

## INFRARED SPECTRA OF THE BEDT-TTF AND DIMET SALTS WITH THE $\text{NO}_3^-$ AND $\text{ClO}_4^-$ ANIONS

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The infrared absorption spectra of the salts  $\alpha$ -(BEDT-TTF)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>, (BEDT-TTF)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>, (DIMET)<sub>2</sub>ClO<sub>4</sub>·xTHF and (DIMET)<sub>x</sub>(NO<sub>3</sub>)<sub>y</sub>(THF)<sub>z</sub> have been investigated in the temperature range 80-300 K. The vibrational bands in the BEDT-TTF crystals result from the coupling between electrons and a<sub>g</sub> modes of the BEDT-TTF molecule. The infrared spectra of the DIMET<sup>9</sup> salts suggest that the electron-molecular-vibration coupling is not limited to totally symmetric modes.

### I. Introduction

The organic conductors based on the bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF) molecule were intensively studied and the most significant advances in the field of organic conductors have been accomplished on the BEDT-TTF crystals in recent years. The other TTF derivatives have been also investigated. One of these derivatives is "unsymmetrical" 4,5-dimethyl-4,5'-ethylenedithiolotetrathiafulvalene (DIMET) molecule [1]. This donor with various anions (e.g. ClO<sub>4</sub><sup>-</sup>, AuI<sub>2</sub><sup>-</sup>, ReO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, I<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>) yields crystals with metallic properties [2-4].

The vibrational spectra of charge transfer organic conductors are dominated by the bands related to the phenomenon of strong electron-molecular vibration (EMV) coupling. From simple symmetry considerations results that only totally symmetric modes (a<sub>g</sub> modes) can couple with charge carriers [5]. The BEDT-TTF molecule has a center of symmetry and

EMV coupling constants are non-zero. On the other hand the DIMET molecule is unsymmetrical and EMV coupling is not allowed. The studies of infrared spectra of BEDT-TTF and DIMET compounds can answer the question about a possibility of other EMV interaction mechanisms.

We have performed the infrared studies as a function of temperature in the following compounds:  $\alpha$ -(BEDT-TTF)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>, (BEDT-TTF)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>, (DIMET)<sub>2</sub>ClO<sub>4</sub>·xTHF and (DIMET)<sub>x</sub>(NO<sub>3</sub>)<sub>y</sub>(THF)<sub>z</sub>. The crystals of these compounds exhibit metallic properties at ambient temperature. The structural investigations [2,6,7] have shown that both BEDT-TTF and DIMET molecules are arranged to form conducting quasi-two-dimensional layers separated by insulating layers of acceptor molecules.

## II. Results and discussion

Infrared spectral investigations were performed in the frequency range 350-4000 cm<sup>-1</sup> using a Perkin Elmer type 577 spectrophotometer with temperature equipment. The range of temperature measurements was from about 80-300 K with a stabilization of about 1 K. The samples were prepared by compressing the finely powdered salts with KBr (weight concentration was 0.05-0.1 %).

The temperature dependences of infrared spectra are presented in Fig.1 and Fig.2 for BEDT-TTF and DIMET salts, respectively. In both cases the spectra are qualitatively similar to other charge-transfer compounds, i.e. they consist of broad electronic band and a series of vibrational lines superimposed on this electronic band.

If one assumes that the BEDT-TTF molecule has D<sub>2h</sub> symmetry, the fundamental mode distribution amongst symmetry species shows that this molecule has 12 modes of symmetry a<sub>g</sub> [8]. Taking into account the fundamental frequencies of BEDT-TTF we have performed the assignment of the bands in  $\alpha$ -(BEDT-TTF)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub> and (BEDT-TTF)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> (Table I).

The assignment of fundamental vibrations of DIMET molecule has not been yet performed. From the fact that DIMET is "unsymmetrical" (C<sub>2v</sub> symmetry) results that the EMV interactions are forbidden. Therefore, the vibrational lines in the infrared spectra of the DIMET salts should be assigned to the infrared active DIMET vibrations of symmetry A<sub>1</sub>, B<sub>1</sub> and B<sub>2</sub> or NO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> vibrations (for NO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> the bands: 1385, 840 cm<sup>-1</sup> and 1120, 1110, 635, 625 cm<sup>-1</sup>, respectively). However, the presence of a strong band at about 440 cm<sup>-1</sup> and its considerable intensity enhancement with lowering the temperature (Figs.2 and 3a) could mean that this band is due to the EMV interaction despite the symmetry arguments. The question is: what alternative mechanism of EMV interaction could be envisaged ?

