2052 © 1991 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 64, 2052—2057 (1991) [Vol. 64, No. 7

Pressure-Induced Neutral–Ionic Phase Transition of a Tetrathiafulvalene–Iodanil Crystal

Susumu MATSUZAKI,* Toshihiro HIEJIMA, and Mizuka SANO†
Department of Chemistry, Faculty of Science, Kumamoto University, Kumamoto 860
† Division of Natural Sciences, International Christian University, Mitaka, Tokyo 181

(Received March 4, 1991)

The pressure dependence of IR spectra measured for a mixed-stack neutral charge-transfer (CT) crystal, tetrathiafulvalene–iodanil (TTF-IA), showed an occurrence of a neutral–ionic (N–I) transition at 1.9 GPa. The N–I transition is accompanied by gradual dimerization of the crystal lattice and a small ionicity jump, in contrast to the case of TTF–chloranil (TTF–CA). Such a quasi-continuous N–I transition is attributable to stronger electron–lattice interaction in TTF–IA than that in TTF–CA.

Organic charge-transfer (CT) crystals with mixed-stack structures are classified into two types with a neutral and an ionic ground electronic states. The occurrence of either ground state is determined by a balance between energy gain by the electrostatic Madelung energy (E_M) of an ionic crystal lattice and energy cost on ionization of a donor–acceptor pair ($I_D - E_A$) in a neutral crystal lattice, where I_D is ionization potential of a donor (D) and E_A is electron affinity of an acceptor (A). When a transfer integral "t" determined by an orbital overlap between the D–A pairs is negligibly small, the neutral–ionic interface is sharp; i.e., degree of ionicity (ρ) takes one of the extreme values, zero or one.[1] The interface diffuses with an increase in "t", and ρ comes to take a value between zero and one. In such a case, the CT crystals are labeled as quasi-neutral ($\rho<0.5$) and quasi-ionic ($\rho>0.5$) compounds.[2]

It has recently been found[3] that application of pressure or lowering of temperature generates a phase transition accompanying an increase in ρ from quasi-neutral to quasi-ionic i.e., N–I transition, for several mixed-stack CT crystals near the neutral–ionic interface. In particular, a mixed-stack CT crystal of tetrathiafulvalene (TTF) and chloranil (CA), TTF–CA, has attracted much attension of physicists and chemists for the pressure-induced[4,5] and temperature-induced[6,7] N–I transitions. Many experimental and theoretical works on TTF–CA have revealed that an increase in E_M with a contraction of the crystal lattice and electron–lattice interaction play important roles in the N–I transition. On the other hand, there are only a few reports on the N–I transition of other CT crystals.[8,9] Experimental studies on various CT crystals are necessary to draw a complete scheme of N–I transitions.

TTF–tetrahalo-*p*-benzoquinones are known to give several CT crystals with segregated- or mixed-stack structure and neutral or ionic ground state;[10,11] e.g., mixed-stack crystals of TTF–FA[12] (FA, fluoranil), TTF–CA,[12] and TTF–IA[11] (IA, iodanil) are neutral, and the crystal of TTF–BA[13] (BA, bromanil) is ionic. We are interested in an effect of halogen-substitution on the ionicity and N–I transition in the TTF–tetrahalo-*p*-benzoquinone crystals. Here, we report a pressure-induced N–I transition in a mixed-stack CT crystal of TTF and iodanil (TTF–IA) and compare the results with those of TTF–CA.

Experimental

Tetrathiafulvalene (Tokyo Kasei Co.) was purified by sublimation in vacuo. Iodanil (tetraiodo-*p*-benzoquinone) synthesized from bromanil and potassium iodide by the method of Torrey and Hunter[14] was purified by repeated recrystalizations from ethyl acetate to give deep purple needle-like crystals. They were identified by elemental analyses and IR spectra.

Charge-transfer complexes of TTF and IA were prepared by mixing of the hot ethyl acetate solutions of each component. When the mixed solution was cooled, two kinds of crystals were simultaneously obtained: One is an orange needle and another is a dark brown plate. The former is a 1:1 CT complex (TTF–IA) and the latter is a 2:1 CT complex, $(TTF)_2IA$. Compositions of these complexes were determined by elemental analyses and X-ray crystal-structure analyses.[15] The results for $(TTF)_2IA$ will be published elsewhere. A potassium salt of IA, K·IA, was prepared from IA and potassium iodide in acetone. Crystals of TTF–CA and TTF–BA were prepared by mixing of the hot acetonitrile solutions of each component.

