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Temperature and Pressure Effects on Intermolecular Interactions in Charge Transfer Crystals of 2-(4-Methoxyphenyl)-1,4-benzoquinone and Quinhydrone

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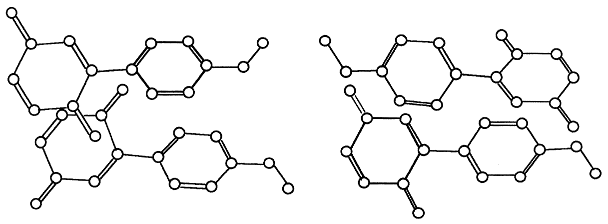
Temperature and pressure effects on the Raman spectra due to the intramolecular vibrations of charge transfer crystals of 2-(4-methoxyphenyl)-1,4-benzoquinone and quinhydrone were studied. In quinhydrone crystals involving the intermolecular charge transfer and the intermolecular hydrogen bonding, the temperature- and pressure-induced frequency shifts of the intramolecular vibrations showed blue and red shifts with decreasing temperature and increasing pressure depending on the vibrational modes. In the yellow crystal of 2-(4-methoxyphenyl)-1,4-benzoquinone involving the intramolecular charge transfer, and in the red crystal involving both the intra- and intermolecular charge transfers, the frequencies of the intramolecular vibrations showed only blue shift with increasing pressure. This blue shift was larger in the yellow crystal than in the red crystal. It was also observed that phase transitions take place under 1.8 and 2.7 GPa in quinhydrone crystal and that the phase transitions take place under 1.5 and 2.5 GPa in the yellow and red crystals of 2-(4-methoxyphenyl)-1,4-benzoquinone, respectively.

The thermal rearrangements of the orientation of molecules due to transition from the yellow to red crystals of 2-(4-methoxyphenyl)-1,4-benzoquinone were studied by many workers.[1–3] It was shown that the difference of the color of crystal is accounted for a difference of the stacking of the molecules in the crystal. The benzoquinone ring overlaps with that of the neighboring molecule (head-to-head stacking) in the yellow crystal, while the benzoquinone ring overlaps with the adjacent methoxyphenyl ring (head-to-tail stacking) in the red crystal as shown in Fig. 1. Since 4-methoxyphenyl is an excellent electron donor and benzoquinone is a fairly good electron acceptor, the intramolecular charge transfer from 4-methoxyphenyl to benzoquinone takes place in the yellow crystal. On the other hand, the intermolecular charge transfer takes place in addition to the intramolecular charge transfer in the red crystal, and intermolecular charge transfer π complex between 4-methoxyphenyl and *p*-benzoquinone is formed.[1–3]

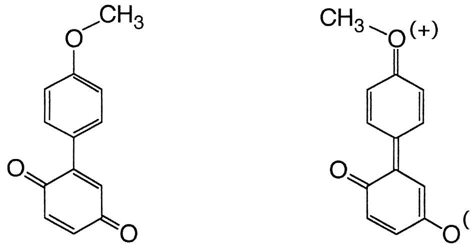
Neutral to ionic phase transition in mixed stacked organic charge transfer compounds was first observed by Torrance et al.[4] They pointed out that the mixed stacked organic charge transfer compounds are either neutral or ionic, while several neutral compounds undergo reversible phase transitions to the ionic ground state under certain pressure.

The quinhydrone charge transfer crystal composed of hydroquinone as a donor and *p*-benzoquinone as an acceptor was studied by many workers.[5–8] It was shown that intermolecular



yellow crystal of *p*-MPB (head to head stacking)

red crystal of *p*-MPB (head to tail stacking)



nonpolar structure of *p*-MPB

polar structure of *p*-MPB

Fig. 1. Molecular structures and packings in the yellow and red crystals of 2-(4-methoxyphenyl)-1,4-benzoquinone (*p*-MPB).

proton transfer coupled with intermolecular charge transfer takes place in quinhydrone crystal, and quinhydrone becomes more ionic compared with other charge transfer complexes where no proton-transfer occurs. Thus a new phase transition from neutral to ionic states takes place in quinhydrone crystal.[8] The mechanism of the new phase transition was discussed through the observation of the pressure effect on the infrared spectrum of quinhydrone crystal.[8]

In this work, temperature and pressure effects on the charge transfer and hydrogen bonding are discussed through the observation of the temperature and pressure effects on the Raman spectra due to the intramolecular vibrations of three types of organic charge transfer complexes: that is, the complexes involving only intramolecular charge transfer, complexes involving both intra- and intermolecular charge transfers, and complexes involving hydrogen bonding in addition to intermolecular charge transfer.

Experimental

Material. 2-(4-Methoxyphenyl)-1,4-benzoquinone (*p*-MPB) was synthesized from *p*-anisidine (Kanto Chemicals) and *p*-benzoquinone (Wako Chemicals) by the method presented by Brassard and L'Écuyer.[9] Yellow crystal of *p*-MPB was obtained by recrystallization of crude sample from benzene–hexane hot solution (1 : 1 in volume ratio). Red crystal of *p*-MPB was obtained by spontaneous evaporation of solution where the crude sample was dissolved in large amounts of benzene–hexane solution. Some yellow crystals varied to red crystal on standing for a few hours at room temperature or on heating. Some yellow crystals varied to red crystal only when the samples were heated above 100 °C.[3]

Quinhydrone was obtained by spontaneous evaporation of acetone solution in which equivalent moles of *p*-benzoquinone and hydroquinone were dissolved. The purification of *p*-MPB and quinhydrone was checked by the melting points and then confirmed by measurements of the NMR spectra.

