BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (10), 2791—2793 (1979)

Charge-transfer Absorption Intensity and Magnetic Property of Solid Ion Radical Salts

Yôichi IIDA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received February 9, 1979)

The electronic spectrum of solid ion radical salt is known to be different from the monomer spectrum of the radical ion and to show an intermolecular charge-transfer transition between ion radicals in the low-energy region. The intensity of the charge-transfer absorption was theoretically obtained by applying one-dimensional half-occupied Hubbard model to the segregated stack of ion radicals of solid ion radical salts. The intensity of the charge-transfer absorption was then correlated to the magnetic properties of those solid ion radical salts.

The prominent magnetic, electrical and optical properties of a number of solid ion radical salts have been the subject of many theoretical and experimental investigations over the past fifteen years.[1–15] In such solid ion radical salts, the planar ion radical molecules are known to form, in themselves, a plane-to-plane stacking into infinite one-dimensional columns so as to make a large overlap between their half-occupied molecular orbitals.[5–8] 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. So far, many investigators have observed such charge-transfer absorptions of solid ion radical salts and attempted to explain the electronic state of segregated stack of ion radicals in terms of an isolated cluster model such as a dimer of ion radicals.[3–5] Rigorously speaking, however, the cluster model approximation is not applicable to one-dimensional column composed of infinite stack of ion radical molecules.

In a previous paper,[9] we applied infinite one-dimensional Hubbard model to the columns of ion radical molecules, and investigated the transition energy and the line shape of such charge-transfer absorptions on the basis of Green's function method. In the present paper, we further attempted to explain the intensity of the charge-transfer absorption of solid ion radical salts in terms of the same model. So far, it has been suggested that ion radical salts with strong intensity of the charge-transfer absorption show almost diamagnetic susceptibility and possess strong antiferromagnetic spin exchange interaction between nearest neighbor ion radical molecules, while ion radical salts with weak charge-transfer absorption show almost free paramagnetism obeying Curie law.[2–5,13–15] By using our theoretical approach, we shall give strong theoretical basis to such a close correlation between the intensity of the charge-transfer absorption and the magnetic properties of solid ion radical salts.

Theoretical

For the sake of simplicity, we consider one-dimensional segregated stacks of ion radical molecules in simple solid ion radical salts where each ion radical has one unpaired electron. Hereafter, we take only the half-occupied molecular orbital of the unpaired electron for one site of the ion radical molecule, and assume a model of non-alternant one-dimensional column composed of infinite number of such sites. In this model, each ion radical site has one identical molecular orbital with equal energy level, and there is one electron per each site. Along such one-dimensional column, an unpaired electron transfers from one site to another site, but a strong repulsive force will take place when an electron happens to come onto a site which is already occupied by another electron with opposite spin. Let us denote the intra-site Coulomb repulsive energy as I, and consider a system of electrons described by the following Hamiltonian, which is often called the Hubbard Hamiltonian,[10]

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

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 repulsive potential, I, appears only when two electrons with up and down spins are at the same site. Since each ion radical site has identical molecular orbital with equal energy level, we put $t_{ii}=0$ without loss of generality. The unperturbed band energy, $\varepsilon_{\boldsymbol{k}}$, of the system is related to t_{ij} by

$$\varepsilon_{\boldsymbol{k}} = \sum_{j} t_{ij} \mathrm{e}^{i\boldsymbol{k}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)}. \tag{2}$$

In the case of non-alternant one-dimensional model, we assume that the transfer matrix elements exist only between nearest neighbor sites. Then, the unperturbed band energy is simply given by

$$\varepsilon_k = 2T \cos ka, \quad \left(-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}\right), \tag{3}$$

where $T(<0)$ is the transfer matrix element between nearest neighbors and a is the lattice separation.

