The neutral-to-ionic phase transition of TTF-CA: a Raman study of the influence of temperature and hydrostatic pressure

A Moreac, A Girard and Y Delugeard

Groupe Matière Condensée et Matériaux, URA au CNRS 804, Université de Rennes I, Campus de Beaulieu, Bâtiment 11B, 35 042 Rennes Cédex, France

Abstract. A low- and high-frequency Raman scattering study of the neutral-to-ionic phase transition of TTF-CA as it relates to the temperature and hydrostatic pressure is reported. Around the transition, the variations of the intensities of several antisymmetric modes permit the determination of the phase diagram and therefore the confirmation of previous results. Under pressure, the more continuous character of the transition is confirmed unambiguously. On the other hand, an evolution under pressure of the mechanism of the transition is clearly shown. The soft mode is still observed at 4 kbar but with a softening which is less critical. Moreover, in the high-temperature phase, the broadening of several totally symmetric modes favours an order–disorder mechanism. So, our study performed under pressure clearly shows that the mechanism of the transition moves from a displacive mechanism to an order–disorder one.

1. Introduction

In a previous paper [1], we have presented a Raman and infrared study of the neutral-to-ionic phase transition induced at low temperature and atmospheric pressure of a mixed-stack charge transfer (C.T.) complex, namely tetrathiafulvalene-p-chloranil (TTF-CA). Following on this study, it appeared that an investigation by varying both pressure and temperature should be very interesting.

Numerous studies have been performed on the neutral-to-ionic phase transition of TTF-CA, and previous publications concerned the effects of applying pressure at room temperature [2–5]. A first infrared study [2] has suggested an increase of the ionicity ρ versus pressure and the authors have shown that the frequencies of several totally symmetric intramolecular modes which appear at the transition are in agreement with those calculated by using a dimer model in the high-pressure phase. Besides this, a second infrared study [3] has shown that the neutral spectrum and the ionic one coexist over a large domain of pressure. This study has also permitted an estimation to be made of the ionicity variation versus pressure. Note that, around the transition, the jump of ionicity ($\approx$0.2) observed under pressure is slightly lower than the one observed at atmospheric pressure ($\approx$0.3) [6]. Moreover, in a Raman study [4], the frequency evolution versus pressure of several totally intramolecular modes has been analysed. By using the dimer and trimer models which take the electron–molecular vibration (e–mv) coupling into account, a new evolution versus pressure of the ionicity has been found at room temperature. Note that this evolution of ρ confirms that the jump observed under pressure is lower that the one observed at atmospheric

pressure. Lastly, conductivity measurements [5] have shown that the evolution of σ versus pressure is clearly continuous, the transition being observed over a large domain of pressure.

Concerning our work, it is to our knowledge the first Raman experiment including a low-frequency study, performed on a single crystal of TTF-CA by varying both pressure and temperature. This work may give important information about the evolution under pressure of the nature of this transition (displacive at atmospheric pressure [1]), and may confirm the evolution of its character (clearly first order at atmospheric pressure [6, 7]) under pressure. Besides this, due to the electron–phonon coupling [8, 9], the evolution versus pressure of the Raman spectrum may give interesting information on the dynamical and electronic properties of this type of C.T. compound. Lastly, simultaneously with a study performed by neutron diffraction [10], this work permits us to plot the phase diagram and thus to confirm or disprove the surprising results obtained earlier by two different techniques [5, 11].

Thus, the present paper describes a Raman investigation of the neutral-to-ionic phase transition of TTF-CA, involving varying both pressure and temperature. The experimental conditions are given in section 2. In section 3 we present the high-frequency spectra and compare our phase diagram with others. In section 4 we describe the influence of pressure on the character of the transition, and in section 5 we study the evolution of its mechanism.

2. Experimental details

TTF-CA single crystals were grown by co-sublimation according to a method described previously [12]. As for our atmospheric pressure study [1], Raman spectra were recorded with a DILOR XY spectrometer using a charge-coupled device (C.C.D.) detector which is very sensitive in the near-infrared spectral range. Due to the high absorption of TTF-CA, the titanium–sapphire laser beam power was adjusted to around 5–6 mW to reduce the heating of the sample. So the experimental conditions are not very different from those defined at atmospheric pressure.