Optical Measurement. The Raman spectra of the yellow and red *p*-MPB crystals and of quinhydrone crystal due to the intramolecular vibrations were measured with a Bio-Rad FT-Raman II Spectrophotometer. The spectra were observed at various temperatures between 370 and 77 K at 1 atm and also at various pressures from 1 atm (1×10^{-4} GPa) to 3.3 GPa at 300 K by the backscattering observation method. The 1064 nm beam from a Nd:YAG laser of Spectra Physics Model T10-106C was used for excitation. A diamond anvil of Toshiba Tungaloy Co. XK-4184 was used for measurements of the Raman spectra at various pressures. The method of observing the Raman spectra was essentially the same as that described previously.[10,11] The thickness from the table to culet of the diamond of 0.16 carats is 2.0 mm and the diameters of the table and culet are 1.7 and 0.6 mm, respectively. A stainless steel gasket with thickness of 0.3 mm and area of 5×5 mm^2 was placed between the culets of the two opposed diamonds. A hole with a diameter of 0.3 mm was made in the center of the gasket, and the sample and ruby chips suspended in nujol were held in the hole. The pressure inside the gasket hole was determined by measuring the wavelength shift of the R_1 fluorescence line at 694.2 nm emitted from the ruby chips according to the equation proposed by Mao et al.[12] The pressure inside the hole was confirmed to be hydrostatic by observing the shapes of the R_1 and R_2 (692.7 nm) fluorescence lines emitted from ruby. No chemical reaction between samples and nujol was detected. A cryostat of OXFORD DN1704 was used for measurements of the Raman spectra at various temperatures. DSC measurement was carried out with a Seiko Instruments Model SII EXSTAR 6000.

Results and Discussion

A. 2-(4-Methoxyphenyl)-1,4-benzoquinone (*p*-MPB).

A-1. Temperature Effect on the Intramolecular Vibrations of *p*-MPB. It was found that *p*-MPB shows dimorphism, having yellow and red colors in the crystal; the yellow crystal gives the absorption band around 420 nm and the red crystal gives the bands around 420 and 500 nm.[1–3] *p*-MPB is the typical intramolecular charge transfer compound, in which electron-donating 4-methoxyphenyl group is directly bonded to electron-accepting *p*-benzoquinone. In the yellow crystal, all *p*-MPB molecules are oriented in head-to-head fashion, while in the red crystal, *p*-MPB molecules are oriented in head-to-tail fashion and the continuous chain of the π complex is formed.[1–3] Projections of the two adjacent molecules in the yellow and red crystals are shown in Fig. 1. The observed absorption bands around 420 nm in the yellow and red crystals, and the band around 500 nm in the red crystal were assigned to the intra- and intermolecular charge transfer bands, respectively.[1–3]

Although the difference of the geometry of the molecules in the yellow and red crystals may be small, the π overlap between the 4-methoxyphenyl and quinone rings may increase the polar character of the molecule in the red crystal compared with the molecule in the yellow crystal as shown in Fig. 1.

The thermograms obtained by differential scanning calorimetric observation for the yellow crystal in heating scan showed a weak endothermic peak at 112 °C in addition to the strong endothermic peak due to melting of the crystal. The observed endothermic peak at 112 °C is assigned to be due to the transformation from the yellow to red crystals, just as described by Desiraju et al.[3]

The Raman spectra of the yellow and red *p*-MPB crystals are shown in Fig. 2. The bands in the lowest wavenumber region around 150 cm^{-1} are due to the intermolecular vibrations. The difference of the spectral structures of the yellow and red crystals is prominent in the region of 1700 –900 cm^{-1}. The Raman spectra of the yellow *p*-MPB (at 300 K), mixture of the yellow and red *p*-MPB (at 330 K), and red *p*-MPB (at 370 K) crystals observed with increasing temperature, together with the spectra of anisol and *p*-benzoquinone crystals observed at 300 K in the region of 1700–900 cm^{-1} are shown in Fig. 3.

The assignments of the Raman bands for *p*-MPB, anisol and *p*-benzoquinone were made according to the vibrational frequencies and modes of the normal vibrations based on the ab initio calculation with the HF/6-31G** method. The calculation showed the following results. (1) The LUMO of *p*-benzoquinone has large anti bonding character in the C=O bond, and therefore, the intermolecular charge transfer to LUMO of *p*-benzoquinone causes a large red shift (more than 100 cm^{-1}) for the C=O stretching vibrational frequency compared with the frequency of *p*-benzoquinone itself. (2) The charge transfer from the HOMO of 4-methoxyphenyl causes a slight increase in bonding character for the benzene ring in 4-methoxyphenyl, and therefore, the 8a vibrational frequency increases slightly (about 40 cm^{-1}) compared with the frequency of 4-

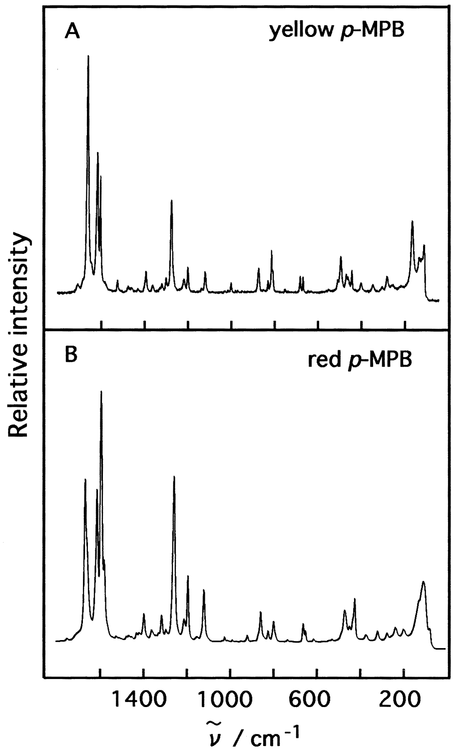


Fig. 2. The Raman spectra of the yellow and red crystals of 2-(4-methoxyphenyl)-1,4-benzoquinone.

methoxyphenyl itself. (3) The Raman band due to the C=O stretching vibration has the strongest intensity in the spectra before and after charge transfer. The calculated results suggest that the C=O stretching and 8a vibrational frequencies show large red and small blue shifts, respectively, after charge transfer. The nomenclature of the vibrational modes is taken from that given by Mair and Honig.[13]