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).[10] The Green's function is given by

$$G_{k\sigma}(E) = \frac{1}{2\pi}\left\{\frac{E_{k\sigma}^{U} - I(1-n_{-\sigma})}{E_{k\sigma}^{U} - E_{k\sigma}^{L}} \frac{1}{E - E_{k\sigma}^{U}} + \frac{I(1-n_{-\sigma}) - E_{k\sigma}^{L}}{E_{k\sigma}^{U} - E_{k\sigma}^{L}} \frac{1}{E - E_{k\sigma}^{L}}\right\}, \tag{4}$$

where

$$n_\sigma = \langle n_{i\sigma} \rangle,$$

$$E^U_{k\sigma} = \frac{1}{2}(\varepsilon_k + I + \sqrt{\varepsilon_k{}^2 + 2(2n_{-\sigma} - 1)\varepsilon_k I + I^2}),$$

$$E^L_{k\sigma} = \frac{1}{2}(\varepsilon_k + I - \sqrt{\varepsilon_k{}^2 + 2(2n_{-\sigma} - 1)\varepsilon_k I + I^2}).$$

Here $E^L_{k\sigma}$ is the energy of an electron with σ-spin which moves about avoiding other electrons with $-\sigma$-spin, while $E^U_{k\sigma}$ is the energy of an electron which propagates mainly among sites already occupied with electrons with $-\sigma$-spin. The optical transition from $E^L_{k\sigma}$ to $E^U_{k\sigma}$ corresponds to the intermolecular charge-transfer absorption of the one-dimensional system of solid ion radical salt. The charge-transfer absorption spectrum corresponds to the real part of frequency-dependent conductivity tensor, $\sigma_{\mu\nu}(\omega)$, which is given by[11]

$$\sigma_{\mu\nu}(\omega) \sim \frac{ie^2}{V} \lim_{\delta \to 0+} \sum_{k,\sigma} \frac{1}{\omega - E^U_{k\sigma} + E^L_{k\sigma} - i\delta} \frac{1}{E^L_{k\sigma} - E^U_{k\sigma}} \times \frac{\partial E^U_{k\sigma}}{\partial k_\mu} \frac{\partial E^L_{k\sigma}}{\partial k_\nu} (f(E^L_{k\sigma}) - f(E^U_{k\sigma})), \tag{5}$$

where ω is the frequency of electromagnetic wave, V is the volume of the system, and $f(E)$ is the Fermi distribution function. If the direction of the one-dimensional column is chosen as x axis, the total intensity of the charge-transfer absorption per unit volume, A, is given by

$$A = \int_0^\infty \mathrm{Re}\, \sigma_{xx}(\omega) \mathrm{d}\omega = -\frac{\pi e^2}{V} \sum_{k,\sigma} \frac{1}{E^L_{k\sigma} - E^U_{k\sigma}} \times \frac{\partial E^U_{k\sigma}}{\partial k_x} \frac{\partial E^L_{k\sigma}}{\partial k_x} (f(E^L_{k\sigma}) - f(E^U_{k\sigma})). \tag{6}$$

We assume a paramagnetic state for simple ion radical salt where each ion radical carries one unpaired electron. This leads to half-occupied Hubbard model with $n_\downarrow = n_\uparrow = 1/2$. In the case when the intra-site Coulomb repulsion energy, I, is much larger than the energy due to the observed temperature, we can well put $f(E^L_{k\sigma}) - f(E^U_{k\sigma}) = 1$. If our system has N one-dimensional chains per unit area perpendicular to the chain axis, we have

$$A = \frac{2\pi N e^2}{L} \sum_{kx} \frac{1}{(\sqrt{\varepsilon_k{}^2 + I^2})^3} \frac{1}{4} (\varepsilon_k + \sqrt{\varepsilon_k{}^2 + I^2}) \times (\sqrt{\varepsilon_k{}^2 + I^2} - \varepsilon_k) \left(\frac{\partial \varepsilon_k}{\partial k_x} \right)^2, \tag{7}$$

where L is the length of the chain. The summation with k_x in Eq. 7 was carried out by integrating with $(L/2\pi)\int \mathrm{d}k_x$ in the first Brillouin zone. By the use of Eq. 3, we have

$$A = Ne^2 \int_{-\pi/a}^{\pi/a} \frac{1}{4} I^2 \frac{(2Ta)^2 \sin^2 k_x a}{(\sqrt{I^2 + 4T^2 \cos^2 k_x a})^3} \mathrm{d}k_x. \tag{8}$$

