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Charge-transfer Absorption of Complex TCNQ Anion Radical Salts: $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{\dot{-}\dot{-}}$ and $(\mathrm{Morpholinium}^+)_2(\mathrm{TCNQ})_3^{\dot{-}\dot{-}}$

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The charge-transfer transition between ion radical molecules is known to take place in solid ion radical salts. The present paper describes some spectroscopic features of the charge-transfer absorptions observed in complex anion radical salts of $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{\dot{-}\dot{-}}$ and $(\mathrm{Morpholinium}^+)_2(\mathrm{TCNQ})_3^{\dot{-}\dot{-}}$. A one-dimensional Hubbard model consisting of equivalent sites with less than half-occupied orbitals was applied to those systems in order to explain the transition energy and the line shape of the charge-transfer absorptions.

In a number of solid ion radical salts, the planar ion-radical molecules are known to form, in themselves, a face-to-face stacking into infinite one-dimensional columns so as to make a large overlap between their half-occupied molecular orbitals.[1–11] In this case, since any individual radical molecule interacts through charge-transfer most strongly with two other neighboring radicals, the electronic spectrum of the solid salt differs distinctly from the monomer spectrum of the radical ion in solution but shows a charge-transfer transition between ion radicals in the low-energy region.[8–11]

It is well known that 7,7,8,8-tetracyanoquinodimethane (TCNQ) forms chemically-stable crystalline anion radical salts with various diamagnetic counter cations.[1–9] We can obtain two kinds of TCNQ anion radical salts depending on their chemical composition.[6–9] One belongs to simple anion radical salts where each TCNQ has one unpaired electron. Another is called complex anion radical salts, which include not only TCNQ anion radicals but also formally neutral TCNQ molecules. In a previous paper,[12] we studied the optical properties of the charge-transfer absorption of simple TCNQ anion radical salts. We applied the one-dimensional Hubbard model to the columns of TCNQ anion radicals by assuming equivalent sites with half-occupied orbitals, and investigated the character of the intermolecular charge-transfer absorption by using a Green's function method. On the other hand, in complex TCNQ anion radical salts, each TCNQ species no longer has one unpaired electron because of the existence of formally neutral TCNQ molecules. In the present paper, by the use of an approach similar to our previous work,[12] we examined the spectroscopic features of charge-transfer transition between TCNQ anion radicals for one-dimensional system of sites with less than half-occupied orbitals. The transition energy and the theoretical line shape of the charge-transfer absorption were derived and were compared with those observed in such complex salts as $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{\dot{-}\dot{-}}$ and $(\mathrm{Morpholinium}^+)_2(\mathrm{TCNQ})_3^{\dot{-}\dot{-}}$.[9]

Results

In order to describe a narrow energy band with strong electron correlation in crystalline ion radical salts, we consider a system of electrons expressed by the Hubbard Hamiltonian;[13–15]

$$\mathscr{H} = \sum_{i,j,\sigma} t_{ij} C_{i\sigma}{}^{+} C_{j\sigma} + I \sum_{i} n_{i\downarrow} n_{i\uparrow}, \tag{1}$$

where $n_{i\sigma} = C_{i\sigma}{}^{+} C_{i\sigma}$, and $C_{i\sigma}{}^{+}$ and $C_{i\sigma}$ are the creation and annihilation operators of an electron with σ-spin at the i-th site, respectively, and where t_{ij} is the transfer matrix element between the i-th and j-th sites, and the intra-site Coulomb repulsive potential, I, appears only when two electrons with up and down spins are on the same site. Hereafter, we confine our system within the framework of the one-particle Green's function given by Hubbard in his first paper (it is often referred to as Hubbard I),[13] and consider one-dimensional stacks of ion radical molecules in the solid state. For the sake of simplicity, we assume a non-alternant linear chain of equivalent sites for which the transfer matrix element is taken only between nearest neighbor sites and is denoted by $T(<0)$, and we only consider the charge-transfer transition between ion radicals. According to the previous paper,[12] the charge-transfer absorption due to the transition of electrons with up spin in such one-dimensional column is given by $\mathrm{Re}\,\sigma_{\mathrm{xx}}(\omega) \propto \mathrm{Re}\,\sigma^{+}(\omega) + \mathrm{Re}\,\sigma^{-}(\omega)$;

