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Pressure-induced neutral-to-ionic phase transition in organic charge-transfer crystals of tetrathiafulvalene-*p*-benzoquinone derivatives

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Infrared and visible absorption spectra have been measured on three kinds of mixed-stack organic charge-transfer crystals of tetrathiafulvalene (TTF) -*p*-benzoquinone derivatives under hydrostatic pressures up to about 50 kbar. In TTF-tetrachloro-*p*-benzoquinone and TTF-trichloro-*p*-benzoquinone crystals, the regularly stacked quasineutral phase at ambient pressure undergoes a change to the dimerized quasi-ionic phase under the increasing pressure, passing through an inhomogeneous mixed state where the quasineutral molecular region and the quasi-ionic molecular region are spatially separated. On the other hand, in TTF-2,5-dichloro-*p*-benzoquinone, a continuous increase in the degree of charge transfer is observed under increasing pressure up to about 50 kbar. The nature of these pressure-induced neutral-to-ionic transitions in the respective TTF-complex crystals is discussed.

I. INTRODUCTION

Physical properties of 1:1 mixed-stack organic charge-transfer (CT) crystals have been extensively investigated in recent years from the interest in their characteristic behaviors related to the quasi-one-dimensional Peierls-Hubbard systems. In particular, in tetrathiafulvalene (TTF) -*p*-chloranil (CA) crystal, extensive studies have been made on the so-called neutral-to-ionic (*N-I*) phase transition induced either by temperature[1] or pressure.[2] Various kinds of measurements have been done to clarify the nature of this unique phenomenon. Through the results it has been found that the temperature-induced *N-I* transition (TINIT) in TTF-CA crystal is characterized by a sharp change in the ionicity (ρ) of molecules,[3] that is, in the degree of CT between the donor (D) and acceptor (A) molecules. The ρ value varies from 0.25–0.30 to 0.65–0.70 at the critical temperature $T_c = 81$ K.[4,5] A simultaneous dimerization of DA stacks occurs below T_c.[4–6] On the other hand, in the case of pressure-induced *N-I* transition (PINIT) at room temperature, the DA stacks are transformed into the dimerized ionic phase[7–9] at about 11 kbar, above which the ρ value increases steadily up to about 0.8 in the higher-pressure region. It is evident from these results that the electron-lattice interaction plays an essential role in the *N-I* phase transition in TTF-CA crystal.[10] In this system, one can regard the dimeric distortion in the lattice as an appropriate order parameter to characterize the *N-I* transition.

As previously reported by Torrance *et al.*,[2] similar PINIT phenomena are observed in the quasineutral mixed-stack CT crystals other than TTF-CA, which are located near the *N-I* boundary. Previously, these PINIT's have been simply interpreted as being predominantly due to an increase in the long-range Coulomb interaction between partially charge-transferred molecules by pressure. However, in the actual mechanism of PINIT, the effect of electron-lattice interaction cannot be ignored in these crystals either. Key information on this effect will be obtained from optical spectra of these CT crystals under pressure. It will be useful to compare these spectra with those of TTF-CA crystal which have been investigated in detail.[2,7,8,9,11]

In this paper, we report the optical spectra of three kinds of mixed-stack complexes composed of TTF as the donor and substituted *p*-benzoquinones as the acceptor. The latter includes tetrachloro-*p*-benzoquinone (QCl_4 or equivalently CA), trichloro-*p*-benzoquinone (QCl_3) and 2,5-dichloro-*p*-benzoquinone ($pQCl_2$). From infrared (ir) measurements, all of these crystals are confirmed to be in the quasineutral phase at ambient pressure and at room temperature. The common donor TTF has the ionization energy of about 6.4 eV.[12] The electron affinity E_A of each acceptor molecule is about 2.5 eV for QCl_4(CA), about 2.4 eV for QCl_3 and 2.3 eV for $pQCl_2$.[13] Therefore, the degree of charge-transfer is expected to decrease in the sequence of TTF-QCl_4 (TTF-CA), TTF-QCl_3, and

TTF-pQCl$_2$. It is interesting to see how such a sequential tendency in the CT interaction manifests itself in the spectral behavior at the PINIT.

II. ir AND VISIBLE SPECTROSCOPY OF TTF COMPLEX: A GENERAL ASPECT

In order to evaluate the change in the ρ value with temperature or pressure and to detect the possible dimeric distortion at the N-I transition, the intramolecular vibration spectroscopy has been proved to be quite effective in TTF-CA.[4,5,7,9,14] From the frequency shift of specific intramolecular vibration bands in the ir spectra, one can estimate the ρ values as a function of temperature or pressure.[15] In the CT complexes presently investigated, the frequency shift of the ir active C=O stretch mode of p-benzoquinones is useful, since it is fairly sensitive to the molecular ionicity. In the case of QCl$_4$(CA) molecule, it shows a fairly large red shift which amounts to about 160 cm^{-1} when a neutral molecule is ionized.[16,17]

On the other hand, information on the dimeric lattice distortion can be obtained from the ir spectra of an a_g mode which is activated by the lattice distortion via the electron-molecular-vibration (EMV) interaction. In a regularly stacked DA lattice with the inversion symmetry, the a_g molecular vibrations are not ir active, but when the symmetry is lowered by the dimeric lattice distortion, they become ir active.[5,14,18] The intensity of such an a_g mode is critically dependent on the following two parameters; the difference between the intradimer and interdimer CT interactions and the EMV coupling. Since the latter effect depends relatively little on the external perturbations by temperature or pressure as compared with the former effect, the intensity of a particular a_g mode can be utilized as a sensitive probe for detecting the dimeric distortion of lattice. A number of a_g modes are usually observed in the ir spectra of dimerized crystals. In this study, a specific mode which is observed around 960 cm^{-1} in p-benzoquinone derivatives in common has been investigated at various pressures. This mode is composed of the stretching vibration of the C—C and C—Cl bonds and the bending vibration of the C—Cl bond in chlorine-substituted benzoquinone molecule.[19]

Besides the infrared molecular vibration spectra, visible electronic absorption spectra have been also measured on the same complex crystals under hydrostatic pressure. Since the energy of the intramolecular electronic excitation band around 2.5 eV is dependent on the degree of CT in these crystals,[3,11,20] the change of this band by pressure is also useful for investigation of the molecular CT state at high pressures.

