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# Electronic and Vibrational Spectra of $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$ Crystals

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**Abstract.** — We present the results of spectral studies of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  salt containing alternating stacks of  $\text{Au}(\text{dmit})_2$  and TCNQ molecules. The polarized transmission spectra of single crystals are measured in the IR region (650 to 6500  $\text{cm}^{-1}$ ) as a function of temperature (90 to 300 K). Moreover, the powder absorption spectra in the frequency range (400 to 40000  $\text{cm}^{-1}$ ) are reported. From spectral evidence results that transferred electrons are localized on  $\text{Au}(\text{dmit})_2$  molecules in the mixed stacks. The intrastack charge transfer between  $\text{Au}(\text{dmit})_2$  and TCNQ molecules ( $\sim 8000 \text{ cm}^{-1}$ ) and the interstack charge transfer transition between  $\text{Au}(\text{dmit})_2$  molecules ( $\sim 5500 \text{ cm}^{-1}$ ) are found. Interactions of electrons with intramolecular vibrations of TCNQ ( $a_g$  modes) and  $\text{Au}(\text{dmit})_2$  (C = C and C = S stretching) are suggested and discussed.

## 1. Introduction

The metal complexes  $\text{M}(\text{dmit})_2$  (M = Ni, Pd, Pt, Au and dmit = 4,5 dimercapto-1,3-dithiole-2-thione; Fig. 1) are known to form many highly conducting salts with different donor molecules or closed-shell cations [1]. In this series three  $\text{Ni}(\text{dmit})_2$  salts and three  $\text{Pt}(\text{dmit})_2$  salts exhibit superconductivity under pressure and one  $\text{Ni}(\text{dmit})_2$  salt becomes superconductor at ambient pressure [1, 2]. Close S · S contacts, shorter than the sum of the corresponding van der Waals radii, promote effective molecular overlap inside and/or between the stacks. Up to now the most widely studied are compounds based on the dmit complexes of Ni, Pd and Pt but an interesting series of highly conducting salts based on  $\text{Au}(\text{dmit})_2$  has been also synthesized [3].

The TCNQ (tetracyano-p-chinodimethane) is another important organic acceptor yielding a great number of conducting charge transfer salts with different cations [4]. The TCNQ molecules stack face-to-face to form linear chains and the overlap of  $\pi$ -molecular orbitals along the stacking direction greatly exceeds interstack coupling. The consequence of such specific crystal structure is a high anisotropy of the physical properties, *i.e.* quasi-one-dimensionality.

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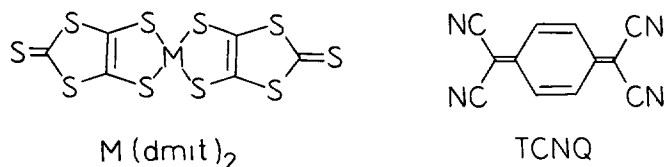


Fig. 1. —  $M(dmit)_2$  and TCNQ molecules ( $M = Ni, Pd, Pt, Au$ ).

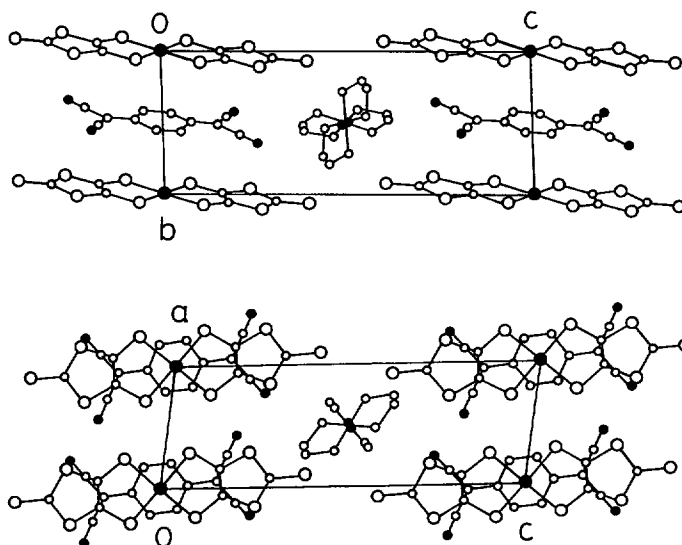


Fig. 2. — Crystal structure of  $Et_4N[Au(dmit)_2TCNQ]$  projected along the  $c$ -axis (above) and  $b$ -axis (below) [3].

Both  $Au(dmit)_2$  and TCNQ form conducting salts with  $Et_4N^+$  (tetraethylammonium) cation. The  $Et_4N(TCNQ)_2$  crystal is a quasi-one-dimensional semiconductor [5], whereas the  $Et_4N[Au(dmit)_2]_2$  compound is known to exist in two modifications  $\alpha$  and  $\beta$ , exhibiting metallic and semiconducting properties, respectively [3]. Moreover, an interesting crystal  $Et_4N[Au(dmit)_2TCNQ]$ , containing mixed  $[Au(dmit)_2TCNQ]^-$  anion, has been also synthesized [3]. The crystal structure data of the  $Et_4N[Au(dmit)_2TCNQ]$  are following: triclinic unit cell, space group  $P\bar{1}$ ,  $a = 6.490(1)$ ,  $b = 7.330(1)$ ,  $c = 17.802(4)$  Å,  $\alpha = 86.51(3)$ ,  $\beta = 81.75(3)$ ,  $\gamma = 78.24(3)^\circ$ ,  $V = 820.08$  Å<sup>3</sup>,  $Z = 1$  [3]. The  $Au(dmit)_2$  and TCNQ molecules alternate each other forming stacks along  $b$  direction (Fig. 2). The stacks are arranged in layers parallel to  $ab$  plane alternating with the layers of  $Et_4N$  cations in  $c$  direction. Slightly shortened  $S \cdots S$  contacts (3.637 Å) are observed between the stacks in the anion layers. The low room temperature conductivity of this crystal ( $\sim 10^{-5}$  S/cm) gives evidence of strong charge localization in the mixed  $[Au(dmit)_2TCNQ]$  stack.