$$\mathrm{Re}\,\sigma^{\pm}(\omega) = \frac{e^2}{2} \frac{I^2 n_{\downarrow}(1-n_{\downarrow})}{\omega^2\sqrt{\omega^2 - 4I^2 n_{\downarrow}(1-n_{\downarrow})}} \times\sqrt{4T^2 - \{-(2n_{\downarrow}-1)I \pm \sqrt{\omega^2 - 4I^2 n_{\downarrow}(1-n_{\downarrow})}\}^2}\,\theta_{\pm}(\omega), \tag{2}$$

where ω is the frequency of electromagnetic wave absorbed by electrons with up spin and $n_{\downarrow} = \langle n_{i\downarrow} \rangle$ is the mean number of electrons with down spin per site, and where $\theta_{\pm}(\omega)$ is the term related to Fermi distribution function. When the intra-site Coulomb repulsion energy is much greater than the observed temperature, we can well put $\theta_{\pm}(\omega) = 1$. If we assume paramagnetic state (*i.e.*, $n_{\downarrow} = n_{\uparrow}$) for our system, an expression of the absorption analogous to Eq. 2 is obtained for electrons with down spin. Therefore, we only consider the absorption due to electrons with up spin, as given in Eq. 2.

Let us examine how the optical absorption of $\mathrm{Re}\,\sigma^{+}(\omega)$ and $\mathrm{Re}\,\sigma^{-}(\omega)$ depends on $n_{\downarrow}$. From Eq. 2, if $2|T| \geq (2n_{\downarrow}-1)I$, that is, if $-T/I + 1/2 \geq n_{\downarrow} \geq T/I + 1/2$, both $\mathrm{Re}\,\sigma^{+}(\omega)$ and $\mathrm{Re}\,\sigma^{-}(\omega)$ make contribution to the charge-transfer absorption of $\mathrm{Re}\,\sigma_{\mathrm{xx}}(\omega)$. We can see that both $\mathrm{Re}\,\sigma^{+}(\omega)$ and $\mathrm{Re}\,\sigma^{-}(\omega)$ have a sharp divergent peak at the energy $\omega_0 = 2I\sqrt{n_{\downarrow}(1-n_{\downarrow})}$, where the spectra have a van Hove singularity in the lower energy side. They have no absorption in the energy region below ω_0, but have absorption in the energy region above ω_0. The absorption intensities of $\mathrm{Re}\,\sigma^{+}(\omega)$ and $\mathrm{Re}\,\sigma^{-}(\omega)$ are the greatest at $\omega = \omega_0$, and decrease progressively with increasing ω. For Re $\sigma^+(\omega)$, the maximum frequency at which absorption can occur is at $\omega_-=\sqrt{4T^2-4IT(2n_\downarrow-1)+I^2}$ where the intensity becomes zero, and the spectrum has a shoulder in the energy region between ω_0 and ω_-. On the other band, for Re $\sigma^-(\omega)$, the maximum frequency takes place at $\omega_+=\sqrt{4T^2+4IT(2n_\downarrow-1)+I^2}$ where the intensity drops to zero, and the spectrum has a shoulder in the energy region between ω_0 and ω_+. Since Re $\sigma_{xx}(\omega)$ consists of the superposition of Re $\sigma^+(\omega)$ and Re $\sigma^-(\omega)$, the charge-transfer absorption spectrum of our system does not have a simple line shape, but has a structure due to the different line shapes of Re $\sigma^+(\omega)$ and Re $\sigma^-(\omega)$. In the case of $n_\downarrow=1/2$, however, as we can see from Eq. 2, Re $\sigma^+(\omega)$ coincides with Re $\sigma^-(\omega)$, so that the charge-transfer absorption of Re $\sigma_{xx}(\omega)$ can be described by a simple line shape of 2Re $\sigma^+(\omega)$ or 2Re $\sigma^-(\omega)$.