Raman measurements under pressure were performed by using a pressure cell in which helium gas is the pressure-transmitting medium. This experimental setting ensures a hydrostatic pressure around the sample. This cell, inserted into a cryostat, can be cooled down between 6 K and 300 K, and permits 4 kbar to be reached and a macroscopic single crystal to be used. The pressure and temperature stabilities are respectively better than 10 bar and 0.1 K. As in the preceding paper [1], the experimental lines have been deconvoluted from the resolution function and then refined by a least-squares method [13].

3. High-frequency Raman spectra and the phase diagram

Two types of experiment have been performed. The first type concerns studies at variable pressure and at different fixed temperatures; the second one is an experiment at 4 kbar versus temperature. Note that this second experiment is directly comparable to that performed at atmospheric pressure since the transition is induced by temperature in the two cases. For these high-frequency Raman scattering experiments under pressure, the recorded spectral range varies from 250 cm^{-1} to 510 cm^{-1}. For example, figure 1 presents some Raman spectra obtained at different temperatures at 4 kbar in the 390–510 cm^{-1} spectrometer window. First, due to the retro-diffusion configuration, note that the lines located at 419 cm^{-1} and 432 cm^{-1} are assigned to the sapphire window of the pressure cell. Despite several experimental modifications, these two lines have never been totally cancelled. At 4 kbar the transition temperature is estimated to be at about 170 K, and between the neutral
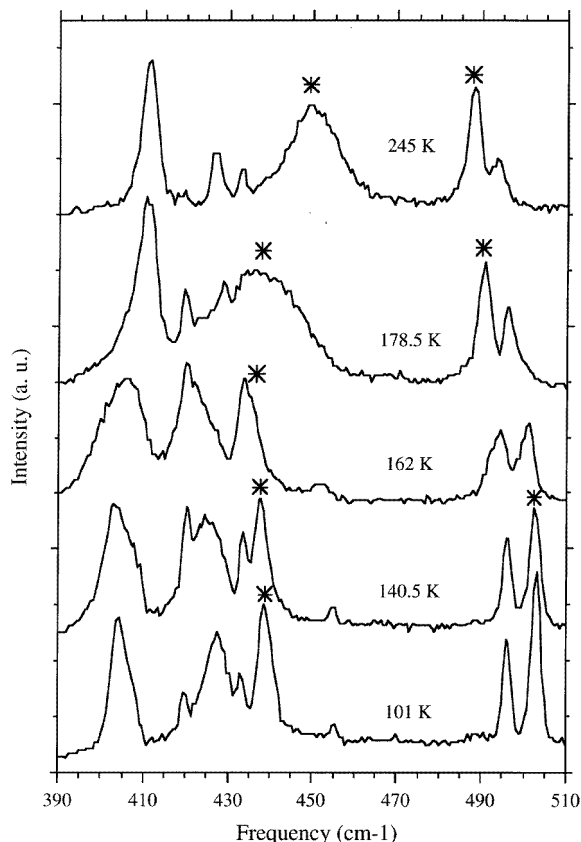
Figure 1. At 4 kbar, the evolution versus temperature of the 390–510 cm^{-1} Raman spectral range of TTF-CA in the neutral phase (245 K), around the transition (178.5 K and 162 K) and in the ionic phase (140.5 K and 101 K). The asterisks indicate the TTF $a_g\nu_6$ and CA $a_g\nu_4$ modes whose frequency and linewidth behaviours are discussed in the text. The modes located at 419 cm^{-1} and 432 cm^{-1} are assigned to the sapphire window of the pressure cell.

phase and the ionic one some important spectral variations, discussed later, are observed in figure 1. In particular, due to the symmetry breaking, an increase in the number of bands is emphasized. The same phenomenon is observed in the experiments performed at low temperature and variable pressure. The explanation for this increase in the number of lines is the loss of the centrosymmetry which makes the antisymmetric modes active in the ionic phase.

