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A New Approach to Protonics in the H-bonded Charge-Transfer Crystals

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Our recent study of the proton transfer in the double-well potential of the H-bonded charge-transfer (CT) crystals is introduced together with several other related topics. Special attention is focused on our investigation into the control of the dynamical motion of protons by using the excess π-electron effect on the hydrogen bonding in the CT-interaction system, which provides useful information in the design of a new molecular function using the H-bonded CT complexes. In this process, optical transitions enhanced by the dynamical motion of protons has been identified as the proton-linked super-CT transitions.

GENERAL REMARKS

As is now well recognized, the nature of the hydrogen bonding (H-bonding) is sensitively altered by changing the charge distribution in the surrounding molecular system.[1–8] It is particularly interesting that there is always a finite probability of the quantum-mechanical proton-transfer between the H-bonded double-well potential, i.e. proton tunneling, in the charge-transfer (CT) complexes, as demonstrated by Rein and Harris following Löwdin's suggestion in the study of a mutation process of the double helix of DNA.[5,6] These theoretical investigations imply that there is a unique possibility for designing a new molecular function based on the proton tunneling in the H-bonded CT complexes by controlling the degree of the electron-transfer by chemical modification or by external perturbations.

The control of the electron transfer in the CT complexes has been a main subject for synthesis of organic semiconductors, metals, or superconductors.[9] The essential viewpoint for producing such an organic conductor is to utilize the specific character of the CT states near the neutral-to-ionic (N—I) interface, where the two characteristic energies are competing, the net ionization energy in donor–acceptor (D—A) pairs and the electrostatic energy gain when the lattice is ionized (i.e., the Madelung energy).[10] Near the interface, the metallic properties apear in some segregated-stacked CT complexes, while in the mixed-stacked materials many anomalous behaviors have been revealed in the semiconducting transport, optical, dielectric and magnetic properties.[11–17] In Figure 1(a) and (b), the conductivity of

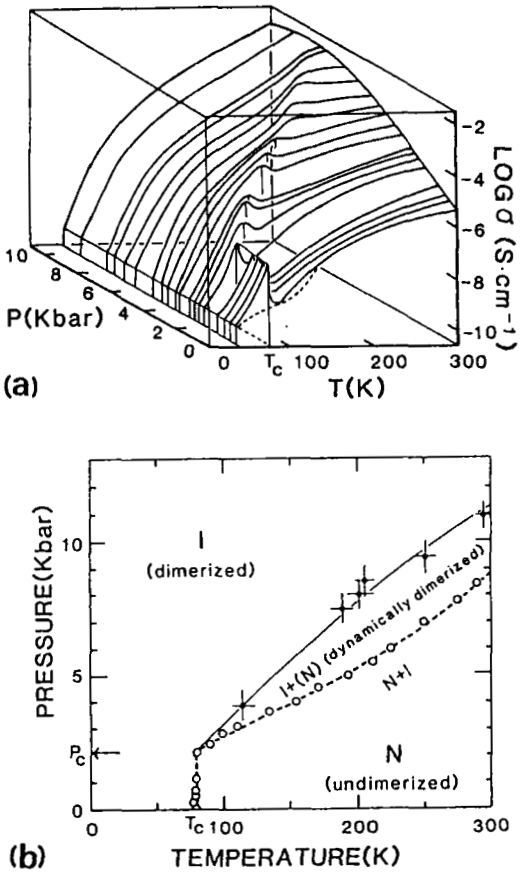


FIGURE 1 (a) A stereographic plot of temperature-dependent electric conductivity σ (P,T) of TTF-*p*-chloranil crystal at various pressure. (b) Experimental phase diagram for the N—I phase transition obtained by projection of the σ (P,T) on the P—T plane. Filled circles present the phase boundary between the dimerized ionic phase and the weakly (or dynamically) dimerized ionic phase detected by infrared molecular vibration spectra.

a prototype of mixed-stacked CT complex, TTF-*p*-chloranil crystal, and its phase diagram are presented as a function of temperature and pressure.[15] Since the neutral and ionic molecules coexist near the interface as shown in Figure 1(a), the anomalous properties, e.g. nonlinear transports and switching phenomena due to the negative resistance, are observed. They could not be explained by an individual excitation of electron or hole but can be attributed to the collective excitation of molecules dynamically coupled with the dimerization of D—A pairs, such as charged and spin solitons or N—I domain walls, as the lowest elementary electronic excitation in the strong electron-lattice-coupling system.[13-18]

Introducing the H-bonding interaction into the CT lattice, another possible phase transition associated with the positively charged proton transfer is expected to exist.

