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Optical and Magnetic Properties of Crystalline Phenothiazine Cation Radical Salts

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Synopsis. Crystalline phenothiazine cation radical salts show charge-transfer transition between cation radicals in the low-energy region. These salts have antiferromagnetic exchange interaction between cation radicals. Their optical and magnetic properties were discussed in terms of one-dimensional Hubbard model.

The prominent magnetic, electrical and optical properties of a number of crystalline ion radical salts have been the subject of many theoretical and experimental investigations over the past fifteen years.[1-8] In such ion radical salts, the ion radical molecules are known to form, in themselves, a segregated stacking into infinite one-dimensional columns so as to make a large overlap between their half-occupied molecular orbitals.[1-8] 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.[1-4] In a previous paper,[6] we applied one-dimensional Hubbard model to the columns of ion radical molecules, and investigated the optical properties of solid ion radical salts. In the present paper, we examined the optical and magnetic properties of several crystalline phenothiazine cation radical salts on the basis of such a model.

Phenothiazine (PT) is a strong electron donating molecule and forms chemically stable cation radical salts with various counter anions. Several years ago,[2] we prepared such cation radical salts as $PT^{+\cdot}Br^-$, $PT^{+\cdot}HSO_4^-\cdot H_2O$, and $PT^{+\cdot}C_6H_2(NO_2)_3O^-$ (picrate). Moreover, Sato *et al.* synthesized the salts with antimony pentachloride anions.[3] The absorption spectrum of the phenothiazine cation radical monomer dissolved in dilute hydrochloric acid has a weak band around 13500 cm^{-1} composed of several vibrational structures at 15000, 13500, and 12200 cm^{-1}, a strong band at 19300 cm^{-1} with a shoulder at 19900 cm^{-1} and a band at 22800 cm^{-1}.[2] On the other hand, the solid-state spectra of $PT^{+\cdot}Br^-$, $PT^{+\cdot}HSO_4^-\cdot H_2O$, and $PT^{+\cdot}C_6H_2(NO_2)_3O^-$ differ markedly from the monomer spectrum of the cation radical.[2] For example, the solid-state spectrum of $PT^{+\cdot}HSO_4^-\cdot H_2O$ is reproduced in Fig. 1, together with the absorption spectrum of the cation radical monomer. The solid-state spectrum shows a strong low-energy band at 12000 cm^{-1}, high-energy bands at 21100 and 23300 cm^{-1}, and a shoulder around 28000 cm^{-1}. The low-energy band at 12000 cm^{-1} has been assigned to the charge-transfer transition between the phenothiazine cation radicals in their segregated stacks, while the high-energy bands at 21100 and 23300 cm^{-1}, to the shifted bands of the cation radical monomer

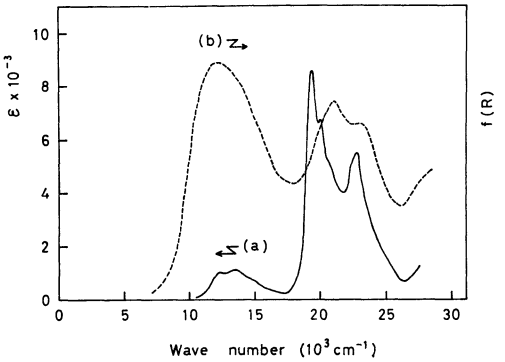

Fig. 1. (a) The absorption spectrum of the cation radical salt of phenothiazine hydrogen-sulfate monohydrate dissolved in hydrochloric acid and (b) the solid-state spectrum of the same salt. The solid-state spectrum was obtained by plotting the diffuse reflection spectrum using the Kubelka-Munk function, $f(R)=(1-R)^2/2R$, where R is the reflectance. See Ref. 2.

at 19300 and 22800 cm^{-1}, respectively.[2] The line shape of the charge-transfer absorption is almost symmetrical with respect to the axis of peak energy. The solid-state spectra of the bromide and the picrate are found to be very similar to that of the hydrogen-sulfate monohydrate salt. The charge-transfer absorptions of the bromide and picrate salts are located at 12900 and 12800 cm^{-1}, respectively.[2] On the other hand, according to Sato *et al.*,[3] the solid-state spectra of $PT^{+\cdot}SbCl_4^-$ and $PT^{+\cdot}SbCl_5^-$ salts are rather similar to the absorption spectrum of the phenothiazine cation radical monomer. The charge-transfer absorptions of these solid salts appear at 9350 and 10000 cm^{-1}, respectively. However, these absorptions have weak intensity and appear as a shoulder in the monomer spectrum of the cation radical.

In a previous paper,[6] we presented the theoretical line shape of the charge-transfer absorption on the basis of non-alternant one-dimensional Hubbard model. The shape of the absorption spectrum is given by

$$\sigma(\omega) \propto \frac{e^2}{4}\frac{I^2}{\omega^2\sqrt{\omega^2-I^2}}\sqrt{4T^2-\omega^2+I^2}. \qquad (1)$$