By replacing the parameters of $k_x a$ and $2T/I$ into x and t, respectively, we have

$$A = \frac{Ne^2}{4a} I(at)^2 \int_{-\pi}^{\pi} \frac{\sin^2 x}{(\sqrt{1 + t^2 \cos^2 x})^3} \mathrm{d}x. \tag{9}$$

This function can be evaluated only in terms of elliptic integral. However, in the limit of small transfer matrix element region of $|t| = |2T/I| \ll 1$, we have an approximation by expanding

$$1/(\sqrt{1 + t^2 \cos^2 x})^3 = 1 - \frac{3}{2} t^2 \cos^2 x + \frac{3 \cdot 5}{2 \cdot 4} t^4 \cos^4 x + \cdots \tag{10}$$

Therefore, we can obtain

$$A = \frac{Ne^2}{4a} I(at)^2 \int_{-\pi}^{\pi} (\sin^2 x - \frac{3}{2} t^2 \sin^2 x \cos^2 x + \cdots) \mathrm{d}x = \frac{N\pi e^2}{4a} I(at)^2 \left(1 - \frac{3}{8} t^2 + \cdots \right). \tag{11}$$

This is the final expression for the absorption intensity of the charge-transfer transition between ion radicals in non-alternant one-dimensional column of simple solid ion radical salt.

Discussion

In the preceding section, the charge-transfer absorption intensity, A, was expressed as a function of intra-site Coulomb repulsion energy, I, and the nearest neighbor transfer matrix element, T. Obviously, if $T=0$, that is, if no transfer of unpaired electron between ion radical molecules takes place in solid ion radical salt, we have $A=0$ in Eq. 11 and no charge-transfer absorption appears in the solid-state spectrum. On the other hand, for non-zero T value, as long as $2|T| \ll I$, the intensity, A, will be non-zero and will increase progressively with the increase of the $|t| = 2|T|/I$ value, as is given by Eq. 11. In most solid ion radical salts, the I values are known to be of the order of 1 eV, while the magnitudes of $|T|$, to be of the order of 0.1 eV or more.[9,13–15] Therefore, in these solid salts, the magnitude of A is not zero, and this is the reason why a number of solid ion radical salts, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion radical salts, show marked charge-transfer absorptions in their solid-state spectra.[3–5] According to our previous paper,[9] we obtained theoretically the transition energy and the line shape of the charge-transfer absorption of the same system as the present model. The peak energy of the charge-transfer absorption corresponds to $\omega = I$. Thus, from the peak position of the observed charge-transfer absorption, we can estimate the I value experimentally. Therefore, by the use of Eq. 11 together with the estimated I value, we can estimate the T value if the absolute intensity measurements are made with the charge-transfer absorption of solid ion radical salt. This procedure will be the most direct way to estimate the I and T values of our Hubbard model.