III. EXPERIMENT

Single crystals of TTF-QCl$_4$ (TTF-CA) were grown by the cosublimation method, and TTF-QCl$_3$ and TTF-pQCl$_2$ crystals were grown from hot acetonitrile solutions. Component materials were purified by the usual recrystallization and sublimation procedures. Optical measurements were made on crystalline powders obtained by pulverizing these single crystals. In the measurement of transmission spectra under hydrostatic pressure, a conventional diamond-anvil technique was utilized. The Nujol mull of crystalline powder was filled in a 0.5-mm-diam hole in a stainless-steel gasket which was sandwiched between diamond anvils. Liquid paraffin in the mull acted as a pressure-transmitting medium. The hydrostatic pressures in the cell were calibrated by the pressure-induced shift of the R_1 emission line of a small ruby crystal in the mull. Accuracy of the pressure measurement was about 0.5 kbar in the pressure range up to about 60 kbar.

IV. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Infrared spectra under hydrostatic pressure

1. TTF-QCl$_4$ (TTF-CA)

The pressure dependence of ir-transmission spectra of TTF-QCl$_4$ (TTF-CA) crystal is shown in Fig. 1, in the frequency ranges around 1600 cm^{-1} (left) and around 900–1000 cm^{-1} (right). The structure A around 1650 cm^{-1} and D around 1540 cm^{-1} in Fig. 1(a) are due to the

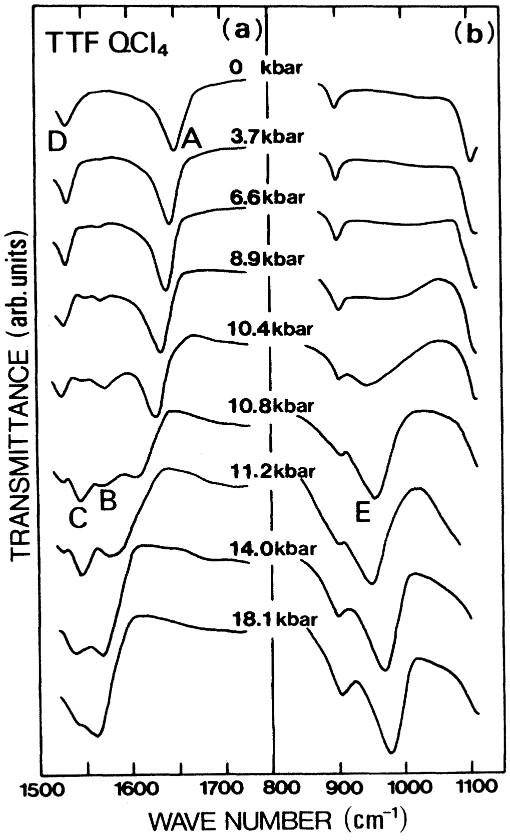

FIG. 1. Transmittance spectra of TTF-QCl$_4$ (TTF-CA) under various hydrostatic pressures. The structures A, B, and C are assigned to the C=O stretch modes of QCl$_4$ (CA) molecules ($A,B;b_{1u},C;a_g$). The structures D and E are assigned to the b_{2u} and a_g modes of QCl$_4$ (CA) molecules, respectively.

b_{1u} (C=O stretch) and b_{2u} modes of QCl_4 (CA) molecule, respectively.[5] The *A* band shows a remarkable change by pressure, whereas the *D* band is almost unchanged with pressure. When pressure is applied, the dip (the absorption peak) of the *A* band shifts gradually to lower frequencies, indicating a continuous increase of ρ with increasing pressure. When pressure is increased above 7 kbar, weak additional dips (labeled *B* and *C*) appear at around 1570 and 1550 cm^{-1}, respectively. The intensities of these bands increase gradually with increasing pressure. When pressure is raised further to about 11 kbar, the main dip *A* is merged into the *B* band. At the same time, a strong enhancement of the absorption intensity is observed in the *B* and *C* bands.

The pressure-induced change is even more remarkable in the spectra shown in Fig. 1(b). At low pressures, a weak dip is observed around 900 cm^{-1}. It is assigned to another b_{1u} mode of the CA molecule.[5] This band is almost unchanged with pressure. However, when pressure is raised to about 9 kbar, a very broad band denoted *E* appears around 960 cm^{-1}. This is attributed to the a_g mode of QCl_4 (CA) molecules which is activated by the lattice distortion.[5] The *E* band is remarkably enhanced with increasing pressure above 11 kbar.

