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R. Swietlik, A. Graja

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Temperature study of infrared reflection spectra on various faces of MTPP(TCNQ)₂ single crystals

R. Świętlik and A. Graja

Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17/19, Poznań, Poland

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Résumé. — Les cristaux du sel d’ion-radical MTPP(TCNQ)₂ subissent une transition de phase structurale du 1er ordre à la température de 315,7 K, se manifestant par des modifications importantes du spectre infrarouge qui seront présentées et discutées. Nous avons observé en outre une hystérèse des spectres de réflexion et avons montré qu’il existe une relation entre les changements du spectre et l’enthalpie de transition.

Abstract. — Crystals of the ion-radical salt MTPP(TCNQ)₂ undergo a first-order structural phase transition at the temperature \( T_p = 315.7 \) K. This phase transition has a pronounced influence on the infrared spectra. In this paper we present and discuss the infrared spectra of MTPP(TCNQ)₂ as a function of temperature. During thermal cycling we have observed an interesting thermal hysteresis of the reflection coefficients for different bands. Moreover, we have related the observed spectral modifications with the enthalpy of the phase transition.

In a previous paper [1] we have described for the first time the infrared reflection spectra of single crystals of methyltriphenylphosphonium bis-tetracyanoquinodimethanide (MTPP(TCNQ)₂) below and above a phase transition. They have been compared and the changes in real \( e'(\omega) \) and imaginary \( e''(\omega) \) parts of the permittivity spectra have been shown as well. We have tried to discuss at a molecular level the factors which could be responsible for the spectral variations due to the phase transition. The role of charge delocalization has also been emphasized.

In this paper we present the reflection spectra on various faces of MTPP(TCNQ)₂ single crystals and discuss the anisotropy of these spectra. The changes in the reflectivity connected with the phase transition at 315.7 K were examined as a function of the temperature. The mechanism of the spectral changes as well as a contribution to the enthalpy of the phase transition were investigated on the basis of our results. The knowledge regarding the structural [3] and thermal dynamic [8] properties of the phase transition was useful for this purpose.

According to the results of crystal structure analysis given by Konno and Saito [3], TCNQ molecules between tetramers is shortened by about 0.02 Å whereas the average interplanar distances in the tetrad are longer by 0.08 and 0.04 Å than the corresponding distances in the low-temperature modification. The overlapping mode of the TCNQ moiety between the tetrad is also changed. The conformation of MTPP⁺ ion is different from that of the low-temperature form; two of the phenyl groups are rotated by about 56° and 45° from the positions observed in the low-temperature form. The conformation of the phosphonium ion is disordered. The structural characteristics of the phase transition of MTPP(TCNQ)₂ are pronounced and rather different from those of the Peierls’ transition typical of the one-dimensional TCNQ salts.

These large changes of the structure are in accord with the changes of electrical conductivity (drop from about \( 4 \times 10^{-3} \) \( \Omega^{-1} \) cm\(^{-1} \) to \( 10^{-2} \) \( \Omega^{-1} \) cm\(^{-1} \) [4, 7]), enthalpy of the phase transition (485.18 cal/mole [8]) as well as other physical properties [5, 13, 14].

The morphology of MTPP(TCNQ)₂ crystal according to Hamann [2] is shown in figure 1. MTPP(TCNQ)₂ crystallizes mainly as a pinacoid in dominating forms \{100\}, \{010\}, \{011\}, and \{211\}; the most important directions of the crystal’s edges are: \{001\}, \{011\} and \{100\}. In this notation the directions \{100\}, \{011\} and \{001\} correspond to the crystallographic axes \( a \), \( b \) and \( c \) in [3] (Fig. 1), respectively.
Fig. 1. — The crystal shape of MTPP(TCNQ)$_2$ single crystal [2]. The direction [011] corresponds to the TCNQ chain direction (b-axis in ref. [3]).