The different intensity behaviours of the antisymmetric modes have been used to define the transition pressure (P_{N-I}) or the transition temperature (T_{N-I}). As an example, figure 2 reports the intensity of the antisymmetric mode located at around 300 cm^{-1} in the ionic phase as a function of pressure for two different temperatures (100 K and 151 K). The transition pressures are determined by the inflexion points of these curves. Similarly, at 4 kbar, the curve obtained versus temperature for the same mode permits us to determine the value of T_{N-I} (170 K). The transition pressures (at 100 K, 119 K, 135 K, 151 K and 163 K) and transition temperatures (at atmospheric pressure [1] and at 4 kbar) so deduced have permitted us to plot the phase diagram of TTF-CA (figure 3). The slope of the phase
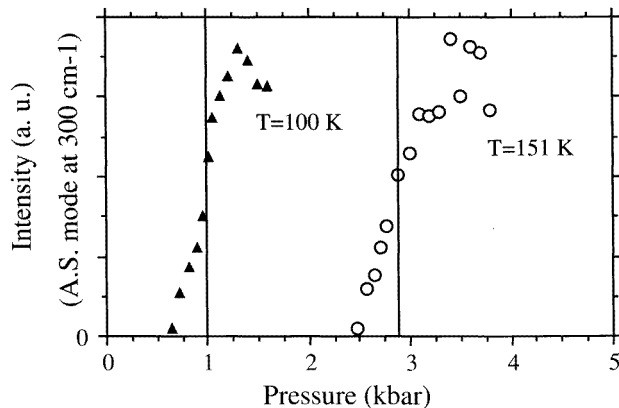
Figure 2. The evolution versus pressure for two temperatures of the intensity of an antisymmetric mode of TTF-CA located at around 300 cm^{-1}. The vertical lines indicate the transition pressure (P_{N-I}) at these two temperatures.
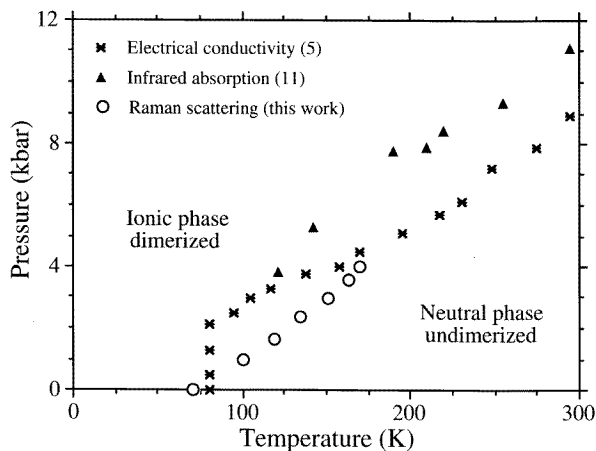

Figure 3. The phase diagram of TTF-CA obtained by three different techniques.

diagram at the origin is $(\mathrm{d}P/\mathrm{d}T)_{P=0} = 33$ bar K^{-1} and the second derivative is positive.

The neutral-to-ionic phase transition is attributed to the competition between the cost in energy $(I - A)$ due to the ionization of the DA pair (I is the ionization energy of the donor molecule and A is the electronic affinity of the acceptor molecule), and the Madelung energy, proportional to $\langle e^2/a \rangle$ (a is the minimum intermolecular distance within the DA pair). Under pressure, the contraction of the intermolecular distances increases the Madelung energy and, consequently, the phase transition is favoured. So, pressure must increase T_{N-I}, which is in agreement with the phase diagram obtained.

On the other hand, in figure 3 we have reported the phase diagrams obtained from electrical conductivity [5] and infrared absorption [11] studies. For the electrical determination of the phase diagram, the very surprising anomaly observed at low pressure ($\mathrm{d}P/\mathrm{d}T$ is infinite) would certainly be due to the use of a clamps cell for which the applied

pressure is not necessarily hydrostatic in this pressure range. Moreover, at low pressure, the relative errors in pressure measurements are important. As for the infrared determination of the phase diagram, the curve is parallel to ours but strongly shifted (by about 60 K) towards low temperatures. Although this determination depends on the same principle as ours (due to the symmetry breaking, the appearance of symmetric modes (infrared) or antisymmetric modes (Raman) in the ionic phase), the results are very different. The most probable reason for this discrepancy is the use of a diamond-anvil cell for which, as for the clamps cell, the hydrostatics and measuring the pressure are very delicate. So, our study has permitted us to correct the low-pressure phase diagram of TTF-CA.

