

# Far-infrared powder spectrum of $(\text{N}(\text{CH}_3)_3\text{D})(\text{I})(\text{TCNQ})$ <sup>1</sup>

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We present the powder absorption spectrum of  $(\text{TMA})(\text{I})(\text{TCNQ})$  in the far-infrared as a function of temperature. Below 160 K new absorption features appear and others increase in intensity. This behaviour supports the electron- and neutron-diffraction evidence of a distortion on the TCNQ chains below the first phase-transition temperature. Effects due to the second phase transition at 89 K are also observed. The results of a group-theoretical analysis are presented. These show that totally-symmetric internal modes  $a_g$  are to be expected in the infrared spectra of this compound even in the undistorted phase.

Nous présentons le spectre d'absorption de poudre de  $(\text{TMA})(\text{I})(\text{TCNQ})$  dans l'infrarouge lointain, en fonction de la température. Au dessous de 160 K, de nouvelles fréquences d'absorption apparaissent et d'autres augmentent d'intensité. Ce comportement confirme les indications de la diffraction des neutrons et des électrons sur l'existence d'une distorsion des chaînes TCNQ au-dessous de la première température de transition de phase. On observe aussi des effets dus à la seconde transition de phase à 89 K. Les résultats d'une analyse par théorie des groupes sont présentés. Ils montrent que des modes internes totalement symétriques ( $a_g$ ) doivent être attendus dans le spectre infrarouge de ce composé, même dans la phase sans distorsion.

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## 1. Introduction

Trimethylammonium iodide tetracyanoquinodimethane  $(\text{TMA})(\text{I})(\text{TCNQ})$ , where  $(\text{TMA})$  is the abbreviation we will use for the partially deuterated form,  $\text{N}(\text{CH}_3)_3\text{D}^+$ , is a ternary compound composed of  $\text{TMA}$  cations and separate chains of  $\text{TCNQ}^{2/3-}$  and  $(\text{I}_3^-)_{1/3}$  anions. It is an organic conductor, with a room-temperature conductivity of around  $20 (\Omega \text{ cm})^{-1}$ . Upon cooling, the conductivity of some crystals immediately decreases (see for example Cougrand *et al.* (1)), while for others the conductivity increases slowly to a broad maximum around 240 K and then decreases (see for example Abkowitz *et al.* (2)). This difference in behaviour may depend on the degree of disorder between the iodine chains (3), which in turn depends on the method of preparation. The iodine chains contain triiodide anions  $\text{I}_3^-$ , as determined by the very strong resonance at  $105 \text{ cm}^{-1}$  seen in Raman measurements (2). These ions are relatively well-ordered within a chain, but there is little correlation between chains in the "disordered" material. All crystals, however, undergo a phase transition at 150 K ( $T_1$ ) (159 K in our deuterated sample (3)). Below this temperature they are semiconductors with an activation energy which extrapolates to an estimated value of 1000 K at 0 K (4). This phase transition is clearly seen in measurements of the direct current

(dc) conductivity (1, 2), microwave conductivity (2), thermoelectric power (2), electron spin resonance (esr) linewidth (5), Young's modulus (6), magnetic susceptibility (7), and the unit-cell parameters (7). Another phase transition at 89 K ( $T_2$ ) is seen in the Young's modulus data (6), microwave dielectric constant,<sup>2</sup> and proton spin-lattice relaxation (8). This latter transition has been associated with the freezing-out of methyl-group rotations (6) and is also the temperature at which the TCNQ molecules develop a tilt so that the  $b$  axis is no longer normal to the molecular plane (4).

The present point of contention centres around the nature of the 150 K phase transition. There are two schools of thought. The authors of references 2, 5, 6, and 8<sup>2</sup> support the view proposed by Epstein (9) to explain the behaviour of several similar compounds. The transition is a semiconductor – semiconductor one in which there is a gap in the density of states at the Fermi level at all temperatures. This produces an *activated* number of conduction electrons, and the "metallic" behaviour of the dc conductivity above  $\sim 240 \text{ K}$  ( $T_M$ ) in the ordered crystals is due to a strongly temperature-dependent mobility with the mobility *decreasing* as the temperature rises. This temperature dependence is brought about by the interaction between the conduction electrons and the molecular vibrations.