The Raman band at 1654 (strongest in intensity), 1608, and 1594 cm^{-1} in the yellow crystal were assigned to the C=O stretching, 8a, and 8b vibrations, respectively, since the molecule in the yellow crystal is expected to have non-polar structure. The bands at 1658, 1604, and 1584 (strongest in intensity) cm^{-1} in the red crystal were assigned to the 8a, 8b, and C=O stretching vibrations, respectively, on the basis of the calculation described above. As a result, the C=O stretching vibrational frequency of the red crystal is nearly equal to that of

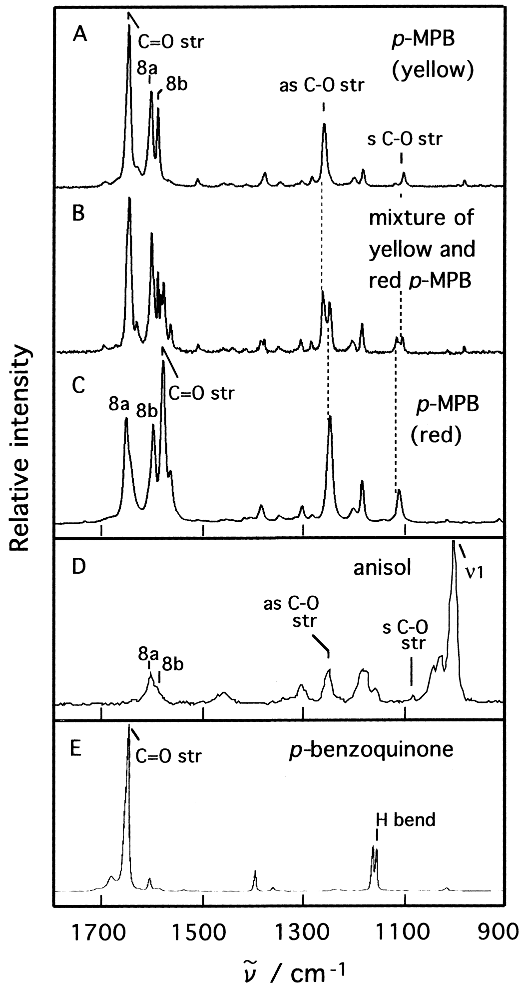


Fig. 3. The Raman spectra of the yellow and red crystals of 2-(4-methoxyphenyl)-1,4-benzoquinone, anisol, and *p*-benzoquinone. A, B, C, D, and E refer to yellow *p*-MPB (at 300 K), mixture of yellow and red *p*-MPB (at 330 K), red *p*-MPB (at 370 K), anisol (at 300 K), and *p*-benzoquinone (at 300 K) crystals, respectively.

quinhydrone involving hydrogen bonding as shown in Table 1. This may be supported by the fact that the C=O stretching vibrational frequency is not so much affected by the hydrogen bond formation; the band in 2-pyridone shifts only about 15

Table 1. Raman Frequencies due to Intramolecular Vibrations of Yellow and Red 2-(4-Methoxyphenyl)-1,4-benzoquinone, and Quinhydrone Crystals at Various Temperatures at 1 atm

Mode	Yellow *p*-MPB		Red *p*-MPB		Quinhydrone		
	300 K $\tilde{\nu}$/cm^{-1}	77 K $\tilde{\nu}$/cm^{-1}	300 K $\tilde{\nu}$/cm^{-1}	77 K $\tilde{\nu}$/cm^{-1}	300 K $\tilde{\nu}$/cm^{-1}	130 K $\tilde{\nu}$/cm^{-1}	77 K $\tilde{\nu}$/cm^{-1}
C=O str	1654	1655	1584	1586	1584	1580	1579
8a	1608	1610	1658	1660	1655	1656	1656
8b	1594	1597	1604	1605			
as C–O–C str	1261	1266	1248	1250			
s C–O–C str	1102	1106	1111	1115			
H′ bend					1237	1242	
C–O str					1161	1162	1162
A band					450	451	451

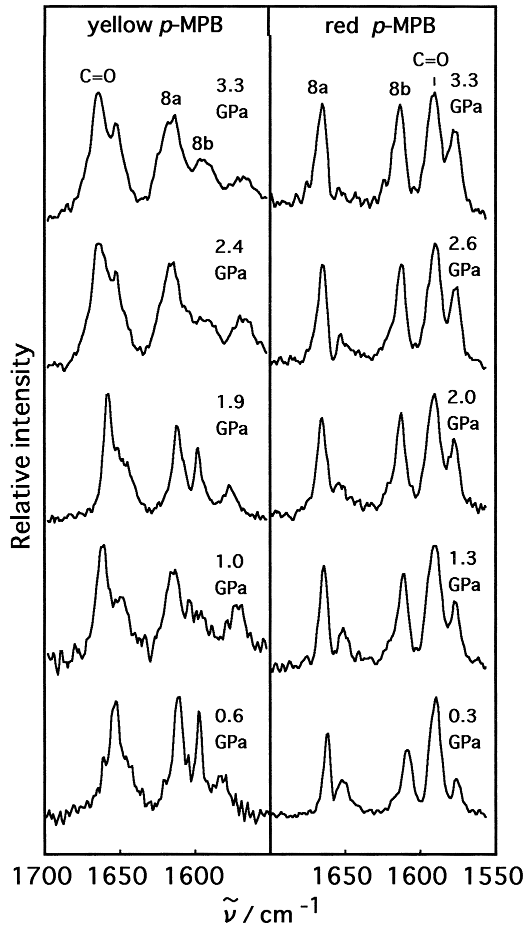


Fig. 4. The Raman spectra of the yellow and red crystals of 2-(4-methoxyphenyl)-1,4-benzoquinone in the 1600 cm^{-1} region observed at various pressures between 0.3 and 3.3 GPa at 300 K.

