

Manifestation of mixed vibronic states in the far infrared spectra of TEA(TCNQ)₂ and their contribution to the dielectric constant

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The reflection band in the far IR spectra of TEA(TCNQ)₂, which determines the high dielectric constant $\epsilon_s \approx 70$ of the crystal, is investigated and explained on the basis of allowance for the interaction between the electrons and the TCNQ molecule vibrations. It is estimated that this mechanism can account for the anomalously large dielectric constants of highly-conducting TCNQ salts.

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Investigations of IR spectra of conducting TCNQ salts, initiated in^[1-3], have revealed an interaction between the quasi-one-dimensional electron system and the intermolecular vibrations (IMV) of TCNQ, which leads to an anomalous structure in the case of the polarization $\mathbf{E} \parallel \mathbf{a}$, where \mathbf{a} is the direction of the TCNQ chains.¹⁾ The structure is located near the frequencies of the fully-

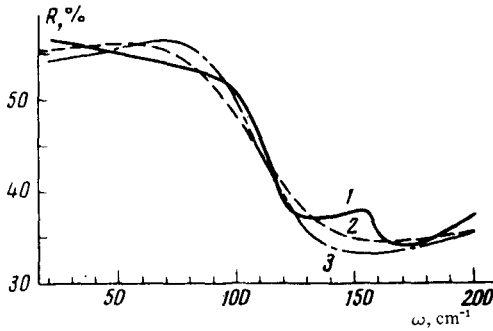


FIG. 1. Reflection spectra of TEA(TCNQ)₂ crystals with polarization $E \parallel a$: 1—experimental data from^[9], 2—calculation by the oscillator model, 3—calculation based on formula (1).

symmetrical (A_g) IMV of TCNQ^[5,6] against the background of the electron absorption band. The constants of this interaction can be determined from an analysis of its spectrum, and this was realized with the framework of the model of mixed vibronic states,^[4] with TEA(TCNQ)₂ as an example.²⁾ A microscopic description has also been proposed by now.^[5] So far, however, principal attention has been paid to the spectral region $\lambda < 10\mu$. We show in this paper, for the first time, that resonances of this type are observed also in the far infrared (FIR) region. These resonances are characterized by high oscillator strengths, and are therefore one of the causes of the anomalously large dielectric constants of highly conducting TCNQ salts, $\epsilon_s = 300-3000$.^[7,8]

The FIR spectra of TEA(TCNQ)₂ were investigated in^[9]. Attention is called to the 20–130 cm⁻¹ high-reflection bands in $E \parallel a$ polarization (Fig. 1, curve 1), which was not discussed in that paper. We have carried out a standard analysis of this band within the framework of the oscillator model $\epsilon(\omega) = \epsilon_e + \epsilon_e(\omega_L^2 - \omega_T^2) / (\omega_T^2 - \omega^2 - ig\omega)$, where ϵ_e is the background dielectric constant in this region, ω_T and ω_L are the transverse and longitudinal frequencies, and g is the damping. A Kramers–Kronig analysis yields $\epsilon_e \approx 20$.^[9] The best description of the experimental spectrum is reached (curve 2) at $\omega_T = 85$, $\omega_L = 130$, $g = 90$ (all frequencies in cm⁻¹). For these values of the parameters we have $\epsilon(0) = \epsilon_e \omega_L^2 / \omega_T^2 \approx 50$. However, since the calculated spectrum is not very sensitive to changes to ω_T , we estimate the oscillator strengths $S = \epsilon_s - \epsilon_e = 30-70$ by using the dielectric constant $\epsilon_s = 70 \pm 20$ measured at radio frequencies.^[10] The known formula $S = 4\pi Nq^2\epsilon_s / \mu\omega_L^2\epsilon_e$, where q and N are the charge and concentration of the oscillators, is then used to estimate the reduced mass μ . Substituting the number $N = 0.72 \times 10^{21}$ cm⁻³ of the unit cells and recognizing that the oscillating charge in each of them is $q \leq 2e$, since each cell has two unpaired electrons, we obtain $\mu \leq 0.7$ proton mass. Such a value cannot be due to the motion of the TEA⁺ and TCNQ⁻ ions corresponding to the external lattice vibrations, and indicate motion of light particles. Neither, however, can the properties of the band be explained by invoking IMV with participation of hydrogen, which produces in TEA(TCNQ)₂ bonds such as C–H and N–H, which are characterized by high oscillation frequencies. In this case it is also difficult to understand the strong polarization of the band. All this suggests that the electrons take part in the oscillator motion.