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<sup>2</sup>W. Gunning, A. J. Epstein, and J. S. Miller. Unpublished.

The probable existence of large on-site Coulomb repulsions in the semiconducting state above  $T_1$  (150 K) is acknowledged (10). Certainly many of the measured properties support the semiconducting state above 150 K, not the least of which is the clearly activated dc conductivity just above 150 K. The mobility in semiconductors is known to be strongly temperature dependent (1). One of the problems is the nature of the phase transition at 150 K. The Epstein supporters maintain that a probable cause of the semiconducting state above 150 K is the periodic potential at the TCNQ chain induced by the triiodide ( $I_3^-$ ) chains. Presumably this may occur even in the disordered materials because the effect of the nearest-neighbour triiodide chains would predominate. While this potential could produce a semiconducting state without actually distorting the TCNQ chains, the view has been taken that the chain is distorted at all temperatures and has an approximately constant energy gap. Indeed, the dc conductivity is analyzed on the basis of a gap of  $\sim 0.14$  eV ( $\sim 1100$  cm $^{-1}$ ) which does not change through  $T_1$ . This is supported by the optical data of Tanner *et al.* (12, 13), who find a conductivity which starts from the dc value of  $20$  ( $\Omega$  cm) $^{-1}$  and rises to a broad peak of  $\sim 170$  ( $\Omega$  cm) $^{-1}$  at approximately  $2000$  cm $^{-1}$ . This is little changed at 80 K and so the authors conclude that at 150 K there is only a small change in the gap, but a large change in the mobility.

The other school of thought may be found in refs. 1, 4, and 7. These authors maintain that the phase transition is a Peierls transition involving the three-dimensional condensation of a charge-density wave. Below this temperature a semiconductor exists due to the Peierls distortion of the conducting TCNQ chain, but above it no distortion exists and the material is metallic. (The periodicity of this distortion would be  $3b$ , due to the one-third-filled band which is a result of the stoichiometry. This periodicity is identical to that produced by the triiodide ( $I_3^-$ ) chains.) The density of states would have no gap above  $T_1$  and the mobility need not be as strongly temperature dependent as required by Epstein ( $T^{-4}$ ). Instead, the various measured properties can be accounted for by assuming electron-electron interactions (7). In particular, the dc conductivity is reduced because of the smaller mean free-path, the paramagnetic susceptibility is enhanced, and a good fit is obtained to the optical data with a maximum in the frequency-dependent conductivity (14). (Apart from electron-electron correlations, another factor which may be contributing to the activated behaviour of the dc conductivity in the metallic phase above 150 K is the disorder. A recent NMR study on  $Qn(TCNQ)_2$  by Devreux *et al.* (15), in which the quinolinium is disordered, showed that the diffusion constant had the same temperature dependence as the conductivity. They

found that the carrier concentration was only weakly temperature dependent, but that the disorder produced a mobility which increased with temperature due to the thermal surmounting of random potentials and barriers.) It should be noted that the electrical, magnetic, and optical properties of  $(TMA)(I)(TCNQ)$  closely resemble those of several other compounds, notably the  $(TMTTF)_2X$  radical-cation salts (with  $X = BF_4^-$ ,  $ClO_4^-$ , or  $PF_6^-$ ). Coulomb effects are important in these materials and they are known as either metals with strong electron correlations (16) or magnetic semiconductors (17). For details on these and related compounds, the reader is referred to the literature (16–18).

The French school, therefore, set out to show that no distortion is present in the TCNQ chains above 150 K and this they have reasonably established. First of all they studied (7) the effect of interchain Coulomb interactions on the metal-insulator transition in a homogeneous series of TCNQ salts where the separation of the TCNQ chains in the  $c$  direction can be varied without affecting the intrachain separation  $b$ . The dependence of the transition temperature on the interchain coupling, assuming a Peierls-type distortion, was successfully demonstrated. A subsequent neutron-scattering study (4) and an electron-diffraction study (19) established the existence of a distortion of periodicity  $3b$  on the TCNQ chains below 150 K. This distortion then changes from a reciprocal-lattice vector  $(0, \pm b^*/3, 0)$  to a  $\pm(xa^*, b^*/3, 0)$  vector with  $0 < x < 1/6$  between 100 and 80 K and finally becomes  $\pm(a^*/6, b^*/3, 0)$  below 80 K.