This conclusion has been confirmed by an another experiment. Indeed, simultaneous with our study, a group in our laboratory has also determined the phase diagram of TTF-CA by neutron diffraction [10]. In this work, T_{N-I} corresponds to the appearance of the characteristic extinctions ($(0k0), k = 2n + 1$) of the neutral phase, which are assigned to the loss of the 2_1 axis. The slope of this phase diagram at the origin (equal to 36 bar K^{-1}) is in agreement with our own value (33 bar K^{-1}). Note that calorimetry and neutron diffraction measurements [14] performed at atmospheric pressure have shown that the value of $\Delta S/\Delta V$ (ΔS: entropy variation; ΔV: volume variation) confirms the slope obtained. Nevertheless, our phase diagram is shifted towards low temperatures from about 6 K. This difference can be explained by the local heating of the sample occurring in the Raman experiment. This heating, which depends on the laser beam power, on the laser beam focusing, and on the absorption versus temperature and pressure, introduces an error in the determination of T_{N-I} or P_{N-I}. Under these conditions, our measured temperature is lower than the temperature of the scattering volume and, consequently, the Raman phase diagram is shifted towards low temperatures. Thus, the low-pressure phase diagrams obtained by Raman scattering and neutron diffraction are in good agreement.

4. Character evolution

At atmospheric pressure [1], we have shown that the discontinuities observed in the evolution versus temperature of the frequency of several totally symmetric intramolecular modes emphasize the clear first-order character of the transition induced at low temperature. Moreover, a coexistence domain which traduces the superposition of the neutral spectrum and of the ionic one exists around the transition temperature called T_{N-I}. The origin of this coexistence domain is assigned to the first-order character of this transition and to the temperature gradient which exists for the scattering volume [1]. Thus, under pressure, the behaviour of these totally symmetric intramolecular modes should be very interesting as regards providing information about the evolution of the character of this transition.

The first example is the CA $a_g v_4$ mode which is located at around 484 cm^{-1} at atmospheric pressure and room temperature. Figure 4(a) shows that, at 4 kbar, the frequency behaviour of this mode is clearly different from that observed at atmospheric pressure. Indeed, at 4 kbar, the frequency of the CA $a_g v_4$ mode continuously increases from 487 cm^{-1} to 503 cm^{-1}, whereas at atmospheric pressure, a discontinuity of the frequency and a coexistence domain are displayed. Note that the discontinuity which is observed at around the transition temperature T_{N-I} at 4 kbar is due to a coupling between this mode and the mode located at 494 cm^{-1} at 280 K. This coupling is characterized by an anticrossing phenomenon in the frequency behaviour of these two modes (figure 4(a)), and by an intensity exchange (figure 1). Moreover, the coexistence domain defined at atmospheric pressure has disappeared at 4 kbar. Another illustration of the disappearance of this coexistence domain is presented in figure 5. In the vicinity of the transition and for different couples
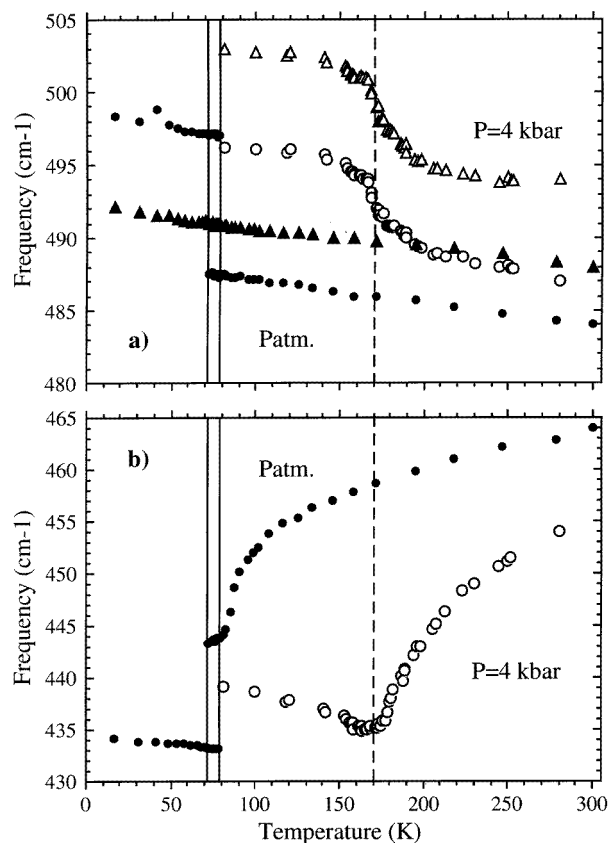
Figure 4. Frequency evolutions versus temperature of two totally symmetric molecular modes of TTF-CA at two pressures: (a) ●, the CA $a_g v_4$ mode at atmospheric pressure; ○, the CA $a_g v_4$ mode at 4 kbar; ▲, the coupled mode at atmospheric pressure; △, the coupled mode at 4 kbar; (b) ●, the TTF $a_g v_6$ mode at atmospheric pressure; ○, the TTF $a_g v_6$ mode at 4 kbar. The temperature domain between full vertical lines (from 72 K to 80 K) corresponds to the coexistence domain observed by Raman scattering at atmospheric pressure, whereas the dashed vertical line indicates the transition temperature at 4 kbar ($T_{N-I} = 170$ K).

