

## FT-IR INVESTIGATIONS OF (BEDT-TTF)<sub>2</sub>I<sub>3</sub> RADICAL SALTS

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### Abstract

Fourier transform infrared absorption spectra of structurally different phases of the radical cation salt (BEDT-TTF)<sub>2</sub>I<sub>3</sub> in the range of the molecular vibrations of the donor are presented. The low-temperature spectra provide exact fingerprints of the different phases as long they have different unit cells. Additional differences concerning the positions of ethylene groups reflect themselves in the CH<sub>2</sub>-stretching vibrations. As a result, it could be shown that the ethylene groups of the  $\alpha_t$ -phase and  $\beta$ -phase must have a different order. Concerning the tempering of the different phases, it is shown that at least  $\alpha_t$ - and  $\kappa_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> are the same.

### Introduction

Because of their ability of forming low-dimensional conductors and even superconductors, radical cation salts synthesized with the donor BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) and triiodide counteranions are investigated since nearly ten years. The very special attraction of the system (BEDT-TTF)<sub>2</sub>I<sub>3</sub> lies in the fact that there exist several different crystallographic phases exhibiting very different transport properties like the metal-insulator phase transition in  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> or the metallic behaviour with superconducting phase transitions with T<sub>c</sub> of 1.3 K, 4 K and 8 K in  $\beta$ -,  $\kappa$ - and  $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> respectively.

Still unsolved questions are e.g. the nature of the M-I phase transition in  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> or the structural relationship between  $\beta$ - and  $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>. Because the molecular vibrations of the BEDT-TTF framework and especially of

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the terminal ethylene groups should give an unmistakable picture of each crystal phase [1], we investigated FT-IR absorption spectra at low temperatures of the above mentioned phases of  $(\text{BEDT-TTF})_2\text{I}_3$ .

## Experimental

The crystals used in this work have been prepared electrochemically in the standard way described earlier [2, 3]. For infrared absorption measurements, 1 mg of crystals were ground with 200 mg KBr in an agate mortar and afterwards pressed to pellets with a pressure of  $9\text{ t/cm}^2$ . Since the pressure during the preparation of the pellets is a hydrostatic one, this procedure does not affect the crystal structure.

The spectra were taken on a commercial Fourier transform spectrometer (BOMEM DA 3.02) with a fast InSb detector in the range of  $5000 - 1800\text{ cm}^{-1}$  and a MCT detector between  $1800\text{ cm}^{-1}$  and  $450\text{ cm}^{-1}$  – the resolution was  $0.5\text{ cm}^{-1}$ . In order to obtain a good signal-to-noise ratio, at least 2000 interferograms were coadded for each spectrum. Measurements were performed in an OXFORD continuous flow helium cryostat with KRS 5 and ZnSe windows at 5 K.

## Results

### A. Vibrations of the BEDT-TTF framework in the triiodide salts

Before the vibrational spectra of the radical cation salts with triiodide counteranions can be interpreted satisfactorily, one should have a reliable assignment of the vibrational modes of the neutral donor BEDT-TTF (which is an insulator) and if possible, of the fully ionized radical cation  $\text{BEDT-TTF}^+$  (e.g. in  $(\text{BEDT-TTF})\text{I}_3$ , which is semiconducting). For both the neutral and the simply charged molecule Kozlov et al. [4,5] have performed a normal coordinate analysis, so that all important bands in the spectra of these molecules can be assigned to fundamental vibrations of the BEDT-TTF molecule.

The spectra in the range between  $1600\text{ cm}^{-1}$  and  $600\text{ cm}^{-1}$  of the investigated 2:1-salts are shown in Fig. 1. They were recorded with a resolution of  $0.5\text{ cm}^{-1}$  and at 5 K in order to obtain narrow bands. In this interval most of the vibrations of the BEDT-TTF framework are found except a few lower lying bands and the  $\text{CH}_2$ -stretching vibrations, which are discussed below.

It can be easily seen, that the spectra of the vibrations of the molecular framework give a precise fingerprint of the respective phase of  $(\text{BEDT-TTF})_2\text{I}_3$  crystals except in the case of the  $\alpha_t$ - and  $\beta$ -phases. In the overall shape there are common features – although the shapes of bands and their degree of splitting differ from one phase to another, the bands are found in nearly the same positions.

This especially applies to some spectroscopic features which cannot be assigned as vibrational bands, either due to their intensity or frequency. Firstly there are always strong bands around  $1450\text{ cm}^{-1}$  with a pronounced antiresonant behaviour, which are assigned as vibronic bands due to an electron-molecular vibration coupling (EMVC) induced by antisymmetric vibrations of the BEDT-TTF molecules constituting a dimer [6,7]. Secondly there is a broad band around  $1350\text{ cm}^{-1}$ , which is more pronounced in spectra taken at room temperature. This band is found as well (in addition to a vibronic band around  $1400\text{ cm}^{-1}$ ) in the 1:1-salt (BEDT-TTF) $\text{I}_3$  at the same position but not in BEDT-TTF radical cation salts with other than  $\text{I}_3^-$ -anions, for which reason it has to be related to the presence of the triiodide counteranions.