The occurrence of such a distortion is often clearly and easily seen in the infrared spectra. Normally infrared-inactive modes of vibration become strongly activated as a result of it. In the case of an incommensurate distortion, the modes are activated by coupling with the phase oscillations of the accompanying charge-density wave (CDW), as shown theoretically by Rice (20). Examples of systems which display this effect are TTF-TCNQ (21, 22) and  $(TEA)(TCNQ)_2$  (23). Alternatively, if the distortion is commensurate, then the activity is due to a "vibronic" effect whereby the symmetric intramolecular modes are accompanied by a charge transfer between the molecules. TTF-TCNQ displays activated modes by this effect also, namely those seen with a polarization perpendicular to the chains. In this direction the CDW has a periodicity of  $4a$  (24). Another example is K-TCNQ in which the TCNQ ions are dimerized (25, 26). In all of these materials the totally symmetric  $a_g$  modes, which are usually the strongest activated modes, are infrared inactive in the undistorted material. In the low-resolution mid-infrared reflectivity studies of  $(TMA)(I)(TCNQ)$  by Tanner *et al.* (12, 13), the strong features have been identified with the  $a_g$  modes, both at room temperature

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and below  $T_1$ , and this has been taken as evidence of a distortion at all temperatures. A similar conclusion is drawn by Graja *et al.* (27, 28). They observed  $a_g$  modes in their mid-infrared powder spectra which were present at room temperature, but increased in intensity below  $T_1$ . We wish to point out, however, that in (TMA)(I)(TCNQ) the TCNQ ions do not sit on inversion centres and the  $a_g$  modes are normally infrared active in this solid. (The group theory is presented in the next section.) They should be expected at room temperature in the undistorted phase even though some may be weak. The effect of a distortion, on the other hand, would be to increase their oscillator strength. The purpose of this paper then is to report on measurements of far-infrared transmission through powders of (TMA)(I)(TCNQ). These show very clearly several activated resonances appearing below 160 K, while others show an increase in oscillator strength below 160 K. This is taken as further evidence of a distortion appearing on the TCNQ chains below 159 K. Preliminary results have been previously reported (29).

## 2. Group theory selection rules

The high temperature structure of  $\text{TMA}^+\text{TCNQ}^{2/3-}$ ,  $(\text{I}_3^-)_{1/3}$  in its ordered form is described by two interpenetrating lattices: the main or A lattice, composed of TMA and TCNQ molecules, and the B lattice composed of  $\text{I}_3^-$  molecules (30, 4). The vibrations due to these two lattices are considered separately.

The A lattice belongs to the space group  $C_{2/m}(C_{2h}^3)$  and has two molecules per primitive unit cell which occupy sites of  $C_5$  symmetry (31). The monoclinic cell's unique axis  $b$  is parallel to the TCNQ stacks and iodine chains. A correlation diagram relating the irreducible representations of the molecular point groups to those of the site group and unit-cell group of the A lattice is given in Table I. The translational and rotational degrees of freedom of TCNQ form the representation  $b_{1u} + b_{2u} + b_{3u}$  and  $b_{1g} + b_{2g} + b_{3g}$ , respectively, whereas for TMA they are  $a_1 + e$  and  $a_2 + e$ , respectively. Because there are two formula units per primitive unit cell, the translational vibrations of the A lattice should form the representation (including acoustic modes)  $4A_g + 2B_g + 2A_u + 4B_u$  and the rotational or librational ones the representation  $2A_g + 4B_g + 4A_u + 2B_u$ . The presence of a hydrogen bond between the TMA and TCNQ molecules, however, means that three translational and three rotational degrees of freedom per hydrogen bonded pair become hydrogen bond vibrations. Thus, the intermolecular vibrations of the A lattice are: six translational modes ( $2A_g + B_g + A_u + 2B_u$ ), three of which are infrared active or acoustic modes; six librations ( $A_g + 2B_g + 2A_u + B_u$ ), three of which are infrared active; and in addition, there are twelve hydrogen bond vibrations ( $3A_g + 3B_g + 3A_u +$