Next, we consider the case of $2|T|<(2n_\downarrow-1)I$, that is, $n_\downarrow>-T/I+1/2$ or $n_\downarrow<T/I+1/2$. In the case of $n_\downarrow>-T/I+1/2$, the charge-transfer absorption of Re $\sigma_{xx}(\omega)$ comes solely from Re $\sigma^+(\omega)$, and there is no contribution of Re $\sigma^-(\omega)$ to Re $\sigma_{xx}(\omega)$. We can easily see from Eq. 2 that, for Re $\sigma^+(\omega)$, the minimum value of ω takes place at $\omega_+=\sqrt{4T^2+4IT(2n_\downarrow-1)+I^2}$, where Re $\sigma^+(\omega)=0$ and no discontinuity exists. As ω increases slightly, Re $\sigma^+(\omega)$ rises very steeply and takes the greatest value of Re $\sigma^+(\omega)$ at the energy just above ω_+. As ω further increases, Re $\sigma^+(\omega)$ decreases progressively and has a shoulder, falling down to zero at $\omega_-=\sqrt{4T^2-4IT(2n_\downarrow-1)+I^2}$. Then, the charge-transfer absorption of Re $\sigma_{xx}(\omega)$ ranges from ω_+ to ω_- with no discontinuity. On the other hand, in the case of $n_\downarrow<T/I+1/2$, the situation is reversed, and the charge-transfer absorption of Re $\sigma_{xx}(\omega)$ comes solely from Re $\sigma^-(\omega)$. The spectrum ranges from $\omega_-=\sqrt{4T^2-4IT(2n_\downarrow-1)+I^2}$ to $\omega_+=\sqrt{4T^2+4IT(2n_\downarrow-1)+I^2}$ with no discontinuity. Re $\sigma^-(\omega)$ has the greatest value at the frequency just above ω_-, and has a shoulder in the region between ω_- and ω_+. It is interesting to note from Eq. 2 that, except for Fermi distribution term, Re $\sigma^-(\omega)$ for $n_\downarrow$ has properties symmetrical to those of Re $\sigma^+(\omega)$ for $1-n_\downarrow$.

In the previous paper,[12] we have already examined the charge-transfer absorption for the system of $n_\downarrow=1/2$. Therefore, in the present paper, we will discuss, as a case of $n_\downarrow\neq1/2$ system, the optical properties of complex TCNQ anion radical salts with composition ratio of (2: 3) such as $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{\bar{\cdot}\bar{\cdot}}$ or $(\mathrm{Morpholinium}^+)_2(\mathrm{TCNQ})_3^{\bar{\cdot}\bar{\cdot}}$. In these systems, three TCNQ molecules share two unpaired electrons. According to X-ray analysis data reported by Arthur *et al.*,[2,3] the crystal structure of $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{\bar{\cdot}\bar{\cdot}}$ belongs to the monoclinic system with space group $P2_1/c$. The crystal structure reported by them is shown in Fig. 1. The structure consists of one-dimensional columns of TCNQ molecules parallel to the b axis with a plane-to-plane stacking. The caesium cations occupy sites between TCNQ columns in such a manner that each Cs$^+$ ion is surrounded by eight nitrogen atoms at the corners of a distorted cube. In one-dimensional stacking of TCNQ molecules, however, the sites are crystallographically no longer equivalent and TCNQ molecules form a triad; in a unit cell two rather ionic TCNQ anions are at noncentric positions and one rather neutral TCNQ molecule is at centric position.[3] On the other hand, the crystal structure of $(\mathrm{Morpholinium}^+)_2(\mathrm{TCNQ})_3^{\bar{\cdot}\bar{\cdot}}$ was determined by Sundaresan and Wallwork.[5] The arrangements of TCNQ molecules were found to be very similar to those of the caesium salt. In both of these anion radical salts, the charge distribution of unpaired electrons depends on the sites, but our present model for the charge-transfer absorption given in Re $\sigma_{xx}(\omega)$ and Eq. 2 is based on homogeneous charge distribution of the electrons along one-dimensional column. This point will be further discussed in the following section. In order to examine the applicability of our model and to explain the character of the charge-transfer absorptions observed in those solid salts, we proceed to consider the system of $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{\bar{\cdot}\bar{\cdot}}$ or $(\mathrm{Morpholinium}^+)_2(\mathrm{TCNQ})_3^{\bar{\cdot}\bar{\cdot}}$ in terms of one-dimensional column consisting of equivalent TCNQ sites where each TCNQ species carries a formal charge of $-2/3$.

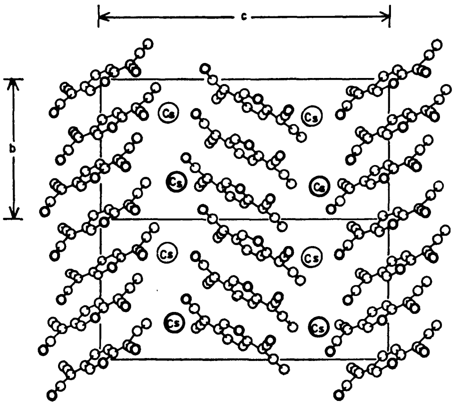

Fig. 1. View of the crystal structure of $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{\bar{\cdot}\bar{\cdot}}$ reported by Chesnut and Arthur and by Fritchie and Arthur. See Refs. 2 and 3.