IR spectra of powder samples were recorded on a JASCO FT/IR-7000 Fourier-transform infrared spectrometer in the pressure region up to 6.3 GPa by use of a diamond anvil cell (DAC). A stainless steel foil 0.03 mm thick was used as a gasket which had a hole of 0.6 mm in diameter. Nujol was used as a pressure medium and the applied pressure was calibrated by use of the R_1 fluorescence line of ruby. Raman spectra of powder samples were recorded on a JASCO R-800 spectrometer equipped with an NEC GLG-3200 Ar^+ laser as an excitation light source at ambient pressure to determine frequencies of totally symmetric vibrations. The fluorescence line of ruby was also recorded on the Raman spectrometer. All the measurements were performed at ambient temperature.

Results and Discussion

Ionicity at Ambient Pressure. Figure 1a shows an IR-spectrum of a TTF–IA powder sample at ambient pressure. A spectrum of TTF–CA obtained in this study is shown in Fig. 1b for comparison. Frequencies and assignment of the IR bands are given in Table 1 with those of IA^0 and IA^-.[11] The frequencies of K·IA are

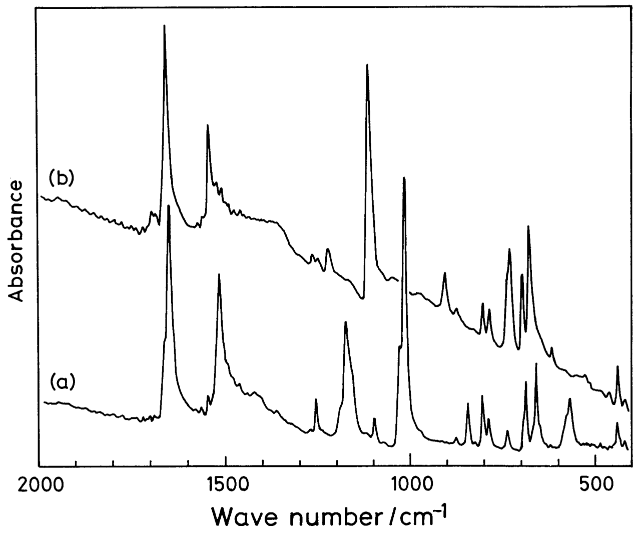

Fig. 1. IR spectra of power samples at ambient pressure. (a) TTF–IA; (b) TTF–CA.

Table 1. IR Frequencies of TTF–IA at Ambient Pressure

TTF–IA	Wave number$^{a)}$/cm^{-1}				Assignment		
	IA^0	IA$^-$	TTF^0	TTF$^+$			
3080			3073		TTF	b_{2u}	ν_{22}
1647	1662	1498			IA	b_{1u}	ν_{10}
1518	1519	1519			IA	b_{2u}	ν_{18}
1510			1530	1478	TTF	b_{1u}	ν_{14}
1255			1254	1237	TTF	b_{2u}	ν_{23}
1172	1177				IA	b_{2u}	ν_{19}
1096			1090	1072	TTF	b_{1u}	ν_{15}
1013	1018	1065			IA	b_{1u}	ν_{11}
841	840	849			IA	b_{1u}	ν_{12}
803			794	825	TTF	b_{2u}	ν_{25}
785			781	836	TTF	b_{1u}	ν_{16}
735			734	751	TTF	b_{1u}	ν_{17}
687	692	688			IA	b_{3u}	ν_{28}
659			639	705	TTF	b_{3u}	ν_{34}
567	567				IA	b_{2u}	ν_{20}
437			427	460	TTF	b_{1u}	ν_{18}

a) Frequencies of TTF^0 and TTF$^+$ are from Ref. 16.

used as those of IA$^-$, and frequencies and assignment of TTF^0 and TTF$^+$ have been reported in the literature.[16] The spectrum of TTF–IA (Fig. 1a) is reasonably explained as a superposition of the spectra of neutral donor (TTF^0) and neutral acceptor (IA^0), as in the case of TTF–CA (Fig. 1b);[17] i.e., TTF–IA is a neutral CT crystal. The degree of ionicity at ambient pressure (ρ_0) is estimated at 0.08 for TTF–IA from the C=O stretching IR frequency (1647 cm^{-1}) of IA on the assumption of a linear relation between the frequency and ρ.[17]