TABLE I. Correlation diagram for the A lattice of  $\text{TMA}^+\text{TCNQ}^{2/3-}(\text{I}_3^-)_{1/3}$

Molecular point group		Site group	Unit-cell group	
$C_{3v}$ (TMA)	$\bar{6}_2$ (TCNQ)	$C_5$	$C_{2h}$	
$a_1(\text{ir,R})$		A'	A <sub>g</sub> (R)	
$e(\text{ir,R})$				B <sub>u</sub> (ir) E1b
$a_g(\text{R})$				
$b_{3g}(\text{R})$				
$b_{1u}(\text{ir})$				
$b_{2u}(\text{ir})$				
$a_2$		A''	B <sub>g</sub> (R)	
$e(\text{ir,R})$				A <sub>u</sub> (ir) E1b
$b_{1g}(\text{R})$				
$b_{2g}(\text{R})$				
$a_u$				
$b_{3u}(\text{ir})$				

ir = infrared active  
R = Raman active

$3B_u$ ), some of which should absorb in the far infrared. The primary far-infrared hydrogen bond vibrations will be the hydrogen bond stretches  $\nu(\text{NH}\cdots\text{N}\equiv\text{C}\cdots)$  and the hydrogen bond deformations  $\delta(\text{NH}\cdots\text{N}\equiv\text{C}\cdots)$  (32). From Table I it can be seen that each intramolecular vibration of the free molecule will yield two vibrations in the solid, one infrared active ( $A_u$  or  $B_u$ ) and one Raman active ( $B_g$  or  $A_g$ ). The low frequency intramolecular vibrations of the free TCNQ molecule are listed in ref. 20 and consist of four normally Raman-active modes  $\nu_{10}(a_g)$ ,  $\nu_{17}(b_{1g})$ ,  $\nu_{31}(b_{2g})$ , and  $\nu_{49}(b_{3g})$ , four normally infrared active modes  $\nu_{20}(b_{1u})$ ,  $\nu_{40}(b_{2u})$ ,  $\nu_{53}(b_{3u})$ , and  $\nu_{54}(B_{3u})$ , and possibly one normally inactive mode  $\nu_{14}(a_u)$ . For TMA the intramolecular vibrations that could absorb below  $450\text{ cm}^{-1}$  are two-methyl torsions  $\nu_8(a_1)$  and  $\nu_{23}(e)$  (33).

The B lattice is pseudomonoclinic with its unique axis  $b_B$  being perpendicular to the TCNQ stacks and iodine B chains (26). The only possible common symmetry element of the A and B lattices is an inversion centre. The unit-cell volume of the B lattice is three times that of the primitive A lattice so there are two  $\text{I}_3^-$  molecules per unit cell. There are only two possible space groups. If the two molecules per unit cell are not equivalent the space group is  $P1$  and then each vi-

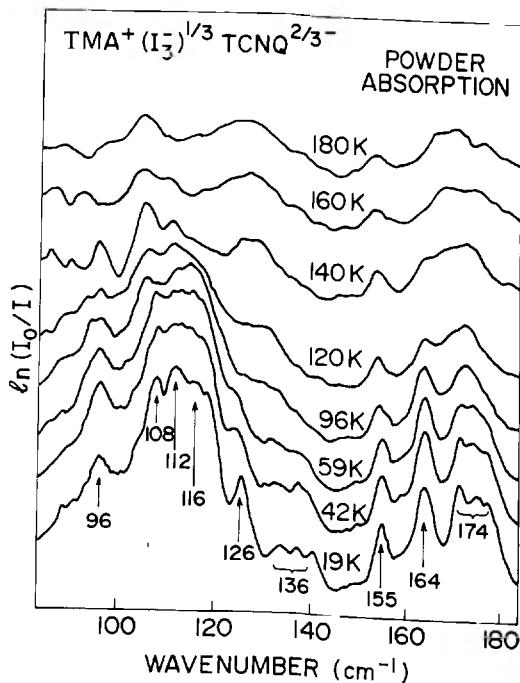


FIG. 1. The lower-wavenumber portion of the powder absorption spectra obtained from one sample, vertically displaced for clarity. The indicated features are discussed in the text and are listed in Table 2. The resolution is  $1 \text{ cm}^{-1}$  below  $60 \text{ K}$ ,  $2 \text{ cm}^{-1}$  for  $60 \text{ K} < T < 120 \text{ K}$ , and  $4 \text{ cm}^{-1}$  for  $120 \text{ K} < T < 180 \text{ K}$ , due to the decreasing signal-to-noise ratio.

