

## CH<sub>2</sub> vibrations in radical cation salts based on the donor BEDT-TTF

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### Abstract

Investigations of the CH<sub>2</sub> stretch vibrations in radical cation salts based on the donor BEDT-TTF and the neutral donor itself are presented. The spectra taken by Fourier transform infrared absorption technique not only demonstrate the importance of the relationship between the possible positions of the CH<sub>2</sub> groups in the BEDT-TTF molecule and the physical properties of the organic metal but also offer the opportunity to achieve structural information by the use of a simple method.

### Introduction

The organic donor molecule bis(ethylenedithio)tetrathiofulvalene, commonly abbreviated to BEDT-TTF, finds high interest because of its ability to form metallic and superconducting radical cation salts with a number of mainly monovalent counter ions [1]. Especially by the use of spherical or linear anions such as ReO<sub>4</sub><sup>-</sup> or I<sub>3</sub><sup>-</sup>, a variety of different phases is obtained, some of which possess identical stoichiometry [2]. Also, the organic superconductors with the highest transition temperatures into the superconducting state are found within this family [1].

With only a few exceptions, all these salts consist of alternating layers of radical cations and anions. As the BEDT-TTF molecule is not flat and the different kinds of layers are inclined with respect to each other, the terminal CH<sub>2</sub> groups at both ends of the donor molecule give rise to contacts shorter than the sum of the van der Waals radii with neighbouring atoms. It has been shown [3] by calculations on model compounds that in BEDT-

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TTF radical cation salts the C-H...anion interactions are more important for the stability of the crystal than the C-H...donor interactions. Small variations in both of these interactions may slightly change the structure of the whole BEDT-TTF molecule. When viewed along the long molecular axis, the two ethylene groups of every BEDT-TTF molecule can occupy two possible positions which are designated as eclipsed and staggered [4]. But as the crystal structure of these compounds is usually very sensitive to the detailed conformations of the donor molecule, any changes have large influence on the physical properties of the radical cation salt. Examples are the different superconducting states in  $\beta$ -,  $\beta_H$ - and  $\alpha_T$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> [5], the thermal conversion from  $\alpha$ - to  $\alpha_I$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> [6, 7] or the destruction of superconductivity in pressed polycrystalline pellets of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> [8].

With this background it would be desirable to observe the CH<sub>2</sub> vibrations in BEDT-TTF radical cation salts directly, either by infrared or Raman spectroscopy. Unfortunately, the broad interband transition which appears in the region above 3000 cm<sup>-1</sup> masks the CH<sub>2</sub> stretch vibrations which are expected to occur around 2900 cm<sup>-1</sup> to such an extent that they become unobservable in the infrared reflectance technique, particularly at room temperature [9]. The only observation published so far (besides some preliminary results presented by the authors themselves [10] at a conference) can be found in a paper by Kornelsen *et al.* [11]. They obtained a weak doublet near 2900 cm<sup>-1</sup> through the use of high resolution polarized reflectance measurements at 25 K in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>.

Therefore we used Fourier transform infrared (FT-IR) absorption spectroscopy which is capable of giving information about bulk phonons without interference of various surface effects in contrast to reflectance techniques. It has been demonstrated [12] that, aside from small differences in the relative intensities of the lines, virtually the same results can be obtained from both reflection and absorption spectra on crystalline samples and polycrystalline pressed pellets, respectively. Thus the application of FT-IR absorption spectroscopy allowed us to investigate the CH<sub>2</sub> vibrations in a number of BEDT-TTF radical cation salts at room temperature. Here we present data in the spectral range around 2900 cm<sup>-1</sup> (2200 cm<sup>-1</sup> for CD<sub>2</sub> vibrations in the deuterated compound) of various phases of (BEDT-TTF)<sub>2</sub>I<sub>3</sub>, of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> and also, for comparison, of the neutral donor BEDT-TTF.