Metzger and Torrance[18] and Girlando, et al.[13] discussed on the difference in ionicity between two mixed stack CT crystals, TTF–CA and TTF–BA: the former is neutral and the latter is ionic. They claimed that BA has larger polarizability than CA and the resulting large polarization energy plays an important role in stabilizing the ionic ground state in TTF–BA. However, their claim appears to be inconsistent with the fact found in this study that TTF–IA has a neutral ground state. Iodanil has larger polarizability than BA as reported by Sato, et al.[19]. They have estimated that the molecular polarizability of IA is about twice as large as that of BA, on the basis of the difference in ionization energy between the gaseous and solid states. The electron affinity of IA, on the other hand, is not so different from the electron affinities of CA and BA.[20] These factors are expected to advantage the ionic ground state also in the case of TTF–IA. Therefore, the neutral ground state found in this study suggests that other factors should be considered to explain the difference in the ionicity of TTF–tetrahalo-*p*-benzoquinone crystals.

Large polarizability of the component molecules in CT crystals stabilizes the energy of D$^+$ and A$^-$. This effect decreases the energy difference, I_D-E_A, and is favorable for the ionic ground state. On the other hand, the large polarizability simultaneously increases dielectric constant (ε) of the crystals, according to Clausius–Mossotti relation. The increased dielectric constant reduces the Madelung energy, $E_M=\alpha e^2/\varepsilon r$, where α, e, and r are Madelung constant, electron charge, and intermolecular distance, respectively; therefore, this effect is favorable for the neutral ground state. Ionicity of the CT crystals is expected to be dominated by the relative importance of these two effects, so that large polarizability of the component molecules does not necessarily produce the ionic ground state.

There is another factor to be taken into consideration, i.e., a packing motif of donor and acceptor molecules in the crystal. The packing motif is expected to affect the ionicity through a change of E_M. Among all the CT crystals of TTF–tetrahalo-*p*-benzoquinones with the mixed stack structure, only TTF–BA is ionic and the others are neutral. The neutral CT crystals, TTF–FA,[12] TTF–CA,[12] and TTF–IA,[15] have packing motifs similar to each other: The crystals are composed of a single mixed stack. On the other hand, the crystal of TTF–BA is composed of two mutually orthogonal mixed stacks; i.e., the packing motif is quite different from those of the three neutral CT crystals. The results suggest that the difference in the molecular packing motif must also play an important role in the occurrence of the ionic ground state of TTF–BA in addition to the polarization effect.

The value of ρ_0 is estimated at 0.18 for TTF–CA[5,17] by use of the C=O stretching frequencies of the complex (1657 cm^{-1}), CA^0 (1693 cm^{-1}), and CA^{-1} (1518 cm^{-1}). The ionicity estimated for TTF–IA (0.08) is considerably smaller than that of TTF–CA. The small value is attributed to the effect of the substitution of large iodine atoms into the acceptor. An interplanar distance between TTF and IA (3.57 Å)[15] is 0.18 Å longer than that of TTF–CA (3.39 Å),[12] because of the larger atomic radius of iodine than that of chlorine. The large interplanar distance in TTF–IA should be responsible for the small value of ρ_0. The ionicity is approximately expressed by the relation, $\rho \propto t^2/(h\nu_{\mathrm{CT}})^2$, where t is a transfer integral and $h\nu_{\mathrm{CT}}$ is energy of charge-transfer absorption. The value of $h\nu_{\mathrm{CT}}$ observed for TTF–IA in a KBr disk is 6300 cm^{-1}, which is not so different from the value for TTF–CA (5300 cm^{-1}).[21] Therefore, the small ρ_0 value of TTF–IA is attributed to a small transfer integral, which results from the large interplanar distance, i.e., a small overlap between π molecular orbitals of donors and acceptors in comparison with TTF–CA.