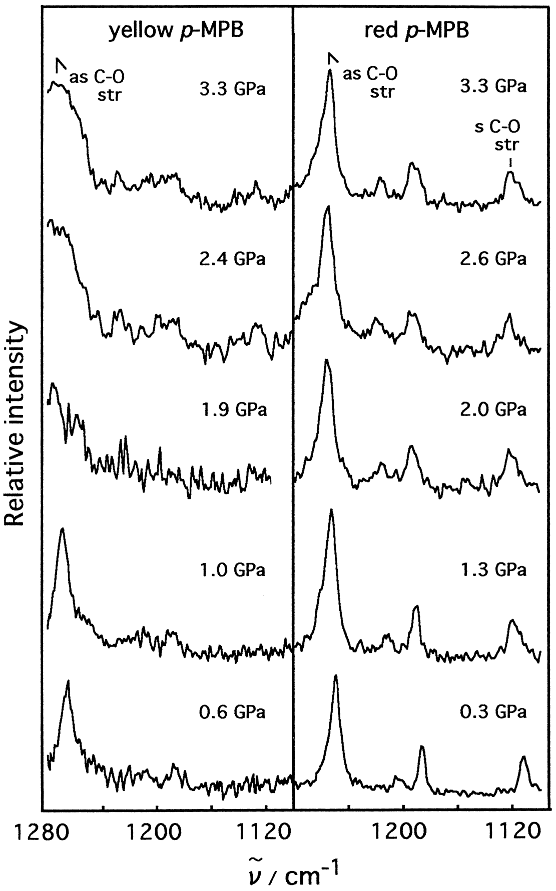


Fig. 5. The Raman spectra of the yellow and red crystals of 2-(4-methoxyphenyl)-1,4-benzoquinone in the 1200 cm^{-1} region observed at various pressures between 0.3 and 3.3 GPa at 300 K.

cm^{-1} to the red side upon the cluster formation with water.[14] The assignment given for the red crystal seems to be reasonable for the present.

The intensities of the Raman bands at 1261 and 1102 cm^{-1} of the yellow crystal decrease gradually and the intensities of the bands at 1248 and 1111 cm^{-1} of the red crystal increase gradually with increasing temperature as can be seen in Fig. 3. The anti symmetric and symmetric C–O stretching vibrations of methoxy aromatic hydrocarbons involving C–O–C bonds are generally observed around 1250 and 1100 cm^{-1}, respectively. The coupling of the two C–O stretching vibrations in the red crystal is weaker than the coupling in the yellow crystal, because the molecule is more polar in the red crystal. Thus the frequency of the anti-symmetric C–O stretching vibration in the red crystal is expected to become lower than that in the yellow crystal; on the other hand, the frequency of the symmetric C–O stretching vibration in the red crystal is expected to become higher than that in the yellow crystal. On the basis of these considerations, the observed bands at 1261 (1248) and 1102 (1111) cm^{-1} in the yellow (red) crystals were assigned to the anti symmetric and symmetric C–O stretching vibrations, respectively. The values in parentheses refer to the frequencies in the red crystal. The vibrational assignments are given in Fig. 3. The frequencies of the C=O stretching, 8a, 8b, anti symmetric C–O stretching, and symmetric C–O stretching vibrations in the yellow and red crystals increase slightly with decreasing temperature. This behavior is induced by increase of the intermolecular repulsive interaction with decreasing temperature. The intramolecular vibrational frequencies observed in the yellow and red crystals of *p*-MPB are given in Table 1 together with the frequencies of quinhydrone.

A-2. Pressure Effect on the Intramolecular Vibrations of *p*-MPB. The Raman spectra around 1700–1550 cm^{-1} and 1280–1100 cm^{-1} regions observed at various pressures at 300 K are shown in Figs. 4 and 5, respectively. The bands assigned to the C=O stretching, 8a, 8b, anti symmetric C–O stretching, and symmetric C–O stretching vibrations were clearly observed under high pressures up to 3.3 GPa. The relation between the observed relative frequency shifts defined by $\Delta\tilde{\nu} / \tilde{\nu}_1$ atm and pressure is shown in Fig. 6, where $\Delta\tilde{\nu} = \tilde{\nu}_{p\,\mathrm{GPa}} - \tilde{\nu}_{1\,\mathrm{atm}}$. The following facts were observed. (1) The relative frequency shifts for the C=O stretching, 8a, 8b, and anti symmetric C–O stretching vibrations of the yellow *p*-MPB crystal increase continuously with increasing pressure up to about 1.5 GPa and show a discontinuous change at about 1.5 GPa. The relative frequency shifts increase again continuously with increasing pressure up to 3.3 GPa. (2) The relative frequency shifts for

Table 2. Raman Frequencies due to Intramolecular Vibrations of Yellow and Red 2-(4-Methoxyphenyl)-1,4-benzoquinone Crystals, and Quinhydrone Crystal at Various Pressures at 300 K

Mode	Yellow *p*-MPB			Red *p*-MPB			Quinhydrone		
	1 atm $\tilde{\nu}$/cm^{-1}	2 GPa $\tilde{\nu}$/cm^{-1}	3.2 GPa $\tilde{\nu}$/cm^{-1}	1 atm $\tilde{\nu}$/cm^{-1}	2 GPa $\tilde{\nu}$/cm^{-1}	3.3 GPa $\tilde{\nu}$/cm^{-1}	1 atm $\tilde{\nu}$/cm^{-1}	1.7 GPa $\tilde{\nu}$/cm^{-1}	5.3 GPa $\tilde{\nu}$/cm^{-1}
C=O str	1653	1662	1665	1584	1586	1585	1584	1562	
8a	1608	1616	1617	1658	1664	1663	1655	1657	1663
8b	1594	1601		1603	1608	1609			
as C–O–C str	1260	1266	1268	1249	1245	1246			
s C–O–C str	1102			1111	1114	1114			
H′ bend							1237	1249	1258
C–O str							1161	1159	1158
A band							450	453	458