(temperature, pressure), figure 5 presents the evolution of the spectral range corresponding to the CA $a_g v_4$ mode. When pressure is weak ($P < 2$ kbar), three lines are present. Among these three lines, two are characteristic of the superposition of the neutral and ionic bands (respectively located at 487 cm^{-1} and 497 cm^{-1}) assigned to the CA $a_g v_4$ mode. Thus, in this case, the transition still appears as a clearly first-order one. When $P > 2$ kbar, the triplet of bands disappears: around the transition, only two broad lines are observed. This observation is especially interesting because a temperature gradient comparable to that observed at atmospheric pressure still exists under pressure (the experimental conditions are almost identical [1]). Thus in agreement with the evolution of the CA $a_g v_4$ mode frequency, the disappearance of the coexistence domain is due to the more continuous character of the transition under pressure.

A last illustration of the evolution of the character concerns the frequency behaviour of several totally symmetric intramolecular modes. These modes—TTF $a_g v_6$, CA $a_g v_3$ and CA $a_g v_5$ (respectively located at 464 cm^{-1}, 982 cm^{-1} and 325 cm^{-1} at (300 K, 1 bar))—
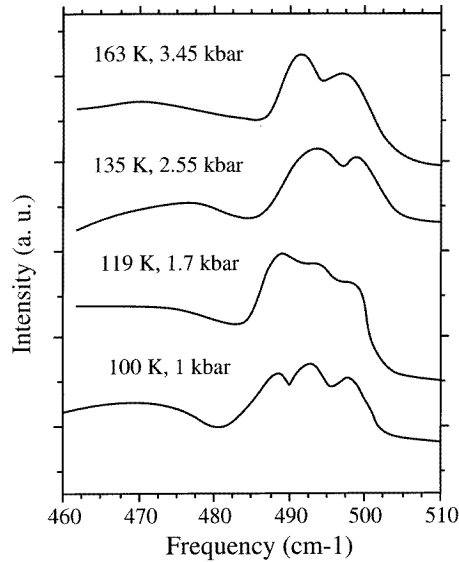
Figure 5. The evolution of the 460–510 cm^{-1} spectral range of the Raman spectrum of TTF-CA for several (temperature, pressure) couples located in the vicinity of the transition.

are highly coupled to the charge transfer [1]. Moreover, at atmospheric pressure, we have shown that their frequencies decrease between the neutral and ionic phases, the jumps being a signature of the first-order character. At 280 K when pressure is applied from 1 bar to 4 kbar, a behaviour in agreement with the one mentioned by Hanfland *et al* [4], is observed. Indeed, when pressure increases, the frequency decreases of these modes are respectively equal to 9 cm^{-1}, 9.5 cm^{-1} and 1 cm^{-1}. Figure 4(b) presents a comparison between the evolution versus temperature of the TTF $a_g v_6$ mode frequency at atmospheric pressure and that at 4 kbar. This figure clearly shows a difference in behaviour between these two studies. Indeed, the evolution at 4 kbar appears totally continuous, whereas at atmospheric pressure a high discontinuity (at around 10 cm^{-1}) is observed. As far as the other two modes are concerned—CA $a_g v_3$ and CA $a_g v_5$—the changes between atmospheric pressure and 4 kbar, in the frequency evolutions versus temperature, are similar. These changes in the frequency evolutions versus temperature between that in the study at atmospheric pressure and that in the one at 4 kbar are another signature of the evolution of the transition character under pressure.

Note that the continuous behaviour of the frequency of the CA $a_g v_4$ and TTF $a_g v_6$ modes has permitted a new assignment of these two modes in the ionic phase. Indeed, for atmospheric pressure, Girlando *et al* [15] have assigned these modes to the lines respectively located at 427 cm^{-1} and 500 cm^{-1}. This study under pressure clearly shows that the assignments are inverse for these two modes.