On the other hand, neutral TCNQ molecule is almost planar, and has sixteen molecular orbitals for sixteen $2p\pi$ electrons.[16] Then, in the ground state of $\mathrm{TCNQ}^{-2/3}$, the molecular orbitals from the lowest to the 8 th are fully occupied, while 2/3 unpaired electron is in the 9 th molecular orbital. The other molecular orbitals are vacant orbitals. In the column of TCNQ molecules, we take only the 9 th molecular orbital with the 2/3 unpaired electron for one site of TCNQ molecule, and assume a model of non-alternant one-dimensional column composed of infinite number of such sites. In this model, each TCNQ molecular site is composed of one identical molecular orbital with equal energy level, and there is 2/3 electron per each site. Then, we have $n_\downarrow=1/3$ if we assume paramagnetic state for our system. Under these situations, we consider the optical absorption (intermolecular charge-transfer absorption) of crystalline $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{\bar{\cdot}\bar{\cdot}}$ and $(\mathrm{Morpholinium}^+)_2(\mathrm{TCNQ})_3^{\bar{\cdot}\bar{\cdot}}$ as expressed by Re $\sigma_{xx}(\omega)$ and Eq. 2. At this time, we have two possibilities for the system of $n_\downarrow=1/3$, depending on the magnitudes of I and T. If $|T|\geq(1/6)I$, the charge-transfer absorption will come from the case of $-T/I+1/2\geq n_\downarrow\geq T/I+1/2$. In this case, as has been mentioned, Re $\sigma_{xx}(\omega)$ has two contributions of Re

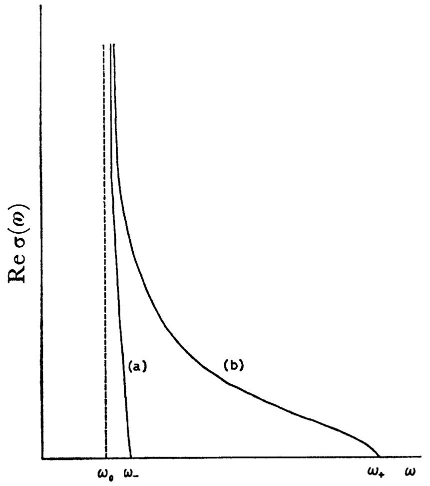

Fig. 2. The intermolecular charge-transfer absorption spectrum Re $\sigma_{xx}(\omega) \propto$ Re $\sigma^{+}(\omega)+$Re $\sigma^{-}(\omega)$, as given by Eq. 2 for the $n_{\downarrow}=1/3$ system with $|T|\geq(1/6)I$, where (a) Re $\sigma^{+}(\omega)$, (b) Re $\sigma^{-}(\omega)$, $\omega_0=(2/3)\sqrt{2}\,I$, and $\omega_{\pm}=\sqrt{4T^2\mp 4IT/3+I^2}$. See text.

$\sigma^{+}(\omega)$ and Re $\sigma^{-}(\omega)$; both of them have a divergent peak at $\omega_0=2\sqrt{2}\,I/3$. The Re $\sigma^{+}(\omega)$ component converges to zero at $\omega_{-}=\sqrt{4T^2+4IT/3+I^2}$, while the Re $\sigma^{-}(\omega)$ component, at $\omega_{+}=\sqrt{4T^2-4IT/3+I^2}$. Since $T<0$ and $\omega_{-}<\omega_{+}$, the band width is determined by $\omega_{+}-\omega_0$. Then, the spectrum of the charge-transfer absorption, Re $\sigma_{xx}(\omega)$, is given by the superposition of Re $\sigma^{+}(\omega)$ and Re $\sigma^{-}(\omega)$; both of them are shown in Fig. 2. On the other hand, if $|T|<(1/6)I$, the charge-transfer absorption corresponds to the case of $n_{\downarrow}<T/I+1/2$. In this case, Re $\sigma_{xx}(\omega)$ comes solely from Re $\sigma^{-}(\omega)$, which ranges from $\omega_{-}=\sqrt{4T^2+4IT/3+I^2}$ to $\omega_{+}=\sqrt{4T^2-4IT/3+I^2}$ with no discontinuity, and has absorption maximum at the energy just above ω_{-}. Then, the spectrum of the charge-transfer absorption, Re $\sigma_{xx}(\omega)$, is schematically given in Fig. 3.

