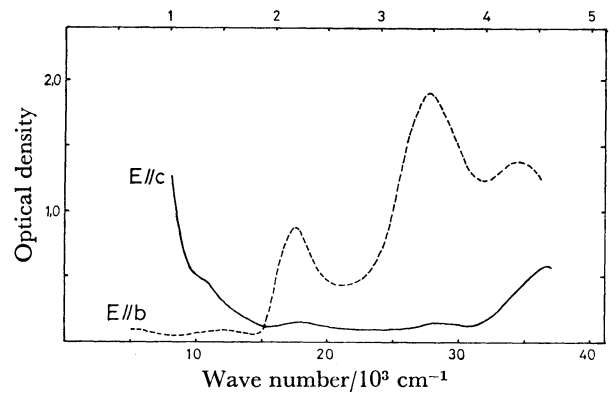

Fig. 6. Polarized absorption spectra observed on the (100) plane of a single crystal of $(TTF)(SCN)_{0.57}$.

shown in Figs. 4, 5, and 6. The wave numbers and relative intensities of the observed bands are listed in Table 3.

One can easily see from the arrangement and orientation of TTF in these salts that an absorption band associated with the intermolecular charge transfer along the TTF stack should appear exclusively in the c-axis spectrum, while the LE bands associated with the intramolecular transitions of $(TTF)^+$ ion and/or TTF molecule, both the long-axis and short-axis polarized ones, should appear only in the b-axis spectrum.

The spectra observed of the three salts are very similar to each other. The c-axis spectrum of each salt exhibit a strong absorption band in the region below $15\times10^3\ \mathrm{cm}^{-1}$, and the b-axis spectrum shows three absorption maxima in the region above $15\times10^3\ \mathrm{cm}^{-1}$. The former must be due to the intermolecular charge transfer and the latter must be due to the local excitations.

Let us first examine the LE bands which appear in the b-axis spectra. All salt exhibit three absorption maxima located at about 18×10^3, 27×10^3, and $34\times10^3\ \mathrm{cm}^{-1}$, respectively. Since the solution spectrum of TTF molecule exhibits no absorption band in the region below $22\times10^3\ \mathrm{cm}^{-1}$, the first maximum at about $18\times10^3\ \mathrm{cm}^{-1}$ cannot be due to the TTF neutral molecule. We can attribute it to the LE band associated with the $17.3\times10^3\ \mathrm{cm}^{-1}$ transition of $(TTF)^+$. The second maximum is very strong, suggesting that it is associated with some strong transitions in the TTF molecule or $(TTF)^+$ ion. Although the TTF molecule has two transitions (at 22.4×10^3 and $28.0\times10^3\ \mathrm{cm}^{-1}$) in the corresponding region, both of them are of very low oscillator strength, and cannot be taken as the origin of the observed strong absorption maximum. The possible origins of the second absorption maximum which is commonly observed in the b-axis spectra of the three mixed-valence salts, would be the 23.0×10^3 or $29.6\times10^3\ \mathrm{cm}^{-1}$ transitions of $(TTF)^+$. It should be noted that the positions of the second absorption maxima observed for the three TTF salts are very close to that of the LE_3 band of $(TTF)(ClO_4)$, but the observed band shapes are considerably broader as compared with the latter. Seemingly, the local excitation bands associated with the 23.0×10^3 and $29.6\times10^3\ \mathrm{cm}^{-1}$ transitions of $(TTF)^+$ are superimposed on each other to give a broad absorption maximum. TTF molecule has a srtong transition at $32.5\times10^3\ \mathrm{cm}^{-1}$.[29,33,34] The third absorption maximum which is located at 33—35×10^3 cm^{-1} in the b-axis spectra, is most likely to be the LE band associated with the above transition of TTF molecule.

As we have described above, all absorption bands observed in the b-axis spectra of the three salts can be interpreted either as a LE band associated with a transition of $(TTF)^+$ or that associated with a transition of $(TTF)^0$. If positive holes are completely delocalized through the TTF stack to give the same fractional charge on every TTF molecule, the TTF stack will exhibits an absorption spectrum composed of the bands which cannot be simply correlated with the transitions of $(TTF)^+$ and $(TTF)^0$. The fact that the observed spectra can be well interpreted in terms of the intramolecular transitions of $(TTF)^+$ and $(TTF)^0$, suggests that, as regards the optical properties, the TTF stack behaves as if it is composed of ions and molecules of TTF in spite of the metal-like high electrical conductivity through the TTF stack.

According to the interpretations of the spectra mentioned above, the intensity ratio of the first and third bands in the b-axis spectrum of each salt must be related to the ratio of $(TTF)^+$ and $(TTF)^0$. Using the molar extinction coefficient of the 17.3×10^3 cm^{-1} band of the solution spectrum of $(TTF)^+$ and that of the 32.5×10^3 cm^{-1} band of the solution spectrum of $(TTF)^0$, we estimated the ionized fraction of TTF from the observed intensity ratio. The ionized fraction of TTF thus obtained is 0.67, 0.58, and 0.62 for $(TTF)Br_{0.71}$, $(TTF)I_{0.71}$, and $(TTF)(SCN)_{0.57}$, respectively. These are very rough values since we have to expect various sources of error in the procedures of obtaining them from the observed crystal spectra. Nevertheless the results are quite reasonable. In particular, it is interesting to see that the ionized fraction is estimated to be appreciably lower in $(TTF)I_{0.71}$ than in $(TTF)Br_{0.71}$. Recently, we showed[5] that the S 2p peaks of the X-ray photoelectron spectra of mixed-valence TTF salts can be well reproduced by superimposing the S 2p peak characteristic of $(TTF)^0$ and that characteristic of $(TTF)^+$, assuming an appropriate intensity ratio. From the above analyses of the observed S 2p peaks we concluded that the ionized fraction of TTF is 0.71 and 0.52 in $(TTF)Br_{0.71}$ and $(TTF)I_{0.71}$, respectively, thus an incomplete charge transfer must be taking place in $(TTF)I_{0.71}$ while a complete charge transfer is taking place in $(TTF)Br_{0.71}$. The results obtained in the present study from the analyses of the intensity ratio of the LE bands are consistent with the above conclusion from the X-ray photoelectron spectra.