The extraordinary crystal structure and the presence of mixed anion prompted us to perform the spectral investigations of  $Et_4N[Au(dmit)_2TCNQ]$  crystals. Optical properties of the alternating stack and first of all the charge distribution are the most interesting problems. It is well known that infrared spectra of crystalline organic conducting systems are dominated

by vibrational bands which are a consequence of electron-molecular vibration (EMV) coupling phenomena [6]. The eventual presence of EMV interactions in  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  crystal is another interesting question.

## 2. Experimental

The plate-shaped  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  crystals of typical dimensions  $1 \times 1 \times 0.03 \text{ mm}^3$  were grown from acetonitrile. The compound  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2]$  in the amount of 0.0216 g ( $3 \times 10^{-5} \text{ mol}$ ) was dissolved in acetonitrile (30 ml) at room temperature. After heating of the solution up to  $t = 72 \text{ }^\circ\text{C}$  the TCNQ (0.02448 g,  $1.2 \times 10^{-4} \text{ mol}$ ) was added. Then the vessel with solution was placed into a thermostat ( $72 \text{ }^\circ\text{C}$ ) and cooled down slowly to room temperature at the rate of  $1 \text{ }^\circ\text{C}/\text{hour}$ . The obtained crystals were filtered off, washed up with acetonitrile and acetone and dried at  $t = 40 \text{ }^\circ\text{C}$ .

Polarized transmission spectra of single crystals, for electrical vector of polarized light parallel and perpendicular to the stacking axis, were measured within the frequency range (650 to  $6500 \text{ cm}^{-1}$ ) by using the FT-IR Perkin Elmer 1725 X spectrometer equipped with a FT-IR microscope. We studied also the spectra of powders dispersed in KBr pellets in the range 400 to  $40000 \text{ cm}^{-1}$ ; three different spectrometers were used: FT-IR Perkin Elmer 1725 X ( $400$  to  $7400 \text{ cm}^{-1}$ ), Specord NIR ( $4000$  to  $13500 \text{ cm}^{-1}$ ) and Specord UV-VIS ( $13000$  to  $40000 \text{ cm}^{-1}$ ). Moreover, temperature dependence of the middle IR transmission of both single crystals and powders in KBr pellets was studied down to  $T = 90 \text{ K}$ . For comparison we measured also room temperature absorption spectra of the compounds  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2]$  and  $\text{Et}_4\text{NI}_3$  using KBr pellet technique. Detailed analysis of infrared spectra and their temperature dependencies was performed after decomposition of the selected spectral features. For this purpose a standard PEAKFIT program was used and the bands were fitted by Lorentzian and/or Gaussian functions.

The value of average charge residing on TCNQ molecule can be estimated from the position of Raman band assigned to the totally symmetric TCNQ mode  $a_g\nu_4$  [7]. For this reason we performed the Raman measurements of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  powders at room temperature using FT-IR Bruker IFS 66 spectrometer equipped with FRA 106 Raman accessory and Nd:YAG laser ( $\lambda = 1.064 \text{ }\mu\text{m}$ ).

## 3. Results and Discussion

**3.1. ELECTRONIC TRANSITIONS AND CHARGE DISTRIBUTION.** — The electronic absorption spectra of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  and  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2]$  powders in KBr pellets are shown in Figure 3. In both compounds three strong, similar bands D, E, F are observed and the salt  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  exhibits additional, weak electronic absorptions A, B, C. The electronic transitions fall into two classes: those at higher energies result from intramolecular electronic excitations and the lower-energy bands are due to the interactions among the molecules and are called charge transfer bands. The assignment of electronic bands has been performed by comparison with the interpreted electronic spectra of other  $\text{Au}(\text{dmit})_2$  [8] and TCNQ [9, 10] salts.

The strong band F at the frequency  $33000$  to  $34000 \text{ cm}^{-1}$  with a shoulder at  $35500 \text{ cm}^{-1}$  is related to a  $\pi-\pi^*$  transition of the dmit ligand. Another  $\pi-\pi^*$  band of the ligand is observed at  $21000 \text{ cm}^{-1}$  for  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  and at slightly lower frequency  $20500 \text{ cm}^{-1}$  for  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2]$  (band D in Fig. 3). The electronic absorptions F and D correspond to the bands at about  $34200 \text{ cm}^{-1}$  and  $21400 \text{ cm}^{-1}$ , respectively, for  $\text{Bu}_4\text{N}[\text{Au}(\text{dmit})_2]_2$  in acetonitrile solution [8]. The band E at  $27000 \text{ cm}^{-1}$  with a weak shoulder at  $25000 \text{ cm}^{-1}$  can be assigned