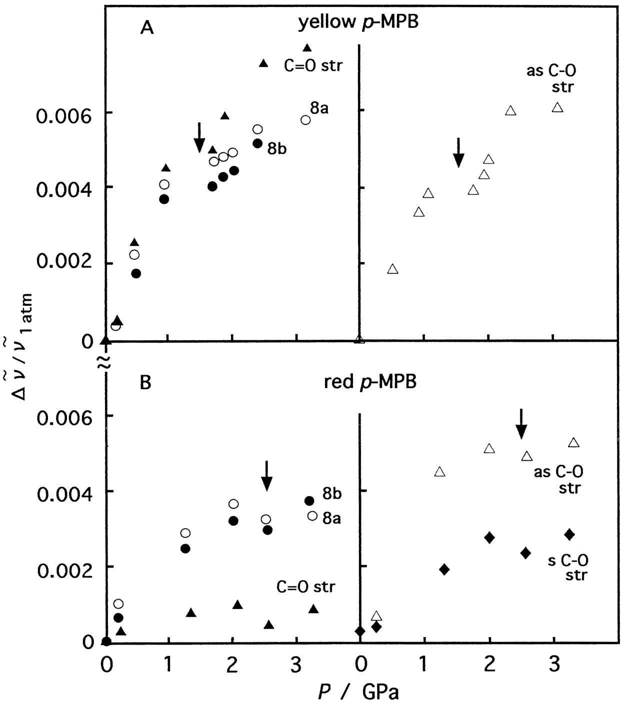


Fig. 6. Pressure-frequency relations for the Raman bands of the yellow and red 2-(4-methoxyphenyl)-1,4-benzoquinone crystals at various pressures between 0.3 and 3.3 GPa at 300 K. A and B refer to the yellow and red crystals, respectively. ▲, ○, ●, △, and ◆ refer to the C=O stretching, 8a, 8b, antisymmetric C–O–C stretching, and symmetric C–O–C stretching vibrations, respectively.

the C=O stretching, 8a, 8b, anti symmetric C–O stretching, and symmetric C–O stretching vibrations of the red *p*-MPB crystal increase continuously with increasing pressure up to about 2.5 GPa and a show discontinuous change at about 2.5 GPa. The relative frequency shifts increase again continuously with increasing pressure up to 3.3 GPa. The observed discontinuous changes of the pressure-relative frequency shift relations for the yellow and red crystals indicate that the phase transitions take place at about 1.5 and 2.5 GPa for the yellow and red crystals, respectively. The attractive interaction resulting from the intermolecular charge transfer from 4-methoxyphenyl to quinone rings in the red crystal compensates the intermolecular repulsive interaction between the 4-methoxyphenyl and quinone rings. Therefore, the phase transition in the red crystal takes place under higher pressure than the pressure in the yellow crystal. The intramolecular vibrational frequencies in yellow and red crystals of *p*-MPB observed at various pressures are given in Table 2 together with the frequencies of quinhydrone.

B. Quinhydrone. B-1. Temperature Effect on the Intramolecular Vibrations of Quinhydrone. Charge transfer quinhydrone crystal shows reversible redox reaction in solution, where proton transfer takes place together with charge transfer. The structure of the crystal is characterized by two sublattices, the hydrogen bonded lattice and the charge transfer mixed-stacked molecular lattice.[6] The cooperative phenomena associated with charge and proton transfers in quinhydrone crystal were studied through observation of the pressure effect on the O–H and C=O stretching vibrations in the infrared spectrum.[7] A new phase transition associated with the proton transfer was observed under the pressure of around 2.5 GPa.[7] The phase composed of the charge transfer-stacked lattice and the phase composed of the lattice formed by proton transfer coupled with the charge transfer will be referred to as phases I and II, respectively. The phase II is more ionic than the phase I.

The Raman spectra of quinhydrone, hydroquinone, and *p*-benzoquinone crystals are shown in Fig. 7. The assignments of the Raman bands for hydroquinone and *p*-benzoquinone crystals were made through the analysis of the normal vibrations based on the ab initio calculation with the HF/6-31G** method. The assignment of the Raman bands for hydroquinone is the same as that made by Tzeng et al.[15] The spectral structure around 1650 cm^{-1} region in quinhydrone strongly resembles the structure observed in the red *p*-MPB. Therefore, the strong bands at 1655 and 1584 cm^{-1} were assigned to the 8a and C=O stretching vibrations, respectively. The frequencies of the H′ bending and C–O stretching vibrations in quinhydrone are higher and lower, respectively, compared with the frequency in hydroquinone owing to the hydrogen bonding, where the medium strong bands at 1237 and 1161 cm^{-1} are assigned to the H′ bending and C–O stretching vibration, respectively. H′ refers to the hydrogen atom in the O–H bond. The very strong band at 450 cm^{-1} (refer to band A) could be assigned to the ν_l vibration. The assignments of the intramolecular vibrations observed in the infrared spectrum were given by Fukushima and Sakurada.[16]

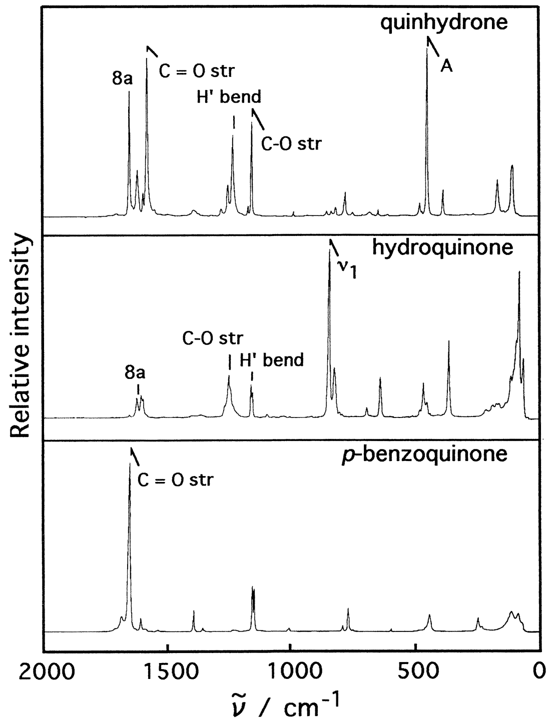


Fig. 7. The Raman spectra of quinhydrone, hydroquinone, and *p*-benzoquinone crystals observed at 300 K at 1 atm. H′ is the hydrogen atom in O–H bond.

