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Bull. Chem. Soc. Jpn., ***56***, *921—922 (1983)*

Absorption Intensity of Charge-transfer Transition between Ion Radicals in One-dimensional System of Crystalline Ion Radical Salts

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(Received August 16, 1982)

Synopsis. The charge-transfer interaction between ion radicals in crystalline ion radical salts was examined with one-dimensional Hubbard model. The intensity of charge-transfer absorption in crystal electronic spectra was estimated with both simple and complex ion radical salts. This approach was then applied to simple cation radical salt of Phenothiazine$^{+}\cdot$Br^{-} and complex cation radical salt of (Phenothiazine)$_2^{+}\cdot$Br^{-}.

Much attention has been paid to the charge-transfer interaction in one-dimensional system of crystalline ion radical salts.[1-5] In simple ion radical salts where each ion radical carries one unpaired electron, the planar ion radical molecules are known to form, in themselves, a plane-to-plane stacking into one-dimensional column so as to make a large overlap between their half-occupied molecular orbitals. The electronic spectrum of crystalline simple salt differs distinctly from the monomer spectrum of the radical ion, but shows a charge-transfer transition between ion radicals in the low-energy region.[1-4] On the other hand, in crystalline complex ion radical salts, ion-radical and its parent neutral molecules are known to stack together to form regular one-dimensional column, where each molecular site is occupied by less-than-one unpaired electron. The electronic spectrum of complex salt is somewhat different from that of simple salt. Usually, the spectrum of complex salt shows two kinds of charge-transfer absorptions.[1,5] One arises from the electronic transition between ion radical and its parent neutral molecule, and the other, from the electronic transition between ion radicals. Although the latter transition is similar to the charge-transfer transition in simple salt, there may be a marked difference in the absorption intensity. In the present paper, we shall derive the absorption intensity of the charge-transfer transition between ion radicals in simple and complex ion radical salts and apply it to certain ion radical salts.

First, we consider the charge-transfer absorption in simple ion radical salts. In previous papers,[3] we applied the one-dimensional half-occupied Hubbard model to the segregated column of ion radicals. This model is a simplification of the real crystal and is expressed by two parameters I and T. $T(<0)$ is the transfer matrix element which describes hopping of an unpaired electron between adjacent molecular ion radical sites, while $I(>0)$ is the on-site Coulomb repulsion between two electrons with up and down spins on the same molecule. This model can well explain the reason why the absorption due to the charge-transfer transition between ion radicals is observable in simple ion radical salts. The previous paper described that the total intensity of the charge-transfer absorption per unit volume, A, was given by[3]

$$A = \frac{n\pi e^2}{4a}I(at)^2\left(1-\frac{3}{8}t^2+\cdots\right), \qquad (1)$$

where n is the number of one-dimensional columns per unit area perpendicular to the column axis, e is the electric charge, a is the lattice separation in one-dimensional column and $t=2T/I$. Hereafter, we only consider the case of $|t|\to 0$ limit and neglect the terms higher than t^4 in Eq. 1. Then, we obtain

$$A = \frac{n\pi e^2}{4a}I(at)^2 = \frac{n\pi e^2a^2}{a}\cdot\frac{T^2}{I}. \qquad (2)$$

Since a is the lattice separation, $(1/a)$ gives the number of sites per unit length in one-dimensional column. Therefore, (n/a) in Eq. 2 gives the number of sites (ion radical molecules) per unit volume in crystalline ion radical salt, being denoted by $N=n/a$. Then, A is expressed by $A=N\pi e^2a^2T^2/I$. Note that N is also equal to the number of unpaired electrons, because each ion radical carries one unpaired electron. The magnitude of A is rewritten by $A=N\pi e^2a^2J/2$, where $J=2T^2/I$ is an antiferromagnetic spin exchange parameter between adjacent unpaired electrons in one-dimensional column.[4]

It has been experimentally known that the charge-transfer interaction between ion radicals gives an antiferromagnetic Heisenberg chain of ion radical salt and that those ion radical salts which possess large J values show strong charge-transfer absorption intensities.[3] These experimental results can be well understood in terms of $A=N\pi e^2a^2J/2$. Here, A is proportional not only to the number of unpaired electrons, N, in the system but also to the magnitude of J. The latter can be explained in the following way. Since the charge-transfer interaction occurs mostly between adjacent ion radicals, the charge-transfer transition can only take place if the unpaired electrons of adjacent ion radicals in the ground state are antiparallel. In this case, the charge-transfer excited state corresponds to occupation of two electrons with up and down spins on the same site of ion radical molecule. If the unpaired electrons of adjacent ion radicals in the ground state are parallel, the charge-transfer transition is forbidden because of Pauli's exclusion principle. Thus, the absorption intensity of charge-transfer transition is closely related to the strength for aligning two unpaired electron spins of adjacent ion radicals antiparallel, and this strength corresponds to the magnitude of J.