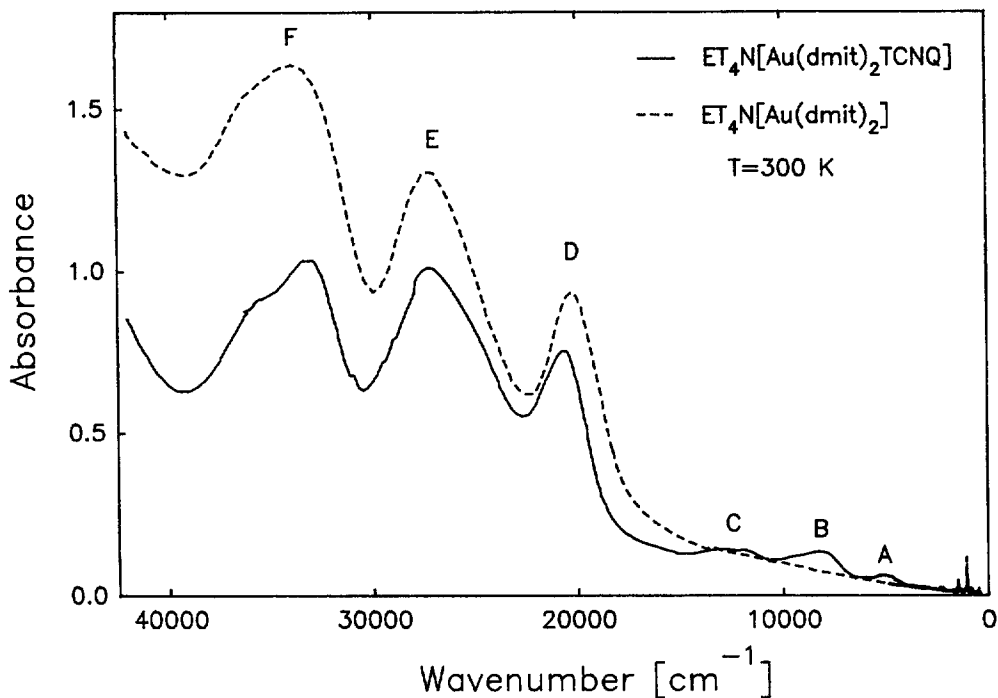


Fig. 3. — Electronic absorption spectra of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  and  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2]$  powders in KBr pellets (weight concentration 1:4000).

to the  $\text{Au}^{\text{III}} \leftarrow \text{S}$  charge transfer excitation but in this frequency region the intramolecular excitation of neutral  $\text{TCNQ}^0$  usually appears (27000 to 28000  $\text{cm}^{-1}$  for different TCNQ salts [9,10]). Therefore, in  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  the band E is a superposition of the  $\text{Au}^{\text{III}} \leftarrow \text{S}$  charge transfer and  $\text{TCNQ}^0$  intramolecular excitation. Analogous electronic absorption was found at 28600  $\text{cm}^{-1}$  with a shoulder at 26300  $\text{cm}^{-1}$  for  $\text{Bu}_4\text{N}[\text{Au}(\text{dmit})_2]_2$  in acetonitrile solution [8].

A striking feature of the electronic spectrum of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  is the absence of a band at about 16000  $\text{cm}^{-1}$  which could be expected from comparison with the electronic spectra of other TCNQ salts — at this frequency the intramolecular excitation of  $\text{TCNQ}^-$  anion is usually observed [9,10]. This fact suggests that the average charge density on TCNQ molecules is close or equal to zero, *i.e.* the transferred electron is mostly localized on  $\text{Au}(\text{dmit})_2$  molecule. This conclusion is confirmed by our Raman measurements of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  since the  $a_g\nu_4$  Raman band is situated at 1450  $\text{cm}^{-1}$ , *i.e.* nearly at the frequency corresponding to neutral  $\text{TCNQ}^0$  molecule (1454  $\text{cm}^{-1}$  [7]).

The relatively weak doublet C (12000 and 13000  $\text{cm}^{-1}$ ) is without doubt related to TCNQ. Analogous electronic feature is always found in spectra of TCNQ salts [9,10], though usually at slightly lower frequency. Since the publication of the paper [9] by Torrance *et al.*, such electronic absorption is generally assigned to the charge transfer process ( $\text{TCNQ}^- + \text{TCNQ}^- \rightarrow \text{TCNQ}^0 + \text{TCNQ}^{2-}$ ). The specific structure of the stacks in  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  and the estimated charge distribution prove that such charge transfer is impossible. Yakushi *et al.* [11] attributed band C to the lowest  $\pi-\pi^*$  band of  $\text{TCNQ}^-$  ion but in  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  there are only neutral  $\text{TCNQ}^0$  molecules in the stacks. In conclusion the nature of TCNQ electronic absorption C remains unclear.