Fig. 3. The intermolecular charge-transfer absorption spectrum Re $\sigma_{xx}(\omega) \propto$ Re $\sigma^{-}(\omega)$, as given by Eq. 2 for the $n_{\downarrow}=1/3$ system with $|T|<(1/6)\,I$, where $\omega_{\pm}=\sqrt{4T^2\mp 4IT/3+I^2}$. See text.

Discussion

Let us compare these theoretical predictions with the experimental electronic spectra of crystalline $(Cs^{+})_2$-$(TCNQ)_3^{\dot{-}\dot{-}}$ and $(Morpholinium^{+})_2(TCNQ)_3^{\dot{-}\dot{-}}$. In a previous paper,[9] we measured those electronic spectra by means of diffuse reflection method. The observed spectra are reproduced in Fig. 4. The Kubelka-Munk function, $f(R)=(1-R)^2/2R$, where R is the reflectance and $f(R)$ is proportional to the absorbance, was plotted *versus* wave number (10^3 cm^{-1} unit).

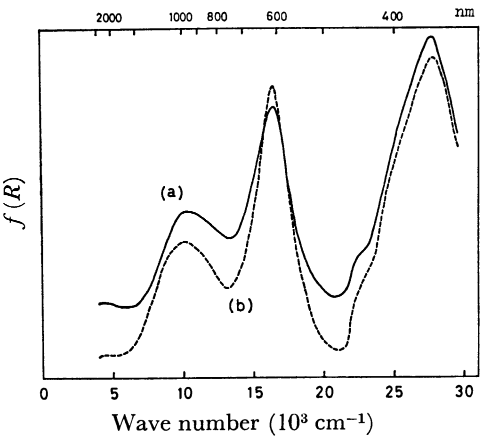

Fig. 4. The experimental results on the diffuse reflection spectra of the solid salts of (a) $(Cs^{+})_2(TCNQ)_3^{\dot{-}\dot{-}}$ and (b) $(Morpholinium^{+})_2(TCNQ)_3^{\dot{-}\dot{-}}$, where the value of Kubelka-Munk function, $f(R)=(1-R)^2/2R$, was plotted *versus* wave number. See Ref. 9.

In the case of $(Cs^{+})_2(TCNQ)_3^{\dot{-}\dot{-}}$, the solid-state spectrum has four absorptions in the energy region from 5000 to 30000 cm^{-1}. The absorptions at 27500 and 16200 cm^{-1} are the shifted bands of the monomer spectrum of the TCNQ anion radical at 22800 and 11900 cm^{-1}, respectively, while the low-energy band at 10100 cm^{-1} characteristic of the solid salt has been assigned to the charge-transfer transition between TCNQ anion radicals in the one-dimensional column.[9] Moreover, the complex salt shows additional weak and broad absorption around the energy region of 4000—6000 cm^{-1}; this band has been assigned to the charge-transfer transition from TCNQ anion radical to the neutral TCNQ.[9] The spectroscopic features of the former three absorptions are very similar to those of simple TCNQ anion radical salts such as K^{+} $TCNQ^{\dot{-}}$,[8,12] while the absorption around 4000—6000 cm^{-1} is characteristic of the complex salt.

The theoretical approach in the preceding section can solely explain the charge-transfer absorption due to the transition between TCNQ anion radicals, but cannot explain the other electronic transitions. Therefore, the absorption at 10100 cm^{-1} of $(Cs^{+})_2(TCNQ)_3^{\dot{-}\dot{-}}$ is of our main interest. If Re $\sigma_{xx}(\omega)$ with $|T|\geq(1/6)I$ and $-T/I+1/2\geq n_{\downarrow}\geq T/I+1/2$ corresponds to this charge-transfer band, the observed peak value of 10100 cm^{-1} should be $\omega_0=2\sqrt{2}\,I/3$ thus giving $I=10700$ cm^{-1}. The absorption band width is related to the $|T|$ value, which should be larger than $(1/6)I$. If we assume $|T|\approx 0.2\,I$ for example, the theoretical band width is $\omega_+-\omega_0\approx 2700\ \mathrm{cm}^{-1}$. This width should only take place in the energy region higher than the absorption peak, and the charge-transfer band shape will have strong asymmetric character with respect to $\omega=\omega_0$. However, as is shown in Fig. 4, the observed charge-transfer absorption at $10100\ \mathrm{cm}^{-1}$ has almost symmetrical line shape with respect to the peak energy axis, although this band overlaps appreciably, in the higher energy region, with the $16200\ \mathrm{cm}^{-1}$ band. Therefore, the case of $|T|\geq(1/6)I$ will not be applicable to the observed charge-transfer absorption.