The frequencies of the *A*, *B*, *C*, and *D* bands are plotted in Fig. 2 against pressure. The frequencies of the C=O stretch mode observed in the neutral ($QCl_4{}^0$) and fully ionic ($QCl_4{}^{-1}$) molecules are indicated by arrows for reference. The *A* band can be attributed to the same C=O stretch band of quasineutral QCl_4 (CA) molecule in the crystal. This band shows a red shift with pressure, indicating that the degree of CT in crystal increases continuously up to about 10 kbar and then shows a discontinuous change into the more ionic CT state at $P_c=11$ kbar. It is evident from this plot that the *B* band observed above P_c is also ascribed to the same C=O stretch mode of the QCl_4 (CA) molecule. Since the *B* band is weakly observed below P_c, part of the QCl_4 (CA) molecules in the lattice are considered to be converted to more ionic molecules before the whole lattice undergoes the PINIT at P_c. In other words, the PINIT in TTF-QCl_4 crystal occurs through an inhomogeneously mixed state in which the lattice is composed of the separated quasineutral and quasi-ionic domains. This mixed state in the pressure region below P_c undergoes a first-order transition at $P_c=11$ kbar. Such a behavior is observed in both powder samples and single crystals,[11] and hence is considered to be an intrinsic feature of the PINIT in TTF-QCl_4 (TTF-CA) crystal.

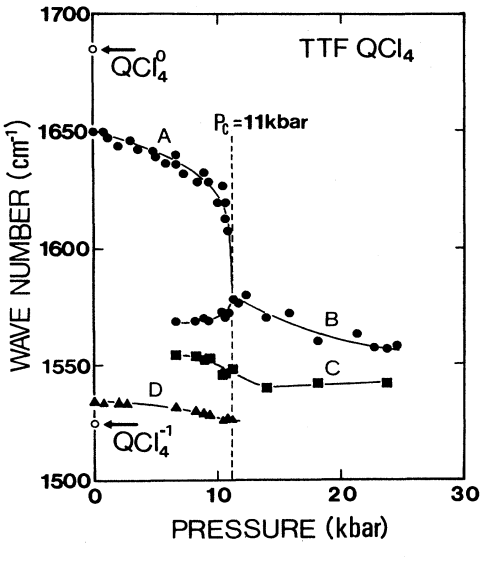

FIG. 2. Frequencies of the *A*, *B*, *C*, and *D* bands of TTF-QCl_4 (TTF-CA) as a function of hydrostatic pressures. The frequencies of the C=O stretch b_{1u} mode in the neutral and fully ionic QCl_4 (CA) molecules are also shown by open circles.

The *C* band is attributable to the C=O stretch a_g mode activated by the lattice dimerization, similar to the *E* band in Fig. 1(b). This assignment is based upon the following reasoning. According to the Raman spectra of neutral and fully ionic QCl_4 (CA) molecules, the frequency of the C=O stretch a_g mode changes from 1693 cm^{-1} [$(CA)^0$] to 1518 cm^{-1} [$(CA)^{-1}$)].[18] These frequencies are close to those of the b_{1u} mode; 1685 cm^{-1} in $(CA)^0$ and 1525 cm^{-1} in $(CA)^{-1}$. However, these two modes can be discriminated, since their frequencies show considerably different dependence on the molecular ionicity ρ in the mixed-stack structure: while the frequency of b_{1u} mode is nearly linear to ρ, the frequency of a_g band is appreciably deviated from a linear dependence upon ρ because of the EMV interaction and must be lower than the b_{1u} band. In the dimer model, the deviation is simply given by $-2g^2\rho(1-\rho)/\omega_{CT}$,[14] where g and ω_{CT} are the EMV coupling constant and the CT excitation energy, respectively. Such a quadratic dependence of the frequency on ρ is in fact observed in the pressure shifts of the *C* and *E* bands, supporting the identification of the *C* band with the C=O stretch a_g band. To summarize, the pressure dependence of the C=O stretch b_{1u} band clearly shows that the ρ value changes rather continuously up to $P_c=11$ kbar, above which the lattice suddenly goes into the ionic dimerized state. At pressure slightly below P_c, however, there is an inhomogeneous region where both quasineutral and quasi-ionic molecules coexist. Such a feature is in contrast with a discontinuous change in ρ in the TINIT, as indicated by a sharp red-shift and a sudden increase in intensity of the same C=O stretch b_{1u} band at $T_c=81$ K. In the TINIT, the coexistence of neutral and ionic states is not observed.

2. TTF-QCl_3

The pressure dependence of infrared transmission spectra of TTF-QCl_3 is shown in Fig. 3 in the two characteristic frequency regions. The features in the ir spectra of QCl_3 are rather complicated as compared with those of QCl_4 (CA), because of the noncentrosymmetric structure of QCl_3 molecule. At $P=0$ kbar, the C=O stretch band consists of doublet structures, *A* and *A*′, located around 1652 and 1625 cm^{-1}, respectively, as shown in Fig. 3(a). This splitting is obviously due to the low symmetry of

QCl_3 molecule. With increasing pressure, both A and A' bands show gradual red shifts. At the same time, another band B appears around 1570 cm^{-1}. Its intensity becomes comparable to that of the A band at about 10 kbar. In addition, another band C becomes observable at high pressures. All three of these bands, A, B, and C, are supposed to be attributed to the $C{=}O$ stretching mode of the QCl_3 molecule. Above 30 kbar, the A and B bands are fused to a single strong band. The D around 1540 cm^{-1} is assigned to the $C{=}C$ stretching mode of QCl_3 molecules. This band is almost unchanged by pressure.