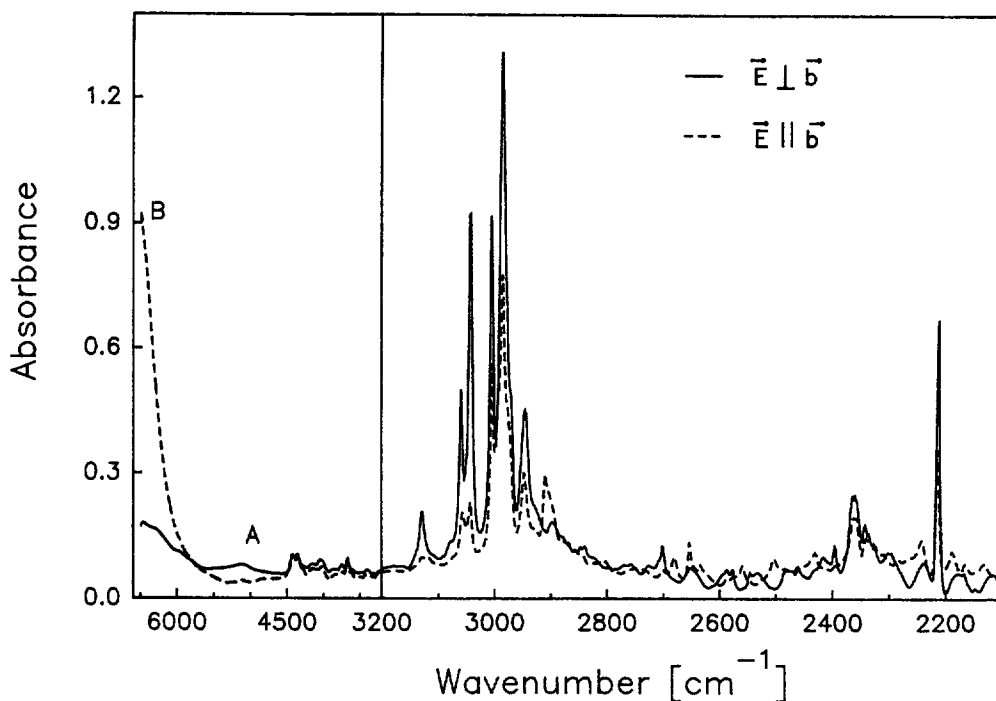


Fig. 4. — Polarized infrared absorption spectra at room temperature of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  single crystal in the region  $6500 - 2100 \text{ cm}^{-1}$ . The electrical vector of polarized light is parallel ( $\mathbf{E} \parallel \mathbf{b}$ ) and perpendicular ( $\mathbf{E} \perp \mathbf{b}$ ) to the stacking axis (note the change of frequency scale at  $3200 \text{ cm}^{-1}$ )

The electronic bands A ( $5500 \text{ cm}^{-1}$ ) and B ( $8000 \text{ cm}^{-1}$ ) in powder spectra (Fig. 3) were also studied using the transmission technique on thin single crystals (Fig. 4). The band A is polarized perpendicular and the band B parallel to the stacking direction  $b$  and we relate them to inter- and intrastack charge transfer, respectively. The band A is very weak and corresponds to the side-by-side charge transfer between  $\text{Au}(\text{dmit})_2$  and TCNQ inside the stack. In single crystal spectrum the band A is centered at lower frequency ( $\sim 5100 \text{ cm}^{-1}$ ) than in powder spectrum ( $\sim 5500 \text{ cm}^{-1}$ ); the band B seems to lie also at lower frequency but it cannot be positioned more precisely since the measurement was made up to  $6500 \text{ cm}^{-1}$ . In powder spectrum band A is weaker than band B but this difference is not so large as in the single crystal spectrum. This could be an indication that band A is polarized perpendicularly to the (001) crystal face and in the single crystal spectrum its component in the  $b$  direction is only observed. Since such electronic transition is rather unexpected, it seems that the difference of relative intensities between powder and single crystal spectra is due to an influence of powdering effect.

**3.2. VIBRATIONAL MODES.** — The specific feature of the organic conductors is the existence of strong electron-molecular vibration (EMV) interactions which manifest themselves by strong bands in the infrared spectra. Obviously, the EMV coupling takes place when the frequency of vibrational mode lies within the region of a suitable, strong charge transfer band. In the  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  salt the high frequency of intrastack charge transfer ( $\sim 8000 \text{ cm}^{-1}$ ) and the very low intensity of interstack charge transfer ( $\sim 5100 \text{ cm}^{-1}$ ) give rise to the weakness of expected infrared bands related to EMV coupling phenomena. The IR spectrum of