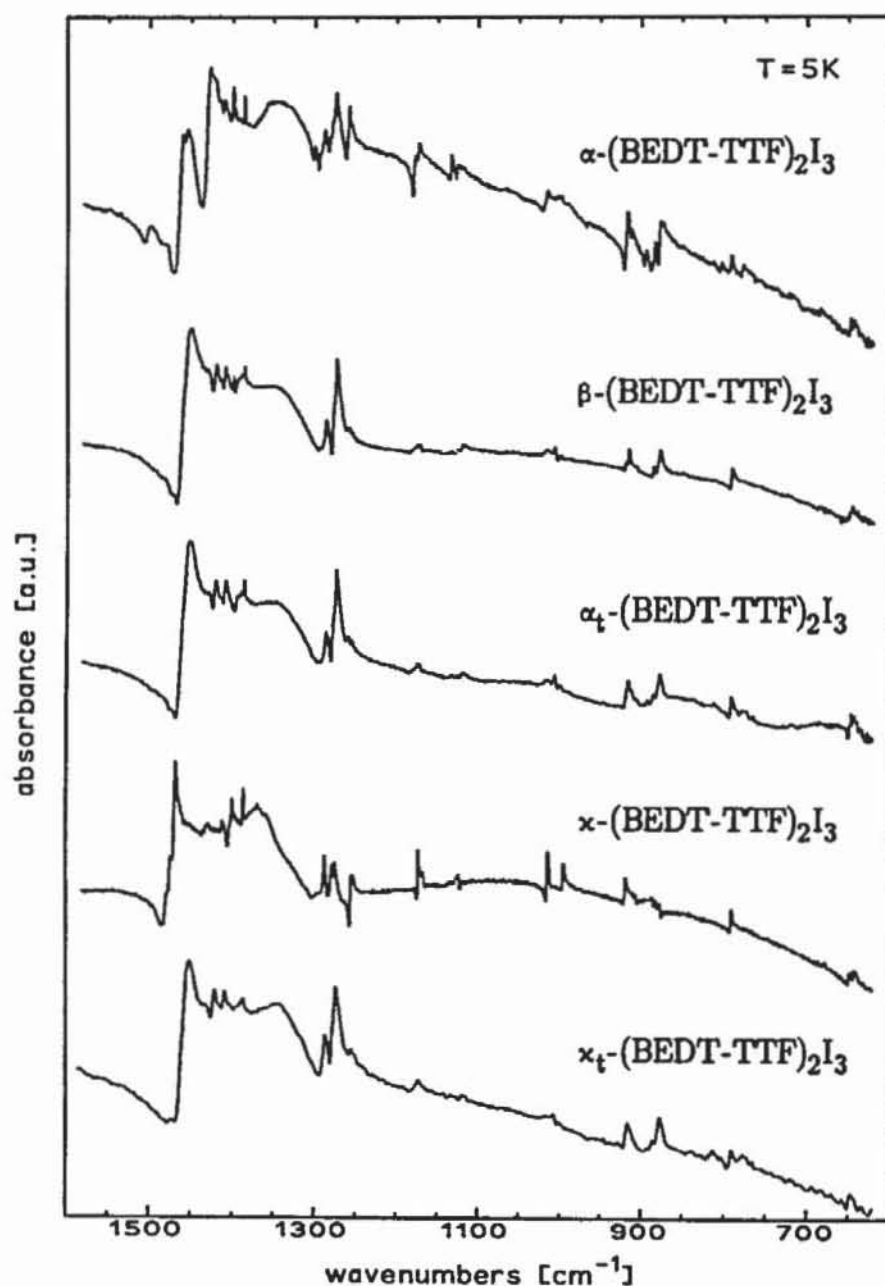


Fig. 1. Vibrational spectra of different phases of  $(\text{BEDT-TTF})_2\text{I}_3$  at 5 K.

## B. CH<sub>2</sub>-stretching vibrations

In the spectra presented above there was no difference found between the  $\beta$ - and  $\alpha_t$ -phase, although their  $T_c$ 's differ significantly (1.3 K and 8 K). It is known that the terminal ethylene groups in  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> suffer from a disorder in their conformation due to the donor-anion contacts mediated through them, which below 200 K results in an incommensurable long-range order [8]. It can be suspected, that even small differences in donor-anion contacts reveal themselves in the spectra of CH<sub>2</sub>-stretching vibrations [1]. The baseline corrected spectra of these vibrational bands at 5 K are shown in Fig. 2.