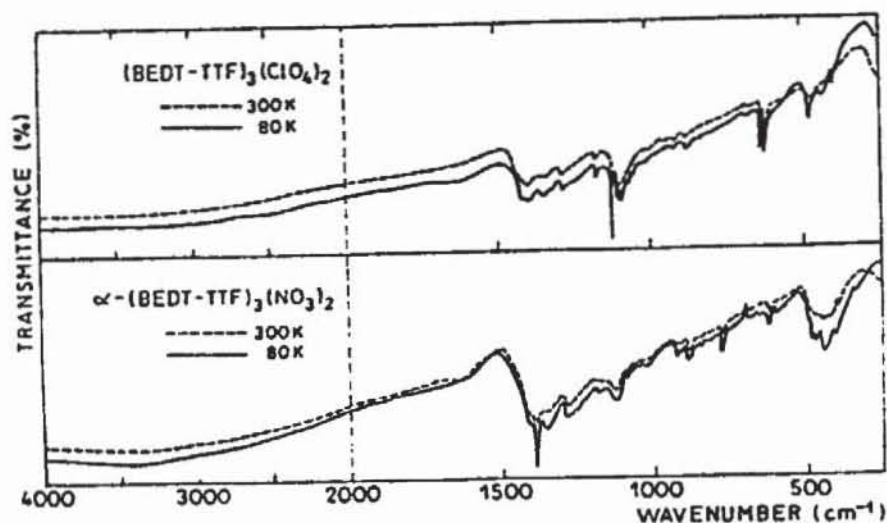


Fig.1. The infrared absorption spectra of  $\alpha$ -(BEDT-TTF) $_3$ (NO $_3$ ) $_2$  and (BEDT-TTF) $_3$ (ClO $_4$ ) $_2$  salts at 300 K and 80 K

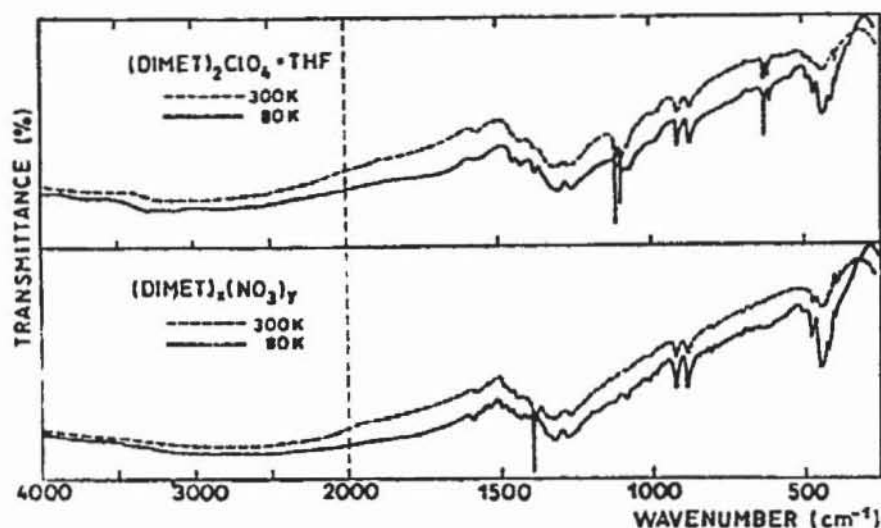


Fig.2. The infrared absorption spectra of (DIMET) $_2$ ClO $_4$ ·THF and (DIMET) $_x$ (NO $_3$ ) $_y$ (THF) $_z$  salts at 300 K and 80 K

In the infrared spectrum of benzene iodine-complex two mechanisms of vibronic intensity enhancement of benzene modes were observed [9]. The first one is a variation of vertical ionization potential with  $a_g$  symmetric vibrations of benzene and the second one is the variation of donor and acceptor wave functions due to out-of-plane benzene vibration of  $e_{1g}$  symmetry (infrared inactive). The origin of the band at about 440  $\text{cm}^{-1}$  could be explained by taking into account the second mechanism

Table I Infrared spectra with the assignment for studied BEDT-TTF salts.

BEDT-TTF [8]	$\alpha$ -(BEDT-TTF) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> T = 300 K	(BEDT-TTF) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub> T = 300 K	Assignment
1494	1440	1440	a <sub>g</sub> (v <sub>3</sub> )
1415	1410	1400	a <sub>g</sub> (v <sub>4</sub> )
	1380		NO <sub>3</sub> <sup>-</sup> e' (v <sub>3</sub> )
	1350	1350	
1285	1280	1290	a <sub>g</sub> (v <sub>5</sub> )
	1170	1180	
	1120	1120	
		1107	} ClO <sub>4</sub> <sup>-</sup> f <sub>2</sub> (v <sub>3</sub> )
		1100	
990	1010	1010	
911	920	920	a <sub>g</sub> (v <sub>7</sub> )
	880	880	
	840		NO <sub>3</sub> <sup>-</sup> a <sub>2</sub> (v <sub>2</sub> )
	770		
653	670	670	a <sub>g</sub> (v <sub>8</sub> )
		635	} ClO <sub>4</sub> <sup>-</sup> f (v <sub>4</sub> )
		623	
	620		
486	480	480	a <sub>g</sub> (v <sub>9</sub> )
440	440	440	a <sub>g</sub> (v <sub>10</sub> )
308	310	310	a <sub>g</sub> (v <sub>11</sub> )