The effect of H-bonding on the electrical conductivity of a series of aromatic acids has been experimentally pointed out by Gravatt and Gross.[19] Matsunaga and Saito have demonstrated the significant contribution of the H-bonding to the CT electronic states by systematic investigations of the CT complexes.[20] By the recent study of a most typical H-bonded CT complex, crystalline quinhydrone, a new phase transition was discovered upon application of hydrostatic pressure,[21] associated with the proton-transfer reaction as $QH_2 + Q \rightarrow QH^- + QH^+$. From the optical and vibrational spectroscopies of this crystal, it was found that the proton and electron transfers were found not to be independent but cooperative through the CT interaction, and also that the proton tunneling plays an essential role in the dynamic properties of the phase transition. Analysis of such experimental data not only provides us with fundamental knowledge for understanding the cooperative phenomena of electron and proton transfer in H-bonded crystals but also has led to some suggestions for the molecular design of "protonics" in the double-well potential system, which includes non-linear optics,[22] proton-transfer-assisted transport,[23] a new mechanism of superconductivity,[24-26] magnetism, and ferroelectricity.

The hydrogen bonding introduced in the CT lattice should be a unique phonon system strongly coupled with the electron system, having a high vibrational frequency well isolated from other phonons. Particularly, when the regular arrangement of protons melts due to the presence of the proton tunneling motion as discussed later in detail, the "protonic" phonons could be propagating in the lattice with a large amplitude between a double-well potential minima. If conductive electrons are introduced in this system by chemical doping or some modification, one would expect a coherent propagation of electrons and the "protonic" phonons, which is quite different from the normal transport mechanism previously developed in organic crystals. In any case, it is essential to establish how to control the dynamical motion of protons in the crystalline state from the microscopic point of view. In the next section, the fundamental research of this subject will be illustrated, using the experimental results on the inter- and intra-molecular proton-transfer in quinhydrone CT complex and some derivatives of *N*-salicylideneaniline, respectively, and then several related topics will be discussed.

CONTROL OF THE H-BONDING BY THE CT INTERACTION

Inter-molecular proton transfer.[21] The crystal structure of the quinhydrone CT complex composed of hydroquinone (QH_2) as a D molecule and *p*-benzoquinone (Q) as an A molecule is characterized by two separate linear chains; the H-bonded D—A chain along the [120] direction and the mixed-stacked D—A chain along the [100] CT axis (Figure 2). When our attention is focused on the H-bonding, the H-bonded D—A chains is considered to form the 2-dimensional proton lattice via the interchain-CT interaction. There exist two different modes of packings of the molecular sheets in crystals; in the triclinic form, all the molecular sheets are stacked with the H-bond axes parallel to each other, and in the monoclinic system, the sheets are piled with the orientation of H-bond axis alternating (see the inset of

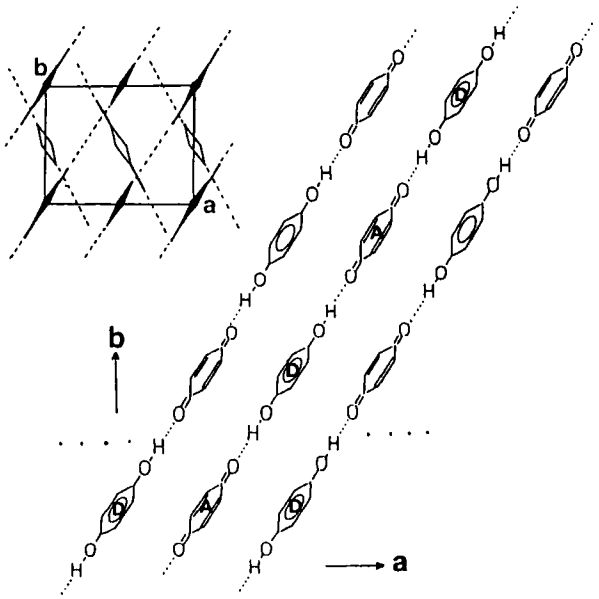


FIGURE 2 Schematic molecular sheets in the [001] plane of monoclinic quinhydrone crystal.

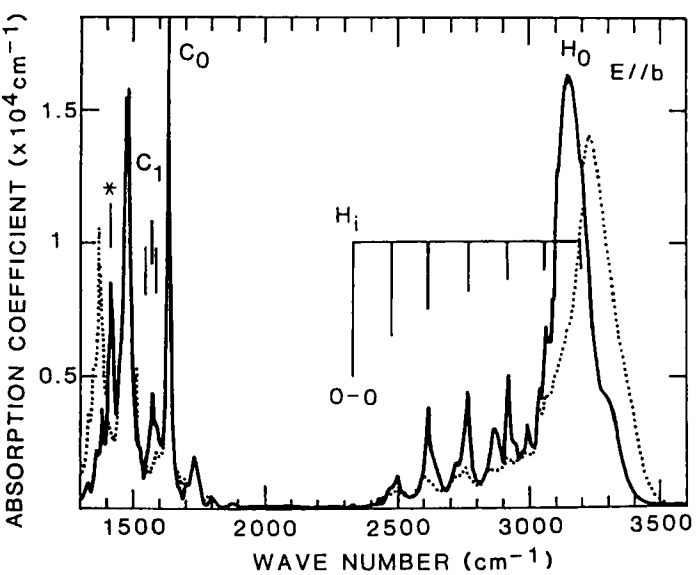


FIGURE 3 The polarized IR absorption spectra of monoclinic quinhydrone single crystal parallel to the *b* axis at 10 K (solid lines) and 300 K (broken lines).