However, because of the lack of suitably thin crystals it was necessary to carry out these absorption measurements on pulverized materials diluted in pressed pellets of KBr. Thus the question arises whether the application of pressure, particularly of the uniaxial component, during the preparation of the sample may lead to any phase transitions. The study of superconductivity in polycrystalline pressed pellets of organic metals [5] shows the importance of this consideration. In order to obtain information concerning this problem both single crystals and polycrystalline pressed samples were taken as starting materials to be diluted in KBr.

## Experimental

All crystals used in this work were prepared electrochemically as described earlier [7, 13]. The samples were made similar to those of Zamboni *et al.* [12] by grinding either single crystals or polycrystalline pressed samples manufactured at a pressure of approx. 10 t/cm<sup>2</sup> in an agate mortar together with dried KBr. Additionally, some of the samples were thermally treated for 3 to 4 days at 70 °C in an oven at different stages during the preparation.

The spectra were taken at room temperature in the range 1800 to 5000 cm<sup>-1</sup> by using a commercial FT-IR spectrometer (BOMEM) which contained a fast and sensitive InSb sandwich detector. Thereby a total resolution of 1 cm<sup>-1</sup> could be achieved. In order to increase the signal-to-noise ratio at least 1000 and up to 10 000 cumulative interferograms were stored. Despite these numbers the times consumed for data acquisition and evaluation of the Fourier transformation only takes approx. 30 min in the first case. As the preparation of the pellets is also rather simple, FT-IR absorption spectroscopy provides a fast and easy alternative to other methods.

As the observable CH<sub>2</sub> stretch vibrations in all the investigated radical cation salts occurred as small peaks on the broad underlying interband transition, a baseline correction was applied to some spectra in order to obtain the exact positions and true relative intensities of the lines when comparing different substances. These spectral properties could be easily reproduced.

## Results

Figures 1 and 2 show a wide-range view of the mid-infrared absorption spectra of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> and  $\alpha$ <sub>T</sub>-(BEDT-TTF)<sub>2</sub>I<sub>3</sub>, respectively. The characteristic feature in both results is the appearance of a broad absorption band above 3000 cm<sup>-1</sup> together with a vibrational structure of much lower intensity in the range between 2900 and 3000 cm<sup>-1</sup> which can be seen extended in the insets of both Figures. In the case of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> in Fig. 1 a sharp doublet with lines occurring at 2111 and 2067 cm<sup>-1</sup> demonstrates the presence of stretching vibrations where the Cu(NCS)<sub>2</sub> anion is involved [12].  $\alpha$ <sub>T</sub>-(BEDT-TTF)<sub>2</sub>I<sub>3</sub> which is obtained from the  $\alpha$ -phase by thermal treatment always shows the same spectrum irrespective of whether the pellet is prepared from preheated material or from untreated  $\alpha$ -phase and thermally treated as a whole.

Figure 3 presents an enlarged view of the baseline-corrected spectra of the neutral donor BEDT-TTF as well as those of  $\alpha$ -,  $\alpha$ <sub>T</sub>- and  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> in the range from 2750 to 3050 cm<sup>-1</sup>. They all clearly reveal four peaks (three in the case of the  $\alpha$ -phase) between 2900 and 3000 cm<sup>-1</sup> which can be identified as the CH<sub>2</sub> stretching modes of the BEDT-TTF molecule as will be discussed later. In the pure isolating donor compound the signal-to-noise ratio is obviously much higher because no interband transition exists and

