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Electronic Spectra and Charge-Transfer Absorption of Solid Anion Radical Salts of 2,3-Dicyano-*p*-benzoquinone and 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone

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Synopsis. The diffuse reflection spectra were measured with solid anion radical salts of 2,3-dicyano-*p*-benzoquinone and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone with rubidium and caesium cations. Strong charge-transfer transition between anion radicals was observed in the low-energy region. The spectroscopic features of the charge-transfer absorption were discussed in terms of one-dimensional Hubbard model.

In most solid ion radical salts, the planar ion radical molecules are known to form, in themselves, a segregated face-to-face stacking into infinite one-dimensional columns so as to make a large overlap between their half-occupied 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]

Several years ago,[1] we examined the solid-state spectra of some stable anion radical salts derived from 2,3-dicyano-*p*-benzoquinone (p-H$_2$QCy$_2$) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (p-Cl$_2$QCy$_2$). We prepared such crystalline salts as Na$^+$ p-H$_2$QCy$_2^{\cdot -}$, K$^+$ p-H$_2$QCy$_2^{\cdot -}$, Na$^+$ p-Cl$_2$QCy$_2^{\cdot -}$, and K$^+$ p-Cl$_2$QCy$_2^{\cdot -}$, where we found strong absorptions due to the charge-transfer transition between anion radicals in the low-energy region. In the case of Na$^+$ p-Cl$_2$QCy$_2^{\cdot -}$ and K$^+$ p-Cl$_2$QCy$_2^{\cdot -}$ salts, the band shape of the charge-transfer absorption was found to be almost symmetrical with respect to the axis of peak energy. However, in the case of Na$^+$ p-H$_2$QCy$_2^{\cdot -}$ and K$^+$ p-H$_2$QCy$_2^{\cdot -}$ salts, the band shape is no longer symmetrical with respect to the axis of peak energy, but has a distinct shoulder in the higher-energy region. Recently, we could well explain those spectroscopic features of the charge-transfer absorptions in terms of one-dimensional Hubbard model.[2,3] In the present paper, we further examined the solid-state spectra of the anion radical salts of p-H$_2$QCy$_2$ and p-Cl$_2$QCy$_2$ with rubidium and caesium cations.

p-H$_2$QCy$_2$ was synthesized from *p*-benzoquinone according to the method of Thiele *et al.*,[4] while p-Cl$_2$QCy$_2$ was commercially available. The anion radical salts of Rb$^+$ p-H$_2$QCy$_2^{\cdot -}$, Cs$^+$ p-H$_2$QCy$_2^{\cdot -}$, Rb$^+$ p-Cl$_2$QCy$_2^{\cdot -}$, and Cs$^+$ p-Cl$_2$QCy$_2^{\cdot -}$ were prepared according to the method described in the previous paper.[1] The solid-state spectra of these anion radical salts were measured by diffuse reflection method. The spectra were recorded on a Beckman DK-2A spectroreflectometer in the range from 4000 to 30800 cm^{-1} at room temperature. In order to avoid cation exchange between the salt and the diluent, the samples were ground and diluted with pure naphthalene. The solid-state spectra were obtained by plotting the diffuse reflection spectra using the Kubelka-Munk function, $f(R)=(1-R)^2/2R$, in which R is the reflectance.

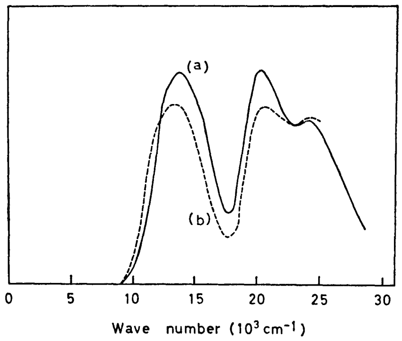

Fig. 1. The solid-state spectra of (a) Rb$^+$ p-Cl$_2$QCy$_2^{\cdot -}$ and (b) Cs$^+$ p-Cl$_2$QCy$_2^{\cdot -}$.

Figure 1, curve (a), is the observed solid-state spectrum of Rb$^+$ p-Cl$_2$QCy$_2^{\cdot -}$ salt, which shows a strong absorption at 13600 cm^{-1} and high-energy bands at 20100 and 24000. These spectroscopic features are found to be very similar to those previously reported on Na$^+$ p-Cl$_2$QCy$_2^{\cdot -}$ or K$^+$ p-Cl$_2$QCy$_2^{\cdot -}$.[1] The band peaked at 13600 cm^{-1} appears in the low-energy region where the p-Cl$_2$QCy$_2$ anion radical monomer does not absorb.[1] This low-energy band seems to be attributable to the charge-transfer transition between the p-Cl$_2$QCy$_2$ anion radicals in the segregated stack of the anion radicals, while the bands at 20100 and 24000, cm^{-1} to the shifted bands of the anion radical monomer at 17100 and 21900 cm^{-1}, respectively. Here, we note that the line shape of the charge-transfer absorption at 13600 cm^{-1} is almost symmetrical with respect to the peak-energy axis and that the high-energy bands at 20100 and 24000 cm^{-1} are appreciably blue-shifted, compared to the corresponding absorptions of the monomer spectrum. On the other hand, Fig. 1, curve (b), is the observed solid-state spectrum of Cs$^+$ p-Cl$_2$QCy$_2^{\cdot -}$ salt, which also shows a strong charge-transfer band peaked at 13400 cm^{-1} and high-energy bands at 20500 and 24200. In this salt, the line shape of the charge-transfer absorption is again almost symmetrical with respect to the peak-energy axis. As the charge-transfer transition occurs in the segregated stack of the p-Cl$_2$QCy$_2$ anion radicals, we can well understand the fact that the energy of the charge-transfer absorption remains nearly constant in going from the rubidium salt to the caesium salt.