Figure 2). In Figure 3, the vibrational absorption spectra of the monoclinic form are shown, in which the main band, H_0, and the multistructure band, H_i, are located in the energy region of the O—H stretching vibrational mode (2300–3300 cm^{-1}), and the sharp peak, C_0, and the satellite structure, C_1, in the C=O stretching region. These characteristic O—H and C=O vibrational structures can be used as a microscopic probe for investigation of the dynamics of the proton, as described below.

When pressure is applied, the energy of the C_0 vibration shifts to a low energy as shown in Figure 4 (a). This indicates that the degree of the π-electron transfer from D to A molecules increases due to the increase of the Madelung energy in the D—A lattice, as observed in the typical CT complex, TTF-*p*-chloranil.[11] The ionicity of molecules can be estimated from the simple CT model[27] to be 30% under ambient pressure. By increasing pressure, it changes to ca. 50%, where the C_0 and C_1 structures coexist, and then the C_0 band disappears. These changes of C=O mode are accompanied by similar changes in the O—H stretching mode under pressure (Figure 4 (b)). The main H_0 band, which is assigned to the asymmetric O—H stretching vibration, disappears by applying pressure. In return, the multiband structures are strongly enhanced, and transforms into the broad band, H_1. This correlation between the C=O and O—H vibrational modes suggests the presence of the strong coupling between the protonic vibration and the π-electron system, promoting the phase transition associated with proton transfer.

Such π-electron transfer between D—A molecules should influence the nature of the hydrogen bonding. Hasegawa *et al.* carried out a quantitative investigation

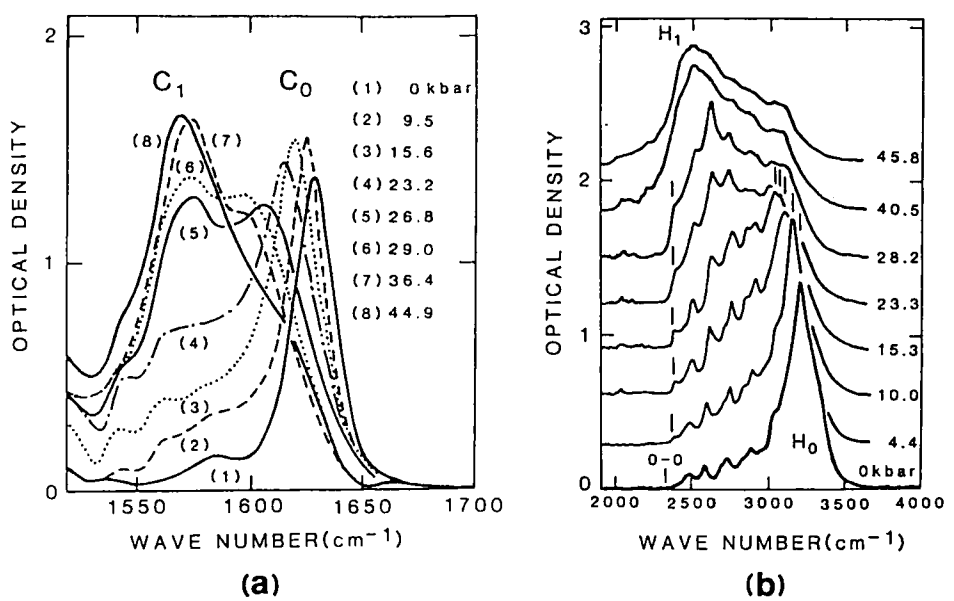


FIGURE 4 The pressure dependences of unpolarized absorption spectra of monoclinic quinhydrone crystals at 300 K in the energy region of (a) C=O and (b) O—H stretching modes.