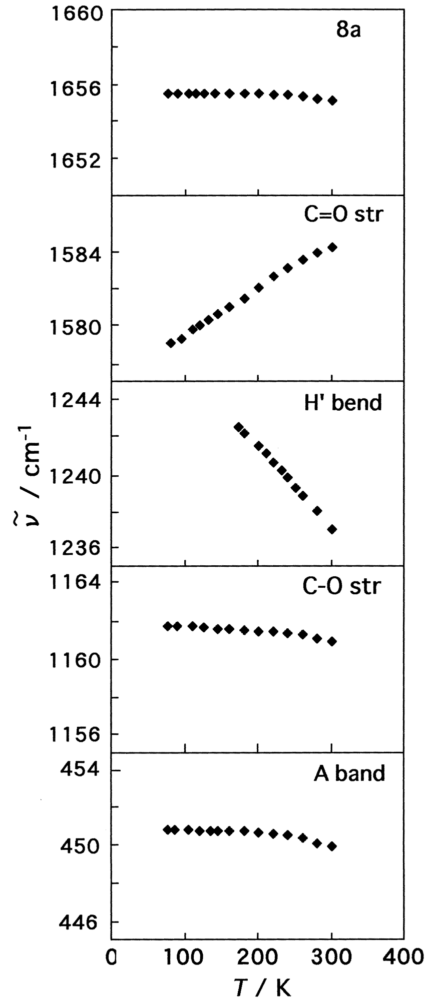


Fig. 8. Temperature-frequency relations for the Raman bands of quinhydrone crystal observed at various temperatures between 77 and 300 K at 1 atm.

The temperature effect on the Raman spectrum of quinhydrone was measured but no change of the spectral structure was observed from 77 to 300 K. The relation between the observed frequencies of the 8a, C=O stretching, H′ bending, C–O stretching, and A vibrations and temperatures is shown in Fig. 8. The band due to the H′ bending vibration was not distinctly detected below 150 K because of overlapping with some other band. The temperature–frequency relations indicate the following facts. (1) The frequencies of the 8a, C–O stretching, and A vibrations slightly increase, (2) the frequency of the C=O stretching vibration markedly decreases, and (3) the frequency of the H′ bending vibration remarkably increases with decreasing temperature.

If the intermolecular potential in molecular crystal involves repulsive and dispersive forces, the repulsive and dispersive forces contribute a large blue shift and a small red shift for the temperature-induced (or pressure-induced) frequency shift of intramolecular vibrations, respectively. Therefore, the vibrational frequency increases with decreasing temperature or increasing pressure. On the other hand, hydrogen bonding causes a red shift for the correlated stretching vibrations such as the C=O stretching mode, and a blue shift for the correlated bending vibrations such as the H′ bending mode.[10,11,17,18]

The observed fact (1) is general behavior of the temperature effect on the vibrational frequency owing to the increase of the repulsive interaction.[10,11,17,18] The observation (2) is explained by the fact that the decrease of frequency of the C=O stretching vibration induced by hydrogen bonding overcomes the increase of the frequency induced by the repulsive interaction with decreasing temperature. The observation (3) is attributed to the cooperation of the increase of the repulsive interaction with strengthening of hydrogen bonding with decreasing temperature. The vibrational frequencies in quinhydrone crystal observed at various temperatures are given in Table 1, together with the frequencies in *p*-MPB crystals.

B-2. Pressure Effects on the Intramolecular Vibrations of Quinhydrone. The Raman spectra observed at various pressures at 300 K are shown in Fig. 9. A new band referred to as Q band came to be observed on the lower wavenumber side of the strong band due to the C=O stretching vibration (referred to P band) with increasing pressure. The intensity of the Q band increases with increasing pressure, and eventually exceeds the intensity of the P band under the pressure above 3.5 GPa. The P band was hardly detected and only the Q band was observed under the pressure above 5 GPa. The relation between the observed vibrational frequencies of the P and Q bands and pressure is shown in Fig. 10. The pressure effects on the intensity of the P and Q bands are the same as the observed effect on the infrared bands assigned to the C=O stretching vibrations in phases I and II,[7] and therefore, the bands P and Q are assigned to the C=O stretching vibration in phases I and II, respectively. The shift from the P to Q bands in the spectrum is discontinuous and both P and Q bands were