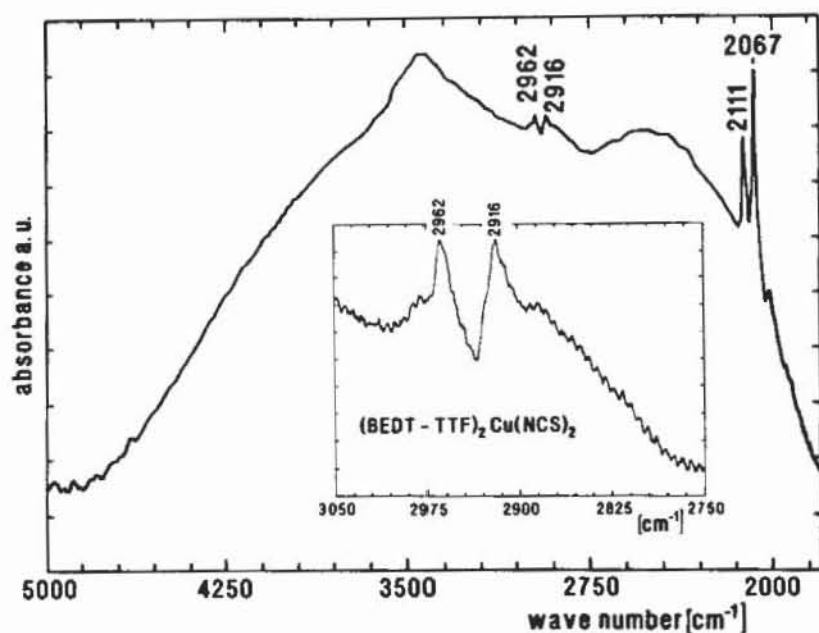


Fig. 1. Mid-IR absorption spectrum of a pressed pellet of  $\kappa$ -(BEDT-TTF) $_2$ Cu(NCS) $_2$  diluted in KBr in the range from 1800 to 5000  $\text{cm}^{-1}$  taken at room temperature. The inset shows an enlarged view of the CH $_2$  stretch vibrations around 2900  $\text{m}^{-1}$ .

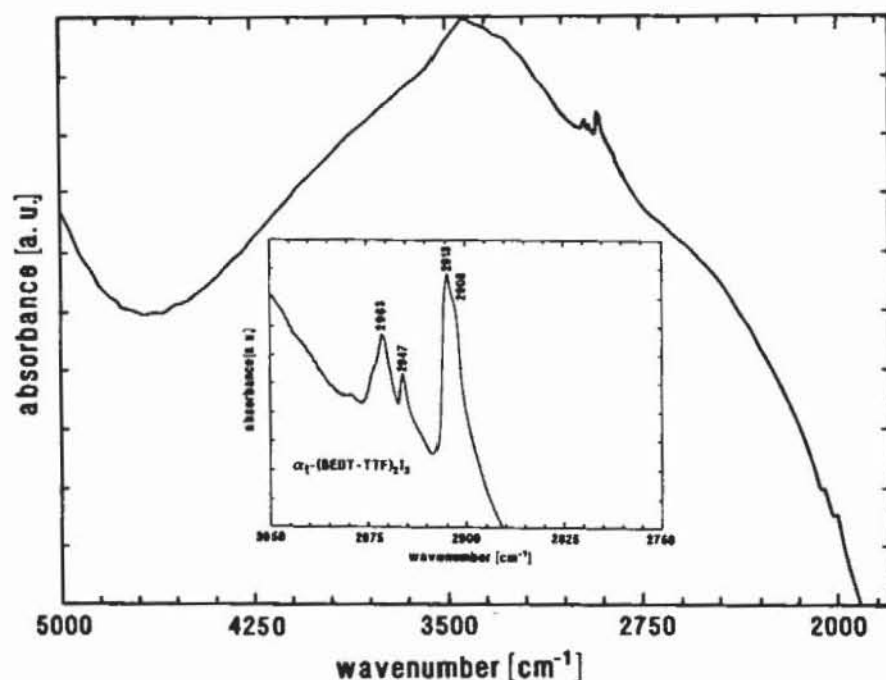


Fig. 2. Mid-IR absorption spectrum of a pressed pellet of  $\alpha_1$ -(BEDT-TTF) $_2$ I $_3$  diluted in KBr in the range from 1800 to 5000  $\text{cm}^{-1}$  taken at room temperature. The inset shows an enlarged view of the CH $_2$  stretch vibrations around 2900  $\text{cm}^{-1}$ .

may cover any vibrations. The further enlarged view in Fig. 4 strikingly demonstrates the occurrence of a very small but distinct difference between  $\alpha_1$ - and  $\beta$ -(BEDT-TTF) $_2$ I $_3$  of 5  $\text{cm}^{-1}$  in the position of the highest energetical vibration (which should be noted exceeds the resolution of the spectrometer system).