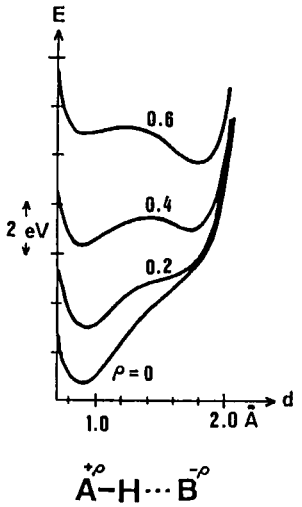


FIGURE 5 The excess π-electron effect on the double-well potential calculated by Hasegawa *et al.* (Reference 7).

of the excess charge effect on potential energy of the molecular system consisting of "A—H···B" atoms, the intraatomic distance of which (A···B = 2.7 Å) is comparable to the O···O distance in quinhydrone crystals.[7] Their result is reproduced in Figure 5. Here the excess $\rho = \rho_D = -\rho_A$ is varied from 0 to 0.6 and the concomitant charge is illustrated. At the neutral state, $\rho_{D,A} = 0$, the double well potential is fairly asymmetric, so that a proton is well localized in one of minima of the potential. The observation of the strong H_0 band as shown in Figure 4(b) corresponds to this case. When the degree of the electron transfer approaches 50%, the potential becomes symmetric, and then the proton is supposedly delocalized due to the increase of the proton tunneling between two minima. This should lead to an increase in the interaction of the asymmetric A—H vibration with the symmetric A—H···B vibration, whose frequency is usually of the order of 100 cm^{-1}.[28] In the case of quinhydrone crystals, the fine structure of the H_i band was found to coincide the energy of the O—H···O vibrations by using polarized synchrotron radiation spectroscopy.[29] Thus, the increase of intensity of the H_i multistructures in quinhydrone crystals may be attributable to the enhancement of such an interaction by increase of the proton tunneling probability. The phase transition characterized by the transformation from the C_0 to C_1 or from the H_0 to H_1 structures is considered to be driven by the proton tunneling assisted by the increase of excess charge of the π-electron. In other words, the periodical regular arrangement of protons as illustrated in Figure 2 undergoes quantum-mechanical melting as the effective Madelung energy increases. More sophisticated analysis of this melting phenomena has been made by using the effective Ising Hamiltonian developed by Zinenko,[30] introducing the effective electrostatic energy and the stabilization energy of the O—H bonding via the CT interaction in the 2-D lattice.[21]

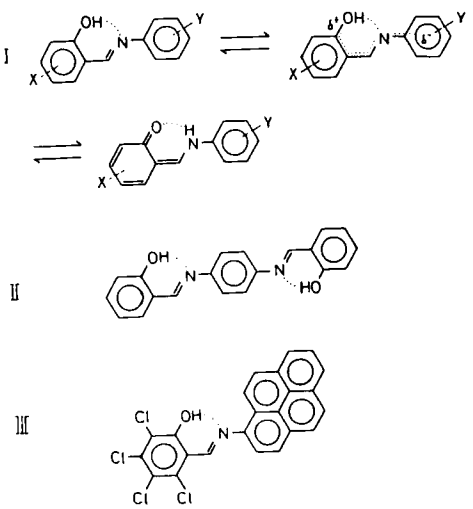


FIGURE 6 Proton transfer in salicylideneanilines (I) and molecular structures of BSP (II) and Cl_4SAP (III).

Intra-molecular proton transfer. The *N*-salicylideneaniline crystal shows photochromism; on irradiation of near UV light, a color change takes place by the self-isomerization through intra-molecular proton transfer from hydroxyl oxygen to imine nitrogen (I in Figure 6).[31] The reverse reaction, i.e. fading of the color, does not occur without irradiating with visible light or heating, indicating that the quantum-mechanical or thermal proton transfer in the H-bonded double well potential is negligible at room temperature. In the case of the derivative of this molecule, *N,N'-bis*(salicylidene)-*p*-phenylenediamine (BSP), which has a symmetric and planer molecular structure (II in Figure 6), lowering the energy difference of the two minima of the double-well potential leads to the observable thermochromism.[32] From the results of the time-resolved spectroscopy,[33] it has been proposed that the thermochromism or photochromism is induced via the intramolecular CT states as an intermediate state in the thermal or optical excitations. This implies that it is rather easy to control the proton transfer by replacing the *X* and *Y* portions of salicylideneaniline by *A*- and *D*-like large molecules. Following this idea, a number of thermochromic derivatives have been recently synthesized by Inabe *et al.*[34] For example, *N*-tetrachlorosalicylidene-1-aminopyrene (CL_3SAP) is presented by III in Figure 6, whose crystal structure and Fourier map with regard to the H-bonded chelate ring at room temperature are illustrated together with those of BSP for comparison in Figure 7(a) and (b).

