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Asymmetric Shape of Charge-transfer Absorption in Crystalline Ion Radical Salts

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Synopsis. Using the one-dimensional Hubbard model, we proposed an asymmetric band shape for the charge-transfer transition between ion radicals in crystalline ion radical salts. The charge-transfer band of the anion radical salts derived from 2,3-dicyano-*p*-benzoquinone was explained in terms of such a model.

In a number of 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-filled molecular orbitals.[1-3] 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.[1-3]

The 2,3-dicyano-*p*-benzoquinone (p-H_2QCy_2) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (p-Cl_2QCy_2) molecules are known to be strong electron acceptors and to form stable anion radical salts with some diamagnetic alkali metal cations. Several years ago,[2] we measured the diffuse reflection spectra of the solid anion radical salts of Na^+ p-$H_2QCy_2^{\overline{\cdot}}$, K^+ p-$H_2QCy_2^{\overline{\cdot}}$, Na^+ p-$Cl_2QCy_2^{\overline{\cdot}}$ and K^+ p-$Cl_2QCy_2^{\overline{\cdot}}$, and found strong absorptions due to the charge-transfer transition between anion radicals in the low-energy region. The observed spectra of the charge-transfer absorptions are reproduced in Fig. 1, where the Kubelka-Munk function, $f(R) = (1—R)^2/2R$, was plotted against wave number. In the case of the Na^+ p-$Cl_2QCy_2^{\overline{\cdot}}$ salt (see (a) or Fig. 1), the peak position of the charge-transfer band is around 12600 cm^{-1} and its band shape is found to be almost symmetrical with respect to the axis of peak energy. On the other hand, the solid-state spectrum of the Na^+ p-$H_2QCy_2^{\overline{\cdot}}$ salt (see (c) of Fig. 1) shows the charge-transfer band with the peak position around 10700 cm^{-1}. However, its band shape is not symmetrical with respect to the axis of peak energy, but has a shoulder in the higher-energy region. Regardless of the species of the counter cations, these distinct differences are also observed for the K^+ p-$Cl_2QCy_2^{\overline{\cdot}}$ and K^+ p-$H_2QCy_2^{\overline{\cdot}}$ salts as are shown in (b) and (d) of Fig. 1. When we first reported those solid-state spectra,[2] we could not fully explain why the anion radical salts derived from p-H_2QCy_2 have asymmetric charge-transfer band with a shoulder in the higher-energy region.

In order to understand the character of this charge-transfer absorption in more detail, we studied in a previous paper the transition energy and the theoretical line shape of such absorption by the use of one-dimensional Hubbard model and the Green's function method.[3] For half-filled band system of simple ion radical salt, we consider non-alternant one-dimensional stack of ion radical molecules with paramagnetic state. We assumed a δ-function for each elementary transition in which the spin and the wave vector of an electron are conserved. The intermolecular charge-transfer absorption, $\sigma(\omega)$, at very low temperature is given by

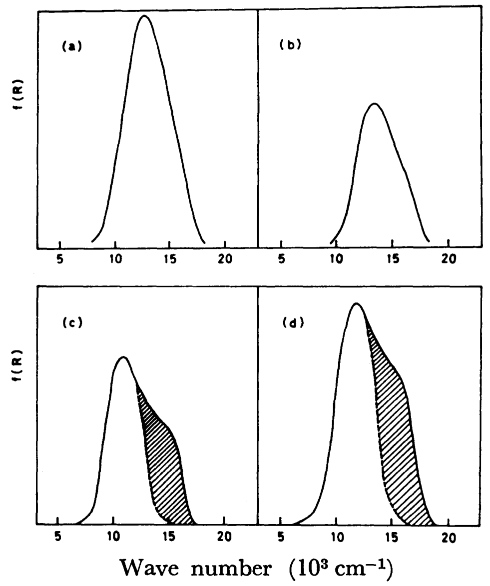

Fig. 1. The observed charge-transfer absorptions of solid anion radical salts as studied by diffuse reflection method (see Ref. 2); (a) Na^+ p-$Cl_2QCy_2^{\overline{\cdot}}$, (b) K^+ p-$Cl_2QCy_2^{\overline{\cdot}}$, (c) Na^+ p-$H_2QCy_2^{\overline{\cdot}}$ and (d) K^+ p-$H_2QCy_2^{\overline{\cdot}}$. The Kubelka-Munk function, $f(R) = (1-R)^2/2R$, was plotted *versus* wave number. For shaded and unshaded parts, see text.