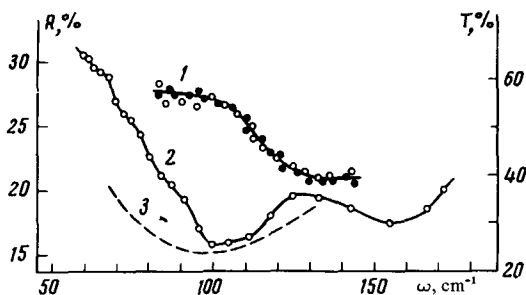


FIG. 2. Reflection spectra (1) of crystals and transmission spectra (2,3) of suspensions of TEA(TCNQ)₂. 1, 2—experimental data, 3—calculated on the basis of formula (1). T °K: ○—300, ●—100

To assess the possible role of the free carriers, we have investigated the reflection of TEA(TCNQ)₂ at $T=300$ and 100 °K. The spectra (Fig. 2) were recorded in unpolarized light with an FIS-21 spectrometer with the crystalline mosaics described in^[4], and agree at 300 °K with the data of^[9]. The changes that occur after cooling to 100 °K are negligible and do not exceed the measurement errors. Figure 2 shows also the transmission spectrum of a TEA(TCNQ)₂ suspension (crystallite dimensions on the order of several dozen microns) in paraffin. The abrupt decrease of the transmission in the region $60-90$ cm⁻¹ is probably due to the enhancement of the scattering of the light by the suspension particles with decreasing wavelength. The absorption near 100 cm⁻¹ discussed below, and the band near 155 cm⁻¹ seems to correspond to IR-active IMV of TCNQ (ω)(B_{3u}) = 146 cm⁻¹.^[11]

The obtained data allow us to reject the assumption that free carriers predominate in the formation of the spectrum. Indeed, if we attempt to connect the band with the plasma reflection edge, then, since the gap in the electron-excitation spectrum of TEA(TCNQ)₂ is ~ 0.3 eV, one should expect a sharp decrease in the free-carrier density n on going from $T=300$ to $T=100$ °K (the electric conductivity ratio is $\sigma_{300K}/\sigma_{100K} \sim 10^6$)^[10] and a decrease in the plasma frequency $\omega_p \sim \sqrt{n}$, which contradict the absence of a band shift.

The position of the intense structure in the reflection of TEA(TCNQ)₂ (minima near $900, 700, 640, 320$ cm⁻¹)^[9] indicates that all the A_g vibrations of TCNQ ($1003, 713, 596, 335, 103$ cm⁻¹)^[11] come into play as a result of the vibronic interaction, just as in the region $\lambda < 10$ μ . It is therefore natural to connect the investigated band with a transition into a mixed vibronic state with $\omega(A_g) = 103$ cm⁻¹. Assuming that the results of^[4] are valid in this case, we used the function proposed there for the dielectric constant at the frequencies $\omega \ll \omega_{Te}$, g_e , where ω_{Te} and g_e are the transverse frequency and damping of the electronic transition; this function takes the form

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_e - \epsilon_\infty}{1 - \gamma_e^2/\omega_{Te}^2(1 - \zeta)(\omega_0^2 - \omega^2 - ig_0\omega)} \quad (1)$$

Here $\zeta = \omega_{Te}^2 \sum_{k \neq 1} \gamma_k^2 \omega_k^{-2} = 0.35$, where g_k and γ_k are the damping and the interaction constants for the vibrations with frequency ω_k , $\epsilon_\infty = 2$, and $\omega_{Te} = 2300$ cm⁻¹.^[4]

Satisfactory agreement is obtained between calculation and experiment at $\omega_0 = 130 \text{ cm}^{-1}$, $g_0 = 70 \text{ cm}^{-1}$, and $\gamma_0^2 \omega_0^{-2} \omega_{Te}^2 = 0.36$ (Fig. 1, curve 3). We have also calculated for these values, on the basis of (1) and the indicated parameters, the transmission spectrum, which describes correctly (Fig. 2) the position of the absorption band; one can hardly expect better agreement, since no account was taken of the light scattering and of the manifestation of surface modes in the spectrum of the minute particles.

Thus, the arguments advanced, as well as the impossibility of attributing the considered band to the usual mechanisms of external or internal vibrations of the crystal lattice or of the free carriers, allow us to speak with assurance of transitions into a mixed state that is due to the interaction of the electrons with the low-frequency IMV of TCNQ.³⁾ It can be assumed that the structure in the FIR spectra of TTF-TCNQ,^[13,14] particularly in the vicinity of 100 and 300 cm^{-1} , is similar. The lower electronic-transition frequency $\omega_{Te} \approx 1000 \text{ cm}^{-1}$ ^[13] lets us assume that the interaction with the low-frequency IMV becomes stronger, but the values of its constants are unknown. Therefore formula (1), with the values $\gamma_k^2 \omega_k^{-2} \omega_{Te}^2$ obtained for TEA(TCNQ)₂ and $\epsilon_e - \epsilon_\infty \approx 80$ ^[13], can yield only a rough estimate of the contribution of the mixed vibronic states to the dielectric constant $\epsilon(0) \sim 200$, merely indicating that it is large for high conductivity salts.

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¹⁾ This structure is remarkable also in that it contains distinct antiresonance.^[4]

²⁾ TEA—triethylammonium, TCNQ—tetracyanoquinodimethane.

³⁾ In view of the strong localization of the electrons, the dielectric state of TEA(TCNQ)₂ is not a pure Peierls state, and the presence of the Fröhlich mode, which also manifests itself in the IFR spectra,^[12] seems little likely.

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