As shown in Figs. 4, 5, and 6, the c-axis spectra of these salts exhibit a strong absorption band extending to the infrared region. Because of the low-energy limit of our microspectrophotometer, we were not able to determine the wave number of the low-energy absorption maximum. The maximum was reported to be at 5000 cm^{-1} in the case of $(TTF)Br_{0.76}$.[22,35] Probably, the maximum is located in the same region also in the cases of the TTF salts studied here. This low-energy band can be safely assigned to an intermolecular CT transition.

There is a shoulder in the tail of the strong band mentioned above. This shoulder is located at 12.5×10^3, 12.4×10^3, and 11.0×10^3 cm^3 cm^{-1} in $(TTF)Br_{0.71}$, $(TTF)I_{0.71}$, and $(TTF)(SCN)_{0.57}$, respectively. Seemingly, this is the second CT band. Since the ionized fraction of TTF is 0.5—0.7 in the three salts, we can expect two types of CT transition. The one is associated with the charge transfer from a $(TTF)^+$ ion to another $(TTF)^+$ ion, and the other is associated with that from a TTF molecule to a $(TTF)^+$ ion. The latter CT transition is expected to be considerably lower in energy than the former one. As we have shown in Fig. 2, the CT band of $(TTF)(ClO_4)$ appears at 12.0×10^3 cm^{-1}, which has been attributed to the charge transfer between $(TTF)^+$ ions. The position of the shoulder observed in the spectra of the mixed-valence TTF salts is almost the same as the above CT band of $(TTF)(ClO_4)$. This fact strongly suggests that the observed shoulder is associated with the charge transfer from a $(TTF)^+$ ion to the neighboring $(TTF)^+$ ion within a TTF stack. Then the strong, low-energy band can be attributed the charge transfer from a TTF molecule to a $(TTF)^+$ ion. We will call the latter CT band as the CT(I) and the former as CT(II). The natures of these two CT transitions can be schematically expressed as follows:[6-8]

$$\mathrm{CT(I)};\ (TTF)^+(TTF)^0 \longrightarrow (TTF)^0(TTF)^+$$
$$\mathrm{CT(II)};\ (TTF)^+(TTF)^+ \longrightarrow (TTF)^0(TTF)^{2+}$$

If we assume the localized model with a strong electronic correlation, we could expect that TTF ions in the mixed valence TTF stack will be separated from each other by TTF molecule. Thus, when the ionized fraction is nearly one half, the following type of arrangement of ions and molecules will be dominant in the TTF stack.

$$\cdots (TTF)^+(TTF)^0(TTF)^+(TTF)^0 \cdots$$

This means that the probability of finding $(TTF)^+$-$(TTF)^+$ pairs in the TTF stack is very small as compared with the probability of finding $(TTF)^+(TTF)^0$ pairs in the salt where the ionized fraction is 0.5—0.7, so that the intensity of the CT(II) band must be very much lower than that of the CT(I) band in the cases of the mixed-valence salts studied here. This is in agreement with the observations.

In the c-axis spectra of the three mixed-valence salts, there is an absorption band with the maximum at 35—37×10^3 cm^{-1}. This cannot be due to acceptor since neither the halogen ions (or atom), nor the $(SCN)^-$ ion, have any absorption band in the corresponding region.[36] The origin of this band is not clear at present. A possible origin would be a π-σ^* or σ-π^* transition of TTF with the transition dipole perpendicular to the molecular plane.

Summary and Conclusion

The polarized absorption spectra over the range of 5000—37000 cm^{-1} were observed on the small single crystals of the mixed-valence TTF salts, $(TTF)Br_{0.71}$, $(TTF)I_{0.71}$, and $(TTF)(SCN)_{0.57}$, which are known to be quasi-one-dimensional conductors. By comparing the observed spectra with the solution spectra of the molecule and monopositive ion of TTF and with the spectrum of the $(TTF)^+(ClO_4)^-$ crystal, we have concluded that the observed spectra can be satisfactorily interpreted in terms of the model which assumes a strong charge localization. The observed spectra also indicate that the ionized fraction of TTF is appreciably smaller in $(TTF)I_{0.71}$ than in $(TTF)Br_{0.71}$. These features are consistent with the conclusion derived from the analyses of the X-ray photoelectron spectra of the mixed-valence TTF salts.

Thus one may conclude that the charges are strongly localized in the TTF stacks of these mixed-valence TTF salts, so that TTF molecules can be considered as being not in the fractionally-charged state, but either in the singly-charged state or in the neutral state, in spite of the metal-like high electrical conductivities displayed by these salts.

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