Next, we examine the case of $|T|<(1/6)I$ and $n_\downarrow<T/I+1/2$. If the $|T|$ value is assumed to be of the order of $0.1\ I$, the theoretical peak value of the absorption is very close to $\omega_-=0.954\ I$, which will correspond to the observed peak value of $10100\ \mathrm{cm}^{-1}$. Therefore, $I=10600\ \mathrm{cm}^{-1}$ and $|T|\approx 1100\ \mathrm{cm}^{-1}$ is estimated for this case. The I and $|T|$ values thus estimated are of quite reasonable magnitudes because of the following explanation. By the use of those I and $|T|$ values, the absorption width, $\omega_+-\omega_-$, is estimated to be $1300\ \mathrm{cm}^{-1}$, and the absorption line shape is then given by Fig. 3 with $\omega_-=10100\ \mathrm{cm}^{-1}$ and $\omega_+=11400\ \mathrm{cm}^{-1}$. As has been discussed in the previous paper,[12)] for many reasons, the actual charge-transfer absorption involves certain width other than the width due to non-zero transfer matrix element, and the actual absorption has a width even in the energy region lower than ω_-. It appears that such a width is of the order of 3500—4000 cm^{-1} and is much larger than the width of $1300\ \mathrm{cm}^{-1}$ due to transfer matrix element. Then, with respect to the axis of peak energy, the charge-transfer absorption will have a width of 3500—4000 cm^{-1} in the lower-energy side and a width of 4800—5300 cm^{-1} in the higher-energy side. The asymmetric character of the line shape of this absorption is so weak that we can well expect almost symmetrical line shape of the charge-transfer absorption with respect to the peak energy axis. This consideration seems to agree well with the observed charge-transfer absorption of $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3{}^{\bar{\cdot}\bar{\cdot}}$ at 10100 cm^{-1}.

The solid-state spectrum (see Fig. 4) of $(\mathrm{Morpholinium}^+)_2(\mathrm{TCNQ})_3{}^{\bar{\cdot}\bar{\cdot}}$ has three strong absorptions at 27600, 16300, and $10000\ \mathrm{cm}^{-1}$ and a broad and weak low-energy absorption around 4000—6000 cm^{-1}.[9)] These spectroscopic features are very similar to those of the caesium salt. From the peak energy and the line shape of the charge-transfer absorption at $10000\ \mathrm{cm}^{-1}$, the magnitudes of I and $|T|$ of the morpholinium salt were found to be almost the same as the corresponding magnitudes of the caesium salt.

Our theoretical treatment for the charge-transfer absorptions of $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3{}^{\bar{\cdot}\bar{\cdot}}$ and $(\mathrm{Morpholinium}^+)_2(\mathrm{TCNQ})_3{}^{\bar{\cdot}\bar{\cdot}}$ assumed a narrow energy band and uniform 2/3-charge distribution in equivalent site systems. This simple model only led to a single charge-transfer transition around $10000\ \mathrm{cm}^{-1}$, which may be interpreted as the transition between $\mathrm{TCNQ}^{-2/3}$ molecules. However, another electronic transition from rather ionic TCNQ to rather neutral TCNQ is actually taking place around 4000—6000 cm^{-1} (see again Fig. 4). This transition thus gives strong evidence for the existence of both rather ionic and neutral TCNQ molecular species in those crystalline complex salts. It is to be noted that one cannot explain such kind of transition as long as one uses uniform charge distribution model. One way of taking those inequivalent TCNQ molecular species into consideration was made by Soos and Klein,[17)] who used the modified Hubbard model to include three crystallographic sites per unit cell in one-dimensional column. Their treatment led to three bands of $N/3$ levels, and the two lower-energy bands accomodate the $2N/3$ electrons of the 1/3-filled Hubbard model. The charge-transfer transition between ionic and neutral sites was interpreted as the transition from the occupied band to the unoccupied band. Our problem will then be to find an appropriate theoretical treatment by the Green's function method for one-dimensional system consisting of inequivalent sites and to explain more quantitatively the charge-transfer transitions between ionic and neutral sites as well as those between ionic sites in $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3{}^{\bar{\cdot}\bar{\cdot}}$ and $(\mathrm{Morpholinium}^+)_2(\mathrm{TCNQ})_3{}^{\bar{\cdot}\bar{\cdot}}$.