Here, a δ-function was assumed for each elementary transition in which the spin and the wave vector of an electron are conserved; I is the intra-site Coulomb repulsion energy, and $T(<0)$ the transfer matrix element between nearest neighbor ion radicals in one-dimensional column of the phenothiazine cation radicals. A schematic representation of the absorption line shape of Eq. 1 has been given in Fig. 1 of Ref. 6. The theoretical charge-transfer absorption has a sharp divergent peak at $\omega=I$. The spectrum has no absorption in the region $\omega<I$, but has a distinct shoulder in the region $I<\omega<\sqrt{I^2+4T^2}$. Actually, however, the

elementary absorption is not a δ-function but involves a finite width, and the spectrum will become more smoothed,[6,7] so that the observed charge-transfer absorption has an intensity even in the energy region lower than the peak position. Then, the absorption peak of the observed charge-transfer band corresponds to $\omega=I$, and its band width comes partly from the width due to the elementary absorptions but partly from the width due to non-zero transfer matrix element, $\sqrt{I^2+4T^2}-I$. We divide the two contributions of the widths in a way similar to the previous work,[7] where the width, $\sqrt{I^2+4T^2}-I$, could be estimated by subtracting with respect to $\omega=I$, the lower-energy side from the higher-energy side of the observed charge-transfer absorption. For example, in the case of the $PT^{+\cdot}$-$HSO_4^-\cdot H_2O$ salt (see Fig. 1, (b)), the observed peak energy of the charge-transfer absorption, 12000 cm^{-1}, thus corresponds to $I=12000$ cm^{-1}. From the observed line shape of the absorption, the width due to the transfer matrix element, $\sqrt{I^2+4T^2}-I$, is estimated to be of the order of 1500 cm^{-1}. This relation, together with $I=12000$ cm^{-1}, leads to the magnitude of the transfer matrix element, $|T|$, of the order of 3000 cm^{-1} or less in the hydrogen-sulfate monohydrate salt. In a similar way, from the observed solid-state spectra, the magnitudes of I for the bromide and the picrate are estimated to be 12900 and 12800 cm^{-1}, respectively. In both salts, the values of the transfer matrix element, $|T|$, again seem to be smaller than 3000 cm^{-1}. As for the $PT^{+\cdot}\,SbCl_4^-$ and $PT^{+\cdot}\,SbCl_5^-$ salts, from the observed charge-transfer absorptions, the I values are estimated to be 9350 and 10000 cm^{-1}, respectively, and the magnitudes of $|T|$ seem to be of the order of 1000 cm^{-1} or less. However, since those charge-transfer absorptions appear as a shoulder in the monomer spectrum of the phenothiazine cation radical, the estimated values of I and $|T|$ should be taken only as an indication.

In order to obtain more exact information on the magnitudes of the transfer matrix elements, we further examined the magnetic properties of solid phenothiazine cation radical salts. In a region of small $|T|$ limit, the Hubbard model leads to a stabilization of the antiferromagnetic state between ion radical molecules. For a pair of nearest neighbor ion radicals, if the small direct exchange is neglected, the energy gap between the parallel and antiparallel spin states is given by $2J=4T^2/I$. Therefore, we can well consider our solid phenothiazine cation radical salts as one-dimensional antiferromagnet with an exchange interaction, J.[8] By measuring the static magnetic susceptibility and its temperature dependence, Sato *et al.* reported the J values for $PT^{+\cdot}\,SbCl_5^-$, $PT^{+\cdot}\,SbCl_4^-$, and $PT^{+\cdot}\,Br^-$ to be 34, 270, and $\approx$970 cm^{-1}, respectively.[3] We also measured the magnetic susceptibility of the hydrogen-sulfate monohydrate.[2] It was found to be almost diamagnetic, indicating the J value of $\approx$800 cm^{-1}. Therefore, by using the relation $J=2T^2/I$, together with the I values determined previously, the $|T|$ values for $PT^{+\cdot}\,SbCl_5^-$, $PT^{+\cdot}\,SbCl_4^-$, and $PT^{+\cdot}\,Br^-$ are estimated to be 410, 1120, and $\approx$2500 cm^{-1}, respectively, while that for the hydrogen-sulfate monohydrate, to be of the order of 2200 cm^{-1}. Although the $|T|$ values estimated previously from the line shape of the charge-transfer absorptions include some uncertainties, for each of the salts the magnitude of the $|T|$ value obtained from the $|T|=\sqrt{J\,I/2}$ relation is found to agree with that estimated only from the spectroscopic data.

Turning back to the optical properties of those phenothiazine cation radical salts, we discuss how the intensity of the charge-transfer absorption is related to the $|T|$ value. According to our preliminary work,[9] the intensity of the charge-transfer absorption is roughly proportional to $|T|^2$. In this respect, the intensities of the charge-transfer absorptions of the bromide and the hydrogen-sulfate monohydrate should be the greatest, that of $PT^{+\cdot}\,SbCl_4^-$ should be intermediate, and that of $PT^{+\cdot}\,SbCl_5^-$, the weakest. In accordance with this prediction, the solid-state spectra observed with the former two compounds differ markedly from the phenothiazine cation radical monomer spectrum and show strong charge-transfer absorptions,[2] while the latter two compounds show only weak charge-transfer absorptions.[3] In particular, the solid-state spectrum of $PT^{+\cdot}\,SbCl_5^-$ is very similar to the monomer spectrum of the phenothiazine cation radical in solution.

On the basis of these considerations, we conclude that the phenothiazine cation radicals in the solid salts of the bromide, the hydrogen-sulfate monohydrate and the picrate stack, in themselves, very closely, while the intermolecular interaction between the phenothiazine cation radicals is weak in the solid $PT^{+\cdot}\,SbCl_4^-$ and $PT^{+\cdot}\,SbCl_5^-$ salts.

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