An extremely important proof for the assignment of the observable lines can be found in Fig. 5. In the completely deuterated pure donor compound

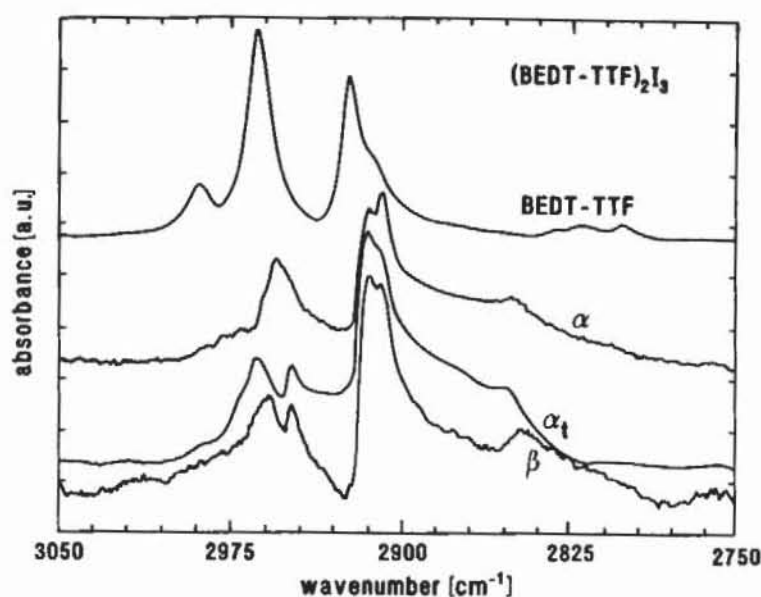


Fig. 3. IR absorption spectra of BEDT-TTF,  $\alpha$ -,  $\alpha_t$  and  $\beta$ -(BEDT-TTF) $_2$ I $_3$  between 2750 and 3050  $\text{cm}^{-1}$ . Baseline correction was applied (see text).

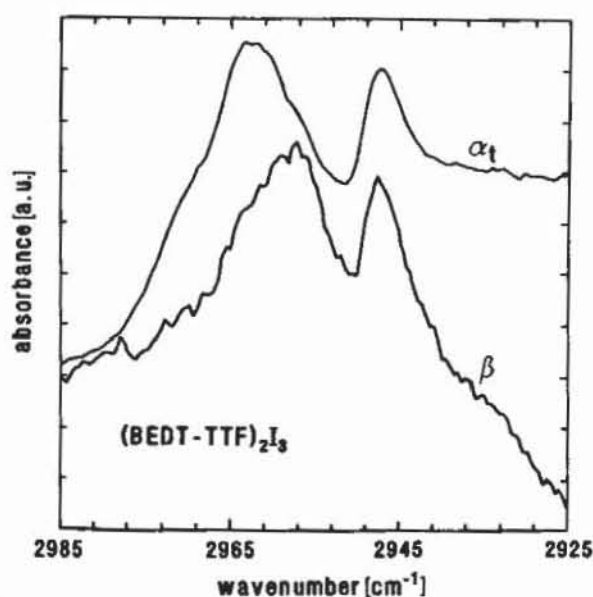


Fig. 4. Enlarged view taken from Fig. 3 demonstrating the significant difference between  $\alpha_t$ - and  $\beta$ -(BEDT-TTF) $_2$ I $_3$  (with baseline correction).

no signs of any vibrations could be detected in the range from 2900 to 3000  $\text{cm}^{-1}$  whereas four new lines appear around 2200  $\text{cm}^{-1}$ .

Experiments concerning the comparison between pressed pellets made of crystalline and polycrystalline starting materials show first results strongly indicating the importance of the details of the preparation. Figure 6 shows the case where a freshly prepared polycrystalline pressed sample of  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  is used as the starting material for a pellet. A striking feature appearing in all samples prepared from polycrystalline pressed materials is the broad line at 2850  $\text{cm}^{-1}$  which is considerably pronounced compared to pellets made from crystalline substances.