It is interesting to note that *D*-like pyrene and *A*-like *o*-chloranil moieties of the CL_4SAP molecule are alternately stacked along the *c*-axis in a manner similar to usual mixed-stacked CT complexes. The mean interplanar spacing of this molecular stack is ca. 3.37 Å, which is indeed shorter than the mean separation of 3.46 Å in pyrene-*p*-chloranil CT complex, suggesting that this CT crystal is more stabilized

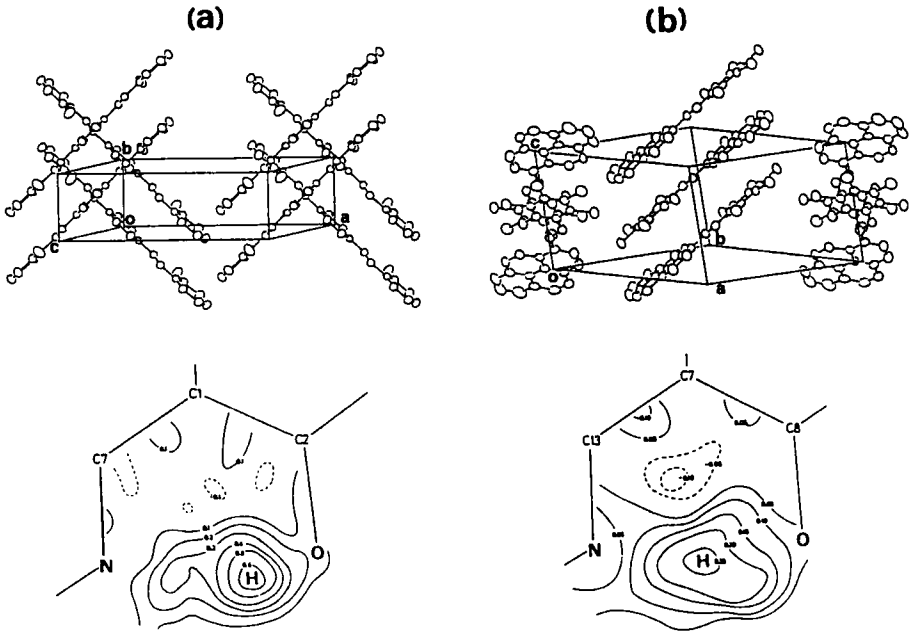


FIGURE 7 The crystal structures and Fourier maps of the H-bonded chelate ring of (a) BSP and (b) Cl_4SAP.

by the intra-molecular CT interaction via the O—H···N interaction. Actually, the O···N distance is as short as 2.53 Å, which is considerably smaller than those of the normal O—H···N bondings in the range of 2.7–2.9 Å.[28] Furthermore, as seen in the Fourier map of Figure 7(b), the hydrogen is mostly located near the center of the hydrogen bond. This situation can be regarded as a case of proton tunneling with extreme high frequency, possibly as a result of cooperation of the intra- and inter-molecular CT interactions. On the other hand, in the case of BSP having a slightly longer O···N distance of 2.61 Å, two minima of the double well potential can be observed in the Fourier map; the O=H···N and O···H=N structures coexist. It has been confirmed from the temperature-dependences of the optical absorption spectra[32] and the NMR signals[35] that the latter state is thermally populated at ambient temperature. Even if the thermal excitation of protons is thoroughly suppressed by lowering temperature, however, the O—H vibrational band does not show sharpening but remains broad and located at a low frequency around 2500 cm^{-1}. This state of matter is similar to the quantum-mechanically melted state of the proton lattice found in the case of quinhydrone crystal. This implies that the periodical arrangement of protons in the BSP crystal is already lost due to the presence of a finite but small probability of the proton tunneling even at ambient pressure, since the inter-molecular proton–proton interaction is considered not to be so large in this molecular crystal.

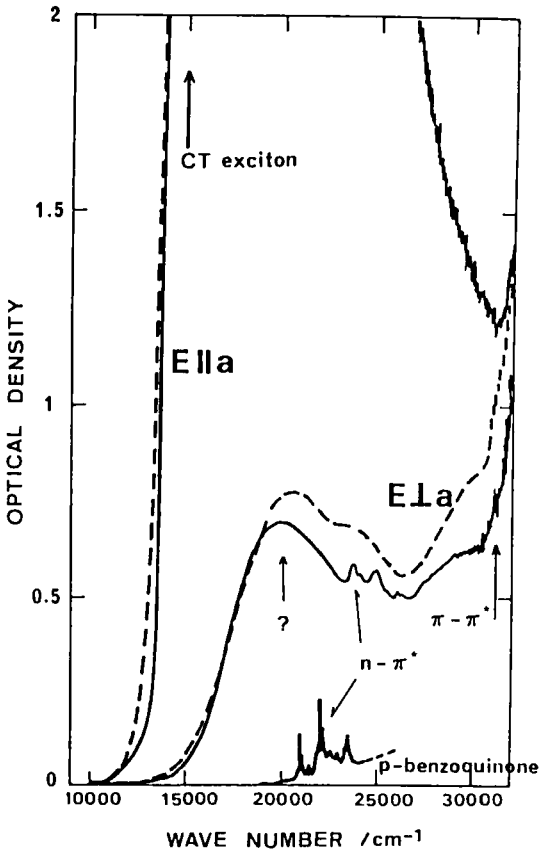


FIGURE 8 The polarized absorption spectra at 10 K (solid curves) and 300 K (broken curves). In a lower part, the polarized absorption spectrum of *p*-benzoquinone crystal parallel to the *p*-axis at 20 K is reproduced (Reference 36).