In the spectra shown in Fig. 3(b), three bands are observed around 860, 950, and 1050 cm^{-1} at ambient pressure. They are attributable to the combined modes between the C—C and C—Cl stretching and C—Cl bending vibrations.[19] The 860- and 1050-cm^{-1} bands do not show observable change by pressure. On the contrary, the intensity of the band (E) around 950 cm^{-1} is significantly enhanced by pressure. Since such a feature is quite similar to that of the E band in TTF-QCl_4 (TTF-CA) crystal [Fig. 1(b)], this effect can be also related to the pressure-induced lattice dimerization in TTF-QCl_3. However, in contrast to the case of TTF-QCl_4 (TTF-CA), the E band in TTF-QCl_3 is weakly observed even at $P=0$ kbar. Evidently this has nothing to do with the dimerization effect but is due to the noncentrosymmetric structure of the QCl_3 molecule. According to an x-ray study, TTF-QCl_3 crystal is regularly stacked at ambient pressure with lattice constants almost equal to those of TTF-QCl_4 (TTF-CA).[20,21] The gradual enhancement of the E-band intensity by pressure indicates that the dimeric distortion in TTF-QCl_3 crystal takes place rather gradually with increasing pressure as compared with an abrupt behavior in TTF-QCl_4 (TTF-CA).

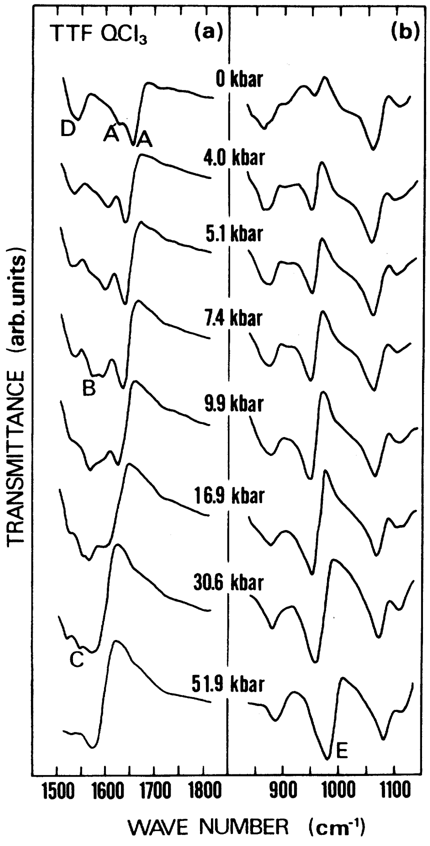

FIG. 3. Transmittance spectra of TTF-QCl_3 under hydrostatic pressures.

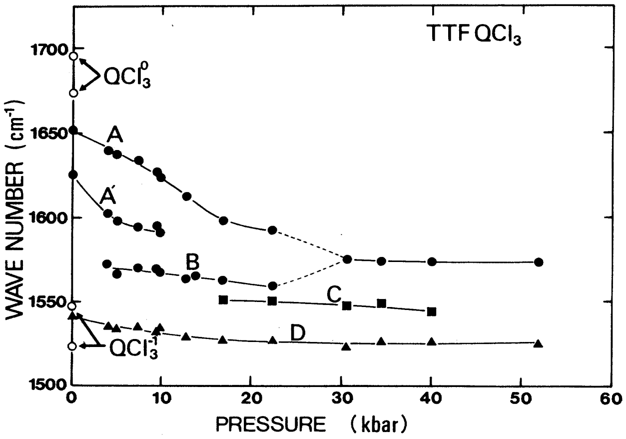

FIG. 4. Frequencies of the A, A', B, C, and D bands of TTF-QCl_3 as a function of hydrostatic pressures. The frequencies of the $C{=}O$ stretch mode in the neutral and fully ionic QCl_3 molecules are also shown by open circles.

The pressure-dependent frequencies of the $A-D$ bands in TTF-QCl_3 are plotted in Fig. 4. Open circles at $P=0$ kbar represent frequencies of doublet $C{=}O$ stretch bands observed in neutral ($QCl_3{}^0$) and fully ionic ($QCl_3{}^{-1}$ in Na-QCl_3) molecules. Definite assignments of the $A-D$ bands in TTF-QCl_3 crystal are not easy because of the considerable overlapping between these bands and also due to a remarkable intensity enhancement effect by the dimerization through the EMV coupling. A tentative assignment is that the doublet A and A' bands are due to the $C{=}O$ strech modes in the quasineutral state and the B band to the same mode in quasi-ionic state, respectively. The C band may be attributed to either a distortion-induced band like the E band, or the partner of the B band, both being split like the A and A' bands in the asymmetric QCl_3 molecule.

3. TTF-pQCl₂

The transmission spectra of TTF-$pQCl_2$ under pressure are shown in Fig. 5. The spectral features are fairly simple and similar to those of TTF-QCl_4 (TTF-CA), as the molecular structure of $pQCl_2$ is again centrosymmetric. The $C{=}O$ stretching b_u mode (A) is observed around 1650 cm^{-1} at ambient pressure. It shows a gradual red shift with pressure up to about 50 kbar. Two bands around 900 and 1000 cm^{-1} at ambient pressure are attributed to the a_u and b_u band, respectively, of $pQCl_2$ molecules. The latter band remains almost unchanged by pressure. In contrast, the intensity of the former band is

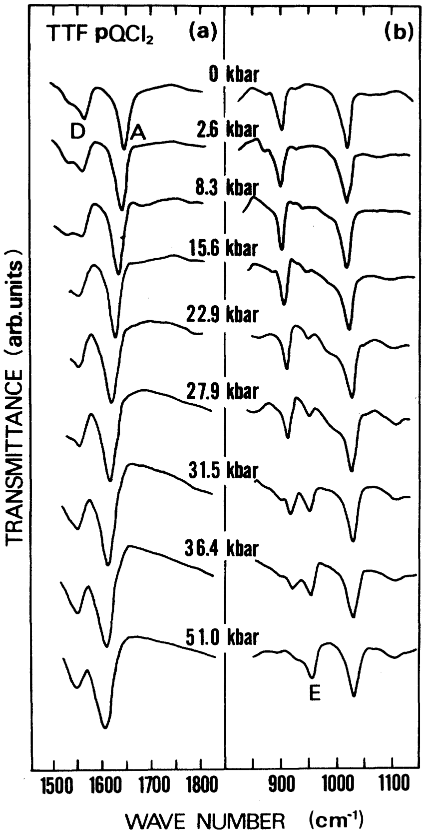

FIG. 5. Transmittance spectra of TTF-pQCl$_2$ under hydrostatic pressures. The structures A and D are assigned to the C=O stretch b_u and other b_u modes of pQCl$_2$ molecules, respectively. The structure E is assigned to the a_g mode of pQCl$_2$ molecules.