Lastly, on approaching T_{N-I}, the association of the inhomogeneity of temperature with the more continuous character observed under pressure makes the Raman spectrum become like a clump of bands for the 420–450 cm^{-1} and 490–505 cm^{-1} spectral ranges. Consequently, the linewidths of several modes can appear to be very important around the transition.

To conclude, in agreement with the literature [5, 10], this Raman study clearly shows that the transition appears to be more continuous under pressure. Nevertheless, in the case of the

TTF-CA opaque sample, Raman scattering seems not to be the most appropriate technique for the study of the character evolution. Indeed, the inhomogeneity of the temperature on the scattering volume which masks the intrinsic coexistence of the neutral and ionic phases at atmospheric pressure [1] has a tendency to hide some weak discontinuities. Thus, at 4 kbar, the character of the transition induced at low temperature could still be weakly of first order.

5. Evolution of the mechanism

At atmospheric pressure, we have shown that the nature of the neutral-to-ionic phase transition of TTF-CA is a displacive one [1]. The soft mode is associated with the dimerization along the stacking axis, which has been observed by neutron diffraction in the ionic phase [16]. The symmetry of this mode is B_u and consequently, as regards Raman scattering, it is only active in the ionic phase. Lastly, at atmospheric pressure, we have shown [1] that this mode is coupled to the mode located at 102 cm^{-1} at 16 K. If we take this coupling into account, the frequency decrease of the soft mode is around 17 cm^{-1} between 16 K and T_{N-I}.
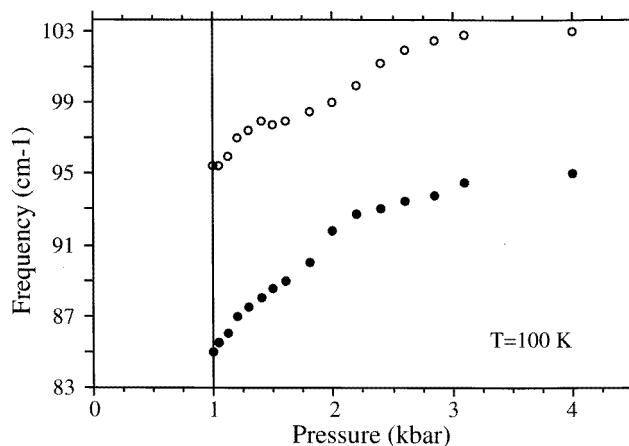

Figure 6. At 100 K, the frequency dependence versus pressure of the Raman soft mode and of the coupled mode observed in the ionic phase of TTF-CA. The vertical line indicates the transition pressure at this temperature ($P_{N-I} = 1$ kbar).

We have performed two studies of the low-frequency dynamics under pressure. The first one has been carried out by varying pressure at a constant temperature (100 K), in the ionic phase. Under these conditions, P_{N-I} is found to be equal to 1 kbar (figure 2). The soft-mode behaviour has been studied from 4 kbar to 1 kbar. Figure 6 presents this frequency evolution versus pressure together with that of the coupled mode. The frequency seems to admit a critical behaviour near P_{N-I}, the frequency decrease being about 10 cm^{-1} between 4 kbar and 1 kbar. If we take the coupling into account, the frequency decrease is about 18 cm^{-1}. This result could show that the nature of the transition is always displacive when we apply pressure at 100 K.

The second experiment has been performed at a constant pressure (4 kbar) and at variable temperature. For the ionic phase, figure 7 compares the evolution versus temperature of the soft-mode frequency at atmospheric pressure and at 4 kbar. In this figure, it is evident
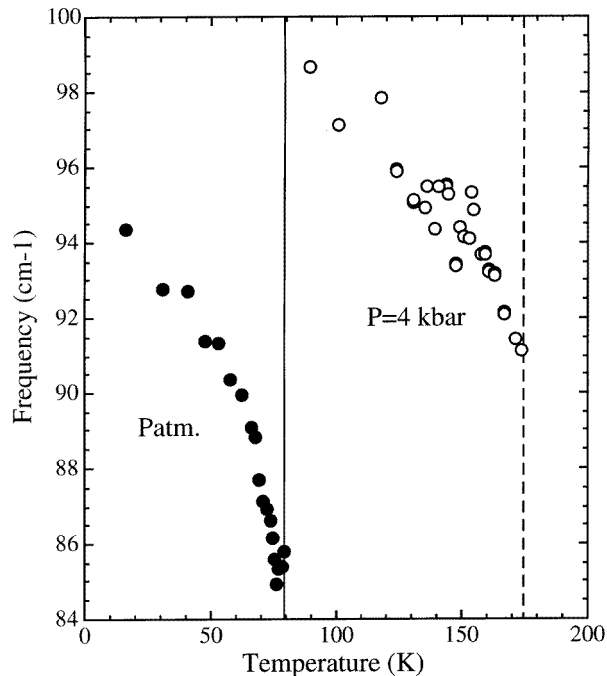
Figure 7. The evolution versus temperature of the frequency of the TTF-CA soft mode at atmospheric pressure and at 4 kbar. The full vertical line and dashed vertical line, respectively, at atmospheric pressure ($T = 80$ K) and at 4 kbar ($T = 175$ K) indicate the temperatures at which the soft mode disappears.