TOPICS OF THE PROTON TRANSFER IN THE CT CRYSTAL

Proton-linked super-CT transitions. In Figure 8, the polarized absorption spectra of monoclinic quinhydrone crystal at 5 K are presented.[29] The weak fine structures with three peaks around 2500 cm^{-1} can be assigned to the $n-\pi^*$ transitions, and the sharp rise at ca. 32,000 cm^{-1} to the intramolecular $\pi-\pi^*$ transitions in *p*-benzoquinones.[36] Below these transitions, a broad band is observed around 20,000 cm^{-1}, which is absent in the spectra of individual constituent molecules, and its tail extends to about 10000 cm^{-1}, although it is not clear in this figure. A possible assignment of this band is a super-CT transition from QH_2 to Q molecules via the hydrogen bonding. Such a possibility has been suggested on the basis of Mulliken's CT theory about 20 years ago, but it has not been identified before. As expected from the crystal structure of the monoclinic form, this transition is polarized perpendicularly to the CT axis and definitely distinguishable from the strong CT

transitions parallel to the CT axis. When pressure is applied, i.e. increasing the proton tunneling, the intensity of the super-CT transitions is remarkably enhanced and the absorption tail reaches a low energy of ca. 6000 cm^{-1}. This transition is analogous to the halogen-linked super-CT exciton in halogen-bridged platinum compounds,[37] if protons are replaced by halide ions. In these compounds, the energy and intensity of the super-CT exciton are dependent on the position of the bridging halide ions between the two platinum atoms. This behaviour has been theoretically explained by Nasu using the 1-D extended Peirls-Hubbard model.[38] It should be noted here that the position of halogen ions is stable but the proton quantum-mechanically moves between the two minima. Thus, if the same model is applied to "proton-bridged" species, the spatial distribution of protons spreaded by the proton tunneling effect would be reflected in the spectral shape of the super-CT transitons. This might be responsible for the observation of the long tail of the super-CT band of quinhydrone crystal. The peak position of the super-CT transitions is located in the same energy region of the normal CT transitions, which may be reasonable assuming considerable mixing of the π-electrons and the lone-pair electrons involved in the H-bonding, as numerically demonstrated in some complexes.[6]

There is a good common feature between such a super-CT transition in the (QH_2, Q) molecular pair and the thermochromism observed in the intra-molecular H-bonded molecules. The thermochromic change and emission spectra of BSP are shown in Figure 9 over a wide temperature range (4–293 K). At the lowest temperature is observed a sharp rise of absorption around 2.8 eV, which is assigned

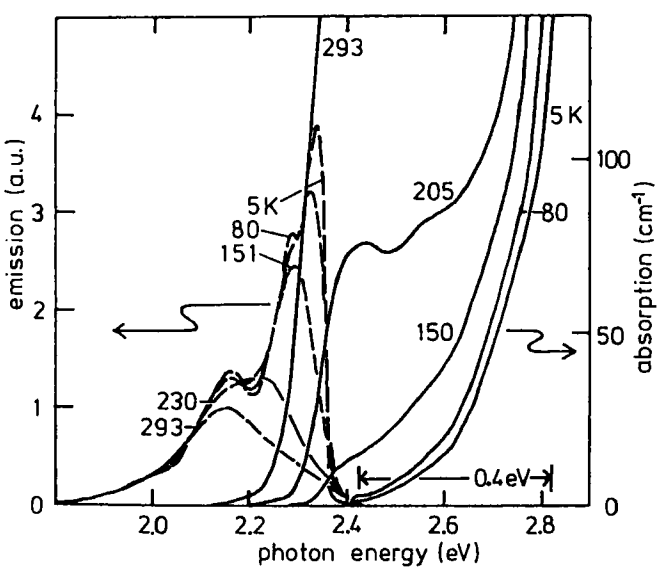


FIGURE 9 The absorption (solid curves) and emission spectra (broken curves) of BSP crystal at various temperatures.

to the $\pi-\pi^*$ transitions. With increasing temperature above 100 K, a broad band appears around 2.4 eV, and subsequently its intensity remarkably increases. This band has been assigned to the $\pi-\pi^*$ transitions from the excited states resulting from the thermal proton transfer onto imine nitrogen sites.[31] On the basis of the CT transition model as illustrated by I in Figure 6, however, this transition can also be regarded as the intra-molecular super-CT transitions. Namely, the transition takes place directly from the ground state to the CT states coupled by the super-transfer integral via protons. At low temperatures, the thermal excitation of protons might be quenched, but there remains a temperature-independent transition considerably below the $\pi-\pi^*$ transition, which starts at 2.4 eV coincident with the edge of the emission band. Thus, this band might be attributable to the intra-molecular super-CT transitions allowed by the presence of a finite amount of the quantum-mechanical tunneling, as suggested from the vibrational study presented above. Roughly speaking, the thermochromic spectral change with increasing temperature presented in Figure 9 seems to reflect the change from the temperature-independent spatial distribution of protons in the double-well potential to that induced by the thermal excitation. Improved CT-coupling in the *D*- and *A*-like moieties in CL_4SAP is expected to yield an enhancement of the temperature-independent super-CT transitions; which has been experimentally confirmed.[34]