The typical size of our crystals was about 5 x 3 x 2 mm$^3$. We investigated the reflectivity $R$ for two polarizations of incident infrared (IR) light (from 4000 cm$^{-1}$ to 200 cm$^{-1}$), in the temperature range 290-350 K, from three well-shaped faces d(100), f(010), and l(011). For the TCNQ salts the reflectivity for light polarization perpendicular to the TCNQ stacks direction is about 7% for all frequencies. Our studies were first of all focused on the spectra obtained with the electrical vector parallel to the TCNQ stacks direction (E // b) because for the TCNQ salts they are the most informative ones.

When we investigated the reflectivities of d(100) and l(011) faces, the electrical vector E of the polarized incident light was parallel to the b direction, that is parallel to the TCNQ stacks. For reflection from the f(010) face the E vector was nearly perpendicular to the stacks and parallel to the long axis of the TCNQ molecules. The reflection spectra of the faces d(100) and l(011) (Fig. 2a) are practically the same (being E // b for both cases). On the other hand the spectrum of the f(010) face is different (Fig. 2b) because the E vector is perpendicular to the stack axis. Figure 2 presents the spectra for low temperature (LT) phase at 300 K.

We also investigated the reflectance for all the three crystal faces with the E vector perpendicular to the above-mentioned polarizations. The light was shone in the same way as in the above-described cases but for faces d(100) and l(011) the E vector was perpendicular to the b direction and for the f(010) face the E vector was perpendicular to the long axis of the TCNQ molecules. In these cases the reflection coefficient was nearly frequency independent and equal to about 0.1.

In order to obtain the dielectric spectrum we have performed the Kramers-Kronig analysis of reflection data. The essence of this analysis lies in determining, by a computer program, the phase shift $\theta$ on the basis of the reflectance $R$ from the Kramers-Kronig integral. Complex reflectivity $R e^{i\theta}$, obtained in this way, is used for evaluation of the optical constants. Since reflection spectra are only available in a restricted frequency range it is indispensable to make reasonable extrapolations. Between the highest measured frequency (4000 cm$^{-1}$) and 23 000 cm$^{-1}$ the reflectance was extrapolated on the basis of the near infrared measurements of Yakushi et al. [5]. The results of these authors indicate the following four absorption bands at this region : $(2 \div 3) \times 10^3$, $10 \times 10^3$, $16 \times 10^3$ and above $25 \times 10^3$ cm$^{-1}$. At very low frequencies (40-200 cm$^{-1}$) we used the far infrared data of Petzelt et al. [6] obtained for the analogous arsonium salt. The IR spectrum of that salt is practically the same as the LT phase spectrum of MTPP(TCNQ)$_2$.

Our reflectance data together with these extrapolations should provide reasonably accurate values for the optical constants in the frequency range 200-4000 cm$^{-1}$ investigated here. The optical constants, i.e. real part of dielectric function $\varepsilon'(\omega)$ and conductivity for IR frequencies $\sigma(\omega) = \varepsilon_0 \omega \varepsilon''(\omega)$, obtained by Kramers-Kronig analysis for LT and HT phases of MTPP(TCNQ)$_2$ are given in figures 4 and 5. One can see that the conductivity $\sigma(\omega)$ for IR frequencies changes appreciably.

Fig. 2. — Infrared reflectivity of the LT phase of MTPP(TCNQ)$_2$ for different crystal faces. The electrical vector E is parallel to the TCNQ stacks direction in the case of faces d(100) and l(011) (Fig. 2a) and is parallel to the TCNQ long axis for f(010) (Fig. 2b).

Fig. 3. — Infrared reflectivity of HT phase of MTPP(TCNQ)$_2$ in the case of faces d(100) and l(011).
The IR spectrum shows pronounced changes due to the phase transition. The spectrum of the high temperature (HT) phase is shown in figure 3. We have also found no differences between the spectra obtained from the l(011) and d(100) faces of the HT phase. The HT phase spectra show weaker reflection within the whole spectral region, especially in the intermolecular electronic excitation region i.e. above 2 000 cm\(^{-1}\). The charge transfer band is shifted to lower frequencies and its intensity decreases considerably; this has been shown in the previous paper [1], where the superposition of the spectra has been presented. These changes are the evidence of an increased electron delocalization due to the modification in the TCNQ stacks. This effect was also observed by Iida et al. [4] as a drop in electrical conductivity by a factor of about 3.5 at the phase transition temperature.