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

where I is the intra-site Coulomb repulsion energy, and $T(<0)$ is the transfer matrix element between nearest neighbor sites in such one-dimensional column.

The theoretical charge-transfer absorption has a sharp divergent peak at the energy $\omega = I$, where the spectrum has a van Hove singularity in the lower energy side. The spectrum has no absorption in the energy region $\omega < I$, but has an absorption intensity in the region $\omega > I$. The intensity is the greatest at $\omega = I$, and decreases progressively with the increase of ω. The highest energy of the absorption takes place at $\omega = \sqrt{I^2+4T^2}$, where the intensity falls down to zero. The spectrum has a shoulder in the region $I < \omega < \sqrt{I^2+4T^2}$. These spectroscopic features are illustrated in Fig. 2.

In this model, the line width, $\sqrt{I^2+4T^2}-I$, of the charge-transfer absorption is solely caused by the ex-

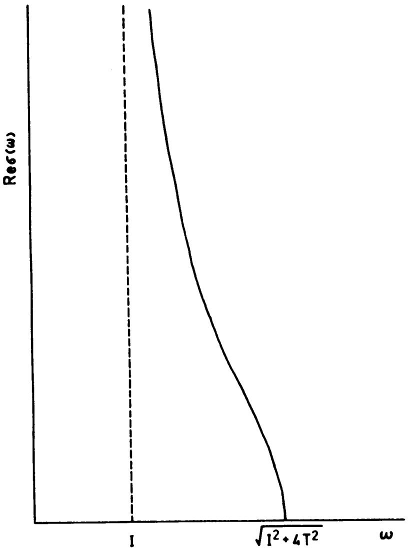

Fig. 2. The theoretical absorption line shape of Eq. 1 due to the charge-transfer transition between ion radical molecules in one-dimensional Hubbard model. See text and Ref. 3.

istence of non-zero transfer matrix element, T. However, as has been mentioned in the previous paper,[3] the actual elementary absorption is not a simple δ-function but involves finite width. Therefore, the actual charge-transfer absorption will have extra width and become more smoothed. If the band width due to the transfer matrix element is much smaller than that of the elementary absorption, the charge-transfer absorption will be governed predominantly by the band shape of the elementary absorption, so that we can well expect almost symmetrical line shape of the charge-transfer absorption with the peak position at $\omega=I$. The charge-transfer absorption of the Na^+ p-$\mathrm{Cl_2QCy_2}^{\overline{\cdot}}$ and K^+ p-$\mathrm{Cl_2QCy_2}^{\overline{\cdot}}$ salts should correspond to this case. In the case of the Na^+ p-$\mathrm{Cl_2QCy_2}^{\overline{\cdot}}$ salt (see (a) of Fig. 1), the observed absorption peak value, 12600 cm^{-1}, corresponds to $I=12600\ \mathrm{cm}^{-1}$. The band width due to the transfer matrix element, $\sqrt{I^2+4T^2}-I$, will be very small compared to that of the elementary absorption, 4000 cm^{-1}, and the $|T|$ value appears less than 1000 cm^{-1}. In a similar way, $I=13300\ \mathrm{cm}^{-1}$ is estimated for the K^+ p-$\mathrm{Cl_2QCy_2}^{\overline{\cdot}}$ salt, and the $|T|$ value of this salt will again be less than 1000 cm^{-1}. In both of these salts, we can well see that a narrow band system with strong electron correlation (*i.e.*, $|T|\ll I$) takes place in one-dimensional column of the p-$\mathrm{Cl_2QCy_2}^{\overline{\cdot}}$ anion radicals.

