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Optical and Magnetic Properties of Solid Cation Radical Salts Derived from Some Aromatic Hydrocarbons

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Synopsis. The optical and magnetic properties of solid cation radical salts derived from 9,10-dimethylanthracene and 9,10-dichloroanthracene were explained in terms of one-dimensional Hubbard model composed of equivalent sites of the cation radicals, while those of perylene cation radical salt, in terms of Hubbard model of cation radical dimer.

There have been made extensive investigations concerning the optical and magnetic properties of a number of crystalline ion radical salts.[1-10] On one hand, a deviation from the Curie or Curie-Weiss law has often been found in the temperature dependence of their magnetic susceptibilities, and this deviation has been explained in terms of an existence of spin exchange interaction between ion radicals.[1-3] On the other hand, the electronic spectrum of such solid ion radical salt is found to be different from the monomer spectrum of the corresponding ion radical molecule, but shows a charge-transfer transition between ion radicals in the low-energy region.[3-5]

In most solid ion radical salts, the planar ion radical molecules are known to form, in themselves, a segregated stacking into one-dimensional columns.[5] In this respect, the intermolecular charge-transfer interaction between ion radical molecules is important for the solid-state properties of ion radical salts. In order to understand this situation in more detail, we have applied half-filled Hubbard model to the segregated stack of ion radical molecules and investigated the optical and magnetic properties characteristic of solid ion radical salts.[6-10] Earlier, Sato *et al.* examined the optical absorptions and the magnetic susceptibilities of crystalline cation radical salts of 9,10-dimethylanthracene (DMA), 9,10-dichloroanthracene (DCA) and perylene (P) with antimony pentachloride and perchlorate anions.[3] In the present paper, we shall explain their experimental results in terms of our Hubbard model and understand the electronic states of those crystalline cation radical salts.

A compound of DMA–SbCl$_5$ was obtained as chemically stable cation radical salt. Its solid-state spectrum showed a band peak at 14400 cm^{-1} and a shoulder around 11600 cm^{-1}.[3] The high-energy peak at 14400 cm^{-1} corresponds to the monomer absorption of the 9,10-dimethylanthracene cation radical at 14800 cm^{-1}. The shoulder in the lower-energy region is characteristic of the solid salt and was assigned to the charge-transfer transition between the 9,10-dimethylanthracene cation radicals.[3] On the other hand, the temperature dependence of the paramagnetic susceptibility of DMA–SbCl$_5$ showed a broad maximum at approximately 80 K. The observed magnetic properties could be well explained in terms of antiferromagnetic linear Ising model with exchange coupling constant $J=56$ cm^{-1}.[3] In order to understand those optical and magnetic properties, we consider a system of non-alternant one-dimensional stack of 9,10-dimethylanthracene cation radicals in terms of Hubbard Hamiltonian, which can be written by

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

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 $T_{ij}(<0)$ is the transfer matrix element between the i-th and j-th sites. The Coulomb repulsion potential, I, appears only when two electrons with up and down spins are at the same site. For non-alternant one-dimensional column of the 9,10-dimethylanthracene cation radicals, we consider the half-occupied molecular orbital of the unpaired electron as one site of cation radical molecule, and take into account only the transfer matrix element between the nearest neighbor sites. Hereafter, it is simply denoted by $T(<0)$. The shape of the intermolecular charge-transfer absorption spectrum of this system, $\sigma(\omega)$, is then given by[6]

$$\sigma(\omega) \propto \frac{e^2}{4} \frac{I^2}{\omega^2\sqrt{\omega^2-I^2}} \sqrt{4T^2-\omega^2+I^2}. \tag{2}$$

Here, a δ-function was assumed for each elementary transition in which the spin and the wave vector of an electron are conserved. The charge-transfer absorption of Eq. 2 has a sharp divergent peak at $\omega=I$ and has a band width of $\sqrt{I^2+4T^2}-I$ in the region $\omega>I$. On the other hand, for the magnetic properties of the same system, the Hubbard model leads to, in a region of small $|T|$ limit, a non-alternant one-dimensional antiferromagnet with an exchange interaction $J\approx 2T^2/I$.[8,9] Therefore, if we combine the experimental data on the peak energy of the observed charge-transfer absorption and the exchange interaction parameter, we can uniquely determine the magnitudes of I and T of Eq. 1. For the cation radical salt of DMA–SbCl$_5$, the observed peak energy of the charge-transfer absorption, 11600 cm^{-1}, thus corresponds to $I=11600$ cm^{-1}. As for the antiferromagnetic exchange interaction, rigorously speaking, the J value of Heisenberg model should correspond to $2T^2/I$, but only the J value estimated with linear Ising model is available at the present time. Therefore, we approximately use the estimated $J=56$ cm^{-1} value as $J\approx 2T^2/I$. By putting the $I=11600$ cm^{-1} value into this relation, we obtain $T\approx -570$ cm^{-1} for the one-dimensional system of the DMA–SbCl$_5$ salt.