On the other hand, Fig. 2, curve (a), is the observed solid-state spectrum of Rb$^+$ p-H$_2$QCy$_2^{\cdot -}$. A strong low-

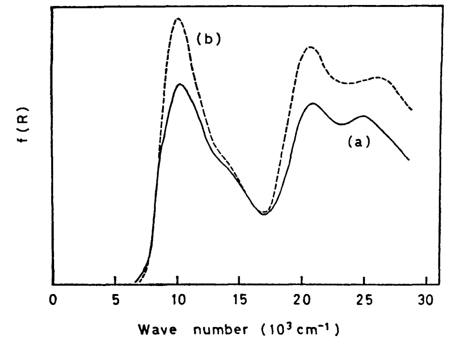

Fig. 2. The solid-state spectra of (a) Rb$^+$ p-H$_2$QCy$_2^{\overline{\cdot}}$ and (b) Cs$^+$ p-H$_2$QCy$_2^{\overline{\cdot}}$.

energy charge-transfer absorption, which arises from the segregated stack of the p-H$_2$QCy$_2$ anion radicals, is found at 10300 cm^{-1} with a shoulder around 13500. High-energy bands are located at 20800 and 25000 cm^{-1}, which originate from the monomer absorptions of the p-H$_2$QCy$_2$ anion radical at 17100 and 21500 cm^{-1}, respectively.[1] Here, we note that the charge-transfer band is broad and has the shoulder in the higher-energy side and that its line shape is no longer symmetrical with respect to the peak-energy axis. The solid-state spectrum of Cs$^+$ p-H$_2$QCy$_2^{\overline{\cdot}}$ is given in Fig. 2, curve (b). In this case, the charge-transfer band and the high-energy bands are located at 10000 cm^{-1} with a shoulder around 13500 and at 20500 and 25800 cm^{-1}, respectively.

Hereafter, we only discuss the spectroscopic features of the observed charge-transfer absorptions on the basis of our previous theoretical approach.[2] To the segregated stacks of the p-Cl$_2$QCy$_2$ or p-H$_2$QCy$_2$ anion radicals in their solid salts, we apply non-alternant one-dimensional Hubbard model composed of ion radical molecules with half-occupied orbitals. In the case of paramagnetic state, the intermolecular charge-transfer absorption, σ (ω), 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) is the transfer matrix element between nearest neighbor ion radicals in one-dimensional Hubbard model. A schematic representation of the absorption line shape of Eq. 1 has been given in Fig. 1 of Ref. 2. 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,[2] so that the observed charge-transfer absorption has an intensity even in the energy region lower than the peak position. Therefore, 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.[3] With respect to $\omega=I$, we subtract the lower-energy side from the higher-energy side of the observed charge-transfer absorption. Then, the part symmetrical with respect to $\omega=I$ will correspond to the contribution of the elementary absorptions, while the remaining asymmetric part, to the width due to non-zero transfer matrix element, $\sqrt{I^2+4T^2}-I$, because the absorption in the $\omega<I$ region is solely attributable to the elementary absorptions and the absorption of Eq. 1 appears only in the $\omega>I$ region.

As for the charge-transfer absorptions of Rb$^+$ p-Cl$_2$QCy$_2^{\overline{\cdot}}$ and Cs$^+$ p-Cl$_2$QCy$_2^{\overline{\cdot}}$, the I values for the rubidium and caesium salts are estimated to be 13600 and 13400 cm^{-1}, respectively, from the observed peak energies. In both salts, the band width due to the transfer matrix element, $\sqrt{I^2+4T^2}-I$, is found to be 400 cm^{-1} or less, and the $|T|$ values are estimated to be 1500 cm^{-1} or less by using the observed I values.

On the other hand, from the observed peak energy, the I values for Rb$^+$ p-H$_2$QCy$_2^{\overline{\cdot}}$ and Cs$^+$ p-H$_2$QCy$_2^{\overline{\cdot}}$ are estimated to be 10300 and 10000 cm^{-1}, respectively. In both salts, however, the broad asymmetric charge-transfer absorption with a distinct shoulder in the $\omega>I$ region implies that the band width due to the transfer matrix element is comparable to the width of elementary absorption. By using the above-mentioned method, the asymmetric part in the higher-energy side of the charge-transfer absorption, $\sqrt{I^2+4T^2}-I$, is found to be 2000 cm^{-1} or less for Rb$^+$ p-H$_2$QCy$_2^{\overline{\cdot}}$ and about 2400 cm^{-1} or less for Cs$^+$ p-H$_2$QCy$_2^{\overline{\cdot}}$. Thus, the $|T|$ values for the rubidium and caesium salts are estimated to be ≤ 3400 and ≤ 3700 cm^{-1}, respectively. These values are found to be considerably larger than the corresponding values for the Rb$^+$ p-Cl$_2$QCy$_2^{\overline{\cdot}}$ and Cs$^+$ p-Cl$_2$QCy$_2^{\overline{\cdot}}$ salts.

In conclusion, the solid-state spectra of M$^+$ p-Cl$_2$QCy$_2^{\overline{\cdot}}$ and M$^+$ p-H$_2$QCy$_2^{\overline{\cdot}}$, (M=Na, K, Rb, and Cs), are predominantly governed by the manner of the segregated stacks of the anion radicals, but are hardly influenced by the species of the counter cations. In such stacks of the anion radicals, the p-H$_2$QCy$_2$ anion radicals stack more closely than do the p-Cl$_2$QCy$_2$ anion radicals. This results in remarkable difference in the charge-transfer absorptions between the p-Cl$_2$QCy$_2$ and p-H$_2$QCy$_2$ anion radical salts.

References

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