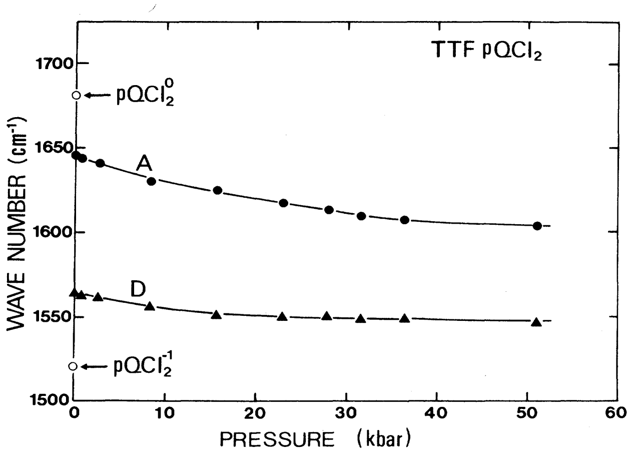

FIG. 6. Frequencies of the A and D bands of TTF-pQCl$_2$ as a function of hydrostatic pressures. The frequencies of the C=O stretch mode in the neutral and fully ionic pQCl$_2$ molecules are also shown by open circles.

considerably weakened by pressure. Above 10 kbar, a new band E emerges around 950 cm^{-1}, and increases with pressure. The E band is assigned to an a_g mode of pQCl$_2$ molecule. These results are in agreement with those recently reported by Girlando *et al.*[22] The frequencies of the A and D bands are plotted in Fig. 6 against pressure. Open circles at $P=0$ kbar indicate the frequencies of the C=O stretch b_u band in the neutral (pQCl$_2^{0}$) and fully ionic (pQCl$_2^{-1}$) molecules.[22] Note that there is no indication of coexisting quasineutral and quasi-ionic molecules in the measured pressure region, in contrast to the cases of TTF-QCl$_4$ and TTF-QCl$_3$.

B. Intramolecular electronic excitation spectra under hydrostatic pressure

Visible absorption spectra of TTF-QCl$_n$ ($n=2,3,4$) crystals at atmospheric pressure are shown in Fig. 7. Two structures, B and C, observed at around 2.5 and 3.3 eV in common are identified with intramolecular excitation bands in TTF molecules.[3,11,20] Since energies and intensities of these bands are dependent on ρ (the degree of CT) in crystal, the pressure dependence of these spectra provides information on the molecular CT state in the lattice under pressure. In this study, such measurements have been made on the B band, since the C band is too strong to make precise determination of the spectral profile in powder transmission spectra. Since the B band is relatively weak, the corresponding molecular exciton is supposed to be fairly localized on a specific TTF molecule as compared with the more intense C exciton.[11,20] This

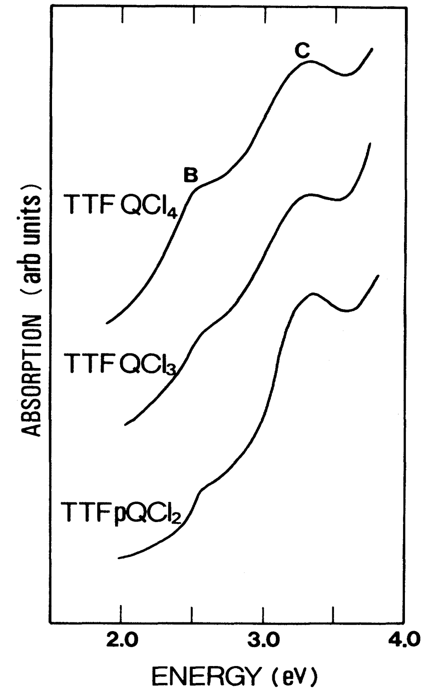

FIG. 7. Visible absorption spectra of TTF-QCl$_4$ (TTF-CA), TTF-QCl$_3$, and TTF-pQCl$_2$ at ambient pressure.

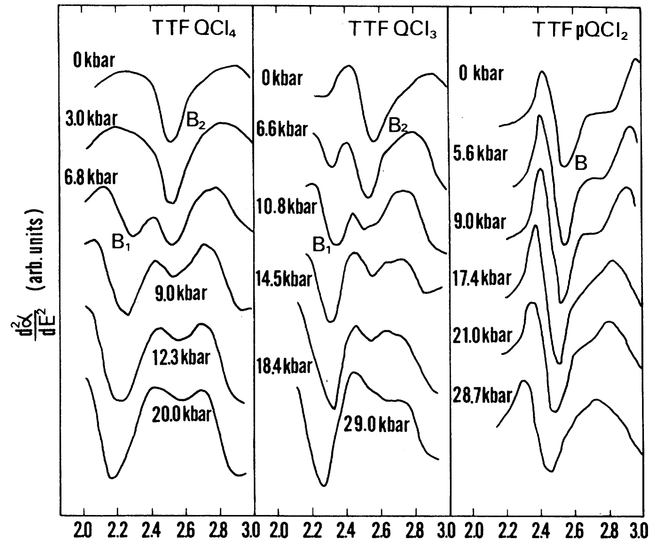

FIG. 8. Second derivatives of visible absorption spectra of TTF-QCl_4 (TTF-CA), TTF-QCl_3, and TTF-$pQCl_2$ under hydrostatic pressures.

feature is favorable for the investigation of molecular ionicity.