of vibronic intensity enhancement in benzene complex. During the out-of-plane intramolecular vibrations of DIMET molecule the electronic overlap and hence the hopping integral  $t$  can be modulated leading to the infrared activity. Without assignment of fundamental vibrations of DIMET molecule it is impossible to analyze the band  $440 \text{ cm}^{-1}$  more carefully. The TTF molecule [10] and the fragments of BEDT-TTF molecule of symmetry  $C_{2v}$  [8] have out-of-plane deformations around  $440 \text{ cm}^{-1}$  and this can be an argument in support of our hypothesis. On the other hand, the assignment of the  $440 \text{ cm}^{-1}$  band to the infrared active DIMET mode or intermolecular lattice mode is quite unlikely because of an enormously enhanced oscillator strength. The overlap of the molecular wave functions and its variation due to vibration are dependent on the geo-

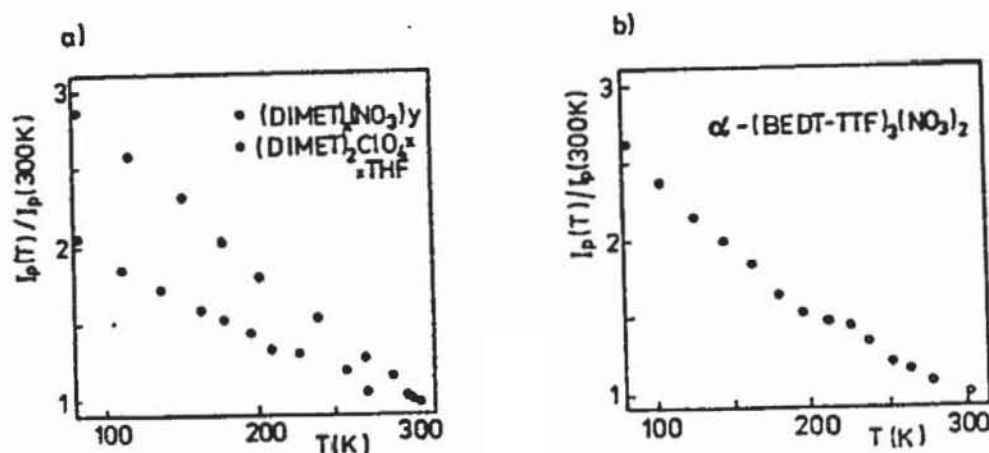


Fig.3 Normalized peak intensities of the band about  $440\text{ cm}^{-1}$  against temperature for DIMET (a) and BEDT-TTF (b) salts

metry of the stack. In  $(\text{DIMET})_2\text{ClO}_4 \cdot x\text{THF}$  crystals the DIMET molecules are alternatively oriented and arranged in dimers [2]. In our opinion, this geometry might facilitate the modulation of overlap of DIMET molecules.

We suggest that the same mechanism of EMV coupling is also present in the BEDT-TTF salts. In the broad band at about  $440\text{ cm}^{-1}$  for  $T = 80\text{ K}$  in  $\alpha\text{-(BEDT-TTF)}_3(\text{NO}_3)_2$  one can distinguish several features; two features at about  $480\text{ cm}^{-1}$  and  $440\text{ cm}^{-1}$  can be assigned to the modes of BEDT-TTF  $a_g(\nu_9)$  and  $a_g(\nu_{10})$ , respectively, and they are superimposed on a broader absorption which can be related to the out-of-plane BEDT-TTF vibration  $b_{2g}(\nu_{40})$  modulating the overlap between molecules. Moreover, the temperature dependence of peak intensity of the band around  $440\text{ cm}^{-1}$  in  $\alpha\text{-(BEDT-TTF)}_3(\text{NO}_3)_2$  is similar to that for DIMET salts (Figs.3a and 3b). In  $(\text{BEDT-TTF})_3(\text{ClO}_4)_2$  the band around  $440\text{ cm}^{-1}$  is weak in comparison with  $\alpha\text{-(BEDT-TTF)}_3(\text{NO}_3)_2$ . This might be explained by the geometry of stacks, i.e. in the  $(\text{BEDT-TTF})_3(\text{ClO}_4)_2$  the modifications of electronic overlap during the vibration are smaller than in the  $\alpha\text{-(BEDT-TTF)}_3(\text{NO}_3)_2$  salt. Nevertheless, in this salt the features at about  $480\text{ cm}^{-1}$  and  $440\text{ cm}^{-1}$  are observed (the modes  $a_g(\nu_9)$  and  $a_g(\nu_{10})$  of BEDT-TTF) but they are superimposed on a much weaker absorption.

Further investigations are under progress.

#### Acknowledgement

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