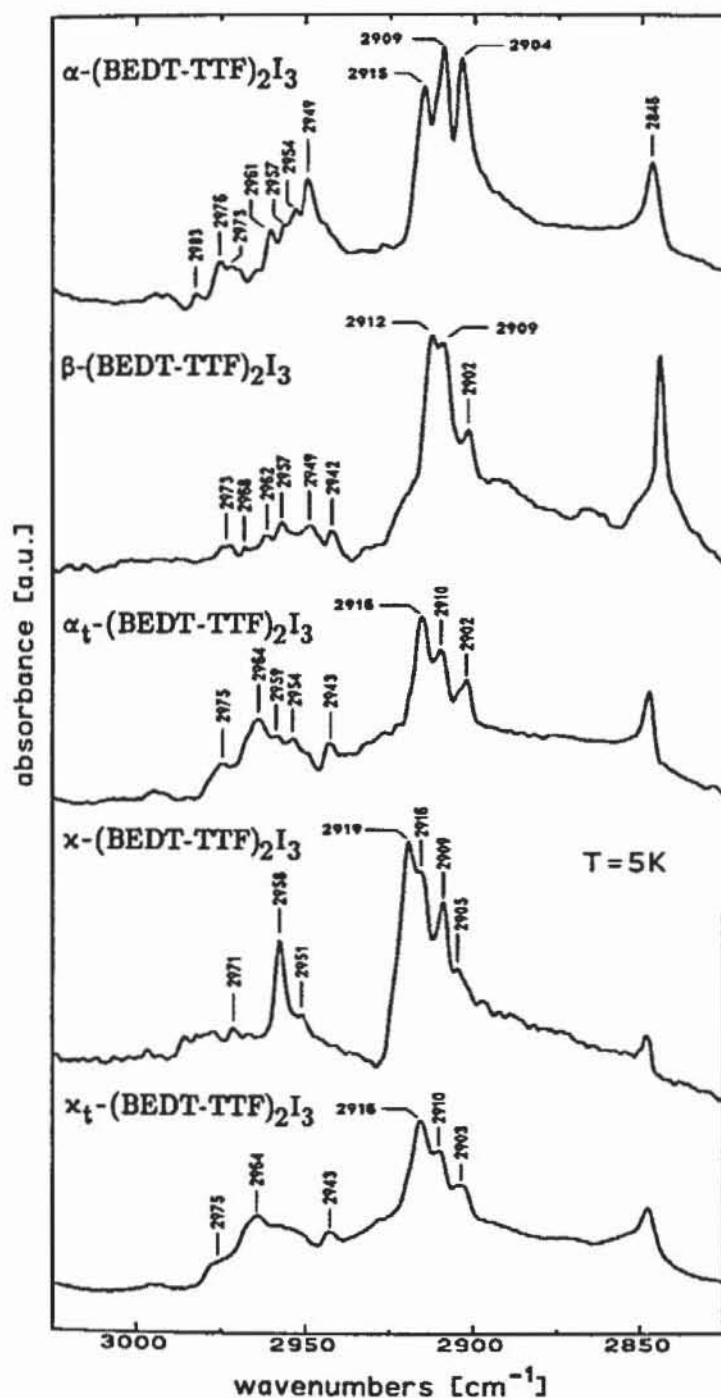


Fig. 2. CH<sub>2</sub>-stretching vibrations of different phases of (BEDT-TTF)<sub>2</sub>I<sub>3</sub> at 5 K.

The spectra of  $\text{CH}_2$ -stretching vibrations exhibit in all phases as well as in the neutral donor BEDT-TTF and its 1:1-salt  $(\text{BEDT-TTF})\text{I}_3$  relatively strong bands in the region between  $2904\text{ cm}^{-1}$  and  $2921\text{ cm}^{-1}$  and a few weaker bands (which at 5 K sometimes are only little above the level of noise) between  $2945\text{ cm}^{-1}$  and  $2983\text{ cm}^{-1}$ . The origin of the relatively sharp and intense band around  $2850\text{ cm}^{-1}$  is not clear yet – it might be due to a pollution in the potassium bromide. But it is evident, that here the characterization of the respective phase has reached a level of maximum precision – even  $\beta$ -phase and  $\alpha_t$ -phase now exhibit a distinct difference of vibrational frequency in one strong line of  $4\text{ cm}^{-1}$ , which compared to the applied resolution of  $0.5\text{ cm}^{-1}$  is a significant value.

## Discussion

As a first result of these investigations it became obvious, that FT-IR absorption spectroscopy on  $(\text{BEDT-TTF})_2\text{I}_3$  salts is a highly accurate method in order to determine a special crystallographic phase, and at the same time a relatively fast one too. Even differences in the position of the ethylene groups with respect to the remainder of the BEDT-TTF framework reflect themselves in the spectra of the  $\text{CH}_2$ -stretching vibrations.