In order to investigate the pressure-induced change of the B band, we have measured the second-derivative absorption spectra $d^2\alpha(E)/dE^2$ at various pressure. The results are shown in Fig. 8. The dips in the derivative spectra correspond to the peaks in absorption spectra. The main dips at $P=0$ kbar correspond to the peaks of the B band around 2.5 eV in the absorption spectra shown in Fig. 8. There are several interesting features in the derivative spectra of TTF complexes under pressure. First, the spectral behaviors are very similar to each other in TTF-QCl_4 (TTF-CA) and TTF-QCl_3. When pressure is applied, a new band denoted B_1 appears on the low energy side of the B_2 band. Its intensity grows gradually with pressure and finally dominates over the B_2 band at high pressures. In contrast, the B band in TTF-$pQCl_2$ shows only a gradual red shift with pressure, but no additional band is induced by pressure.

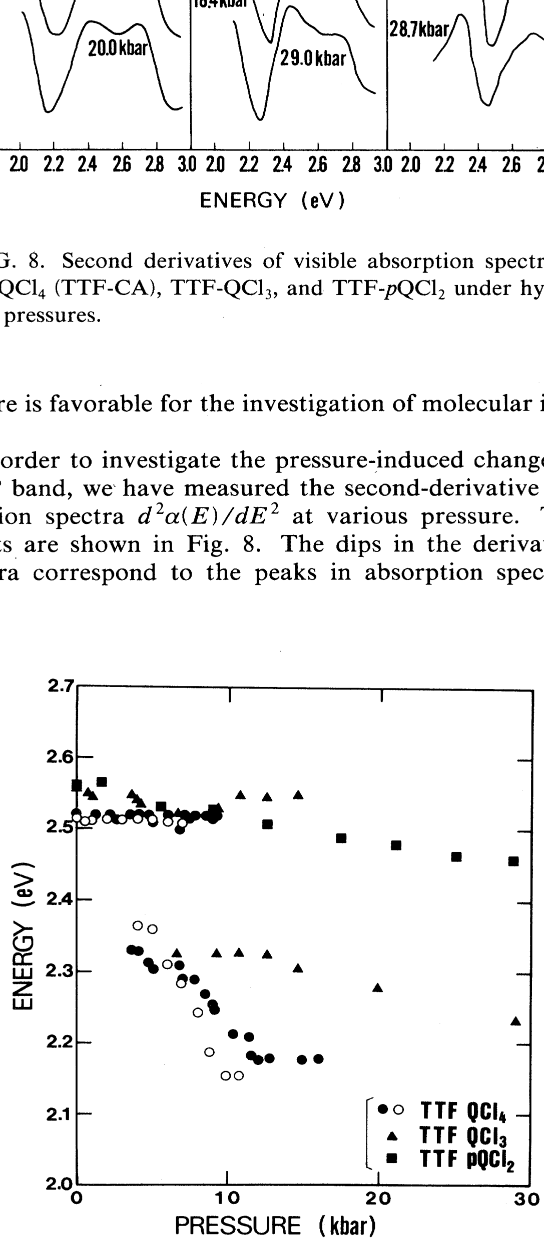

FIG. 9. Peak energies of the B bands of TTF-QCl_4 (TTF-CA) [(● in this work and ○ in Ref. 16)], TTF-QCl_3 (▲), and TTF-$pQCl_2$ (■) at various pressures.

The energies of these dips are plotted in Fig. 9 as a function of pressure. The pressure-induced change in the B band has been previously measured by Kaneko *et al.* in the reflection spectra of the TTF-QCl_4 (TTF-CA) single crystal.[11] Their results are also plotted in Fig. 9 by open circles, which are in good agreement with the present results (solid circles). The red shifts of the B band with pressure indicate that the ρ value of TTF molecules becomes larger with pressure. The apperance of the B_1 band in TTF-QCl_4 (TTF-CA) and TTF-QCl_3 implies that two kinds of TTF molecules having different degrees of charge transfer ρ are induced in these crystals by pressure, whereas no mixed phase is induced in TTF-$pQCl_2$. These results are in good accord with the conclusion derived from the infrared molecular vibration spectra in the preceding section.

C. The ρ value and lattice dimerization in the PINIT

The ρ values and their pressure dependences as well can be estimated from the frequency shifts of C$=$O stretch modes relative to those in the neutral and fully ionic molecules. In the ir spectra of TTF-QCl_4 (TTF-CA) and TTF-$pQCl_2$ (Figs. 1 and 5), the A and B bands have been assigned to the antisymmetric C$=$O stretch modes. In the ir spectra of TTF-QCl_3 (Fig. 3), spectral features are somewhat complicated by the appearance of A, A', B, and C bands, so we have used the main A and B bands for the estimation of the ρ values. The approximate ρ values for these complexes have been evaluated from the frequencies of respective bands at various pressures, assuming that the frequency shifts are linear to ρ between the neutral ($\rho=0$) and fully ionic ($\rho=1$) molecular states. The experimental values which were estimated in this way for TTF-QCl_4 (TTF-CA), TTF-QCl_3, TTF-$pQCl_2$, are plotted in the upper part of Fig. 10 as a function of pressure.[23]

