Cooperative Phenomena Associated with Electron and Proton Transfer in Quinhydrone Charge-Transfer Crystal

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Studies of the IR vibrational spectroscopy of single crystals of the H-bonded quinhydrone charge-transfer complexes show that a new phase transition occurs upon application of hydrostatic pressure, associated with the proton transfer in the 2D proton lattice. The temperature- and pressure-induced changes in the $O-H$ vibrational spectra are accounted for in terms of the melting of the proton lattice due to the proton tunneling effect.

The quinhydrone charge-transfer complex composed of hydroquinone (QH_2) as a donor (D) and p-benzoquinone (Q) as an acceptor (A) shows a reversible redox reaction in solution, in which proton transfer takes place coupled with electron transfer.[1] The crystal structure of this complex is characterized by two sublattices, the 2D hydrogen-bonded lattice and the 1D charge-transfer (CT) mixed-stacked molecular lattice.[2] When the temperature is reduced or when pressure is applied, some quasi-1D mixed-stacked CT complexes undergo a phase transition associated with the electron transfer between D and A molecules induced by the increase of the Madelung energy of the lattice.[3-7] In the H-bonded quinhydrone crystals, another pressure-sensitive interface associated with the proton transfer is expected to exist,[1] which is supposedly cooperative with the electron transfer. This provides a unique opportunity for the study of the dynamics of the 2D proton lattice coupled with the electron transfer and for our experimentally testing the possibility of the order-disorder transition of the proton lattice as discussed from theoretical[8] and experimental points of view.[9] General interest in the hydrogen bonding of crystalline organic materials has been recently stimulated by the observation of the "anomalous" IR absorption peaks and the multiband structure in the $N-H$ stretching mode of acetanilide.[10,11]

In this Letter, attention is concentrated on the $C=O$ and $O-H$ vibrational modes of quinhydrone, which are particularly sensitive to temperature and pressure. The temperature dependence of the $O-H$ spectra of quinhydrone crystals exhibits a number of characteristics analogous to those of acetanilide, and the pressure-dependent spectra provide more information on the proton-proton interaction in the H-bonded lattice. Especially noted is that the isotope effect on the hydrogen bonding is clearly manifested in the $O-H$ (or $O-D$) vibrational spectra at high pressures, where the proton-tunneling effect con-

tributes to the melting of the 2D proton lattice.

The absorption measurements under hydrostatic pressure were performed by use of a diamond-anvil high-pressure cell.[12] The thin-flake quinhydrone crystals used in the measurements were crystallized in a monoclinic form from a methanol-toluene solution.[2] In Fig. 1, the polarized IR absorption spectra parallel to the b axis at 10 and 300 K are presented. From the characteristic temperature dependence of the $O-H$ vibrational spectra in the frequency region of 2400–3500 cm^{-1}, it was found that the spectra are composed of two separate bands; the strong broad band, H_0, located at 3230 cm^{-1} at 300 K, which has been assigned to the $O-H \cdots O$ asymmetric stretching mode,[13] and the multistructure band, H_i, in the energy range of 2350–3200 cm^{-1}. The
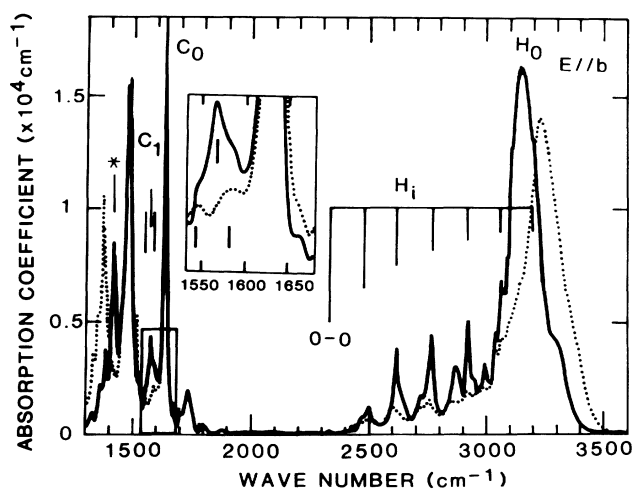