Next, we examine how the intensity of the charge-transfer absorption is related to the magnetic properties of solid ion radical salt. In a region of small $|T|$ limit, the system of the present Hubbard model leads to a stabilization of antiferromagnetic state between ion radical molecules.[12] For a pair of nearest neighbor ion radicals, if the direct small exchange interaction is neglected, the energy gap between the parallel and antiparallel spin state is given by $2J = 4T^2/I$. The stabilization of the antiparallel spin state is caused by the intermolecular charge-transfer effect of the unpaired electrons. Therefore, we can well consider our system of simple solid ion radical salt as one-dimensional Heisenberg antiferromagnetic system with an exchange interaction, J. On the other hand, the charge-transfer absorption intensity, A, in Eq. 11 can be approximated as $A \approx N\pi e^2 I(at)^2/4a = N\pi e^2 a\, T^2/I$ in a region of small $|T|$ limit, where we neglected the terms higher than t^4. In this case, we obtain the relation of $A \approx N\pi e^2 aJ/2$, so that A is nearly proportional to the magnitude of J. The physical meaning of this situation is as follows. Those solid ion radical salts which have very weak charge-transfer absorption intensity will possess very small J values, and thus, show the magnetic properties of almost free paramagnetism obeying Curie law.[14–16] On the other hand, those ion radical salts which have very strong charge-transfer absorptions will possess large J values, and thus, show almost diamagnetic susceptibilities.[2–5,13] So far, these theoretical correlations between the optical and magnetic properties have agreed qualitatively with the experimental observations in a number of solid ion radical salts.[2–5,13–16] Here, we note that, in such ion radical salts, as the I values are of the order of 1 eV and the $|T|$ values are of the order of 0.1 eV, the condition of the small $|T|$ limit approximation is fulfilled. More quantitative measurements of the charge-transfer absorption intensity together with the J values are required to confirm our theoretical relationship $A \propto J$ as well as to determine the magnitudes of the I and $|T|$ values of those solid ion radical salts in more detail.

References

1) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

2) W. J. Siemons, P. E. Bierstedt, and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963); R. G. Kepler, *J. Chem. Phys.*, **39**, 3528 (1963).

3) Y. Iida, *Bull. Chem. Soc. Jpn.*, **42**, 71, 637 (1969); **43**, 2772 (1970); **44**, 663, 1777 (1971); **45**, 105, 624 (1972); Y. Iida and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **41**, 2615 (1968).

4) Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, *Bull. Chem. Soc. Jpn.*, **42**, 3051 (1969); Y. Oohashi and T. Sakata, *Bull. Chem. Soc. Jpn.*, **46**, 3330 (1973).

5) J. Tanaka, M. Tanaka, T. Kawai, T. Takabe, and O. Maki, *Bull. Chem. Soc. Jpn.*, **49**, 2358 (1976).

6) H. Kobayashi, Y. Ohashi, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **26**, 459 (1970), and the references cited therein.

7) J. L. deBoer and Aafje Vos, *Acta Crystallogr., Sect. B*, **28**, 835, 839 (1972).

8) M. Konno, H. Kobayashi, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **46**, 1987 (1973).

9) Y. Iida, *Bull. Chem. Soc. Jpn.*, **50**, 1445 (1977).

10) J. Hubbard, *Proc. R. Soc. London, Ser. A*, **276**, 238 (1963).

11) K. Kubo, *J. Phys. Soc. Jpn.*, **31**, 30 (1971).

12) Z. G. Soos and D. J. Klein, *J. Chem. Phys.*, **55**, 3284 (1971); M. Takahashi, *Prog. Theor. Phys. (Kyoto)*, **42**, 1098 (1969).

13) Y. Iida, *Bull. Chem. Soc. Jpn.*, **51**, 2523, 3637 (1978).

14) Y. Iida, *Bull. Chem. Soc. Jpn.*, **52**, 689 (1979).

15) Y. Iida, *Bull. Chem. Soc. Jpn.*, **52**, 1523 (1979).

16) The theoretical approach in the present paper is applicable not only to solid ion radical salts but also to crystals of neutral free radicals such as 2,2-diphenyl-1-picrylhydrazyl (DPPH). DPPH crystals show antiferromagnetic spin exchange interaction between unpaired electrons of nearest neighbor DPPH molecules but have the exchange interaction parameter as small as $J = 1.55 \times 10^{-5}$ eV. In accordance with this small exchange interaction, the electronic spectrum of solid DPPH is very similar to the spectrum of free DPPH in solution and shows no intermolecular charge-transfer absorption (*i.e.*, $A \approx 0$). See, for example, Z. G. Soos and R. C. Hughes, *J. Chem. Phys.*, **46**, 253 (1967), and H. Inokuchi, Y. Harada, and Y. Maruyama, *Bull. Chem. Soc. Jpn.*, **35**, 1559 (1962).