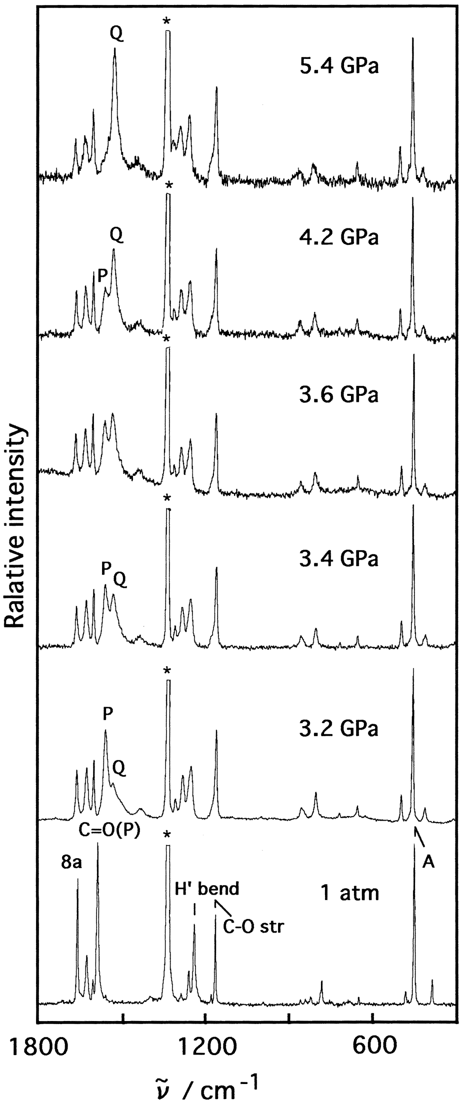


Fig. 9. The Raman spectra of quinhydrone crystal observed at various pressures between 1 atm and 5.4 GPa at 300 K.

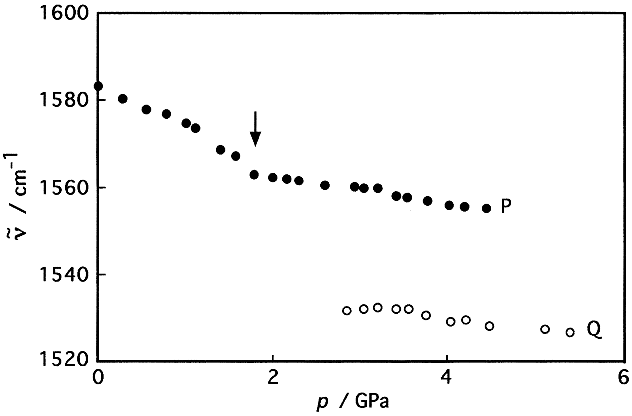


Fig. 10. Pressure–frequency relations for the Raman P and Q bands in quinhydrone crystal observed at various pressures between 1 atm and 5.4 GPa at 300 K.

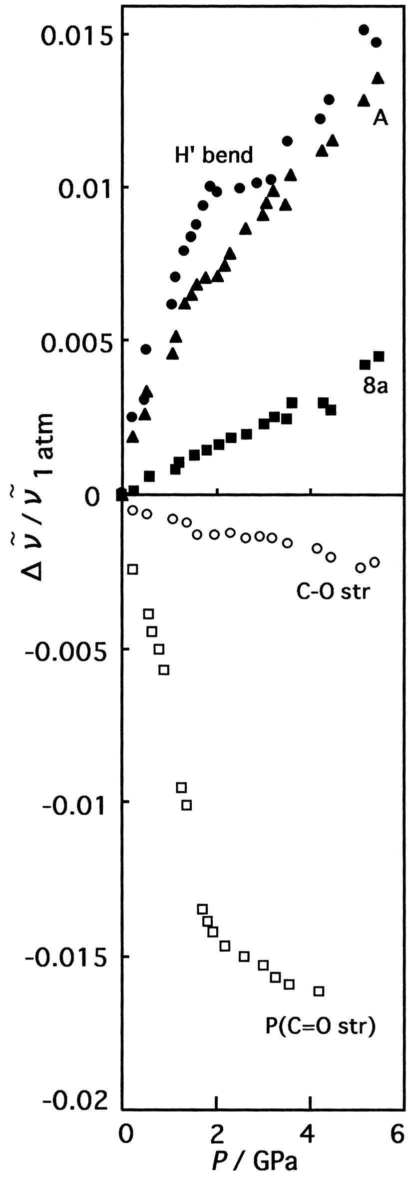


Fig. 11. Pressure-relative frequency shift relations for the Raman bands in quinhydrone crystal observed at various pressures between 1 atm and 5.4 GPa at 300 K. ●, ▲, ■, ○, and □ refer to the H bending, A mode, 8a, C–O stretching, and C=O stretching vibrations, respectively.

observed in the wide pressure range between 2.7 and 4.5 GPa. This fact suggests coexistence of phases I and II in the pressures between 2.7 and 4.5 GPa.

The relation between the observed relative frequency shifts defined by $\Delta\tilde{\nu} / \tilde{\nu}_{1\,\mathrm{atm}}$ and pressure is shown in Fig. 11, where $\Delta\tilde{\nu} = \tilde{\nu}_{p\,\mathrm{GPa}} - \tilde{\nu}_{1\,\mathrm{atm}}$. Figure 11 shows the following facts. (1) The relative frequency shift for the 8a vibrational band increases almost continuously with increasing pressure up to 5.5 GPa. (2) The relative frequency shift for the A vibrational band increases markedly with increasing pressure up to 5.5 GPa and a discontinuous change of the slope of the $p - \Delta\tilde{\nu} / \tilde{\nu}_{1}$ atm relation is detected under about 1.8 GPa. (3) The relative frequency shifts for the C–O and especially for the C=O stretching vibrational bands decrease with increasing pressure, and discontinuous changes of the slopes of the $p - \Delta\tilde{\nu} / \tilde{\nu}_{1\,\mathrm{atm}}$ relations are detected at about 1.8 GPa. The slopes become gentle over about 1.8 GPa. (4) For the H′ bending vibrational band, the relative frequency shift increases markedly with increasing pressure up to 1.8 GPa and above 2.7 GPa, but the shift increases very slightly at between 1.8 and 2.7 GPa.

