Infrared Studies of the Phase Transition in TEA(TCNQ)$_2$

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Polarised infrared and optical spectra were measured at temperatures between 5 and 300 K to study the 210 K structural phase transition in the organic charge transfer salt TEA(TCNQ)$_2$. At high temperatures, characteristic spectral features of semiconducting 1:2 TCNQ salts are observed. At low temperatures, several changes are found. First, the electronic charge transfer sharpens and has enhanced oscillator strength in the low-temperature phase. Second, the vibrational lines split into clear doublets, whose appearance is associated with a sharp decrease in the phonon damping at low temperatures.

KEYWORDS IR; TEA(TCNQ)$_2$; phase transition

INTRODUCTION

TEA(TCNQ)$_2$, triethylammonium-7,7,8,8-tetra-cyano-p-quinodimethane; one of the best-known TCNQ salts because large single crystals have been available for a long time, is considered to be a good 1D semiconductor ($\sigma_{\parallel,300\,K} \approx 5.7 \; \Omega^{-1} \; cm^{-1}$). The structure shows the typical irregular stacking of the TCNQ molecules. The unit cell is triclinic with the c-axis along the TCNQ stacks; it contains two chemical units and the space group is $P\bar{1}$. The transferred electron from TEA is shared by two non-equivalent molecules TCNQ(A) ($\rho_A = 0.6e$) and TCNQ(B) ($\rho_B = 0.4e$). Compared with other 1:2 organic charge transfer salts, TEA(TCNQ)$_2$ has relatively weak electron–electron correlations.[1]

The temperature dependence of the c-axis DC conductivity in TEA(TCNQ)$_2$ shows an anomaly between 200 and 220 K: an increasing jump with temperature of about one order in magnitude. An anomaly is observed in the thermal expansion in the same temperature range. The structural modification in this region is quite subtle. The intermolecular spacings decrease with temperature, each by a different extent, leading to small changes in tetradic structure of the TCNQ molecules.[2–4] However, the space group and the number of chemical units in the unit cell do not change throughout the transition regime.

The optical properties of TEA(TCNQ)$_2$ have been studied by a number of workers.[5–10] The first polarised measurements were done by Brau et al.,[5] who used a Kramers–Kronig analysis to estimate the dielectric function and optical conductivity. Owing to the strong electron–molecule vibrational (EMV) coupling in this system, TEA(TCNQ)$_2$ has been a prototype for the study of these effects. Belousov et al.[7] used a phenomenological formula for optical conductivity to determine EMV coupling constants of this 1:2 salt. Rice et al.[6] calculated the coupling constants within a model

for the phase oscillation of a charge density wave (CDW). By extending the Hubbard model, Yartsev[11] developed a four-site (tetramer) model and applied it to $TEA(TCNQ)_2$. The coupling constants of the four strongest peaks in the spectrum were determined.

Despite the previous spectroscopic work, no comprehensive optical measurements have been made at temperatures in the vicinity of the phase transition. More generally, the present work has been motivated by our interest in relating optical spectra in organic molecular conductors to different kinds of structural anomalies (such as the phase transition found at 200–220 K in $TEA(TCNQ)_2$) and crystallographic phases.

RESULTS AND DISCUSSION

Polarized reflectance measurements at near-normal incidence were made on single-crystal samples of $TEA(TCNQ)_2$. Experiments were performed in two polarizations: with the electric field parallel and perpendicular to the TCNQ chain axis. Far-infrared (FIR) and mid-infrared (MIR) measurements ($30–5000 \text{ cm}^{-1}$) used a Bruker IFS 113v Fourier transform infrared spectrometer equipped with a liquid-helium-cooled Si bolometer for the FIR and a DTGS detector for the MIR. For low-temperature measurements (15–300 K) the sample was mounted on the cold finger in a continuous-flow helium cryostat. Data were taken at several temperatures, concentrated around the structural phase transition. A Perkin-Elmer grating spectrometer was used to measure the spectra in the infrared to the ultraviolet ($1000–30,000 \text{ cm}^{-1}$). These data were collected only at room temperature. It should be noted that two types of $TEA(TCNQ)_2$ crystals exist: needles and platelets. We studied the platelet form here.

The real and imaginary parts of the dielectric function ε_1 and ε_2 and the optical conductivity σ_1 related by $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_1(\omega) + 4\pi i\sigma_1(\omega)/\omega$ were determined from the power reflectance by means of a Kramers–Kronig analysis. At the low-frequency end the spectrum was extrapolated to zero frequency by a constant reflectance, a common procedure for semiconducting materials. At high frequency the reflectivity was extended as $R \approx \omega^{-4}$.