Pressure Dependence of Ionicity and N-I Transition. Figure 2 shows pressure dependence of the IR spectra for TTF–IA. The IR band A of an IA C=O stretching vibration (b$_{1u}$ ν_{10}) shows a large low-frequency shift with increasing pressure. At 1.9 GPa (Fig. 2c), a new band A′ appears as a shoulder on the low-frequency side of band A. On further compression, intensity of band A′ increases and band A disappears as shown in Fig. 2e. The crystals of TTF–IA were found to decompose gradually when storaged in a desiccator to give neutral iodanil. The decomposition is probably attributed to sublimation of TTF molecules which leaves IA^0 molecules on the crystal surface. An IR band of the IA^0 molecules is marked with an asterisk in the figure. The rate of decomposition was so slow that no spectral change induced by the decomposition was observed during the measurements of pressure dependence.

Pressure dependence of the IR frequencies (Fig. 3) shows that band A changes to band A′ at 1.9 GPa with a slight frequency jump. The degrees of ionicity are estimated at 0.36 and 0.42 for bands A and A′, respectively, at 1.9 GPa. With further compression, the frequency of band A′ gradually decreases and the degree of ionicity increases up to 0.57 at 6.3 GPa which is the highest pressure in this study. The C=O stretching frequencies of IA and K·IA are practically independent of applied pressure as shown in Fig. 3. Therefore, ionicity at every pressure was estimated by use of the frequencies of IA and K·IA at ambient pressure.

Even at the highest pressure, the R$_1$ fluorescence line of ruby showed only small inhomogeneous broadening. The broadening is known as a measure of non-hydrostatic compression in a pressure medium.[22] Small inhomogeneous broadening observed shows negligible pressure distribution in the gasket hole of the DAC. Such negligible pressure distribution is also demonstrated by absence of inhomogeneous broadening of bands A and A′ of which widths are expected to be sensitive to the non-hydrostatic compression because of the large frequency shifts by pressure. (See Fig. 2.)

An increase in ρ at P_c is also indicated by frequency

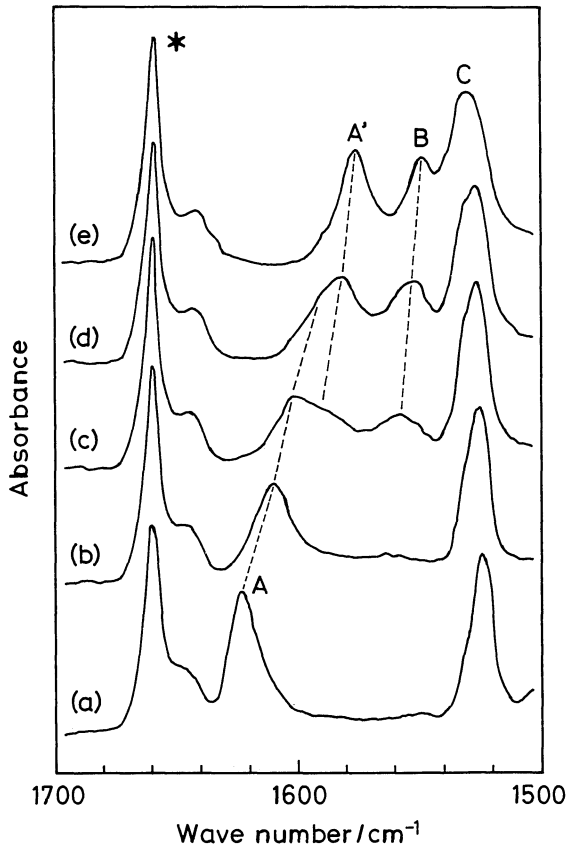

Fig. 2. IR spectra of TTF–IA in the region of C=O stretching vibrations at high pressures. (a) 1.2; (b) 1.7; (c) 1.9; (d) 2.3; (e) 2.7 GPa. *; a band of IA^0.