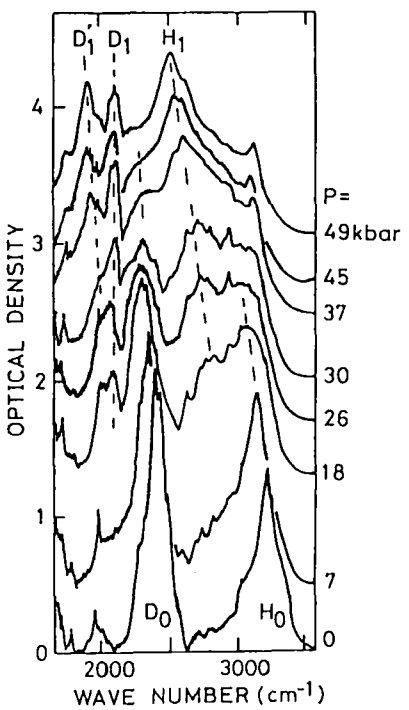
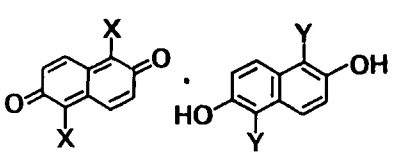


FIGURE 10 Pressure dependence of the unpolarized absorption spectra of the O—H and O—D vibrational modes in the 85% deutrated quinhydrone crystal at 300 K.

The isotope effect in the proton tunneling.[21] As mentioned above, there are two types of melting of the regular arrangement of protons, thermally or quantum-mechanically. One of more direct methods to specify these processes is one using the isotope effect on the vibrational spectra. Our results on 85% deuterated quinhydrone crystal are shown in Figure 10, in which distinction between the O—H and the deuterated O—D stretching modes under hydrostatic pressure is clear. After the melting of the proton lattice around 25 kbar, the O—D vibrational band splits into two sharp bands, D_1 and D_1'. The magnitude of splitting increases with increase of pressure, which may be attributable to increase of an energy difference of the double-well potential minima for $\rho > 0.5$ in Figure 5. For the case of the H-bonded species, such a splitting is smoothed out by the quantum fluctuation of protons between the minima to give a broad line shape to the H_1 band.

Further modification of the inter-molecular proton transfer. As an extension of our study of the cooperative phenomena observed in quinhydrone crystals, naphthoquinhydrone complexes composed of naphthohydroquinone and naphthoquinone Figure 11) have been newly synthesized by Nakasuji *et al.*[39] These complexes have similar H-bonded mixed-stacked CT chains with the same O···O bond distance of 2.71 Å. In spite of a slight increase of the inter-planar spacing, the excitation energy of the CT exciton is considerably lowered by an amount of ca. 0.3 eV by reduction of the HOMO-LUMO gap of the complex due to the delocalization of the conjugated π-electrons. The aim of this modification is to reveal the phase transition associated with the proton transfer without an application of presure. Preliminary experimental data including the vibrational structures in the C=O and O=H modes indicate that the proton transfer easily takes place compared with the case of quinhydrone, and provide a suggestion for realizing an additional reaction in solids, which can be expressed by the type of $QH_2 + Q \rightarrow 2\dot{Q}H$ with a simultaneous and discontinuous transfer of an electron and a proton into the neutral molecules. It is apparently similar to the reaction, $QH_2 + Q \rightarrow QH^- + QH^+$, if a large transfer integral between QH^+ and QH^- molecules exists. By reduction of the transfer integral, however, an essential difference may be induced between them; the $\dot{Q}H$ system may give rise to a phase transition into the Spin-Density-Wave state, in which the magnetic gap always exists. This phase is quite attractive since it is expected to show a unique magnetism coupled with the proton transfer. Thus the chemical modifications along this line may be promising, and further work is now in progress.



X,Y = Cl,Br,CH_3

FIGURE 11 Molecular structures of naphthoquinhydrone complexes.

