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# Infrared study on structural phase transition in $(\text{NMe}_4)_2\text{TCNQ}_3$

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## Abstract

Temperature dependence of linearly polarized infrared absorption spectrum has been measured in  $(\text{NMe}_4)_2\text{TCNQ}_3$  single crystals. Strongly temperature dependent electron-molecular-vibration coupled bands are observed at 2173, 1576, 1351, and 1170  $\text{cm}^{-1}$ . The singular behaviour of the intensity of these bands is discussed in relation to the structural phase transition observed previously by visible to near-infrared optical absorption and X-ray measurements, where the slipped TCNQ radical dimers in the low-temperature phase tend to be eclipsed in the high-temperature phase.

*Keywords: infrared spectroscopy, phase transition*

## 1. Introduction

$(\text{NMe}_4)_2\text{TCNQ}_3$  is one of the 1:2 TCNQ neutral/radical mixed complexes which are reported to exhibit a ferromagnetic behaviour at room temperature[1]. A structural phase transition in this substance was suggested from the temperature dependence of the satellite band ( $S_1$ ) observed at 1.3 eV in the E//a polarization of the optical absorption spectrum, where E and a are the electric field of light and a-axis of the monoclinic crystal structure, respectively[2]. The  $S_1$  band diminishes continuously with increasing temperature to disappear at  $T_C = 65^\circ\text{C}$ . The X-ray diffraction study has shown that second-order structural phase transition takes place at the same temperature[3]. In the low-temperature phase the two TCNQ anion radicals form a slipped dimer, in which they are displaced against each other in the direction of short molecular axis. In the high-temperature phase the dimers are perfectly eclipsed.

Here we report on the infrared approach to the above mentioned structural phase transition.

## 2. Experiment

The as-grown single crystals are used as the samples. The linearly polarized infrared absorption spectra are

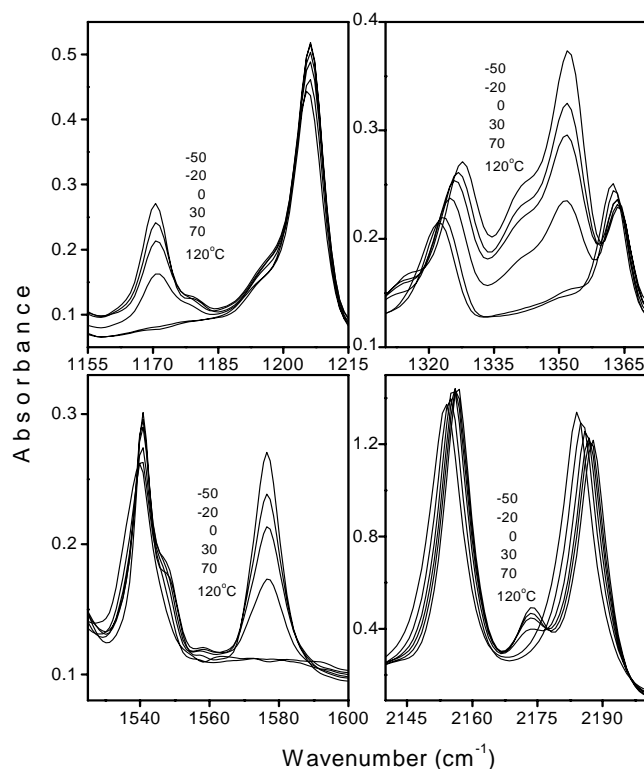


Fig. 1. Infrared absorption spectra for E//a in several spectral regions at various temperatures.

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measured using a spectrometer system (Jasco FT/IR-410) equipped with a microscope and temperature-controllable optical cell (Linkam TH-600PM).

Fig.1. shows the infrared absorption spectra for E//a in several spectral regions at various temperatures. In addition to the normally infrared active  $a_u$  modes, which are almost independent of temperature, of the TCNQ molecules, there appear strongly temperature dependent bands at 1170, 1351, 1576, 2173  $\text{cm}^{-1}$  and so on. We note that the behaviour of the latter bands is very much resemble to that of the  $S_1$  band: They diminish with increasing temperature to disappear at around 65°C.