that at 4 kbar a softening of this mode is still observed. Indeed, the frequency decreases from 97 cm^{-1} at 110 K to 91 cm^{-1} at 175 K. At T_{N-I}, the line assigned to this mode disappears, indicating that the symmetry of this mode is ungerade in the high-temperature phase. Although, as previously seen, the character of this transition is more continuous under pressure, the softening is smaller at 4 kbar than at atmospheric pressure. Indeed, the frequency decrease is around 6 cm^{-1} between $T_{N-I} - 64$ K and T_{N-I} at 4 kbar, whereas it is around 9.5 cm^{-1} between $T_{N-I} - 64$ K and T_{N-I} at atmospheric pressure. Thus this result shows that the transition still has a displacive nature at 4 kbar, but it also displays an evolution of the mechanism under pressure, the displacive nature becoming less important.

This evolution of the mechanism under pressure is confirmed by the behaviour versus temperature of the linewidth of several totally symmetric internal modes (TTF $a_g \upsilon_6$, CA $a_g \upsilon_3$ and CA $a_g \upsilon_5$ modes). As previously seen at atmospheric pressure [1], these modes are highly coupled to the charge transfer and present an increase of their coupling constant between the neutral phase and the ionic one. Moreover, at atmospheric pressure, we have shown that the linewidths of the TTF $a_g \upsilon_6$ (figure 8) and CA $a_g \upsilon_3$ modes increase in the neutral phase in the approach to T_{N-I}. This linewidth increase is related [1] to the increase in charge transfer (from 0.2 to 0.3) which is observed between 100 K and T_{N-I} [6].

First, at 280 K, when we apply pressure, the linewidths of these three modes increase. Besides this, at 4 kbar, when the sample is cooled down, a similar behaviour of the linewidths of the TTF $a_g \upsilon_6$ and CA $a_g \upsilon_3$ modes is observed. As an example, the evolution versus temperature of the linewidth of the TTF $a_g \upsilon_6$ mode at 4 kbar is presented and compared
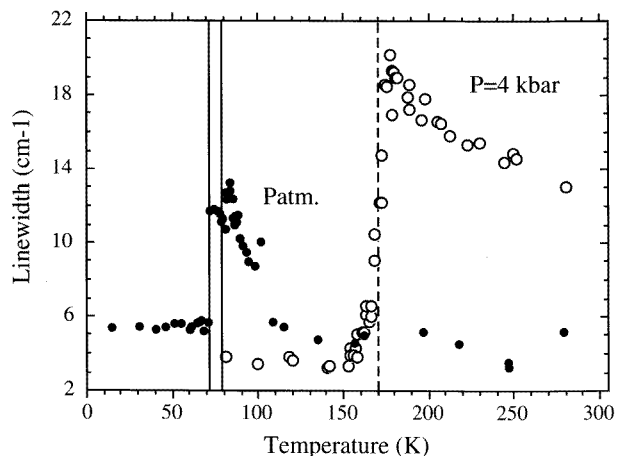
Figure 8. The linewidth dependence versus temperature of the TTF $a_g \nu_6$ mode of TTF-CA single crystal, at atmospheric pressure and at 4 kbar. The temperature domain between full vertical lines (from 72 K to 80 K) corresponds to the coexistence domain observed via Raman scattering at atmospheric pressure, whereas the dashed vertical line indicates the transition temperature at 4 kbar ($T_{N-I} = 170$ K).
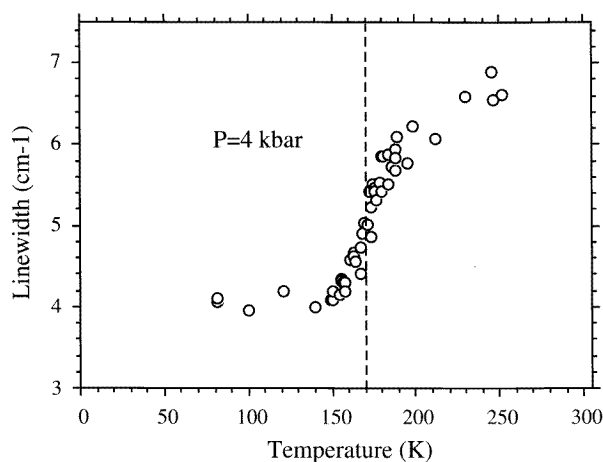