Besides the pressure-induced change in ρ, the infrared molecular vibration spectra provide information on the lattice deformation by molecular dimerization. The integrated intensity of the E band, which is induced around 960 cm^{-1} by the dimerization, is useful for the experimental measure of the lattice dimerization by pressure. The results obtained from Figs. 1, 3, and 5 are plotted against pressure in the lower part of Fig. 10. The intensities are normalized by the intensities of the C$=$O stretch band in the respective complexes at $P=0$ kbar. The E band is normally forbidden at $P=0$ kbar in TTF-QCl_4 and TTF-$pQCl_2$. (In TTF-QCl_3, the E band is weakly activated at $P=0$ kbar by the low molecular symmetry of

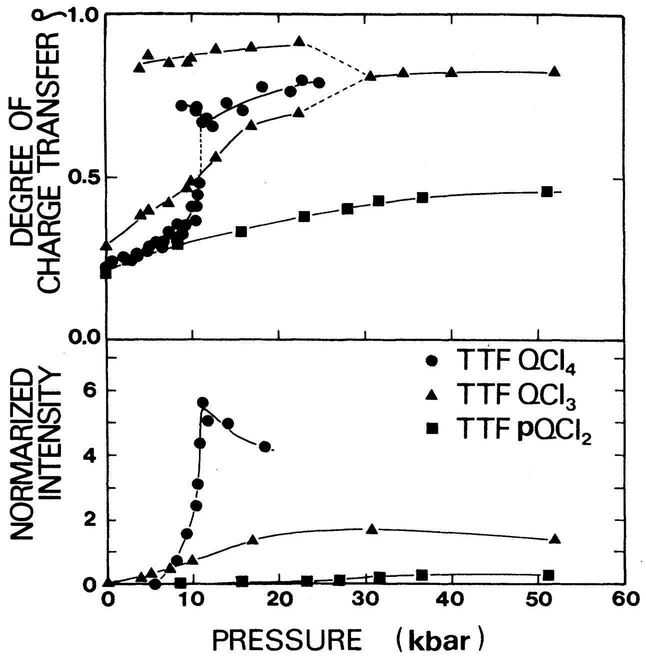

FIG. 10. The approximate ρ values estimated from the frequency shifts of C$=$O stretch bands (upper plot) and the normalized intensities of the E band which is activated by the dimeric lattice distortions (lower plot) in TTF-QCl$_4$ (TTF-CA) (●), TTF-QCl$_3$ (▲), and TTF-pQCl$_2$ (■).

QCl$_3$.) When the lattice is dimerized, the E band gains the intensity from the CT excitation band via the EMV coupling effect. According to a simple dimer model, the intensity is proportional to $\rho(1-\rho)$.[14]

In the regularly stacked TTF-QCl$_4$ (TTF-CA) crystal, the pressure-induced intensity of the E band can be directly related to the degree of lattice dimerization by pressure. A sharp increase in the E-band intensity at about 11 kbar indicates an onset of the dimerized phase. (A slight decrease of the intensity above 11 kbar is due to the intensity change of the CT excitation.) But, contrary to the TINIT,[4] the PINIT is not so sharp, passing through an inhomogeneous quasineutral and quasi-ionic mixed state below P_c as mentioned before. Since the $E(a_g)$ band gains intensity at the same time as the low-frequency component of the C$=$O stretch (b_{1u}) mode due to the quasi-ionic QCl$_4$ (CA) molecule becomes observable, the ionic domains induced by pressure below P_c must be also dimerized. In the case of TINIT, there is no indication of an inhomogeneous state in the optical spectra. (However, a possibility of a devil's-staircase behavior has been suggested to occur in a small temperature range around T_c from recent electric conductivity measurements.[24])

From the above experimental results, the (PINIT) in TTF-QCl$_4$ (TTF-CA) is interpreted as follows. As the Madelung energy is increased with pressure, the energy of the dimerized quasi-ionic state is lowered. At intermediate pressures just below P_c, the quasineutral state and the dimerized quasi-ionic state become nearly degenerate (yet the energy of the latter is still higher than the former). The collective excitations of quasi-ionic regions are thermally generated in the quasineutral DA stacks. In this quasi-one-dimensional system, the energy of the quasi-ionic state is supposed to be lowered by the dimerization. When pressure is further increased to P_c, all molecules are ionized to form a uniformly dimerized quasi-ionic lattice.

In the case of TTF-QCl$_3$ crystal, the E band around 960 cm^{-1} is considerably enhanced by pressure as seen in Fig. 10(b), indicating a pressure-induced lattice dimerization in this system, too. Simultaneous enhancement of the B band around 1570 cm^{-1} is obviously due to the appearance of quasi-ionic QCl$_3$ molecules. From these results, it is evident that the pressure-induced quasi-ionic molecular region is dimerized, being surrounded by the coexisting quasineutral region. Such an N-I mixed state is observed in a large pressure range from about 6 to 25 kbar at room temperature. The pressure-induced change of visible absorption spectra shown in Fig. 8 is consistent with this interpretation. When pressure is sufficiently high, the entire lattice is converted to the homogeneous quasi-ionic-dimerized phase. The critical pressure P_c ($\simeq 25$ kbar) for this PINIT in TTF-QCl$_3$ is considerably higher than P_c ($=11$ kbar) in TTF-QCl$_4$ (TTF-CA). This is understandable as due to the smaller electron affinity of QCl$_3$ than that of QCl$_4$ (CA) molecule.