brational, translational, or rotational degree of freedom of the free molecule will yield two infrared and Raman active modes. If the molecules of the unit cell are related by an inversion centre, the space group is  $P\bar{1}$  and each vibrational, translational, or rotational degree of freedom of the free molecule gives one infrared-active and one Raman-active mode.

The  $\text{I}_3^-$  molecule has four vibrational degrees of freedom which are described by  $\nu_1$ , the symmetric stretch;  $\nu_2$ , the asymmetric stretch, and  $\nu_3$ , the doubly degenerate bend. All of these absorb at low frequency (34). Thus, for the B lattice there should be six translational modes (including acoustic ones), four librational modes, and eight intramolecular modes. If the space group is  $P1$  then all eighteen modes should be infrared-active or acoustic modes. If it is  $P\bar{1}$  there should only be nine such modes.

To summarize then, the far-infrared spectrum of the high-temperature ordered form of  $\text{TMA}(\text{I})\text{TCNQ}$  should be complex. There will be absorption due to at least three translational and five librational modes (six translational and seven librational modes if the B lattice has the space group  $P1$ ). All of the intramolecular modes will have at least one infrared-active component. There will also be absorption due to hydrogen bond

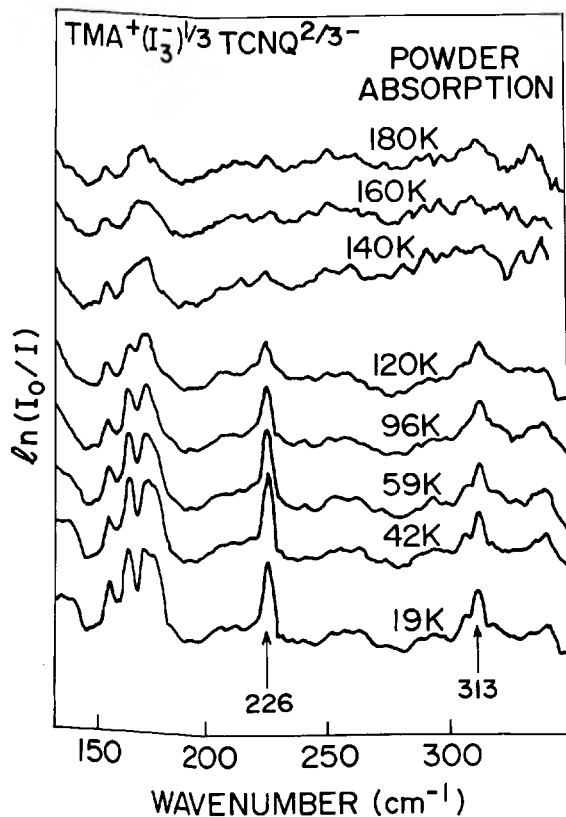


FIG. 2. The upper-wavenumber portion of the powder absorption spectra obtained from the same sample, vertically displaced for clarity. The indicated features are discussed in the text and are listed in Table 2. The resolution is  $4 \text{ cm}^{-1}$ .

vibrations which typically are the stronger far-infrared-active bands (33).

### 3. Experimental

The crystals of  $(\text{N}(\text{CH}_3)_3\text{D})(\text{I})(\text{TCNQ})$  were grown by one of us (J. S. M.) and were ground in nujol for about 20 min. The mull was then spread on a wedged TPX window, which was inserted into a Janis super-variant dewar. The dewar was cooled using cold helium gas and sits at the focus of an RIIC Michelson interferometer. An Infrared Labs commercial bolometer was used to measure the transmitted intensity.