FIG. 1. Polarized IR absorption spectra of quinhydrone single crystal parallel to the b axis at 10 (solid lines) and 300 K (broken lines). Inset: Magnified spectra in the region of the C_0 and C_1 bands.
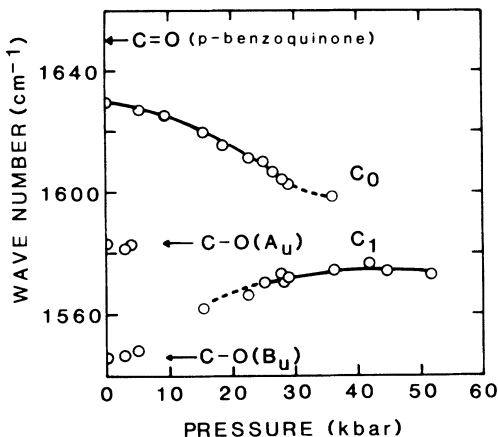
FIG. 2. Peak positions of the IR spectra associated with C=O stretching mode in quinhydrone crystal as a function of pressure. The positions of the A_u and B_u C—O stretching modes are indicated by arrows.

FIG. 3. Pressure dependence of the unpolarized absorption spectra of the O—H stretching mode in quinhydrone single crystal at 300 K.

former band shifts to lower frequency by 80 cm^{-1} (3230 cm^{-1} at room temperature) on lowering of the temperature to 10 K, while the peaks of the H_i multistructure band slightly shift to higher frequency with an almost constant spacing of about 145 cm^{-1} and the intensity of the peaks increases considerably. This structure is attributable to the phonon side band due to the O—H $\cdots$ O symmetric stretching mode.[13] In the frequency region of the C=O stretching mode, the main band, C_0, is observed at 1630 cm^{-1} with two weak shoulderlike structures at frequencies of 1582 and 1545 cm^{-1}. The latter peaks have been assigned to the A_u and B_u vibrational modes of the C—O stretch.[13] If we lower the temperature, the vibrational spectrum in this region is considerably altered, and a new band, C_1, appears at 1566 cm^{-1} as shown in the inset. In the frequency region of the O—H $\cdots$ O bending mode, another new band was observed at 1415 cm^{-1} indicated by an asterisk.

At pressures below 10 kbar, the C=O stretching mode showed quite similar behavior to that observed by the lowering of the temperature. As the pressure is increased further, the intensity of the C_1 band goes up, and eventually exceeds that of the C_0 band at pressures above 25 kbar. At even higher pressures, only the C_1 band is apparent. The positions of the C_0 and C_1 bands also depend on the pressure as shown in Fig. 2. The C_0 band shifts to a lower energy until it disappears at about 40 kbar, suggesting that the CT lattice becomes more ionic from ca. 30% to 60%, which can be estimated from the charge-transfer model.[6] The C_1 band shows a rather slight high-energy shift up to about 52 kbar. The transformation from the C_0 to C_1 bands is discontinuous and both phases coexist in the wide pressure region between 10 and 30 kbar.

The spectral change in the C=O mode clearly has parallels in the profiles of the O—H vibration under pres-
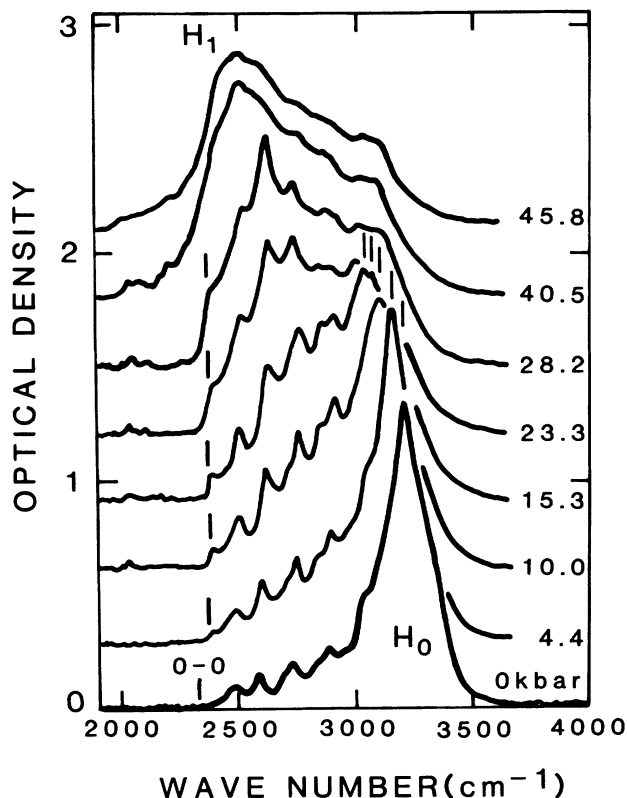
sure, as presented in Fig. 3. The evident spectral change at low pressure is the shift of the H_0 band, which is similar to the temperature-induced shift shown in Fig. 1. If the magnitude of the shift is assumed to be due to the shortening of the O $\cdots$ O bond length,[14] the change in the bond length up to 10 kbar should be about 0.03 Å, which is a small perturbation for the considerably long bond (2.71 Å).[2] However, the intensity of the H_0 band starts to decrease beyond this pressure and it seems to disappear around 40 kbar. Meanwhile, the vibronic structures, H_i, grow with increasing pressure and eventually become a broad band, H_1, around 30 kbar. The total oscillator strength of the O—H vibrational modes is almost constant under the transformation.