Some Remarks

Finally, we compare some spectroscopic features of the charge-transfer absorption of $n_\downarrow\neq 1/2$ system (complex ion radical salts) with those of $n_\downarrow=1/2$ system (simple ion radical salts) on the basis of $\mathrm{Re}\ \sigma_{xx}(\omega)$ and Eq. 2. As for the peak energy, the $n_\downarrow=1/2$ system, where each site has one unpaired electron with paramagnetic state, has a divergent peak at $\omega_0=I$.[12)] On the other hand, the $n_\downarrow\neq 1/2$ system with $-T/I+1/2\geq n_\downarrow\geq T/I+1/2$ has a divergent absorption peak at $\omega_0=2I\sqrt{n_\downarrow(1-n_\downarrow)}$, which is definitely less than the ω_0 value of the $n_\downarrow=1/2$ system. The $n_\downarrow>-T/I+1/2$ system has absorption peak at the energy close to $\omega_+=\sqrt{4T^2+4IT(2n_\downarrow-1)+I^2}$, while the $n_\downarrow<T/I+1/2$ system, at the energy close to $\omega_-=\sqrt{4T^2-4IT(2n_\downarrow-1)+I^2}$. For these cases, since $T<0$ and $\omega_\pm<I$, the peak energy is again smaller than the I value. Therefore, the peak energy of the charge-transfer absorption of less than half-occupied or more than half-occupied orbital system is definitely smaller than that of half-occupied orbital system.

Next, we consider the band width, which is related to the magnitudes of $|T|$ and I. Therefore, by using the constant values of $|T|$ and I, we examine how the band width of the charge-transfer absorption depends on $n_\downarrow$. For the $n_\downarrow=1/2$ system, the band width is given by $\sqrt{I^2+4T^2}-I$.[12)] In the system of $n_\downarrow\neq 1/2$, however, the band widths are $|\omega_+-\omega_-|$ for the case of $n_\downarrow>-T/I+1/2$ or $n_\downarrow<T/I+1/2$, $\omega_--\omega_0$ for the case of $-T/I+1/2\geq n_\downarrow>1/2$, and $\omega_+-\omega_0$ for the case of $1/2>n_\downarrow\geq T/I+1/2$. In all cases, the band width for the $n_\downarrow\neq 1/2$ system becomes much broader than the width for the $n_\downarrow=1/2$ system. The reason is as follows. As has been discussed in the previous paper,[12)] in the Hubbard Hamiltonian of Eq. 1, the unperturbed band energy, ε_k, of unpaired electron system splits into two subbands, $E_{k\sigma}{}^L$ and $E_{k\sigma}{}^U$, through correlation effect. Here, $E_{k\sigma}{}^L$

is the energy of an electron with σ-spin which moves about avoiding other electrons with $-\sigma$-spin, while $E_{k\sigma}{}^U$ is the energy of an electron which propagates mainly among sites already occupied with electrons with $-\sigma$-spin. The charge-transfer absorption is then composed of elementary transitions from $E_{k\sigma}{}^L$ to $E_{k\sigma}{}^U$ in the first Brillouin zone by conserving $\boldsymbol{k}$ and σ (*i.e.*, vertical transition). In the $n_\downarrow=1/2$ system, however, since the sites occupied by electrons with $-\sigma$-spin and those unoccupied exist with equal probability, the energy spectra of the two subbands have nearly the same shape. Therefore, the charge-transfer absorption of the $n_\downarrow=1/2$ system becomes narrow and has a steep peak at the energy $\omega=I$. On the other hand, in the case of $n_\downarrow>1/2$, the $E_{k\sigma}{}^L$ subband becomes flat but the $E_{k\sigma}{}^U$ subband has strong $\boldsymbol{k}$ dependence with considerable width, while in the case of $n_\downarrow<1/2$, the situation is reversed. Therefore, in both cases, the charge-transfer absorption spectra become much broader than that of the $n_\downarrow=1/2$ system.

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