Figure 9. The linewidth dependence versus temperature of the CA $a_g \nu_5$ mode of TTF-CA single crystal, at 4 kbar. The dashed vertical line indicates the transition temperature at 4 kbar ($T_{N-I} = 170$ K).

to that observed at atmospheric pressure (figure 8). This figure shows that the linewidth behaviour of this mode is clearly different at atmospheric pressure from that observed at 4 kbar. At atmospheric pressure, the linewidth of this mode is the same in the neutral phase and in the ionic one ($\sim$5 cm^{-1}), a linewidth increase only being observed in the neutral phase as T_{N-I} is approached. At 4 kbar in the ionic phase, the linewidth is around 3.5 cm^{-1}. As T_{N-I} is approached, the linewidth increases, and in the neutral phase, it is around 13 cm^{-1} at 280 K. Thus at 4 kbar, figure 8 clearly shows that there is an intrinsic broadening of the TTF $a_g \nu_6$ mode between the ionic phase and the neutral one. Note that

in the neutral phase, the broadening observed at atmospheric pressure in the approach to the transition is still observed at 4 kbar, indicating that ionicity variations always exist under pressure in the neutral phase. Similar broadenings are observed for the CA $a_g v_3$ mode. For the CA $a_g v_5$ mode, at 4 kbar, a continuous broadening between the ionic ($\sim$4 cm^{-1} at 80 K) and the neutral ($\sim$6.5 cm^{-1} at 255 K) phases is observed (figure 9), whereas at atmospheric pressure, no anomaly has been observed between these two phases. Thus, at 4 kbar for the TTF $a_g v_6$, CA $a_g v_3$ and also CA $a_g v_5$ modes, there are intrinsic broadenings between the ionic phase and the neutral one.

In structural transitions, mode broadenings between the low- and high-temperature phases are generally assigned to an order–disorder dynamics which implicates the loss of the translation symmetry in the high-temperature phase [13, 17]. Mostly, lattice phonons are highly perturbed by the crystalline environment and, consequently, they are dispersed in the Brillouin zone.

The internal modes are generally weakly perturbed by the crystalline environment and so they are weakly dispersed in the Brillouin zone. Thus, lattice phonons are more sensitive than the internal modes to an order–disorder mechanism.

For the neutral-to-ionic phase transition of TTF-CA under pressure, it can appear surprising that these broadenings are observed on intramolecular modes. Nevertheless, TTF $a_g v_6$, CA $a_g v_3$ and CA $a_g v_5$ modes are highly coupled to the charge transfer [1]. Moreover, at atmospheric pressure, we have shown that their electron–phonon coupling constants increase between the neutral and ionic phases [1]. Consequently, due to the electron–phonon interaction, these modes may appear to be sensitive not only to the crystalline environment, but also to the electronic one. Thus, their broadenings (only observed under pressure) can be related to an order–disorder mechanism—including structural and electronic effects—which would appear under pressure.

Unfortunately, due to a large enhancement of the elastic and/or quasi-elastic scattered line in the neutral phase, the too weak scattered signal in the lattice phonon spectral range prevents us from performing a reliable study of the linewidth behaviours of the external modes between the ionic phase and the neutral one.

Nevertheless, at 4 kbar, the less critical softening observed in the low-frequency spectral range in the ionic phase, and the broadenings of several intramolecular modes between the ionic phase and the neutral one, show that at 4 kbar the mechanism of the transition is intermediate between a displacive and an order–disorder one, whereas at atmospheric pressure the mechanism is displacive. So, it appears that, under pressure, the transition mechanism moves from being a displacive one towards being an order–disorder one, the origin of this disorder being related to structural effects and/or due to the electron–phonon coupling to electronic effects.

Acknowledgment

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