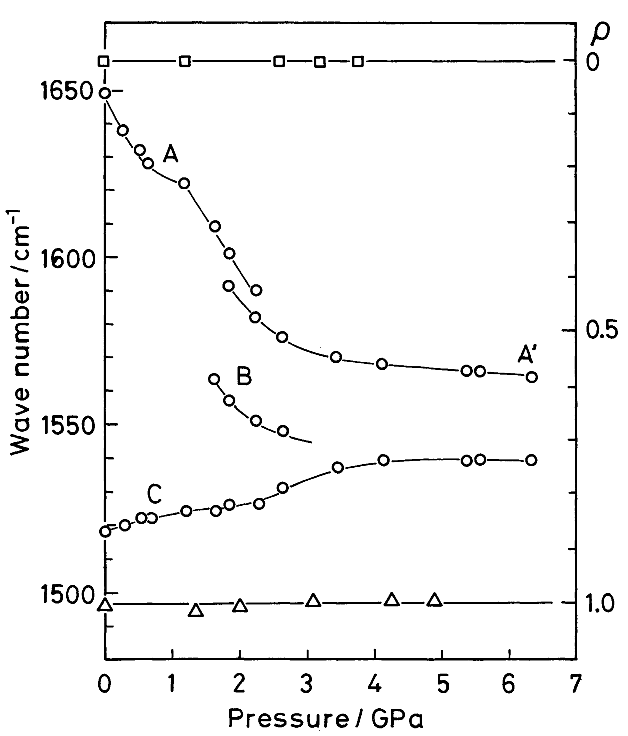

Fig. 3. Pressure dependence of IR frequencies of TTF–IA in the region of C=O stretching vibrations. (○) TTF–IA; (□) IA^0; (△) IA$^-$.

shifts of TTF C–S stretching vibrations (bands E, F, and G) in Fig. 4. Bands E, F, and G are assigned to b_{2u} ν_{25}, b_{1u} ν_{16} and b_{1u} ν_{17}, respectively, as given in Table 1. These bands show considerable high-frequency shifts (20—40 cm^{-1}) on ionization of TTF as shown in the table, and can be used as indicators for ionicity of TTF. Figure 5 shows the pressure dependence of the three bands. The corresponding frequencies of TTF^0 and TTF$^+$ are also plotted versus applied pressure in the figure: frequencies of TTF–BA are used as those of TTF$^+$. The figure shows that the pressure dependence of the frequencies clearly changes at P_c and the frequencies gradually approach to those of TTF$^+$ above P_c: band F comes to be concealed by band E. However, ionicity of TTF could not be precisely estimated because of the nonlinear relations between the frequencies and ionicity, which were found by use of the frequencies of TTF^0, TTF·Br$_{0.76}$ and TTF$^+$.

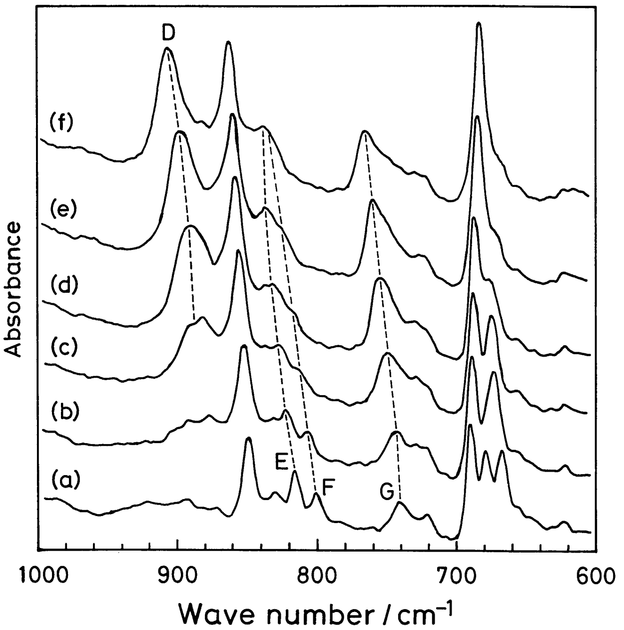

Fig. 4. IR spectra of TTF–IA in thee region of C–S stretching vibrations at high pressures. (a) 1.2; (b) 1.7; (c) 1.9; (d) 2.3; (e) 2.7; (f) 3.5 GPa.