### 4. Results and discussion

Figures 1 and 2 show the lower and upper wavenumber regions respectively of the powder spectra obtained at various temperatures. These spectra are displaced vertically for ease of comparison, but of course the background free-carrier absorption does increase with temperature following the dc conductivity. This, together with thermal broadening, makes the vi-

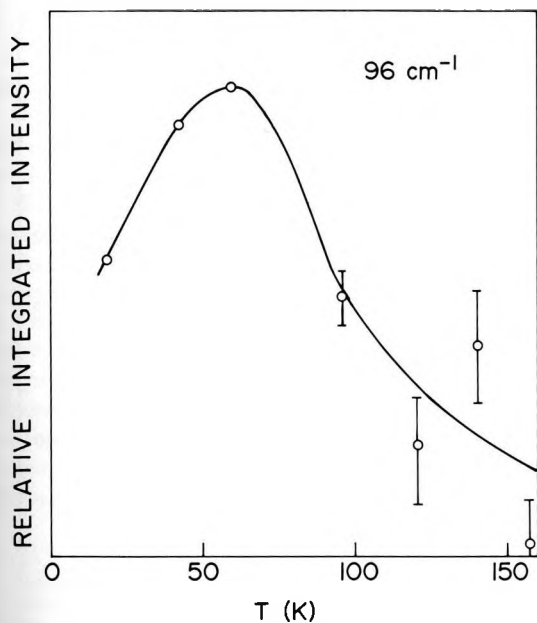


FIG. 3. The relative integrated intensity, in arbitrary units, of the  $96\text{ cm}^{-1}$  feature of Fig. 1 versus temperature. There is a large error in the high-temperature points, but an increase in intensity below  $160\text{ K}$  is evident.

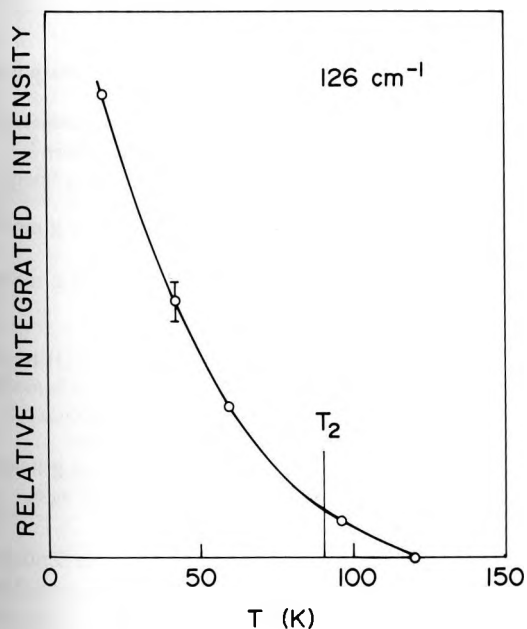


FIG. 4. The relative integrated intensity, in arbitrary units, of the  $126\text{ cm}^{-1}$  feature of Fig. 1 versus temperature. The feature appears only below  $120\text{ K}$ , seeming to follow the second phase transition at  $89\text{ K}$ .

brational features at high temperatures less distinct. Nevertheless, it is apparent that activated features are

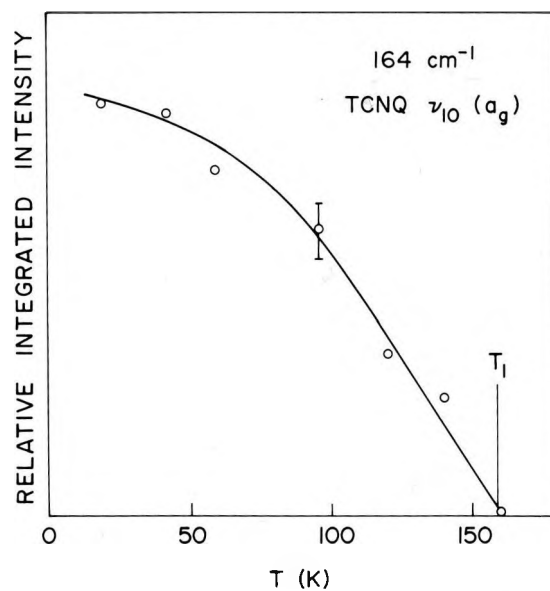


FIG. 5. The relative integrated intensity, in arbitrary units of the  $164\text{ cm}^{-1}$  feature of Figs. 1 and 2 versus temperature. It is assigned to the lowest totally symmetric internal mode of TCNQ,  $\nu_{10}(a_g)$ . It is clearly activated below  $T_1$  at  $159\text{ K}$ .