Fig. 1 shows the measured reflectance over the entire spectral range from 30 to $30,000 \text{ cm}^{-1}$ at

room temperature. The data were taken for polarizations $E \| c$ (along the TCNQ stacks) and $E \perp c$. The data show the well-known structure of intramolecular vibrations, charge transfer bands along the c-axis at about 2200 and $10,000 \text{ cm}^{-1}$ and localised excitons $\perp c$ at about 10,000 and $23,000 \text{ cm}^{-1}$. Because a broad spectral region was covered, the Kramers–Kronig analysis as described above provides accurate results for the optical constants. The reflectance and the real part of the conductivity at 15 and 300 K are shown in Fig. 2. The features which appear here are in good agreement with previous spectra. In addition, because our data were taken by a Fourier transform spectrometer, we were able to achieve high enough resolution to see fine structure in the spectra (the intramolecular vibrations are split into doublets) not observed in previous measurements.

To obtain a deeper physical insight into the origin of the spectral features, we fit our spectra with the Yartsev model[11] for EMV coupling in isolated tetramers. This model gives a very good fit to our spectra, as can be seen in Fig. 3 for the low-frequency part of both the optical conductivity and reflectance. At room temperature the best agreement is found for the Hubbard model parameters $t = 1580 \text{ cm}^{-1}$, $t' = 0.8t$, $U = 9840 \text{ cm}^{-1}$, $V = 0.4U = 3940 \text{ cm}^{-1}$ and $\Delta = 403 \text{ cm}^{-1}$. The optimum values for the EMV coupling constants g_i and damping constants γ_i are listed in Table 1.

The doublets which are observed in the spectra are nothing else than Davydov's splitting,[12] which is known in the theory of Frenkel excitons in crystals with two inequivalent molecules in the unit cell. The doublets appear in a spectrum only if the damping of the intramolecular vibrations is small enough. Otherwise the fine structure smears out and disappears from the spectrum.

The temperature dependence of the doublet structure in σ_1 is displayed in Fig. 4. The fine structure gradually becomes more pronounced as the temperature decreases. At the same time the oscillator strength of all bands increases with decreasing temperature. It is interesting that this growth is not caused by the increase in the EMV coupling constants but is due to the increase in oscillator strength of the electronic charge transfer transition. The charge transfer band is very broad and is centred at about 2200 cm^{-1}.

From this point of view it is interesting to look at the temperature dependence of the $TEA(TCNQ)_2$ spectra around the phase transition temperature. The crystallographic study[2] shows
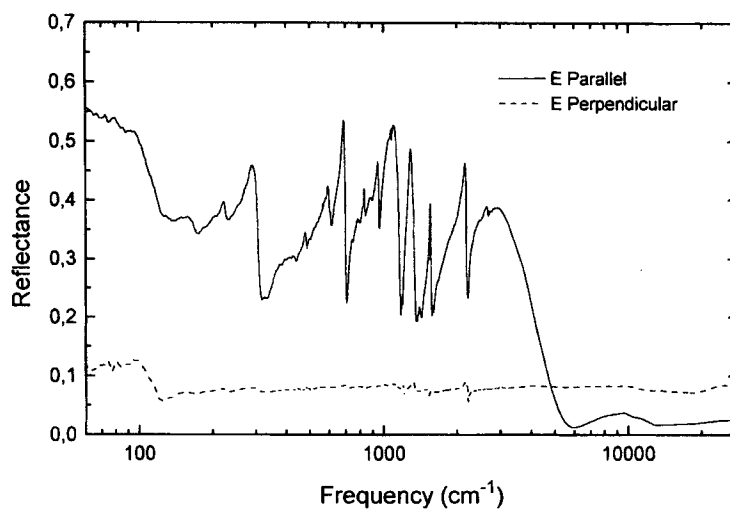
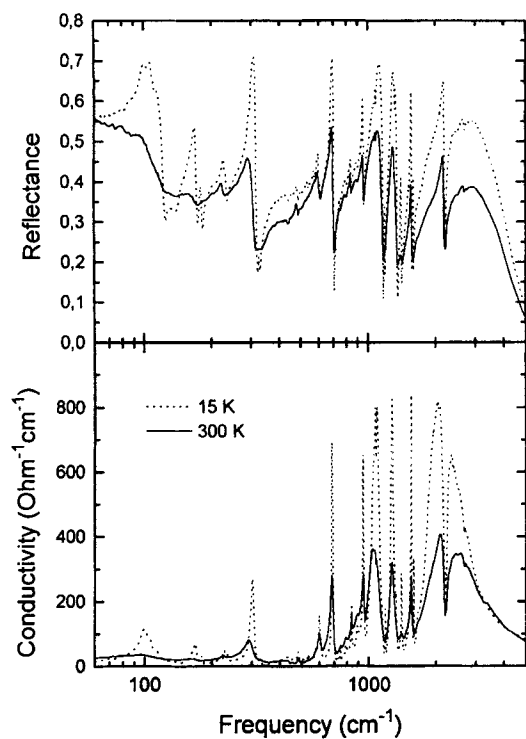Fig. 1. Polarised reflectance of TEA(TCNQ)₂ at room temperature for electric field vector parallel and perpendicular to TCNQ chain direction

