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Spectroscopic Similarity of Charge-Transfer Absorptions in Crystalline Complex Ion Radical Salts

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Synopsis. Charge-transfer transition between ion radical molecules takes place in crystalline ion radical salts. Spectroscopic similarity of the charge-transfer absorptions between certain systems of complex ion radical salts has been studied with use of a one-dimensional Hubbard model.

In most 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.[1–5] 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, showing a charge-transfer transition between ion radicals in the low-energy region.[6,7]

Two kinds of solid ion radical salts are known:[1–7] (a) simple ion radical salts in which each ion radical molecule has one unpaired electron, considered to be a one-dimensional system of sites with half-occupied orbital; (b) complex ion radical salts, which include not only ion radicals but also formally neutral parent molecules, belonging to a one-dimensional system of sites with less than half-occupied orbital. In the present paper, it is shown that the charge-transfer absorption of the system with less than half-occupied orbital has spectroscopic properties similar to those for the system with more than half-occupied orbital.

In order to describe a narrow energy band with strong electron correlation in the crystalline ion radical salts, we consider a system of electrons expressed by the Hubbard Hamiltonian,[8)]

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

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, t_{ij} is the transfer matrix element between the i-th and j-th sites, the intra-site Coulomb repulsive potential, I, appearing only when two electrons with up and down spins are at the same site. We consider one-dimensional stack of planar molecules including unpaired electrons in the solid state, and apply the one-particle Green's function given by Hubbard (often referred to as Hubbard I).[8] For the sake of simplicity, we assume non-alternant linear chain of equivalent sites for which the transfer matrix element, denoted by $T<0$, is taken only between the nearest neighbor sites. Discussion is restricted to the spectroscopic feature of the charge-transfer absorption. The charge-transfer absorption due to the transition of electrons with up spin in such one-dimensional column is given by[9]

$$\mathrm{Re}\,\sigma_{xx}(\omega) \propto A_{+}(\omega)\theta_{+}(\omega) + A_{-}(\omega)\theta_{-}(\omega), \tag{2}$$

$$A_{\pm}(\omega) = \frac{e^2}{2}\frac{I^2 n_{\downarrow}(1-n_{\downarrow})}{\omega^2\sqrt{\omega^2-4I^2n_{\downarrow}(1-n_{\downarrow})}}\sqrt{4T^2-\varepsilon_{\pm}(\omega)^2}, \tag{3}$$

$$\varepsilon_{\pm}(\omega) = -I(2n_{\downarrow}-1) \pm \sqrt{\omega^2-4I^2n_{\downarrow}(1-n_{\downarrow})}, \tag{4}$$

where ω is the frequency of electromagnetic wave absorbed by electrons with up spin, $n_{\downarrow}=\langle n_{i\downarrow}\rangle$ being the mean number of electrons with down spin per site in the Hartree-Fock scheme.[8] $\theta_{\pm}(\omega)$ is the term related to Fermi distribution function, $f(E)$, and is given by $f(E_{\pm}{}^{L})-f(E_{\pm}{}^{U})$, where

$$E_{\pm}^{L} = \frac{1}{2}\left\{\varepsilon_{\pm}(\omega)+I-\sqrt{(\varepsilon_{\pm}(\omega)+I)^2-4I(1-n_{\downarrow})\varepsilon_{\pm}(\omega)}\right\}, \tag{5}$$

$$E_{\pm}^{U} = \frac{1}{2}\left\{\varepsilon_{\pm}(\omega)+I+\sqrt{(\varepsilon_{\pm}(\omega)+I)^2-4I(1-n_{\downarrow})\varepsilon_{\pm}(\omega)}\right\}. \tag{6}$$

If we assume a paramagnetic state (*i.e.*, $n_{\downarrow}=n_{\uparrow}$), an expression of the charge-transfer absorption similar to Eqs. 3 and 4 is obtained for electrons with down spin. Hereafter, we take only the absorption due to electrons with up spin. The character of the charge-transfer absorption of a complex ion radical salt with mean number of electrons, $n_{\downarrow}$, then depends strongly on $n_{\downarrow}$, $(0\leq n_{\downarrow}\leq 1)$.