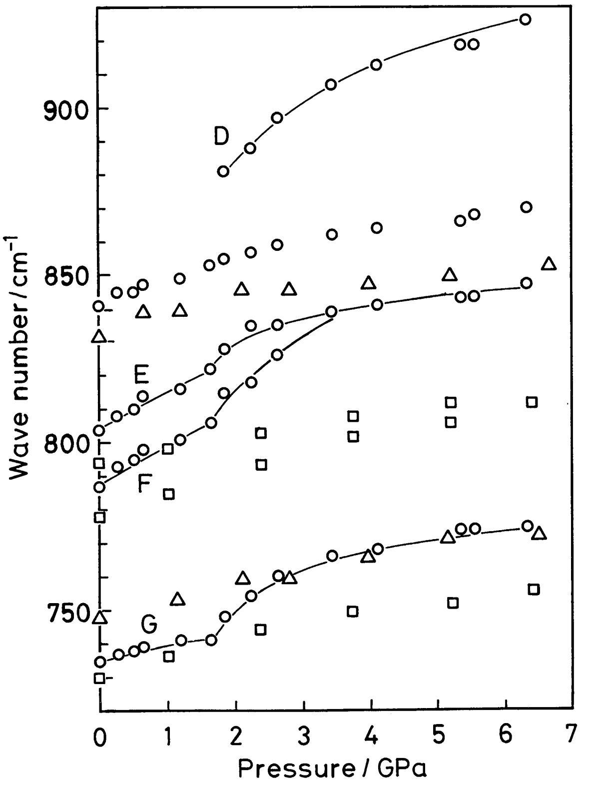

Fig. 5. Pressure dependence of IR frequencies of TTF–IA in the region of C–S stretching vibrations. (○) TTF–IA; (□) TTF^0; (△) TTF$^+$.

A new band B appears around 1560 cm^{-1} at P_c, as shown in Fig. 2c. This band is assigned to the totally-symmetric C=O stretching vibration of IA (a_g ν_1) from its frequency value. Band B shows a low-frequency shift with an increase in pressure as shown in Fig. 3 and is concealed by the band C of an IA C=C stretching vibration (b_{2u} ν_{18}) at ca. 3 GPa. Another new band D appears around 880 cm^{-1} at P_c, as shown in Fig. 4c. This band is assigned to a totally-symmetric ring-deformation vibration of IA (a_g ν_3) from its frequency value. Figure 5 shows that the frequency of band D increases with an increase in pressure. This is consistent with an observed high-frequency shift of the a_g ν_3 Raman band of IA on ionization: 870 cm^{-1} for IA^0 and 935 cm^{-1} for IA$^-$.

IR activation of these bands B and D, which are intrinsically IR-inactive, is attributed to a kind of vibronic interaction, i.e., electron–molecular vibration (e–mv) interaction, between TTF and IA.[23] The appearance of vibronically-activated IR bands demonstrates dimerization of a crystal lattice, because such IR activation is not expected to occur in CT crystals with regular mixed-stack structures.[23] Such dimerization of a crystal lattice is the same as that observed in the N–I transition of TTF–CA,[5] and is produced by electron–lattice interaction. Consequently the anomaly observed for the IR spectra of TTF–IA at 1.9 GPa is attributed to a pressure-induced N–I transition accompanied by dimerization of the crystal lattice. Upon this transition, a yellow sample of TTF–IA was found to turn red, which is attributable to a change in the electronic state of the complex at P_c. The state of the high-pressure phase should rather be labeled as "quasi-ionic" in spite of the result that ionicity of the high-pressure phase is less than 0.5 at P_c as mentioned above. Such a "quasi-ionic" phase is theoretically suggested to exist in the case of strong electron–lattice interaction.[24]

There is another possible assignment of the C=O stretching IR bands A′ and B: band A′ is assigned to a_g ν_1 and band B to b_{1u} ν_{10}. The frequencies of bands A′ and B are 1591 and 1557 cm^{-1} at P_c, respectively. If this assignment is accepted, the phase transition of TTF–IA should be accompanied by a large ionicity jump from

0.36 to 0.64, which is almost equal to that of TTF–CA. However, this assignment is unacceptable because of the following reason. The two C=O stretching vibrations of IA^0 are almost equal to one another: 1656 cm^{-1} (a_g ν_1) and 1659 cm^{-1} (b_{1u} ν_{10}). Furthermore, magnitudes of the low frequency shifts on ionization are also almost equal to one another: 171 cm^{-1} (a_g ν_1) and 161 cm^{-1} (b_{1u} ν_{10}). Therefore, frequencies of the two vibrations are expected to be almost equal to one another at every ionicity if the frequencies are not affected by the e–mv interaction. In fact, frequencies of totally-symmetric vibrations are decreased by the e–mv interaction. On the other hand, non-totally symmetric vibrations are free from any influence by the interaction.[23] Consequently, the frequency of a_g ν_1 must be less than that of b_{1u} ν_{10}.