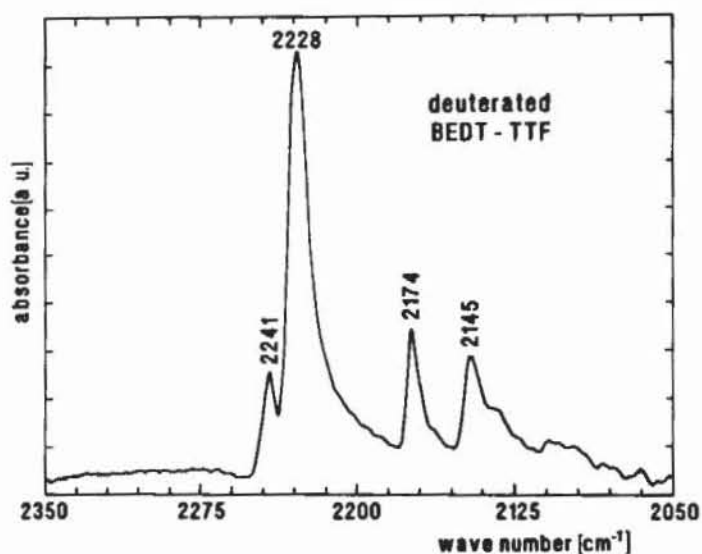


Fig. 5. IR absorption spectrum of the completely deuterated donor BEDT-TTF showing the  $\text{CD}_2$  stretch vibrations (baseline correction applied).

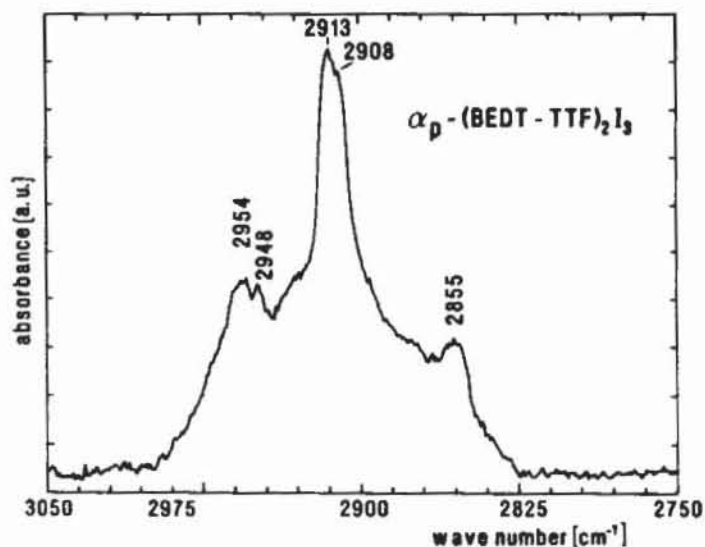


Fig. 6. IR absorption spectrum of a sample prepared from a pressed pellet of  $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$ . For explanation refer to the text. This spectrum has been baseline corrected.

## Discussion

The infrared spectra of radical cation salts based on the donor BEDT-TTF are characterized by a broad absorption band above  $3000\text{ cm}^{-1}$  together with a rich vibrational structure caused by the coupling of the intramolecular vibrations to the conduction electrons of the organic metal [9–12, 14–16]. The first feature has been generally ascribed to inter- and intramolecular electronic transitions of the donor molecule, particularly to transitions between split bands [16–18] where the splitting is caused from strong interactions between donors which are arranged as dimers in these compounds. This

broad band is usually designated as the plasma spectrum and could be found in all BEDT-TTF radical cation salts investigated so far. As it shows a very similar behaviour in the different metals, only two examples are presented in Figs. 1 and 2.

The main vibronic region starts with a sharp increase in absorption just below  $1500\text{ cm}^{-1}$ . This observation has been made in a good number of experiments under various conditions [9–12, 16–21] and also in the samples investigated here. Much effort has been spent to find out criteria in order to distinguish between different phases of a given substance by the use of certain spectral lines appearing in this region. One example are the C–C–H bending modes of the BEDT-TTF molecule which show slight variations depending on details of the molecular arrangement within the unit cell [9]. As these differences are difficult to detect and the expected variations should be much larger in the  $\text{CH}_2$  stretch vibrations, we did not pursue further the range below  $2000\text{ cm}^{-1}$  in this work.