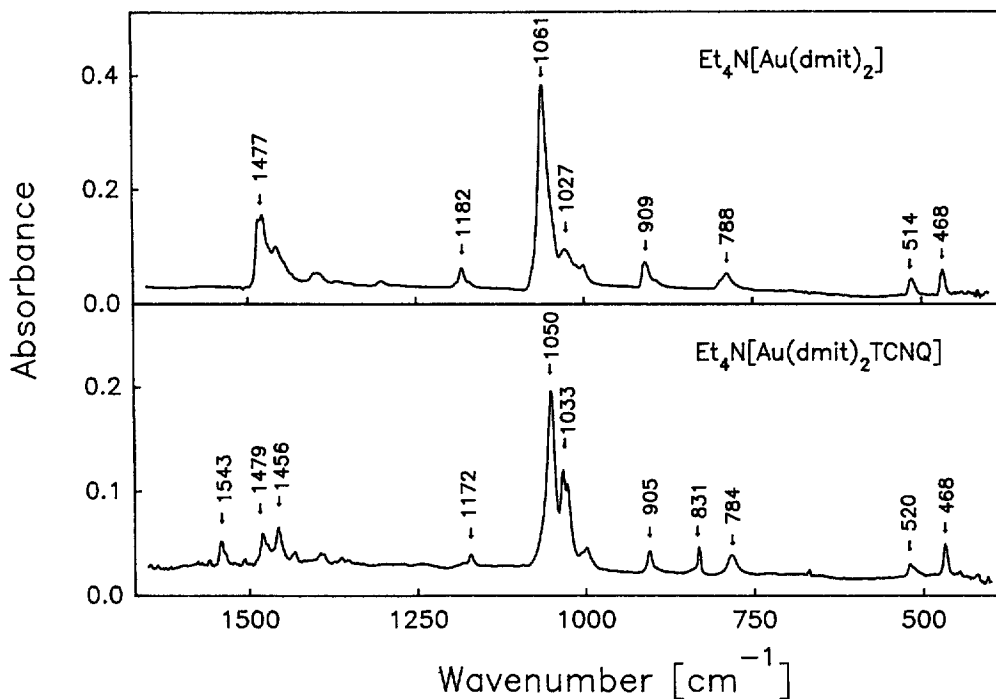


Fig. 5. — Infrared absorption spectra at room temperature of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2]$  and  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  powders in KBr pellets in the region  $1650 - 400 \text{ cm}^{-1}$  (weight concentration 1:1000).

$\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  should be dominated by IR active vibrations of  $\text{Au}(\text{dmit})_2$ , TCNQ as well as cation molecules, nevertheless the presence of weak EMV features is also expected.

The IR absorption spectra of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2]$  and  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  powders are illustrated in Figure 5. The spectra of both compounds are similar and several additional bands in  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  are due to TCNQ molecule. In  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2]$  spectrum the bands are of higher intensity, especially those at  $1477 \text{ cm}^{-1}$  and  $1061 \text{ cm}^{-1}$  related to C = C and C = S stretching vibrations of  $\text{Au}(\text{dmit})_2$  molecule, respectively. The structure of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2]$  is not known but it may be supposed that  $\text{Au}(\text{dmit})_2$  molecules interact stronger (probably face-to-face interaction) than in  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$ , therefore the IR effect of EMV coupling is stronger. The IR transmission spectra on  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  single crystals were investigated in two polarizations: the electrical vector of polarized light was parallel or perpendicular to the stacking direction  $b$  (Figs. 4 and 6). The transmission method on partially transparent single crystal is very useful for measurements of very weak modes, therefore, the single crystal spectra are very rich and in comparison to powder spectra the relative intensities of many bands are different. The FT-NIR Raman spectrum of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  is dominated by the strong TCNQ bands:  $1609 \text{ cm}^{-1}$  ( $a_g\nu_3$ ),  $1450 \text{ cm}^{-1}$  ( $a_g\nu_4$ ),  $1196 \text{ cm}^{-1}$  ( $a_g\nu_5$ ),  $952 \text{ cm}^{-1}$  ( $a_g\nu_6$ ),  $708 \text{ cm}^{-1}$  ( $a_g\nu_7$ ) and  $345 \text{ cm}^{-1}$  ( $a_g\nu_9$ ); the other strong bands at  $906 \text{ cm}^{-1}$ ,  $497 \text{ cm}^{-1}$  and  $325 \text{ cm}^{-1}$  may be related to  $\text{Au}(\text{dmit})_2$  molecule.

The frequencies of IR bands at room temperature and their assignment are listed in Table I. The attributions of  $\text{Au}(\text{dmit})_2$  vibrational bands are based upon those previously established for other molecules containing dmit ligand [12–15] or analogous molecules [16] since the normal

Table I. — Frequencies ( $\text{cm}^{-1}$ ) and assignments of the infrared spectra of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2]$  and  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  at room temperature ( $T = 300 \text{ K}$ ).