Comparison of N-I Transitions between TTF-IA and TTF-CA. In the pressure-induced N–I transition of TTF–CA at room temperature, IR bands as well as visible bands of the ionic species appear at pressures considerably lower than P_c. The bands of the neutral and ionic phases are both observed in the pressure region between 0.7 and 1.1 GPa.[5] On the other hand, in the temperature-induced N–I transition of TTF–CA at 81 K, such coexistence of the two phases is not observed.[7] The coexistence is attributed to thermal excitation of the ionic state which has an energy not far off the neutral state near the transition point.[24] Also in the case of TTF–IA, such coexistence is observed as shown in Figs. 2 and 3. The N–I transitions of TTF–IA and TTF–CA are similar to one another on this point but there are a few remarkable differences between the two CT crystals.

Table 2. Comparison of N-I Transitions in TTF-IA and TTF-CA

Complex	ρ_0	$\frac{P_c}{\text{GPa}}$	$\Delta\rho$	IR intensity of totally symmetric vibrations above P_c
TTF–IA	0.08	1.9	0.06 (0.36→0.42)	Gradual increase
TTF–CA[a]	0.18	1.1	0.30 (0.34→0.64)	Abrupt increase

a) Refs. 5 and 6.

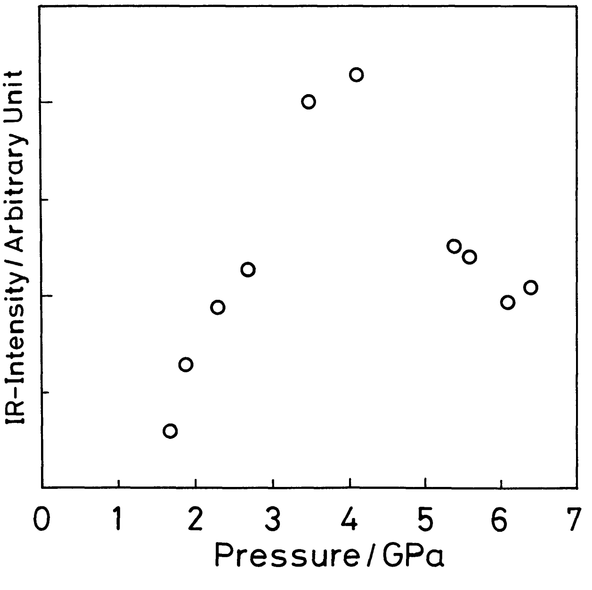

Fig. 6. Pressure dependence of IR intensity observed for a totally-symmetric vibration (IA a_g ν_3) of TTF–IA.

Characteristic features of the N–I transition in the two systems are shown in Table 2. In the case of TTF–CA, a large ionicity jump of 0.3 (from 0.34 to 0.64) is observed at the transition pressure (1.1 GPa): The average of ρ for the neutral and ionic phases at P_c is almost equal to 0.5. On the other hand, in the case of TTF–IA, the ionicity shows only a slight jump of 0.06 (from 0.36 to 0.42) at the transition pressure (1.9 GPa): The average of ρ is clearly less than 0.5. There is a difference also in the IR activation of the totally symmetric vibrations between the two CT crystals. An abrupt increase is observed for the IR intensity of CA (a_g ν_3) in TTF–CA at P_c.[5] In the case of TTF–IA, on the other hand, intensity of the corresponding IR band of IA (a_g ν_3) gradually increases with an increase in pressure above P_c, as shown in Fig. 6. The intensity of the vibronically-activated totally symmetric vibrations is known as a measure of dimerization of crystal lattice,[23] so that Fig. 6 demonstrates gradual dimerization in TTF–IA.