On the other hand, we consider the case when the band width due to transfer matrix element is comparable to or larger than that of the elementary absorption. In this case, the peak position of the charge-transfer absorption is still at $\omega=I$, but the line shape is no longer symmetrical with respect to $\omega=I$. Because of asymmetric component of Fig. 2, the charge-transfer absorption will have a distinct shoulder in the energy region $\omega>I$, and the total band width will arise partly from the width due to the elementary absorption but partly from the width due to the non-zero transfer matrix element. As are shown in (c) and (d) of Fig. 1, the charge-transfer absorption of the Na^+ p-$\mathrm{H_2QCy_2}^{\overline{\cdot}}$ and K^+ p-$\mathrm{H_2QCy_2}^{\overline{\cdot}}$ salts should correspond to this case. In the case of the Na^+ p-$\mathrm{H_2QCy_2}^{\overline{\cdot}}$ salt, the observed absorption peak value, 10700 cm^{-1}, thus corresponds to $I=10700\ \mathrm{cm}^{-1}$. As for the band shape, note that the effect of transfer matrix element gives no contribution to the absorption intensity in the region $\omega<I$. Therefore, we divide, for the sake of simplicity, the observed charge-transfer absorption into symmetrical and asymmetrical parts by subtracting, with respect to $\omega=I$, the lower-energy side from the higher-energy side. This is shown in (c) of Fig. 1, where the unshaded and shaded parts are the symmetrical and asymmetrical ones, respectively. Then, the band width of the shaded part will come mostly from the width due to the non-zero transfer matrix element, $\sqrt{I^2+4T^2}-I$, and this width is found to be of the order of 3000 cm^{-1} or less. By putting $I=10700\ \mathrm{cm}^{-1}$ into this relation, the magnitude of the transfer matrix element is estimated to be $|T|\leq 4300\ \mathrm{cm}^{-1}$. Similarly, in the case of the K^+ p-$\mathrm{H_2QCy_2}^{\overline{\cdot}}$ salt, it is found that $I=11700\ \mathrm{cm}^{-1}$ and $\sqrt{I^2+4T^2}-I\leq 3000\ \mathrm{cm}^{-1}$, so that the magnitude of the transfer matrix element is estimated to be $|T|\leq 4500\ \mathrm{cm}^{-1}$.

On the basis of these considerations, we can well understand the spectroscopic features of the charge-transfer absorptions characteristic of the Na^+ p-$\mathrm{H_2QCy_2}^{\overline{\cdot}}$ and K^+ p-$\mathrm{H_2QCy_2}^{\overline{\cdot}}$ salts as well as of the Na^+ p-$\mathrm{Cl_2QCy_2}^{\overline{\cdot}}$ and K^+ p-$\mathrm{Cl_2QCy_2}^{\overline{\cdot}}$ salts. The magnitude of $|T|$ of the p-$\mathrm{H_2QCy_2}$ anion radical salts appears to be considerably larger than that of the p-$\mathrm{Cl_2QCy_2}$ anion radical salts. This result is also strongly supported by the following reason. The p-$\mathrm{Cl_2QCy_2}$ anion radical molecule includes bulky chlorine substituents, while the p-$\mathrm{H_2QCy_2}$ anion radical molecule does not. Therefore, in one-dimensional stacking of anion radicals, the p-$\mathrm{H_2QCy_2}$ anion radicals will stack, in themselves, more closely than do the p-$\mathrm{Cl_2QCy_2}$ anion radicals, so that the magnitude of $|T|$ of the p-$\mathrm{H_2QCy_2}$ anion radical salts will be definitely larger than that of the p-$\mathrm{Cl_2QCy_2}$ anion radical salts.

At the present time, it is desirable to make sure of the magnitudes of $|T|$ of those anion radical salts by another approach. For this purpose, it will be quite useful to measure the exchange interaction parameters in their magnetic properties and the energy gaps in their semiconductivities. However, more useful approach is to measure absolute intensity of the charge-transfer absorption, because the total intensity will be roughly proportional to $|T|^2$. In this respect, the intensites of the charge-transfer absorptions of the p-$\mathrm{H_2QCy_2}$ anion radical salts may be much stronger than those of the p-$\mathrm{Cl_2QCy_2}$ anion radical salts.

References

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2) Y. Iida, *Bull. Chem. Soc. Jpn.*, **44**, 1777 (1971), and the references cited therein.

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