TCNQ <sup>0</sup> [17]		$\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$			$\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2]$ powder	Assignment	
obs	calc	crystal		powder			
		<b>E    b</b>	<b>E ⊥ b</b>				
3065	3041	3059	3059	3058	3000	TCNQ $b_{1u}v_{18}$	
3053	3050	3043	3043	3043		TCNQ $b_{2u}v_{32}$	
		3006	3006	3005		$\text{Et}_4\text{N}$	
		2986	2986	2986		$\text{Et}_4\text{N}$	
		2976		2973		2976	$\text{Et}_4\text{N}$
		2946	2946	2945		2940	$\text{Et}_4\text{N}$
		2910		2922			$\text{Et}_4\text{N}$
				2852			
				2218			
2229	2230	2217					TCNQ $a_gv_2$
2228	2226		2217			TCNQ $b_{2u}v_{33}$	
2228	2230	2214	2213			TCNQ $b_{1u}v_{19}$	
				2181			
			1921				
			1614				
1602	1602	1598				TCNQ $a_gv_3$	
1545	1542	1543	1543	1543		TCNQ $b_{1u}v_{20}$	
1540	1530	1537	1535	1537		TCNQ $b_{2u}v_{34}$	
		1483			1483	$\text{Et}_4\text{N}$	
		1474	1476	1479	1477	$\text{Au}(\text{dmit})_2$ C=C	
1454	1454	1461				TCNQ $a_gv_4$	
		1457	1457	1456	1457	$\text{Au}(\text{dmit})_2$ C=C	
		1450	1454	1450		$\text{Au}(\text{dmit})_2$ C=C	
		1446	1446	1446	1446	$\text{Et}_4\text{N}$	
		1432	1431	1432	1435	$\text{Et}_4\text{N}$	
		1411	1411			$\text{Et}_4\text{N}$	
1405	1404		1394		1397	TCNQ $b_{1u}v_{21}$	
		1389		1391	1391	$\text{Et}_4\text{N}$	
		1385	1385			$\text{Et}_4\text{N}$	
		1363	1363	1363	1365	$\text{Et}_4\text{N}$	
1354	1360	1353	1353			TCNQ $b_{2u}v_{35}$	
		1331	1331				
			1268				
			1246				
1207	1207	1195				TCNQ $a_gv_5$	
		1185	1185	1181	1182	$\text{Et}_4\text{N}$	
		1174	1168	1172	1171	$\text{Et}_4\text{N}$	
1125	1119		1128			TCNQ $b_{2u}v_{17}$	
			1118				
			1110				
			1094				
		1054				$\text{Et}_4\text{N}$	
		1061	1059	1056		$\text{Et}_4\text{N}$	
		1052	1051	1050	1061	$\text{Au}(\text{dmit})_2$ C=S	
		1035	1035	1033	1027	$\text{Au}(\text{dmit})_2$ C=S	
		1028	1030	1026		$\text{Au}(\text{dmit})_2$ C=S	
998	1013	1006	1006	1005		TCNQ $b_{1u}v_{22}$	
		996	998	998	1001	$\text{Et}_4\text{N}$	
		991	992				
962	961		961			TCNQ $b_{1u}v_{23}$	
		905	907	905	909	$\text{Au}(\text{dmit})_2$ C-S	
859		831		831		TCNQ $b_{3u}v_{10}$	
		783	787	784	788	$\text{Et}_4\text{N}$	
			776	778		$\text{Et}_4\text{N}$	
				520		$\text{Au}(\text{dmit})_2$ Au-dmit	
				514	514	$\text{Au}(\text{dmit})_2$ Au-dmit	
				468	468	$\text{Au}(\text{dmit})_2$ Au-S	



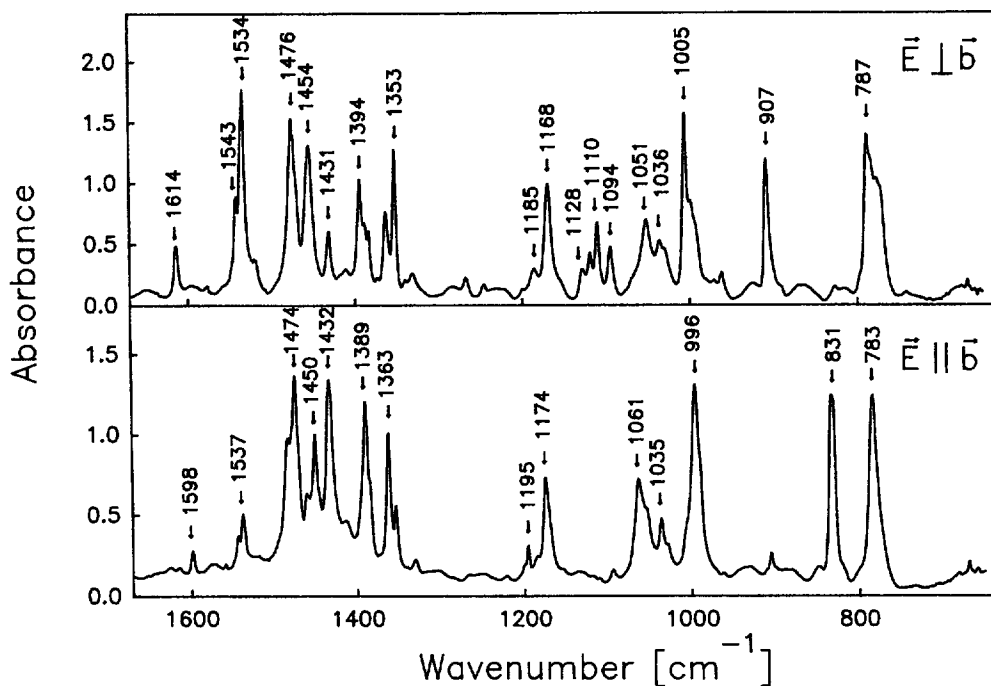


Fig. 6. — Polarized infrared absorption spectra (1670 – 650  $\text{cm}^{-1}$ ) at room temperature of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  single crystal for the electrical vector of polarized light parallel ( $\mathbf{E} \parallel \mathbf{b}$ ) and perpendicular ( $\mathbf{E} \perp \mathbf{b}$ ) to the stacking direction.

mode analysis of  $\text{M}(\text{dmit})_2$  molecule has not been done as yet. The TCNQ bands are assigned according to the paper [17] and the bands of  $\text{Et}_4\text{N}$  cation on basis of our IR data on  $\text{Et}_4\text{NI}_3$  salt. In order to make the best use of experimental evidence the band attribution has been carried out very carefully considering orientation of the molecules with respect to the crystal face (001), the powder and single crystal spectra, the relative intensities for different polarizations as well as the temperature dependencies.