Aside from possible overtones and frequency combinations which, however, are much weaker in intensity, the only other lines above  $1500\text{ cm}^{-1}$  arising from the BEDT-TTF molecule itself are the  $\text{CH}_2$  stretch vibrations which generally occur in the region around  $2900\text{ cm}^{-1}$ . This view is theoretically supported by Kozlov *et al.* [20, 21] who calculated the molecular normal modes of neutral BEDT-TTF and obtained a wave number of  $2912\text{ cm}^{-1}$  for the  $\nu_1(a_g)$  vibration in the protonated compound and a shift of  $772\text{ cm}^{-1}$  for the deuterated molecule. Furthermore, all lines which are not degenerate, unresolved, or heavily damped should appear as quartets as there exist four possibilities of the  $\text{CH}_2$  groups of a BEDT-TTF molecule to vibrate in and out of phase together [11].

Figures 1–5 confirm this expected behaviour. In the neutral donor BEDT-TTF as well as in  $\alpha_1$ - and  $\beta$ -(BEDT-TTF) $_2$ I $_3$  four different lines can be detected in the range from  $2900$  to  $3000\text{ cm}^{-1}$ . In  $\kappa$ -(BEDT-TTF) $_2$ Cu(NCS) $_2$  and  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  the observation of only two and three lines, respectively, points to the occurrence of a degeneracy in the  $\text{CH}_2$  stretch vibrations of both radical cation salts. Also Fig. 5 strongly supports this assignment. In the completely deuterated pure donor BEDT-TTF, four lines are observed which are shifted by an average amount of  $750\text{ cm}^{-1}$  to lower frequencies. This agrees well with the calculated value mentioned above.

Furthermore, it is noteworthy that all vibrations in these compounds are shifted to lower wave numbers with respect to the crystalline neutral donor. This well-known phenomenon [15, 16] is attributed to ionization of the donor molecules.

The infrared spectrum of  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  in the range from  $2900$  to  $3000\text{ cm}^{-1}$  as presented in Fig. 3 shows the same overall behaviour as the spectra of  $\alpha_1$ - and  $\beta$ -(BEDT-TTF) $_2$ I $_3$  in the same region together with decisive differences. Whereas in the  $\alpha_1$ - and  $\beta$ -phases the peak appearing at  $2913\text{ cm}^{-1}$  is always more intense than the one at  $2908\text{ cm}^{-1}$ , the relative amplitudes of these two lines are reversed in the  $\alpha$ -phase. Unlike in the case of  $\alpha_1$ - and  $\beta$ -(BEDT-TTF) $_2$ I $_3$  where two different peaks can be distinguished around  $2950$

$\text{cm}^{-1}$ , only a single line which shows no sign of any splitting occurs at  $2954 \text{ cm}^{-1}$  in  $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$ .

Additionally, Fig. 4 demonstrates that there exists a small but distinct difference between  $\alpha_1\text{-}$  and  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$ . This highly enlarged view of the range from  $2925$  to  $2985 \text{ cm}^{-1}$  clearly shows a significant shift of  $5 \text{ cm}^{-1}$  in the highest energetical peak between these two phases. This finding is very remarkable as it indicates from a structural point of view that both phases are not completely identical.

We expect a strong correlation between the positions and intensities of the various infrared features and the possible conformations of the BEDT-TTF molecule. As a given  $\text{CH}_2$  group is involved in short  $\text{C-H}\cdots$  donor and  $\text{C-H}\cdots$  acceptor contacts depending on its immediate neighbourhood, the detailed surroundings of every  $\text{CH}_2$  group will determine the exact frequency and position of the observable vibrations. However, the crystal structures of the investigated materials are rather complex and often a high degree of overlap between neighbouring atoms is found. Thus it has been impossible so far to assign any of the detected lines to certain  $\text{CH}_2$  group positions of the donor molecule.