On the basis of this discussion, we consider the charge-transfer transition between ion radicals in complex ion radical salts. As was mentioned, we assume a regular one-dimensional column composed of ion radical and its parent neutral molecule. Each molecular site is occupied by less-than-one unpaired electron, the average number of unpaired electron per site being denoted by ρ, $(0 \leq \rho \leq 1)$. Then, we can apply one-dimensional less-than-half occupied Hubbard model to such a column. Here, we again use the parameters of I, T and a, which are common to those used in half-occupied Hubbard model. If we denote N as the total number of molecular sites (ion radicals + parent neutral molecules), the number of unpaired electrons is given by $N\rho$. As for the spin exchange interaction, Shiba and Klein-Seitz have shown that the magnetic susceptibility of a uniform stack of less-than-half occupied molecules $(\rho < 1)$ is related to the magnetic susceptibility of a uniform stack of half-occupied molecules $(\rho = 1)$ in simple ion radical salts.[6,7] If the value of I is much larger than that of $|T|$, the less-than-half occupied one-dimensional Hubbard model becomes equivalent to an antiferromagnetic Heisenberg chain with exchange interaction,

$$J = \frac{2T^2\rho}{I}\left(1 - \frac{\sin 2\pi\rho}{2\pi\rho}\right). \tag{3}$$

As was mentioned, the absorption intensity of charge-transfer transition between ion radicals is proportional not only to the number of unpaired electrons but also to the magnitude of J. If we apply this approach to the absorption intensity, A, of less-than-half occupied system of complex ion radical salts, we have $A \propto N\rho J = (2NT^2\rho^2/I)(1 - \sin 2\pi\rho/(2\pi\rho))$. As our model requires, if $\rho = 1$, A should become identical with $N\pi e^2a^2T^2/I$ in simple ion radical salts. This condition means that A of complex ion radical salts is given by $A = (N\pi e^2a^2T^2\rho^2/I)(1 - \sin 2\pi\rho/(2\pi\rho))$. In this equation, if $\rho \to 0$, that is, if average unpaired electron density approaches zero, the magnitude of A tends to zero, and we can observe no charge-transfer absorption in such a system. The value of A becomes greatest at $\rho = 1$, so that we obtain maximum intensity of the charge-transfer absorption in simple ion radical salt. On the other hand, if $|T| \to 0$, that is, if no charge-transfer interaction acts between adjacent ion radicals, the magnitude of A also tends to zero, and no charge-transfer absorption appears in such a case.

Let us apply this approach to certain crystalline ion radical salts. For example, we take a simple cation radical salt of Phenothiazine$^{+\cdot}$ Br$^-$ and a complex cation radical salt of (Phenothiazine)$_2^{+\cdot}$ Br$^-$. The crystal electronic spectrum of the simple salt was measured by the present author,[2] while that of the complex salt, by Doi and Matsunaga.[5] The simple salt shows a strong low-energy band at 12900 cm^{-1}, which was assigned to the charge-transfer transition between phenothiazine cation radicals.[4] The one-dimensional half-occupied Hubbard model was applied to the system of the simple salt, and the parameter values of I = 12900 cm^{-1} and $T = -2500$ cm^{-1} were estimated. On the other hand, the complex salt shows two charge-transfer absorptions at 5200 cm^{-1} and 12600 cm^{-1}.[5] The former was assigned to the transition from neutral phenothiazine to its cation radical, while the latter, to the transition between the cation radicals. We discuss only the latter absorption. Application of regular one-dimensional less-than-half occupied Hubbard model to the complex salt gave values of I = 12900 cm^{-1}, $T = -2500$ cm^{-1} and $\rho = 1/2$.[4] We denote the intensities of the charge-transfer absorptions per mol for the simple and complex salts as A(simple) and A(complex), respectively. The molecular sites per mol for the simple and complex salts are $N = N_A$ (Avogadro's number) and $N = 2N_A$, respectively. As for the lattice separation, we have no data on the crystal structures, and assume common value of a for both the salts. By putting those parameter values into the equation of A, the ratio of A(complex)/A(simple) was calculated as 1/2. Therefore, the intensity of the charge-transfer absorption of the complex salt at 12600 cm^{-1} appears to be half of that of the simple salt at 12900 cm^{-1}.

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