From the crystallographic data results that molecular planes of  $\text{Au}(\text{dmit})_2$  and TCNQ are nearly perpendicular to the (001) crystal face and the long molecular axes are tilted in this way that they have components in the direction perpendicular to the stacks (Fig. 2). Such orientation of the molecules with respect to the (001) crystal face causes that in-plane, IR active  $b_{1u}$  and  $b_{2u}$  modes should be mainly registered in the direction perpendicular to the stacks whereas the out-of-plane  $b_{3u}$  modes parallel to the stacks. This agrees with the polarization of the bands related to IR active TCNQ modes of  $b_{1u}$  and  $b_{2u}$  symmetry, and their frequencies are close to those for neutral molecule (Fig. 6 and Tab. I). The band  $831 \text{ cm}^{-1}$  polarized parallel to the stacks, corresponds to the out-of-plane  $b_{3u}\nu_{50}$  TCNQ mode and exhibits larger shift from the  $\text{TCNQ}^0$  frequency; it seems to us that it can be due to an influence of the neighbouring  $\text{Au}(\text{dmit})_2$  anions. In the direction parallel to the stacks  $\mathbf{E} \parallel \mathbf{b}$  we find several bands which can be attributed to the totally symmetric  $a_g$  modes of TCNQ molecule. The best example is the mode  $a_g\nu_3 = 1598 \text{ cm}^{-1}$  but also  $a_g\nu_2 = 2217 \text{ cm}^{-1}$  and  $a_g\nu_5 = 1195 \text{ cm}^{-1}$  are well separated by the decomposition procedure. We observe also  $a_g\nu_4 = 1461 \text{ cm}^{-1}$  but this band is difficult to analyse since it strongly overlaps with  $\text{Au}(\text{dmit})_2$  and  $\text{Et}_4\text{N}$  bands. The  $a_g$

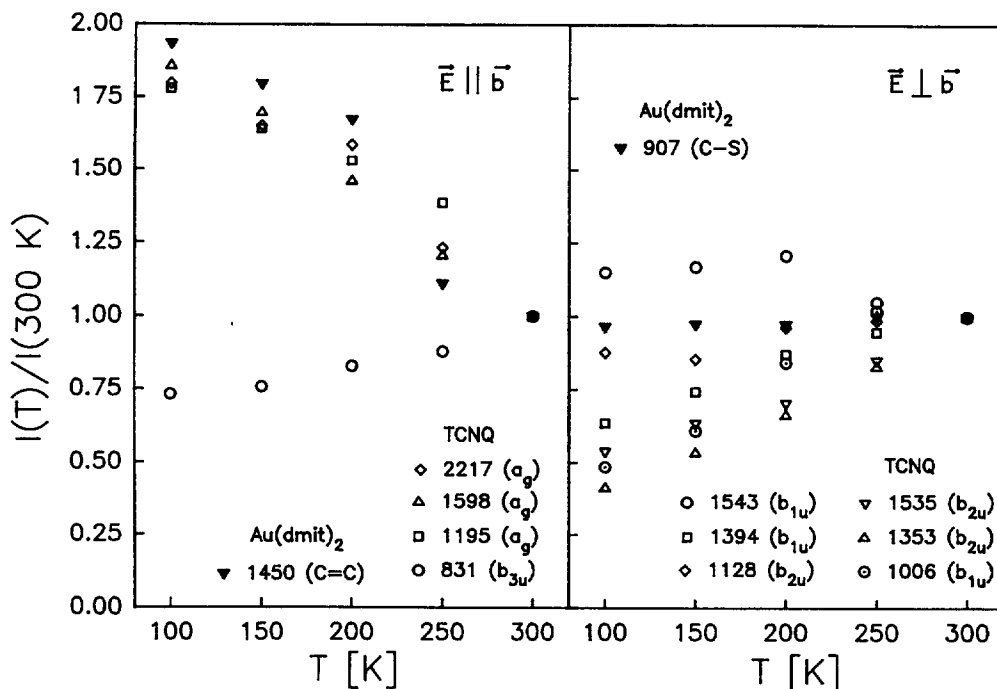


Fig. 7. — Temperature dependence of the relative integral intensity of some IR bands in the polarized absorption spectra of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  single crystal. Note the bands assigned to the  $\text{Au}(\text{dmit})_2$  and TCNQ molecules and different polarizations ( $\vec{E} \parallel \vec{b}$  and  $\vec{E} \perp \vec{b}$ ).

modes are normally IR-inactive but their weak IR activity may appear due to the influence of lower symmetry crystal field or to the effect of coupling to charge transfer. To answer this question we studied temperature evolution of the IR spectra assuming that the bands being a consequence of EMV coupling phenomenon strongly increase the intensity when temperature decreases. The temperature dependence of the relative integral intensity for different TCNQ and  $\text{Au}(\text{dmit})_2$  bands is shown in Figure 7. The intensity of TCNQ  $a_g$  bands grows strongly when the temperature decreases, what suggests that the  $a_g$  modes are activated by coupling with charge transfer transition between  $\text{Au}(\text{dmit})_2$  and TCNQ in stacks. It is interesting that the intensities of the greater part of  $b_{1u}$  and  $b_{2u}$  TCNQ bands grow weaker when temperature decreases (Fig. 7) with the exception of  $b_{1u}\nu_{20} = 1543\text{ cm}^{-1}$  and  $b_{2u}\nu_{33} = 2217\text{ cm}^{-1}$  ( $b_{2u}\nu_{33}$  coincides with  $a_g\nu_2 = 2217\text{ cm}^{-1}$  and it can be the reason of different behaviour). We do not understand the temperature dependence of TCNQ IR active modes — may be it is a sign of continuous structural modifications and/or changes of charge distribution.