In the above discussion, the pressure-induced splitting of the C$=$O molecular vibration band and that of the intramolecular electronic excitation B band are both regarded as experimental evidence for the N-I mixed structure in TTF-QCl$_4$ (TTF-CA) and TTF-QCl$_3$. However, when one compares detailed behaviors of these bands, one finds that there is a significant difference between them: In the electronic excitation spectra, the separation between the B_1 and B_2 bands tends to increase gradually with pressure (cf. Fig. 9). To the contrary, the separation between the C$=$O stretch A and B bands decreases with pressure as seen in Fig. 2 and 4. We suggest that these results manifest the dynamical properties of the N and I regions in the N-I mixed state. It is supposed that the N and I domains in the mixed phase are not statically distributed but are thermally fluctuating in the lattice. Such a fluctuating N-I domain model has been proposed to explain a remarkable increase in the electric conductivity by pressure.[11,25] The average period of this fluctuation is considered to become shorter as pressure approaches P_c. At high pressures near P_c, this period will become comparable to the difference between the molecular vibration frequencies for the quasineutral and quasi-ionic molecules. Then the vibration frequency does not depend on the instantaneous ionicity of specific molecules but tends to depend on the time-averaged molecular ionicity. The decrease of the C$=$O band splitting in TTF-QCl$_4$ (TTF-CA) and TTF-QCl$_3$ crystals with increasing pressure may be accounted for by this interpretation. For the electronic excitation band B, the fluctuation effect must be negligibly small.

Next we consider the case of TTF-pQCl$_2$ crystal. In this crystal, the pressure-induced change of ρ is continuous and becomes almost constant (~ 0.5) at high pressures, as seen in Fig. 10(a). (The ρ values at high pressures may be slightly underestimated at high pressures, since molecular-vibration frequencies for both neutral and fully ionic molecules in crystal usually tend to increase with pressure.) Since there is no detectable splitting in both the C=O stretch vibration band and the *B* excition band at high pressure, we can conclude that the *N-I* mixed state as observed in TTF-QCl_4 (TTF-CA) and TTF-QCl_3 is not induced in TTF-$pQCl_2$ by pressure.

Another point to be noted is that the intensity of the *E* band in TTF-$pQCl_2$ is considerably weaker as compared to that of TTF-QCl_4 (TTF-CA) or TTF-QCl_3. The relative intensities of the *E* band in three kinds of TTF complexes give a crude idea of pressure-induced dimerization in these crystals. For more quantitative discussion, we need the value of the EMV coupling constant for this band which is not known for TTF-$pQCl_2$ and TTF-QCl_3. However, since the C=O stretch a_g band (the *C* band) is not detected in TTF-$pQCl_2$ even at $P=50$ kbar, one may conclude that the lattice distortion must be very small in TTF-$pQCl_2$. As for the *E* band, it is evident that its intensity mainly comes from the nearby a_u band (out-of-plane intramolecular vibration mode) which is located around 900 cm^{-1}. A similar intensity transfer effect between antisymmetric and symmetric modes has been previously observed in TMPD-CA.[26]

Aside from quantitative discussion, qualitative features of the ir and visible spectra have revealed that the electron-lattice interaction in TTF-$pQCl_2$ is not so large as compared to those in TTF-QCl_4 (TTF-CA) and TTF-QCl_3. This difference may be attributed to the molecular geometries in the respective complexes. Since the electron-lattice interaction is determined by the degree of modulation of the intermolecular transfer integral by the particular lattice phonon, it will depend sensitively on the overlapping of molecular orbitals in the donor and acceptor molecules. In TTF-$pQCl_2$, the *N-I* phase transition is not observed up to about 50 kbar. In this complex, the electron-lattice interaction is supposedly not large enough to make the energy of the quasi-ionic state lower than that of the quasineutral state even at about 50 kbar. At higher pressures, an increase in the Madelung energy will become favorable for the *N-I* transition. But at the same time, the transfer integral will be also increased, giving rise to a hindrance effect to the *N-I* transition. Such an interpretation may explain the saturated value for TTF-$pQCl_2$ at high pressures as seen in Fig. 10.

V. CONCLUSIONS

The pressure-induced *N-I* transition (PINIT) has been investigated on three kinds of TTF-*p*-benzoquinone derivatives [TTF-QCl_4 (TTF-CA), TTF-QCl_3, and TTF-$pQCl_2$] by means of the ir and visible absorption spectroscopy under hydrostatic pressure. From detailed behaviors of these spectra under hydrostatic pressure, the following features have been revealed for the pressure-induced *N-I* transition (PINIT) for respective complexes: In TTF-QCl_4 (TTF-CA) and TTF-QCl_3 the undimerized quasineutral state is converted to the dimerized quasi-ionic state by pressure primarily due to an increase of the Madelung energy. The critical pressure P_c for the pressure-induced *N-I* transition (PINIT) is 11 kbar for TTF-QCl_4 (TTF-CA) and about 25 kbar for TTF-QCl_3. At pressures below P_c, the coexistence of quasineutral and quasi-ionic states is observed. This quite notable feature, that is, the formation of an inhomogeneous structure, has a significant influence upon the electric properties of these systems.[11,25] In contrast with the cases of TTF-QCl_4 (TTF-CA) and TTF-QCl_3, the degree of charge transfer ρ in TTF-$pQCl_2$ increases gradually with pressure. The ρ value amounts to about 0.5 at 50 kbar. No discontinuous changes nor spectral features indicating an inhomogeneous CT state are observed. A weak lattice distortion is observed to occur, but it does not seem to play an important role in the change of ρ in this crystal. In the three TTF-complex crystals investigated, the electron-lattice interaction plays a significant role in addition to the electrostatic Madelung energy.

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