The optical and magnetic properties of DCA–

$SbCl_5$ salt can be understood in quite a similar way. Sato *et al.* observed a weak charge-transfer absorption at 11200 cm^{-1}.[3] The observed temperature dependence of the magnetic susceptibility was again analyzed in terms of antiferromagnetic linear Ising model with exchange coupling constant $J=56$ cm^{-1}. Then, the application of non-alternant one-dimensional Hubbard model gives $I=11200$ cm^{-1} and $T\approx-560$ cm^{-1} for the cation radical salt of DCA–$SbCl_5$.

Next, we consider the electronic state of P–ClO_4 salt. Its magnetic susceptibility was weakly paramagnetic and the intrinsic paramagnetism decreased with decrease of temperature. The observed magnetic susceptibility *versus* temperature curve fitted closely to the curve calculated from the singlet-triplet model, where the excited triplet state lies 1370 cm^{-1} above the ground singlet state.[3] Therefore, the perylene cation radicals appear to form dimers in the solid state. In contrast to the DMA–$SbCl_5$ and DCA–$SbCl_5$ salts, the electronic spectrum of the solid P–ClO_4 salt showed a strong low-energy absorption at 7700 cm^{-1}, which was attributable to the charge-transfer absorption of the dimer of the perylene cation radicals.[3] We consider the above optical and magnetic properties of the P–ClO_4 salt in terms of the dimer model of Hubbard Hamiltonian, which can be written by

$$\mathscr{H} = \sum_{\sigma} T(C_{1\sigma}{}^{+}C_{2\sigma}+C_{2\sigma}{}^{+}C_{1\sigma}) + I(n_{1\downarrow}n_{1\uparrow}+n_{2\downarrow}n_{2\uparrow}), \tag{3}$$

where the notations are common to those in Eq. 1. The suffixes, 1 and 2, denote two sites of perylene cation radicals in a dimer, and $T(<0)$ is the transfer matrix element between the cation radicals in the dimer. If we again take the half-occupied molecular orbital of the cation radical for each site, there are six bases of the wave functions for the dimer. After solving the eigenvalue problem, we have three singlet states and one triplet state. A detail of the wave functions and the energy levels are described in a previous paper.[8] The energy of the charge-transfer absorption, $h\nu_{\mathrm{CT}}$, and the singlet-triplet energy separation, δ, are given by

$$h\nu_{\mathrm{CT}} = \{(I/2)^2+(2T)^2\}^{1/2} + I/2, \tag{4}$$

$$\delta = \{(I/2)^2+(2T)^2\}^{1/2} - I/2. \tag{5}$$

This dimer model was then applied to the above optical and magnetic properties of the P–ClO_4 salt. By putting the observed values of $h\nu_{\mathrm{CT}}=7700$ cm^{-1} and $\delta=1370$ cm^{-1} into Eqs. 4 and 5, we obtain $I=h\nu_{\mathrm{CT}}-\delta=6330$ cm^{-1} and $T=-1630$ cm^{-1}, respectively.

The transfer matrix elements thus estimated are considered as a measure of the intermolecular interaction between cation radicals in the solid state. In this respect, the intermolecular interaction in the dimer of the perylene cation radicals of the P–ClO_4 salt should be strongest, while the intermolecular interactions between the 9,10-dimethylanthracene cation radicals in the DMA–$SbCl_5$ salt and between the 9,10-dichloroanthracene cation radicals in the DCA–$SbCl_5$ salt will be of the same order but will be much weaker than that of the P–ClO_4 system. Sato *et al.* noted that the intensity of the charge-transfer band observed in solid spectrum was correlated to the magnitude of exchange coupling constant.[3] In fact, solid P–ClO_4 shows the large values both in exchange coupling constant and intensity of the charge-transfer band, while DMA–$SbCl_5$ and DCA–$SbCl_5$ have weak charge-transfer absorptions and small exchange coupling constants. Although their suggestion was qualitative, we can verify quantitatively their idea on the basis of our Hubbard model. According to our theoretical work,[10] in the region of small $|T|$ limit, the intensity of the intermolecular charge-transfer absorption in non-alternant one-dimensional system of ion radicals is given by CT^2/I, where C is a constant including electric charge, unit cell length and number of sites of the system. On the other hand, the absorption intensity in the dimer model is expressed by $C'T^2/I$,[8] where the constant C' is somewhat different from C. Regardless of this minor difference, the intensity of charge-transfer absorption is predominantly governed by the magnitude of T^2/I. If we take into consideration the T and I values estimated above, the charge-transfer absorption intensity of the P–ClO_4 salt will be ten times or more stronger than those of the DMA–$SbCl_5$ and DCA–$SbCl_5$ salts. Moreover, we have found that, since the antiferromagnetic exchange coupling constant is given by $J\approx 2T^2/I$, the charge-transfer absorption intensity is approximately proportional to the magnitude of J.[10] In this respect, Sato's suggestion that the observed charge-transfer absorption intensity in solid spectrum may be greatly dependent on the magnitude of J receives strong evidence from our Hubbard model.

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