We next consider complex ion radical salts in which the mean number of electrons with down spin is given by $1-n_{\downarrow}$. We also assume a paramagnetic state and magnitudes of I and T common to those of the $n_{\downarrow}$ system, respectively. The charge-transfer absorption of the $(1-n_{\downarrow})$ system is given by

$$\mathrm{Re}\,\sigma'_{xx}(\omega) \propto A_{+}'(\omega)\theta_{+}'(\omega) + A_{-}'(\omega)\theta_{-}'(\omega), \tag{7}$$

where $A_{\pm}'(\omega)$ and $\theta_{\pm}'(\omega)$ are derived from $A_{\pm}(\omega)$ and $\theta_{\pm}(\omega)$ by replacing $n_{\downarrow}$ by $1-n_{\downarrow}$, respectively. However, if we pay attention to the forms of Eqs. 3 and 4, we note that

$$A_{\pm}'(\omega) = \frac{e^2}{2}\frac{I^2 n_{\downarrow}(1-n_{\downarrow})}{\omega^2\sqrt{\omega^2-4I^2n_{\downarrow}(1-n_{\downarrow})}}\sqrt{4T^2-\varepsilon_{\pm}'(\omega)^2}, \tag{8}$$

$$\varepsilon_{\pm}'(\omega) = -\varepsilon_{\mp}(\omega). \tag{9}$$

Thus, we obtain

$$A_{\pm}'(\omega) = A_{\mp}(\omega). \tag{10}$$

The charge-transfer absorption of the $(1-n_{\downarrow})$ system is then given by

$$\mathrm{Re}\,\sigma_{xx}'(\omega) \propto A_{-}(\omega)\theta_{+}'(\omega) + A_{+}(\omega)\theta_{-}'(\omega). \tag{11}$$

As for the term related to the Fermi distribution function, the Fermi energy for the $(1-n_{\downarrow})$ system differs from that for the $n_{\downarrow}$ system. However, if the intra-site Coulomb repulsion energy is much greater than the energy due to the observed temperature, we can put $\theta_{\pm}(\omega) \approx 1$ and $\theta'_{\pm}(\omega) \approx 1$. The magnitudes of I for a number of organic ion radical salts have been reported to be of the order of 1 eV.[9] This is found to be much larger than the room-temperature energy of ≈ 0.026 eV. Under these conditions, the charge-transfer absorption of $\mathrm{Re}\sigma'_{xx}(\omega)$ for the $(1-n_{\downarrow})$ system has spectroscopic properties identical with those of $\mathrm{Re}\sigma_{xx}(\omega)$ for the $n_{\downarrow}$ system, except for a difference between $\theta_{\pm}(\omega)$ and $\theta'_{\mp}(\omega)$. The symmetrical point with respect to the number of electrons with down spin is then at $n_{\downarrow}=1/2$. The system $n_{\downarrow}=1/2$ corresponds to the half-occupied orbital system of simple ion radical salt where each site has one unpaired electron. If we consider a system of complex ion radical salt with $n_{\downarrow}<1/2$, we can expect another kind of complex ion radical salt of $1-n_{\downarrow}>1/2$ with the common I and T values. Thus the spectroscopic features of the charge-transfer absorptions of both less than half-occupied orbital system (the $n_{\downarrow}$ system) and more than half-occupied orbital system (the $1-n_{\downarrow}$ system) are similar.

With respect to negatively charged ion radical salts, 7,7,8,8-tetracyanoquinodimethane (TCNQ) has been known to form a number of complex anion radical salts, as well as simple anion radical salts, with various counter cations.[1-6] Different stoichiometries of the type $(\mathrm{M}^+)_m(\mathrm{TCNQ})_n^{m-}$ are obtainable even for a single cation, M$^+$. For example, morpholinium–TCNQ forms $(m:n) = (1:1)$, $(2:3)$, and $(3:4)$ crystalline anion radical salts,[5,10] while methyltriphenylphosphonium–TCNQ gives $(1:1)$ and $(1:2)$ salts.[1,6] The salts with $(1:1)$ composition correspond to simple anion radical salts of half-occupied orbital system, while those with other compositions are complex anion radical salts. Not only simple TCNQ anion radical salts but also complex ones show strong charge-transfer absorptions due to the transitions between unpaired electrons in the low-energy regions.[6,9] So far, only the complex salts with less than half-occupied orbital system (*i.e.*, $m<n$) are known. No experimental data have been given on the formation and thus the spectroscopic properties of the complex salts with more than half-occupied orbital system (*i.e.*, $m>n$). However, the above theoretical prediction strongly suggests that the spectroscopic features of the charge-transfer absorption of $(\mathrm{M}^+)_m(\mathrm{TCNQ})_n^{m-}$, $(m<n)$, salt are very similar to those of $(\mathrm{M}^+)_{2n-m}(\mathrm{TCNQ})_n^{(2n-m)-}$ salt of more than half-occupied orbital system, as long as the assumptions for deriving Eqs. 2—11 hold for these two compounds.

As for positively charged ion radical salts, few compounds are known to form crystalline complex cation radical salts with diamagnetic counter anions. For example, tetrathiafulvalene (TTF) forms such cation radical salts as $(\mathrm{TTF})_n^{m+}(\mathrm{I}^-)_m$, $(m:n = 0.7:1)$.[11] There should be spectroscopic similarity of the charge-transfer absorptions between complex cation radical salts of less than half-occupied and more than half-occupied orbital systems. The situation would be analogous to that of complex anion radical salts.

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