A further problem arises in the case of  $\alpha_1\text{-(BEDT-TTF)}_2\text{I}_3$ . Although it is known [5] that the unit cell data and the molecular arrangement of the constituents are identical in  $\alpha_1\text{-}$  and  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$ , the detailed crystal structure of the  $\alpha_1\text{-}$  phase could not be resolved yet due to the mosaic-type crystals obtained by thermal conversion from  $\alpha\text{-}$  to  $\alpha_1\text{-(BEDT-TTF)}_2\text{I}_3$ . Nevertheless, other measurements establish a small structural difference between the  $\alpha_1\text{-}$  and  $\beta\text{-}$  phases. Whereas  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  is a superconductor with  $T_c = 1.3 \text{ K}$ ,  $\alpha_1\text{-(BEDT-TTF)}_2\text{I}_3$  shows superconductivity at  $8 \text{ K}$ . Both superconducting states are stable in contrast to  $\beta_{\text{H}}\text{-(BEDT-TTF)}_2\text{I}_3$  which is obtained by a special temperature–pressure cycle and has only a metastable superconducting state at  $8 \text{ K}$ . In the latter compound all terminal  $\text{CH}_2$  groups of the BEDT-TTF molecules within the unit cell possess the staggered form [4] while in untreated  $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$  both conformations exist in neighbouring stacks [13]. Thus we suggest from the result presented in Fig. 4 that in  $\alpha_1\text{-(BEDT-TTF)}_2\text{I}_3$  the terminal  $\text{CH}_2$  groups do not have all the staggered conformation. They might either possess all the eclipsed conformation or rather take the same ordering as in the  $\alpha\text{-}$  phase where both kinds of conformations exist in neighbouring stacks.

Superconductivity is not only observed in single crystals but also in polycrystalline pressed samples of  $\alpha_1\text{-}$  and  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  [5]. So the question arises whether application of pressure, particularly of any anisotropic component, during the preparation of the sample might change their infrared properties due to structural changes.

First experiments show that the observable wave numbers and relative intensities are very sensitive to details of the preparation procedure. One example is presented in Fig. 6. By comparison with Fig. 3 it can be seen that the spectrum of the pressed pellet of  $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$  is different with respect to the crystalline  $\alpha\text{-}$  or  $\alpha_1\text{-}$  phase. On the other hand, thermal treatment



of this sample for 3 days at 70 °C results in a sample which shows exactly the same spectrum as  $\alpha_1$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>, demonstrating that annealing leads to a structural transition into the  $\alpha_1$ -phase.

The spectra of powdered single crystals diluted in KBr resemble the 'true' spectra since these materials are subject to an isotropic pressure during the preparation of the pellet. This isotropic pressure, which is due to the fact that KBr becomes fluid under pressure, seems not to result in any structural phase transition of the investigated materials. Nevertheless, further investigations are necessary in order to obtain more information about the various processes which might occur during the application of pressure.

The weak intensity of the lines around 2830 and 2850 cm<sup>-1</sup> for the neutral donor and the radical cation salts, respectively, varies from sample to sample and is considerably enhanced in all pellets prepared from polycrystalline pressed materials as can be noted by comparing Fig. 6 with Figs. 1–3. These lines may simply arise from imperfections introduced by both iso- and anisotropic pressure to the crystals. It is noteworthy that these frequencies coincide with the  $2\nu_3(a_g)$  vibration calculated by Kozlov *et al.* [21] but it is not clear at the moment if any correlations exist.

## Conclusions

The CH<sub>2</sub> stretch vibrations in some radical cation salts containing the donor molecule BEDT-TTF have been detected at room temperature by using FT-IR absorption spectroscopy. The obtained results demonstrate the value of this simple technique besides the rather sophisticated polarized IR reflectance spectroscopy in determining structural aspects of organic metals. FT-IR absorption spectroscopy can be applied as an easy method, e.g., to distinguish between different phases of certain radical cation salts based on BEDT-TTF and related compounds.

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