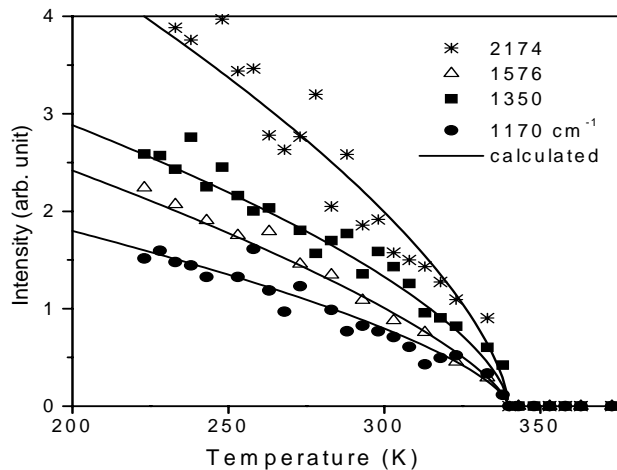


Fig. 2. Temperature dependencies of integrated intensity of the e-mv bands.

The integrated intensity of 1170, 1351, 1576, and 2173  $\text{cm}^{-1}$  bands are plotted in Fig. 2. The variation of the intensity can be expressed in term of the power law

$$I(T) = A\left(1 - \frac{T}{T_C}\right)^\alpha, \quad (1)$$

where  $T$  is the sample temperature,  $A$  is an adjustable coefficient, and  $\alpha$  is a numerical constant. The least-squares fit of eq. (1) to the experimental data yields  $T_C = 340$  K, and  $\alpha = 0.62$ - $0.70$  for all the bands. The values of  $\alpha$  are compared with  $\alpha = 0.63$  and  $0.66$ , which are obtained for the intensity of the  $S_1$  band and (018) Bragg reflection of the X-ray diffraction, respectively[2,3].

The temperature dependence of peak positions of respective bands are shown in Fig.3. The bands at 1351 and 2173  $\text{cm}^{-1}$  are slightly red-shifted with increasing temperature, whereas the bands at 1170 and 1576  $\text{cm}^{-1}$  are blue-shifted.

### 3. Discussion

The above mentioned temperature dependent bands correspond in the spectral position well to the electron-molecular-vibration (e-mv) coupled modes of anionic

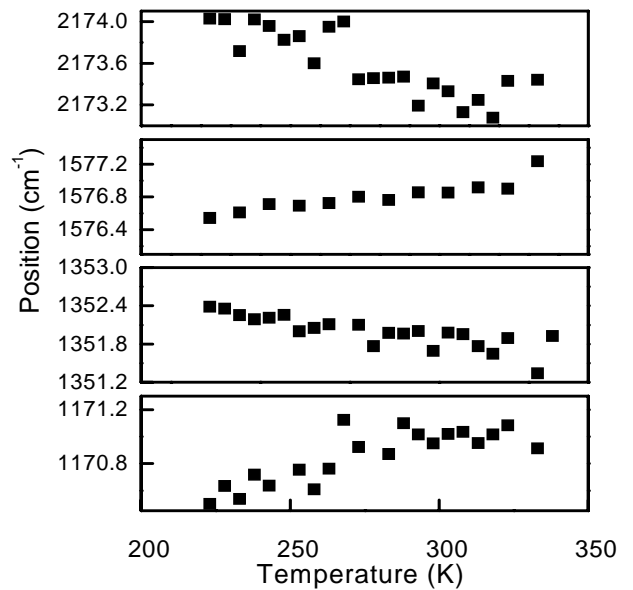


Fig. 3. The temperature dependencies of the peak position of e-mv bands

TCNQ molecules[4] in  $\text{Cs}_2\text{TCNQ}_3$ . According to Painelli et al., the origins of the e-mv modes are the totally symmetric ( $a_g$ ) molecular vibrations of TCNQ molecules. If TCNQ molecules are isolated the  $a_g$  modes have no electric dipole moment, and therefore are infrared-inactive. However, if consecutive TCNQ molecules are dimerized the anti-symmetric combination of an  $a_g$  mode may couple directly to the charge transfer excitations of the dimer. There is no doubt that the bands observed at 1170, 1351, 1576 and 2173  $\text{cm}^{-1}$  below 65°C in the present substance are due to those e-mv modes.

In case of the present substance, the good resemblance of the temperature dependence between the e-mv bands and the  $S_1$  band suggests that the e-mv modes arise from coupling of  $a_g$  vibrations with the charge transfer that drives the  $S_1$  band. In the previous report the  $S_1$  band is suggested to be associated with the charge transfer transition peculiar to the slipped TCNQ radical dimers[2]. Since the electric dipole moment is parallel to the radical TCNQ molecules, this transfer becomes forbidden when the dimers are perfectly eclipsed. In the high temperature phase, therefore, those vibrations recover the infrared-inactive nature.

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