This especially applies to the question of the difference between the  $\beta$ - and  $\alpha_t$ -phase. From the spectra in Fig. 1 it is strongly suggested, that in both phases we are dealing with the same unit cell. This result was already obtained by solid state NMR, Raman spectroscopy, ESR measurements [9] and a Debye-Scherrer picture (the correct structure of  $\alpha_t$ - $(\text{BEDT-TTF})_2\text{I}_3$  is unknown due to the mosaic type of the crystals after the structural transformation). Hence any difference between the two phases must be caused by the order or disorder in the conformation of the ethylene groups, which is proved by their different  $\text{CH}_2$ -stretching vibration bands. Because of the relatively high  $T_c$  (8 K) of  $\alpha_t$ - $(\text{BEDT-TTF})_2\text{I}_3$  it is supposed that in the latter the ethylene groups are ordered (probably together with an absence of the modulation in the positions of the BEDT-TTF molecules and the iodide anions) in contrast to the  $\beta$ -phase, where this groups suffer from a conformational disorder. One question still remains open: Why does the growth of crystals of the  $\beta$ -phase lead to disordered ethylene groups of the donor molecule, whereas a thermal treatment of the  $\alpha$ -phase with a totally different unit cell (in which these groups are ordered) leads to the same unit cell as in  $\beta$ -phase, but ordered ethylene groups in the BEDT-TTF stacks?

Concerning thermal treatment of the various phases it has to be concluded from the spectra of  $\alpha_t$ - and  $\alpha_t$ - $(\text{BEDT-TTF})_2\text{I}_3$ , that these tempered crystals are converted into the same phase. In the case of the  $\alpha_t$ -phase this result is supported by the fact, that  $T_c$  of those crystals, which have been tempered for 12 h at  $75^\circ\text{C}$  rises from 4 K to 8 K [10]. In the case of the  $\beta$ -phase this conversion to a higher  $T_c$

takes several weeks at the same temperature [11], which increases the amount of neutral BEDT-TTF on the surface of the crystals to a degree that makes it impossible to obtain meaningful results from IR spectroscopy. But the simple fact that tempering of crystals with such different unit cells as observed in the  $\alpha$ - and  $\kappa$ -phase respectively results in crystals with an identical unit cell is still surprising.

Another point of interest is the phase transition of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>, which at 135 K turns from the metallic phase to a semiconducting one. As it can be seen from Fig. 1, a splitting of the vibronic band around 1440 cm<sup>-1</sup> is observed in contrast to the other phases, and this splitting has its onset at around 150 K [12]. Additionally at low temperature the number of observed bands in the spectra of  $\alpha$ -phase crystals is higher than in other phases, which cannot be simply explained by the fact that there are four BEDT-TTF molecules in each unit cell. Especially concerning this phase transition further work is in progress.

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## References

- [1] S.Gärtner, D.Schweitzer, H.J.Keller; *Synth. Met.* 44 (1991), 227
- [2] D.Schweitzer, P.Bele, H.Brunner, E.Gogu, U.Haeberlen, I.Hennig, Th.Klutz, R.Swietlik, H.J.Keller; *Z. Phys. B - Condensed Matter* 67 (1987), 489
- [3] K.Bender, I.Hennig, D.Schweitzer, K.Dietz, H.Endres, H.J.Keller; *Mol. Cryst. Liq. Cryst.* 108 (1984), 359
- [4] M.E.Kozlov, K.I.Pokhodnia, A.A.Yurchenko; *Spectrochim. Acta* 43A, No.3 (1987), 323
- [5] M.E.Kozlov, K.I.Pokhodnia, A.A.Yurchenko; *Spectrochim. Acta* 45A, No.4 (1989), 437
- [6] M.J.Rice; *Solid State Comm.* 31 (1979), 93
- [7] R.Bozio, C.Pecile in  
L.Alcacer (ed.), *The Physics and Chemistry of Low Dimensional Solids*, Dordrecht 1980, 165
- [8] P.C.W.Leung, T.J.Emge, M.A.Beno, H.H.Wang, J.M.Williams, V.Petricek, P.Coppens; *J. Am. Chem. Soc.* 107 (1985), 6184
- [9] D.Schweitzer, H.J.Keller in  
R.Delhaes, P.Drillon (ed.), *Organic and Inorganic Low-Dimensional Crystalline Materials*, Plenum Press, New York 1987
- [10] E.Balthes, A.Breining, S.Kahlich, J.Moldenhauer, D.Schweitzer, I.Heinen, B.Nuber, H.J.Keller; *these Proceedings*
- [11] S.Kahlich, D.Schweitzer, H.J.Keller; *Solid State Comm.* 79, No.7 (1990), 933
- [12] J.Moldenhauer, K.I.Pokhodnia, D.Schweitzer, H.J.Keller; *To be published*