We studied also the temperature evolution of the  $\text{Au}(\text{dmit})_2$  bands in the IR spectra of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$ . For polarization parallel to the stacks  $\vec{E} \parallel \vec{b}$  the  $\text{Au}(\text{dmit})_2$  band at  $1450\text{ cm}^{-1}$  (C = C stretching) exhibits temperature changes analogous to those of TCNQ  $a_g$  modes. We suggest that it is also a consequence of the coupling of  $\text{Au}(\text{dmit})_2$  vibration to charge transfer transition within the stacks. For polarization  $\vec{E} \perp \vec{b}$  similar strong temperature dependence has not been found for any band, *i.e.* the  $\text{Au}(\text{dmit})_2$  vibrational modes do not interact with interstack charge transfer.

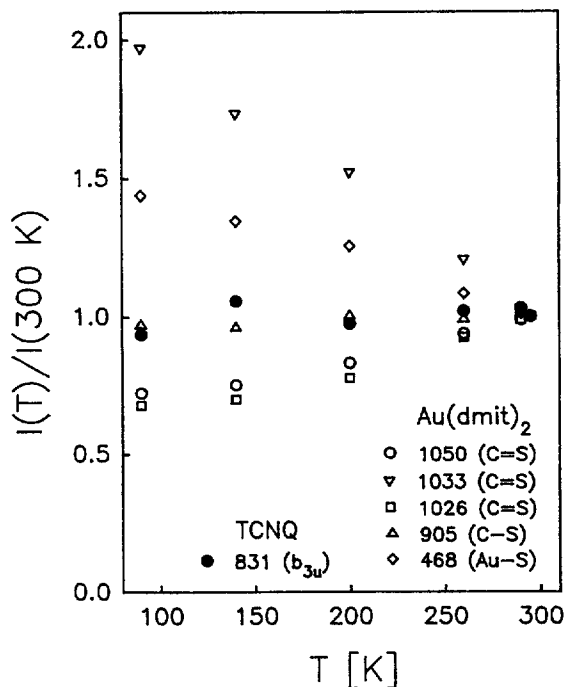


Fig. 8. — Temperature dependence of the relative integral intensity of some IR bands in the absorption spectra of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  powders in KBr pellet (note the  $\text{Au}(\text{dmit})_2$  and TCNQ bands).

Another interesting fragment of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  spectrum is the region of C = S stretching vibrations ( $1070 - 1020 \text{ cm}^{-1}$ ). The comparison of powder and single crystal spectra shows that the C = S bands are weak in single crystal spectra for both polarizations but are very strong in powder spectrum (Figs. 5 and 6). It means that these bands are polarized nearly perpendicularly to the (001) crystal face, probably parallel to the long molecular axis. For this reason the C = S bands were mainly analysed in the spectra of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  powders. In Figure 8 we show temperature dependence of the relative integral intensity of C = S, C-S and Au-S bands of  $\text{Au}(\text{dmit})_2$  molecule, and  $b_{3u}$  band of TCNQ molecule as found from the powder spectrum. The C = S band at  $1033 \text{ cm}^{-1}$  grows strongly when temperature decreases, whereas the bands  $1050 \text{ cm}^{-1}$  and  $1026 \text{ cm}^{-1}$  decrease their intensity (similar behaviour was found for analogous bands in single crystal spectra). The high intensity and strong temperature dependence of the band  $1033 \text{ cm}^{-1}$  could be due to the strong interaction of C = S vibration with the electrons. It is important to emphasize that the C = S mode seems to be polarized along the long axis of  $\text{Au}(\text{dmit})_2$  molecule, *i.e.* it can be  $b_{1u}$  mode. Analogous suggestion about coupling of electrons with  $b_{1u}$  modes was recently made for crystals based on BEDT-TTF molecule [18, 19].

#### 4. Conclusions

We have performed the studies of the electronic and vibrational spectra of  $\text{Et}_4\text{N}[\text{Au}(\text{dmit})_2\text{TCNQ}]$  crystal with the extraordinary stacks consisting of alternating TCNQ and  $\text{Au}(\text{dmit})_2$  molecules. In the analysis of the spectra we mainly focused our attention on the problem

of charge distribution and the electron-molecular vibration coupling phenomena. From the electronic and Raman spectra results that the transferred electrons are localized on Au(dmit)<sub>2</sub> molecule. In the low-energy region of electronic spectrum two charge transfer bands are observed: the intrastack transition between Au(dmit)<sub>2</sub> and TCNQ molecules at about 8000 cm<sup>-1</sup> and the weak interstack transition between neighboring Au(dmit)<sub>2</sub> molecules at about 5500 cm<sup>-1</sup>. We suggest that the C = C vibrations of Au(dmit)<sub>2</sub> and the a<sub>g</sub> modes of TCNQ couple with the intrastack charge transfer excitation. Any signs of the electron-molecular vibration coupling with the interstack charge transfer are not found. On the other hand, it is supposed the interaction of electrons with C = S vibrations polarized along the long axis of Au(dmit)<sub>2</sub> molecule. The intensities of the bands related to IR active vibrations of Au(dmit)<sub>2</sub> and TCNQ molecules decrease when the crystal is cooled down.

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