According to a quantum Monte Carlo simulation by Nagaosa,[24] the N–I transition of the mixed-stack CT crystal changes from the discontinuous transition of the first order to the continuous one of the second order with an increase in the electron–lattice interaction, which is due to a variaton of a transfer integral with a change in the interplanar distance between the donor and acceptor. The quasi-continuous transition observed for TTF–IA, i.e., the small ionicity jump and the gradual dimerization of the crystal lattice, are characteristic to the case of large electron–lattice interaction in comparison with TTF–CA. The simulation, on the other hand, predicts a decrease in the transition pressure for the case of large electron–lattice interaction if other conditions are unchanged. This disagrees with the increased transition pressure in TTF–IA compared with TTF–CA as shown in Table 2. This disagreement may be due to the large interplanar distance between TTF and IA[15] and the large polarizability of IA.[19] These two factors decrease the electrostatic Madelung energy and are expected to push up the transition pressure.

This work was partially supported by a Grant-in-Aid for Scientific Research No.01540381 from the Ministry of Education, Science and Culture.

References

1) H. M. McConnell, B. M. Hoffman, and R. M. Metzger, *Proc. Natl. Acad. Sci. U.S.A.*, **53**, 46 (1963).

2) Z. G. Soos and S. Mazumdar, *Phys. Rev. B*, **18**, 1991 (1978).

3) J. B. Torrance, J. E. Vasquez, J. J. Mayerle, and V. Y. Lee, *Phys. Rev. Lett.*, **46**, 253 (1981).

4) A. Girlando, C. Pecile, A. Brillante, and K. Syassen, *Solid State Commun.*, **57**, 891 (1986).

5) H. Okamoto, T. Koda, Y. Tokura, T. Mitani, and G. Saito, *Phys. Rev. B*, **39**, 1339 (1989).

6) J. B. Torrance, A. Girlando, J. J. Mayerle, J. I. Crowley, V. Y. Lee, P. Batail, and S. J. La Placa, *Phys. Rev. Lett.*, **47**, 1747 (1981).

7) Y. Tokura, T. Koda, G. Saito, and T. Mitani, *J. Phys. Soc. Jpn.*, **53**, 4445 (1984).

8) A. Girlando, C. Pecile, A. Brillante, and K. Syassen, *Synth. Met.*, **19**, 503 (1987).

9) Y. Iwasa, T. Koda, Y. Tokura, A. Kobayashi, N. Iwasawa, and G. Saito, *Phys. Rev. B*, **42**, 2374 (1990).

10) J. B. Torrance, J. J. Mayerle, V. Y. Lee, and K. Bechgaad, *J. Am. Chem. Soc.*, **101**, 4748 (1979).

11) S. Matsuzaki, T. Moriyama, M. Onomichi, and K. Toyoda, *Bull. Chem. Soc. Jpn.*, **56**, 369 (1983).

12) J. J. Mayerle, J. B. Torrance, and J. I. Crowley, *Acta Crystallogr., Sect. B*, **35**, 2988 (1979).

13) A. Girlando, C. Pecile, and J. B. Torrance, *Solid State Commun.*, **54**, 753 (1985).

14) H. A. Torrey and W. H. Hunter, *J. Am. Chem. Soc.*, **34**, 702 (1912).

15) M. Murase, M. Konno, S. Matsuzaki, T. Hiejima, and M. Sano, 59th National Meeting of the Chemical Society of Japan, Yokohama, March 1990, Abstr., 2F212.

16) R. Bozio, I. Zanon, A. Girlando, and C. Pecile, *J. Chem. Phys.*, **71**, 2282 (1972).

17) A. Girlando, F. Marzola, C. Pecile, and J. B. Torrance, *J. Chem. Phys.*, **79**, 1075 (1983).

18) R. M. Metzger and J. B. Torrance, *J. Am. Chem. Soc.*, **107**, 117 (1985).

19) N. Sato, K. Seki, and H. Inokuchi, *J. Chem. Soc., Faraday Trans. 2*, **77**, 1621 (1981).

20) E. C. M. Chen and W. E. Wentworth, *J. Chem. Phys.*, **63**, 3183 (1975); E. C. M. Chen and W. E. Wentworth, *Mol. Cryst. Liq. Cryst.*, **171**, 271 (1989).

21) C. S. Jacobsen and J. B. Torrance, *J. Chem. Phys.*, **78**, 112 (1983).

22) G. J. Piermarini, S. Block, and J. S. Barnett, *J. Appl. Phys.*, **44**, 5377 (1973).

23) A. Painelli and A. Girlando, *J. Chem. Phys.*, **84**, 5655 (1986).

24) N. Nagaosa, *J. Phys. Soc. Jpn.*, **55**, 2754 (1986).