Relatively large anomalies of the polarized optical reflectance have been found near 2 220, 1 580, 1 350, 1 150 and 690 cm\(^{-1}\) i.e. at the region where the a\(_g\) modes of the internal vibrations of the TCNQ molecules are excited due to their coupling to the intermolecular oscillations of the electrons [9-12]. The assignment of these bands has been shown previously [1, 6]. The bands near 2 220, 1 590, 1 410 and 1 190 cm\(^{-1}\) almost disappear in the HT phase, whereas the reflection coefficient of the band 2 160 cm\(^{-1}\) abruptly decreases at \(T_p\). The other bands lower their reflectance by a factor of about 1.1; simultaneously, these bands become broader. The broadening is presumably caused by the increase of the fluctuation of the electric charge at each TCNQ molecule in the HT phase. The increase of these fluctuations means that the charges on TCNQ molecules are more delocalized. This corresponds to the lower energy of charge transfer band. The changes in population of the vibrational energetic levels are the reason of the decrease in reflectance.

One notices that some bands are split in the LT phase [1]. This means that in this phase the TCNQ molecules exist in two different molecular environments. In the HT phase two of the phenyl groups are rotated from the positions observed in the LT phase. Moreover, the average interplanar distances between TCNQ molecules in the stacks are more equalized [3]. These are the reasons why all the TCNQ molecules are approximately in the same environment in the HT phase and why some bands disappear in this phase.

The spectrum measured for the face f(010) also shows some small changes due to phase transition. It is worth noticing that some of the bands in the reflection spectrum of the f(010) face have exactly the same frequencies as one of components of the doublets observed for the l(011) or d(100) faces. This is particularly clear for the 2 210 cm\(^{-1}\) frequency. The other bands which disappear have also their counterparts for l(011) and d(100) spectra. It means that the bands observed for the f(010) face, although polarized along the TCNQ long axis, have their counterparts for perpendicular polarizations. The only possible explanation of this phenomenon is that the symmetry of the a\(_g\) modes is broken as an effect of interaction between the CN groups of the TCNQ anions with nearest phenyl groups of the cations. This break of symmetry of the vibrations does not necessarily make the electron-phonon coupling impossible.

The question is whether these spectral changes occur
Fig. 6. — Typical temperature dependence of the reflection coefficients for the bands which exhibit pronounced changes due to the phase transition. The solid lines are drawn through the data points.

stepwise or softly, if these changes are reversible or not. The measurements of the reflectivity for light polarized parallel to the stacks direction were performed systematically in the temperature range 290-350 K, for temperatures going up and down. The results for all bands which exhibit distinct changes due to the phase transition are similar (Fig. 6). We observed discontinuities in reflectance at 314 K on heating and 309.5 K on cooling; the temperature hysteresis observed is fully reproducible. Similar hysteresis was found e.g. by Iida [7] for electrical conductivity measurements. These observations emphasize the relation between optical properties and electron transport.

The results for other bands are not interesting. The reflectivity decreases when the temperature increases; these changes are also reversible.

From the structural investigations performed by Konno and Saito [3] we know that the phase transition in MTPP(TCNQ)$_2$ is a structural one of the first order. The main changes in the crystal structure are : 1) two of the phenyl groups are considerably rotated, 2) interplanar distances in the TCNQ tetrades are somewhat changed, 3) overlap between the two adjacent tetrades is also changed.