A possible interface of charge transfer associated with the positively charged proton transfer in the quinhydrone crystal is schematically described in Fig. 4, neglecting the electron-transfer energy along the CT axis, T, and the proton-tunneling energy, Γ, in the hydrogen bonding. The intermolecular transfer of protons takes place accompanied by a rearrangement of the electronic configuration of the Q molecules into the ionic state. This phase separation can be characterized by the competition of two main interactions; (a) the net dissociation energy of protons from QH_2 to Q molecules, E_d,[1] and (b)
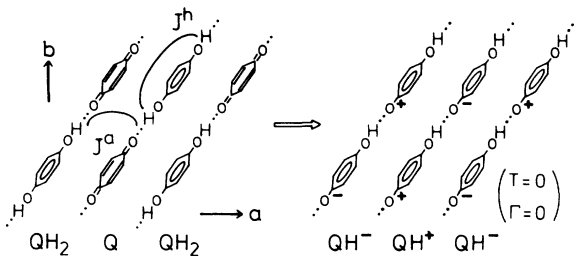
FIG. 4. Schematic molecular sheets in the (001) plane of the quinhydrone (QH_2, Q) crystal under pressure.

the electrostatic Madelung energy of the ionized lattice. The energy difference between the two phases for the N (QH_2,Q) molecular pairs may be given as $E = -N(E_d - M)$, where M is an averaged Madelung energy per molecular pair. The two molecular sheets presented in Fig. 4 form the degenerate ground states at $E_d = M$. If we take into account the contribution of T, the nature of the interface might be considerably modified, because electron and proton charge transfers may not be independent. With this contribution in mind, introduction of effective energies of E_d and M is now possible.

On the basis of the model mentioned above, the phase transition observed in the quinhydrone crystal under pressure can be qualitatively understood by the double-well potential of the hydrogen bond in the mean-field approximation. At atmospheric pressure, the potential is considered to be asymmetric because of the large energy difference $E_d - M$, where the proton tunneling between the two minima is supposed to be quite small. However, the protons can move in the almost symmetric potential well when the magnitude of $E_d - M$ approaches zero by application of pressure. The characteristic change in the O—H vibrational spectra leads us to prove the presence of such a proton-tunneling field. The intensity of the fine structure of the H_i band, which is viewed as the phonon side band associated with the proton-transferred O—H vibration, increases with decrease of $E_d - M$, and the O—O band at high pressure coincides with the absorption edge of the broad H_1 band, as shown in Fig. 3. Such an enhancement of the coupling of the O—H stretching mode with the O—H $\cdots$ O symmetric stretching vibration indicates a delocalization of protons due to the proton tunneling between double-well minima. Near $E_d - M = 0$, the multistructure band H_i transforms to the H_1 band, presumably being affected by coupling with other vibrational modes. The spectral shape after the transformation resembles those observed in the H-bonded species in solution.[15]