The observation (1) is the general behavior of the pressure effect on the vibrational frequency owing to the increase of the repulsive interaction with increasing pressure.[10,11,17,18] The observation (2) suggests that a phase transition takes place at 1.8 GPa, and the A vibration is a mode sensitive to intermolecular charge transfer. The observation (3) suggests that the decrease of frequency of the C=O stretching vibration due to formation of the hydrogen bonding greatly overcomes the increase of frequency induced by the repulsive interaction with increasing pressure. On the other hand, the decrease of frequency of the C–O stretching vibration due to the hydrogen bonding slightly overcomes the increase of frequency induced by the repulsive interaction with increasing pressure. The observation (4) and figure 10 suggest that phase transitions take place at 1.8 and 2.7 GPa. The large frequency shift of the H′ bending vibration observed up to 1.8 GPa is induced by the increase of the repulsive interaction together with strengthening of hydrogen bonding with increasing pressure. The phase transition observed at 2.7 GPa corresponds to the transition from phase I to phase II. The phase transition detected at 1.8 GPa gives a characteristic effect on the frequency shift of the H′ bending vibration. Although the frequency of the C=O stretching vibration in phases II was observed to be different from the frequency in phase I, the differences of the frequencies of the 8a, H′ bending, A mode, and C–O stretching vibrations between phases I and II were not resolved. The vibrational frequencies in quinhydrone crystal observed at various pressures are given in Table 2, together with the frequencies in *p*-MPB crystals.

C. Comparison of Pressure Effect on the Intramolecular Vibrations of Quinhydrone with the Effect of *p*-MPB.

The crystal structure of the yellow *p*-MPB is characterized by a stacked molecular lattice formed by the repulsive and dispersive forces, and the structure of the red *p*-MPB is characterized by the intermolecular charge transfer mixed stacked molecular lattice in addition to the lattice formed by the repulsive and dispersive forces. The crystal structure of quinhydrone is characterized by two sublattices, the intermolecular charge transfer lattice and the hydrogen bonded lattice in addition to the lattice formed by the repulsive and dispersive forces. It is discussed now how differences of the lattices in the yellow *p*-MPB, red *p*-MPB and quinhydrone crystals depend on the frequencies of the intramolecular vibrations.

The observed pressure-relative frequency relations for the 8a and C=O stretching vibrations in the yellow *p*-MPB, red *p*-MPB and quinhydrone crystals are shown in Fig. 12. For the 8a vibration, the values of the relative frequency shift are all plus for the yellow *p*-MPB, red *p*-MPB and quinhydrone crystals and the values decrease in the order of the yellow *p*-MPB, red *p*-MPB and quinhydrone crystals. These facts indicate that the attractive interaction due to hydrogen bonding acts effectively on the quinhydrone crystal in addition to intermolecular attractive charge transfer and intermolecular repulsive interaction. The polar structure of the molecule increases more effectively in quinhydrone crystal than that in the red *p*-MPB crystal. For the C=O stretching vibration, the relative frequency shifts for the yellow *p*-MPB, red *p*-MPB, and quinhydrone crystals give large plus, small plus, and very large minus values, respectively. The largest plus value of the relative frequency shift for the yellow *p*-MPB crystal among the three crystals indicates that the intermolecular repulsive interaction reveals most prominently in the yellow crystal. The small plus value of the relative frequency shift for the red crystal indicates that attractive interaction resulting from intermolecular charge transfer acts on the red crystal in addition to the intermolecular repulsive interaction. Thus the blue shift caused by the intermolecular repulsive interaction was depressed by the red shift caused by the attractive interaction due to the intermolecular charge transfer. In the red crystal, the ratio of polar to non polar structures shown in Fig. 1 may increase with increasing pressure.

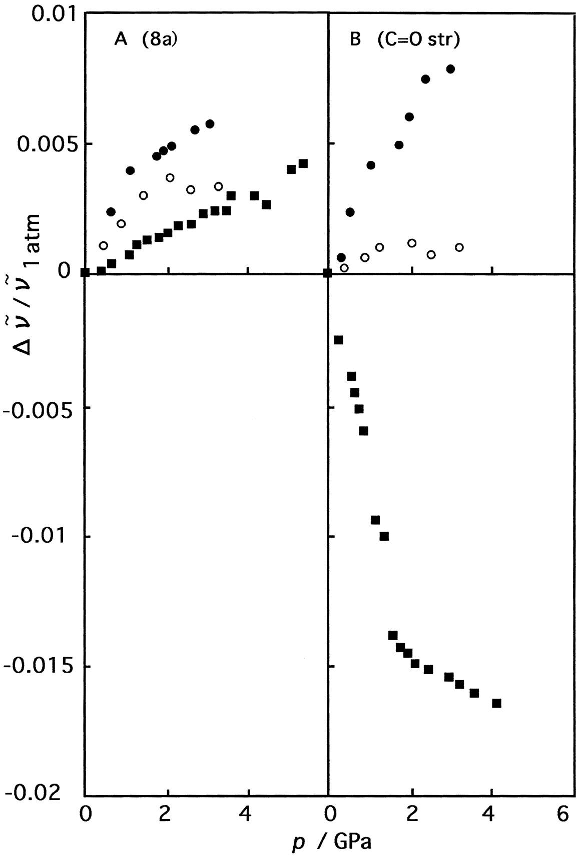


Fig. 12. Comparison of pressure-relative frequency shift relations for the Raman bands in the yellow and red 2-(4-methoxyphenyl)-1,4-benzoquinone crystals with those in quinhydrone crystal observed at various pressures between 1 atm and 5.4 GPa at 300 K. A and B refer to the 8a and C=O stretching vibrations, respectively. ●, ○, and ■ refer to the yellow 2-(4-methoxyphenyl)-1,4-benzoquinone, red 2-(4-methoxyphenyl)-1,4-benzoquinone, and quinhydrone crystals, respectively.

In conclusion, among the three types of intermolecular interactions of repulsive interactions (type I), attractive interactions due to charge transfer (type II), and attractive interactions due to hydrogen bonding (type III), type I acts on the yellow *p*-MPB crystal, types I and II on the red *p*-MPB crystal, and types I, II, and III on the quinhydrone crystal. The differences of the mechanism of the intermolecular interactions were well reflected in temperature- and pressure effects on the intramolecular vibrations of yellow *p*-MPB, red *p*-MPB, and quinhydrone crystals.

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