The internal energy change may be considered as a sum of the free energy of rotation and free energy of translation:

$$E = E_{\text{rot}} + E_{\text{trans}}.$$  

(1)

The internal energy is equivalent to enthalpy of transition because the volume of the unit cell is practically unchanged. The relative change equals to about 0.1 %. The part of rotation is predominant and for this reason we discuss the rotational part of the entropy of transition. The rotation of the phenyl groups from the positions observed in the LT phase induces changes of the charge distribution in the TCNQ stacks, that is changes of electron polarization. We assume that this polarization can be expressed by the function:

$$P_n = P_0 \exp(-\Delta H_n/kT)$$  

(2)

similar to the function describing e.g. the equilibrium of rotational conformers; the index $n = 1$ at $T < T_p$ and $n = 2$ for $T > T_p$, $\Delta H_n$ denotes the enthalpy of the change of configuration of the phenyl groups.

The polarization of the crystal is:

$$P_n = EN \alpha_n$$  

(3)

where $\alpha_n$ is the radical electron polarizability, $E$ is local field, $N$ is the number of TCNQ molecules per unit volume. The electron distribution related to the electron polarization undergoes an abrupt change at the phase transition temperature.

The limit value of the polarizability is:

$$\alpha_n^* = \lim_{T \to T_p} \alpha_n = \alpha_0 e^{-\Delta H_n/kT_p}.$$  

(4)

Putting

$$\Delta H_1 = \Delta H'$$  

and

$$\Delta H_2 = \Delta H' + \Delta H,$$

we can express the ratio of polarizabilities at $T_p$ as:

$$\frac{\alpha_1^*}{\alpha_2^*} = \frac{\alpha_0 e^{-\Delta H_1/kT_p}}{\alpha_0 e^{-\Delta H_2/kT_p}} =$$

$$\frac{e^{-\Delta H'/kT_p}}{e^{-\Delta H'/kT_p} e^{-\Delta H/kT_p}} = e^{\Delta H/kT_p}.$$  

(5)

In spite of the fact that the static polarizability of organic solid $\alpha^*$ differs from that at the IR frequency $\alpha^*(\omega)$, the ratio of the static polarizability of the LT and that of the HT phase is similar to the ratio of the polarizability at the IR frequency. This conclusion can be drawn from the comparison of the dielectric permeability $\varepsilon(\omega)$ obtained by the analysis of the reflectance (Fig. 4) and that at microwave region [14], as well as their changes at the phase transition temperature (both permeabilities increase abruptly by a few per cent at the transition).

Unfortunately we cannot measure these polarizabilities directly, however, we can measure the reflection coefficients.

One can easily prove that:

$$\frac{\varepsilon_1(\omega)}{\varepsilon_2(\omega)} = \frac{R_1}{R_2},$$  

(6)

Thus

$$\frac{R_1}{R_2} = e^{\Delta H/kT_p}$$  

(7)

or

$$\ln \left(\frac{R_1}{R_2}\right) = \Delta H/kT_p$$

$$\Delta H = kT_p \ln \left(\frac{R_1}{R_2}\right).$$

Expressing the enthalpy of transition in units of cal/mole, we have:

$$\Delta H = RT_p \ln \left(\frac{R_1}{R_2}\right).$$  

(8)
This formula permits us to calculate the enthalpy of the phase transition on the basis of the measurement of the reflectivity of the light polarized parallel to the TCNQ stacks direction.

The average value of rotational enthalpy calculated for the bands changed by the phase transition is about 360 cal/mole whereas the total enthalpy found by Kosaki et al. [8] from the heat capacities measured with an adiabatic calorimeter is 485.18 cal/mole.

If one adds a translational part of enthalpy presumably much smaller than the rotational part, one would obtain a value of the total enthalpy close to the thermodynamic value of Kosaki.

In conclusion we would like to stress that the relatively small changes in the molecular neighbourhood of TCNQ molecules in the phase transition can distinctly modify the IR spectrum, in particular the reflection spectrum of MTPP(TCNQ)$_2$ salt. Analysis of the reflectivity for two light polarizations informs us about the stack configuration, the electron-phonon coupling, the nature of the phase transition, and the optical constants and their changes in the phase transition.

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