In order to confirm the presence of the proton-tunneling field, the hydrogen isotope effect under hydrostatic pressure was investigated. The sample was 85% deuterated to permit a direct comparison of the pressure dependence of the O—H and O—D spectra recorded to-
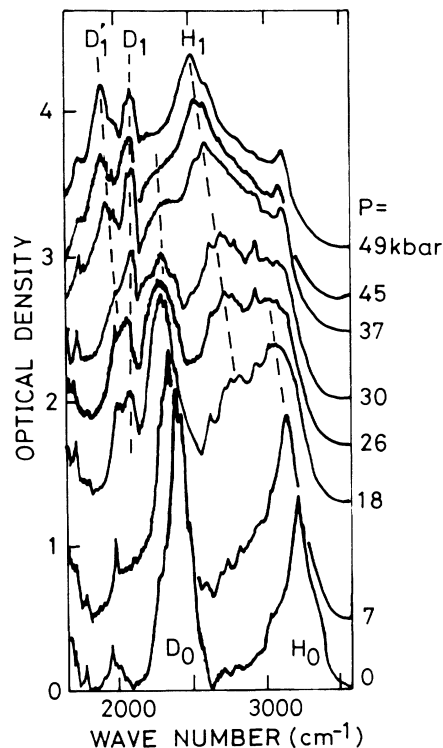

FIG. 5. Pressure dependence of the unpolarized absorption spectra of the O—H and O—D stretching modes in the 85% deuterated quinhydrone crystal at 300 K.

gether. As shown in Fig. 5, with respect to the O—H vibration of the remaining undeuterated species, the behavior of the H_0 band under pressure behaves in almost the same manner as in pure quinhydrone. The O—D vibration band in the deuterated species, D_0, clearly disappears at high pressures. An appreciable isotope effect is observed in the D_1 band above the critical pressure, $P_c \simeq 25$ kbar, which may correspond to a pressure for $E_d = M$. Above P_c, the D_1 band splits into two sharp bands, D_1 and D_1', and the splitting gradually increases with increasing pressure. Its magnitude is about 200 cm^{-1} at the highest pressure (49 kbar), which is attributable to the difference of the double-well potential minima for deuterated species in $E_d - M < 0$. For the case of the H-bonded species, such a splitting could not be observed because of the tunneling motion of the proton, indicating a quantum melting of the hydrogen-bonding lattice. On the other hand, the observation of the splitting in the deuterated species suggests the thermal melt or disordering of the host lattice.

A more sophisticated description of the proton-transfer–induced phase transition is given by the Ising-model Hamiltonian,[8] $H = -\frac{1}{2}\sum_{ij}J_{ij}^{h,a}S_i^z S_j^z - \Gamma\sum_{ij}S_i^x$. Here, J_{ij}^h and J_{ij}^a are the effective interactions between nearest-neighbor protons along the direction of the O—H bonding and the CT axis, respectively. J^h is approximately given by $-(E_d - M)$ and J^a, which corresponds
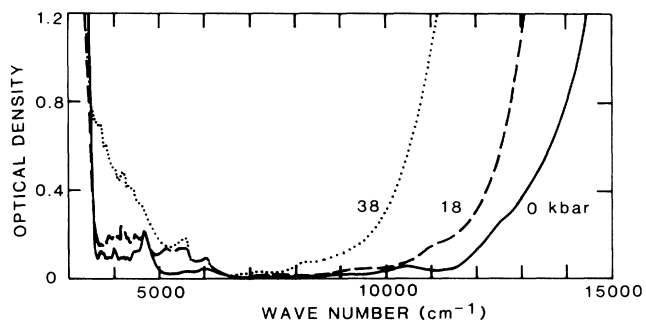
FIG. 6. Pressure dependence of the unpolarized absorption spectra near the edge of the CT exciton in quinhydrone single crystal at 300 K.

to the stabilization energy of the CT coupling along the a axis, and may be expressed in terms of an antiferroelastic coupling, $-T^2/E_{CT}$, where E_{CT} is the lowest excitation energy of the CT exciton. If the proton-tunneling frequency, Γ, is larger than the magnitudes of J^a and J^h, the lattice will melt. The antiferroelastic coupling constant J^a is estimated to be about 250 cm^{-1} by use of the values $E_{CT} \simeq 16000$ cm^{-1},[16] and $T \simeq 2000$ cm^{-1}.[5] Thus, near P_c $(E_d - M \simeq 0)$, the magnitude of the proton-tunneling frequency is considered to be more than 250 cm^{-1}, which satisfies the condition for the smoothing of the fine-structure splitting of the H_1 band even at the highest pressure (see Fig. 5). Finally, the pressure dependence of the electronic spectra near the edge of the CT exciton is shown (Fig. 6) for a demonstration of the melting effect on the electronic states, in which the edge of the CT exciton having a long absorption tail shows a fairly large shift to low energy. The detailed experimental results concerned with the electronic states will be reported shortly.

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