Acknowledgments

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References

1. N. D. Sokolov, *Dokl. Akad. Nauk. SSSR*, **58**, 611 (1947).
2. L. Pauling, *J. Chim. Phys.*, **46**, 435 (1949).
3. K. Nukasawa, J. Tanaka, and S. Nagakura, *J. Phys. Soc. Jpn.*, **8**, 792 (1953).
4. H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **27**, 445 (1954).
5. P.-O. Löwdin, *Rev. Mod. Phys.*, **35**, 724 (1963).
6. R. Rein and F. E. Harris, *J. Chem. Phys.*, **41**, 3393 (1964); **42**, 2177 (1965); **43**, 4415 (1965); **45**, 1797 (1966).
7. M. Hasegawa, K. Daiyasu, S. Yomosa, *J. Phys. Soc. Jpn.*, **27**, 999 (1969); **28**, 1304 (1970).
8. A. Igawa and H. Fukutome, *Bull. Chem. Soc. Jpn.*, **47**, 34 (1974).
9. See for example, *Extended Linear Chain Compounds*, ed. by J. S. Miller (Plenum, New York, 1982) Vol. 1–3.
10. H. M. McConnell, B. M. Hoffman, and R. M. Metzger, *Proc. Natl. Acad. Sci.* U.S.A., **53**, 46 (1965).
11. J. B. Torrance, A. Girlando, J. J. Mayyerle, J. I. Crowley, V. Y. Lee, P. Batail, and S. J. LaPlaca, *Phys. Rev. Lett.*, **47**, 1747 (1981).
12. Y. Tokura, T. Koda, T. Mitani, and G. Saito, *Solid State Commun.*, **43**, 757 (1982).
13. T. Mitani, G. Saito, Y. Tokura, and T. Koda, *Phys. Rev. Lett.*, **53**, 842 (1984).
14. Y. Kaneko, S. Tanuma, Y. Tokura, T. Koda, T. Mitani, and G. Saito, *Phys. Rev.*, **B35**, 8024 (1987).
15. T. Mitani, Y. Kaneko, S. Tanuma, Y. Tokura, T. Koda, and G. Saito, *Phys. Rev.*, **B35**, 427 (1987).
16. H. Okamoto, T. Komatsu, Y. Iwasa, T. Koda, Y. Tokura, S. Koshihara, T. Mitani, and G. Saito, *Synthetic Metals*, in press.
17. Y. Tokura, H. Okamoto, T. Koda, T. Mitani, and G. Saito, *Phys. Rev.*, **B** in press.
18. N. Nagaosa, *J. Phys. Soc. Jpn.*, **55**, 2757 (1986); **55**, 3497 (1986).
19. C. C. Gravatt and P. Gross, *J. Chem. Phys.*, **46**, 413 (1967).
20. Y. Matsunaga and G. Saito, *Bull. Chem. Soc. Jpn.*, **44**, 958 (1971).
21. T. Mitani, G. Saito and H. Urayama, *Phys. Rev. Lett.*, **60**, 2299 (1988).
22. T. W. Barrett, *Energy Transfer Dynamics* (ed., by T. B. Barrett and H. A. Pohl, Springer-Verlag, 1987) pp. 24–48.
23. A. S. Davydov, *Solitons in Molecular Systems* (D. Reidel, Dordrecht, 1985), Chap. 12, pp. 227–241.
24. A. S. Davydov, *phys. stat. sol. (b)*, **146**, 619 (1988).
25. N. M. Plakida, V. L. Aksenov, and S. L. Drechsler, *Int. J. Mod. Phys. B*, **1**, 1071 (1987).
26. T. D. Lee, *Nature*, **330**, 460 (1987).
27. Y. Tokura, H. Okamoto, K. Koda, T. Mitani, and G. Saito, *Solid State Commun.*, **57**, 607 (1986).
28. W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids* (W. A. Benjamin, New York, 1968) Chap. 3, pp. 73–128.
29. T. Mitani and G. Saito, *Synthetic Metals*, in press.
30. V. I. Zinenko, *Phys. Status Solidi*, **B78**, 721 (1976).
31. M. D. Cohen and G. M. J. Schmidt, *J. Phys. Chem.*, **66**, 2442 (1962).
32. N. Hoshino, T. Inabe, T. Mitani, and Y. Maruyama, *Bull. Chem. Soc. Jpn.*, in press.
33. P. F. Barbara, P. M. Rentzepis, and L. E. Brus, *J. Am. Chem. Soc.*, **102**, 2786 (1980).
34. T. Inabe, N. Hoshino, T. Mitani, and Y. Maruyama, to be published.
35. S. Takeda and H. Chihara, private communication.
36. J. W. Sidman, *J. Chem. Phys.*, **78**, 2363 (1956).
37. Y. Wada, T. Mitani, M. Yamashita, and T. Koda, *J. Phys. Soc. Jpn.*, **54**, 3143 (1985).
38. K. Nasu, *J. Phys. Soc. Jpn.*, **52**, 3865 (1983); **53**, 302 (1984).
39. K. Nakasuji, H. Yamamoto, and I. Murata, to be published.