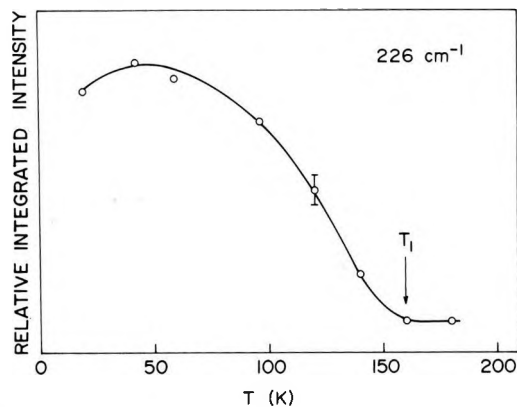


FIG. 6. The relative integrated intensity, in arbitrary units, of the  $226\text{ cm}^{-1}$  feature of Fig. 2 versus temperature. It grows strongly below  $T_1$  at  $159\text{ K}$ .

present in the low-temperature spectra which are not visible at  $180\text{ K}$ . These include the indicated features at  $96$ ,  $112$ ,  $116$ ,  $126$ , and  $164\text{ cm}^{-1}$ . The higher-wavenumber modes at  $226$  and  $313\text{ cm}^{-1}$  are much stronger at low temperatures, but are still visible at  $180\text{ K}$ . The normally active modes which are present in all of the spectra are at  $108$ ,  $136$ ,  $155$ , and  $174\text{ cm}^{-1}$ .

Figures 3, 4, 5, and 6 show the relative integrated intensity of four of the activated features. Three of them, at  $96\text{ cm}^{-1}$  (Fig. 3),  $164\text{ cm}^{-1}$  (Fig. 5), and  $226\text{ cm}^{-1}$  (Fig. 6) grow suddenly and strongly below

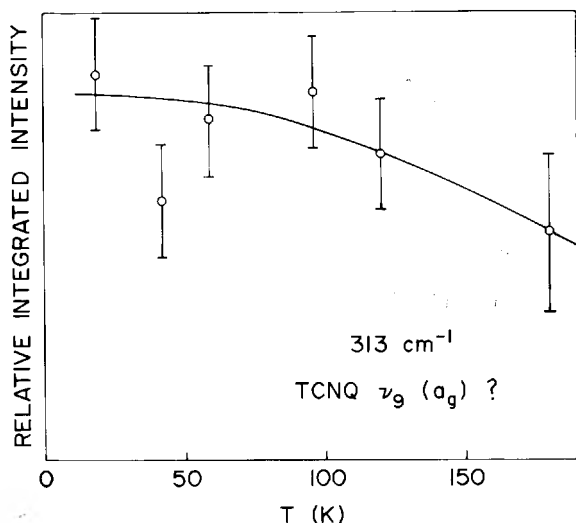


FIG. 7. The relative integrated intensity, in arbitrary units of the  $313\text{ cm}^{-1}$  feature of Fig. 2 versus temperature. It can probably be assigned to TCNQ  $\nu_9(a_g)$ . The temperature dependence is weak with the feature still strong at room temperature.