Fig. 2. Chain axis reflectance and optical conductivity of TEA(TCNQ)₂ at 15 and 300 K
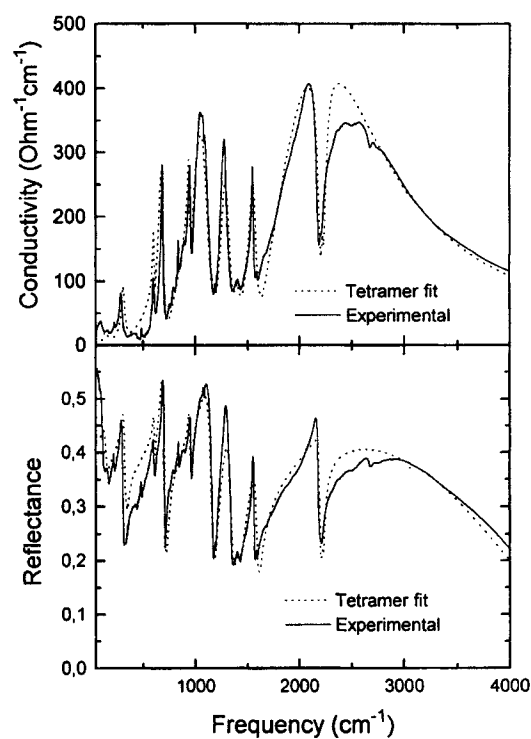
Fig. 3. Theoretical tetramer fit to 300 K reflectance and frequency-dependent conductivity
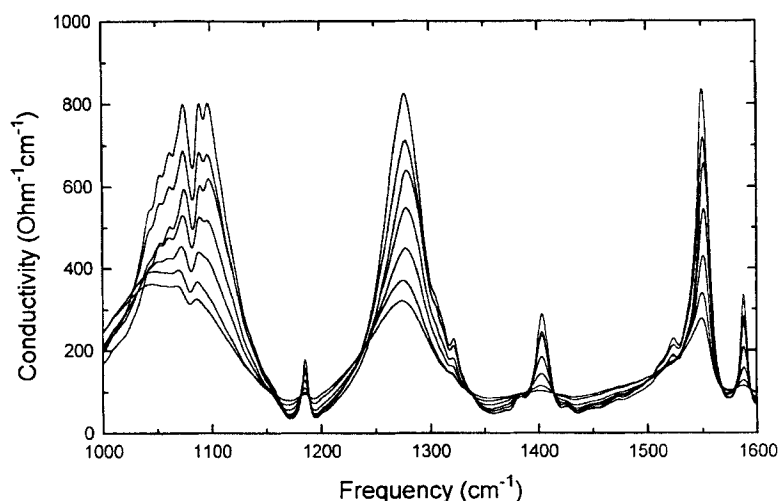
Fig. 4. Detail of temperature dependence of doublet phonon structure in frequency-dependent conductivity. Seven temperatures are shown: 15, 50, 100, 150, 200, 250 and 300 K

Table 1. Vibronic band parameters (cm^{-1}) in $TEA(TCNQ)_2$ at 300 K

i	ω_{iA}	ω_{iB}	g_i	γ_i
1	3048	3061	20	30
2	2206	2229	20	220
3	1602	1622	40	300
4	1366	1424	50	380
5	1171	1184	50	300
6	945	962	5	70
7	711	722	20	200
8	602	613	5	50
9	330	340	30	150
10	144	160	40	100

that tetrameric structure is always present in the TCNQ stacks, even though the distances between particular molecules of the tetramer vary with temperature. The low-temperature data indicate that each chain contains BAAB tetrads, where the notation BAAB means that the longest distance is between B—B molecules. At room temperature the distances between A—A and B—B molecules are equal and larger than A—B. A chain looks like to be made of AB diads. The stacks tend to form ABBA tetrads with the longest spacing between A—A molecules for temperatures above 330 K. In contrast with the structural phase transition in $NPrQn(TCNQ)_2$,[13] where the phase transition leads to formation of the tetramers, we suppose that in $TEA(TCNQ)_2$ the appearance of vibrational

doublets is mostly a result of a narrowing of spectral features due to a decrease in their damping. This conclusion is supported by the fact that weak indications of doublet structure in the vibrational pattern can be observed at room temperature as well. The phase transition at about 210 K is of the order—disorder type and can be attributed to the TEA cation subsystem.[2]

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