159 K, the phase-transition temperature in our samples, indicating that the phase transition involves the appearance of a periodic lattice distortion (PLD). The  $164\text{ cm}^{-1}$  feature which is not visible at all above 150 K has been assigned to TCNQ  $\nu_{10}(a_g)$  because this is the wavenumber at which it was found in TTF-TCNQ. This means that the PLD involves the TCNQ chains. TCNQ  $\nu_9(a_g)$  was assigned to the  $317\text{ cm}^{-1}$  feature in TTF-TCNQ by Bozio and Pecile (35), and so our  $313\text{ cm}^{-1}$  feature may be this mode. Figure 7 shows the integrated intensity which, however, appears much less strongly temperature dependent than those modes in Figs. 3-6, and is still visible at room temperature. This behaviour resembles that observed for the higher-frequency  $a_g$  modes in the mid-infrared (11, 12, 26, 27). Figure 4 shows the unexpected temperature dependence of the  $126\text{ cm}^{-1}$  mode which starts to grow strongly only below 100 K. This corresponds to the growth of the second distortion which precedes the phase transition at 89 K. The mode could, therefore, be a torsion of the methyl groups if their rotation is indeed frozen out at this temperature, or it may be one for which the intensity depends strongly on the angle of tilt of the TCNQ molecules.

Another interesting observation is the apparent appearance of triplets at 136 and  $174\text{ cm}^{-1}$  in Fig. 1. This could be due to the Brillouin-zone folding which follows from the  $b^*/3$  reciprocal lattice vector of the distortion.

Figure 8 shows the frequency dependence of all the indicated features. Lattice or intermolecular modes will

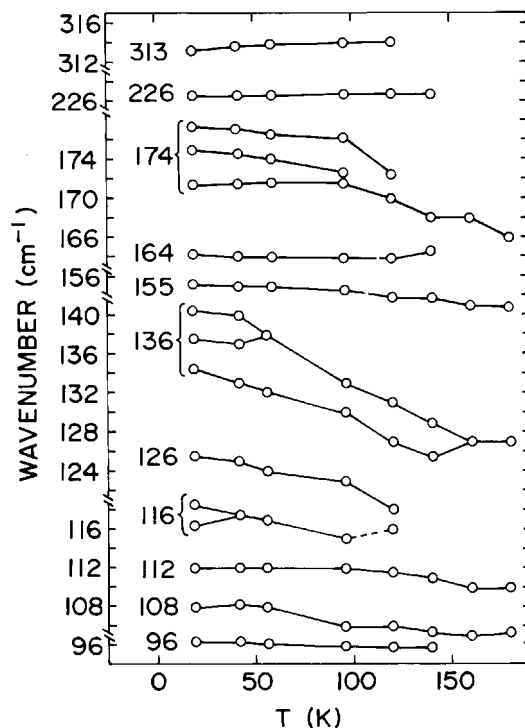


FIG. 8. The temperature dependence of the peak frequencies of the powder features in Figs. 1 and 2.

TABLE 2. Description and possible assignment of the powder features

Wavenumber	Description	Possible assignment
96	Activated <160 K	Internal g mode
108	Normally active	
112	Activated <180 K	Internal g mode
116	Activated <140 K	
126	Activated <96 K	
136	Normally active	Lattice (H-bond?)
155	Normally active	Internal u mode
164	Activated <160 K	TCNQ $\nu_{10}(a_g)$
174	Normally active	Lattice
226	Strong <140 K	Internal g mode
313	Strong <140 K	TCNQ $\nu_9(a_g)$

normally have a much stronger temperature dependence than internal or intramolecular modes. Good candidates for lattice modes are, therefore, the 108, 126, 136, and  $174\text{ cm}^{-1}$  features. Without spectra of the compound with various isotopic substitutions, it is impossible to further assign the powder features of Figs. 1 and 2 to various internal, lattice,  $I_3$ , or hydrogen-bonded modes. Our incomplete descriptions of the modes responsible for the features resulting from this study are presented in Table 2.

## 5. Conclusion

In conclusion, the results presented support the electron and neutron diffraction studies of a phase transition at 150 K (in the protonated sample) which distorts the TCNQ chain, and presumably determines the nature of the semiconducting state. The temperature dependence of the intensity of some of the far-infrared vibrational features, in particular that assigned to TCNQ  $\nu_{10}(a_g)$ , strongly resembles that found in TTF-TCNQ where a Peierls distortion occurs. The persistence of absorption due to high-wavenumber  $a_g$  modes at temperatures above 150 K is due to the lack of an inversion centre in this material. This makes these totally symmetric internal modes infrared active. A Peierls distortion would indicate a metallic state above 150 K; however, these results cannot rule out a semiconducting state which involves no distortion on the TCNQ chains.

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