

DETECTION OF CH₂ STRETCH VIBRATIONS IN α^- , α_t^- and β^- -(BEDT-TTF)₂I₃ by FT-IR ABSORPTION SPECTROSCOPY

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ABSTRACT

We have investigated the CH₂ stretch vibrations of α^- , α_t^- and β^- -(BEDT-TTF)₂I₃ as well as those of the protonated and deuterated pure donor BEDT-TTF by FT-IR absorption spectroscopy. The crystals were pulverized and diluted in pressed pellets of KBr. Results in the spectral range around 2900 cm⁻¹ taken at room temperature are presented. The spectra clearly reveal absorption lines varying in position and intensity between the different species in a characteristic manner.

INTRODUCTION

The organic donor BEDT-TTF [bis(ethylenedithio)tetrathiofulvalene] finds large interest because of its ability to form metallic and superconducting radical cation salts with a number of counter ions [1]. Especially by the use of I₃⁻ anions, a variety of different phases is obtained by electrocrystallisation; some of them even show identical stoichiometry [2].

With only a few exceptions, these salts all 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 CH₂-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 by calculations on model compounds [3] that in BEDT-TTF radical cation salts the C-H...anion interactions are more important for the stability of the crystals than the C-H...donor interactions. Small changes in these interactions may change the structure of the whole BEDT-TTF molecule slightly and thus have large influence on the physical properties of the radical cation salt. Examples are the different superconducting states in β^- , β_H^- and α_t^- -(BEDT-TTF)₂I₃ [4]. It is known that the unit cell data and the arrangement of the molecules in β_H^- and α_t^- -(BEDT-TTF)₂I₃ are the same although the detailed structure of α_t^- -(BEDT-TTF)₂I₃ could not be resolved yet due to the mosaic type crystals obtained by the thermal conversion from α^- to α_t^- -(BEDT-TTF)₂I₃. Nevertheless, the structures cannot be identical since β_H^- -(BEDT-TTF)₂I₃ has only a metastable superconducting state at 8 K while α_t^- -(BEDT-TTF)₂I₃ shows a stable superconducting state at this temperature. Thus it was suggested that any difference only exists in the ordering of the terminal CH₂-groups of the BEDT-TTF molecules [4]. When viewed along the long molecular axis, the two (CH₂)₂-groups of every BEDT-TTF molecule can occupy one of two possible

positions which are designated as eclipsed and staggered [5]. While in $\beta_{\text{H}}^-(\text{BEDT-TTF})_2\text{I}_3$ all terminal CH_2 -groups have the staggered form [5], in $\alpha_{\text{t}}^-(\text{BEDT-TTF})_2\text{I}_3$ they either possess the eclipsed form or even more plausible they might be ordered as in $\alpha^-(\text{BEDT-TTF})_2\text{I}_3$ where both conformations exist in neighbouring stacks [6].

With this background it would be desirable to observe the CH_2 vibrations in the BEDT-TTF salts directly, either by Raman or infrared spectroscopy. Unfortunately, the broad plasma band which appears above 3000 cm^{-1} masks the CH_2 stretch vibrations to such an extent that they become unobservable in reflectance spectra, particularly at room temperature [7].

Therefore we used FT-IR absorption spectroscopy which is able to give information about bulk phonons without interference of various surface effects [8]. It has been demonstrated [8] that, with small differences in the relative intensities, the same results can be obtained by both reflection and absorption spectra on crystals and pressed pellets, respectively. This technique allowed us to investigate the CH_2 vibrations in a number of BEDT-TTF radical cation salts at room temperature.

EXPERIMENTAL

All crystals used in this work have been prepared electrochemically as described earlier [6]. The samples were prepared similar to ref. 8 by grinding single crystals in an agata mortar together with dry KBr. The spectra were taken at room temperature from 1800 to 5000 cm^{-1} by using a BOMEM FT-IR spectrometer with a fast and sensitive InSb detector at a resolution of 1 cm^{-1} . In order to increase the signal-to-noise ratio, up to 10 000 cumulative interferograms were stored. As the CH_2 stretch vibrations occur as small peaks on the broad plasma band, a baseline correction was necessary to obtain the true positions and relative intensities of the observable lines. The reproducibility of these criteria was excellent.

RESULTS

As an example, figure 1 shows a wide range view of the mid infrared absorption spectrum of $\alpha_{\text{t}}^-(\text{BEDT-TTF})_2\text{I}_3$ obtained from 10 000 cumulative interferograms. The characteristic feature is the appearance of a broad absorption band above 3000 cm^{-1} together with a low intensity vibronic pattern occurring around 2900 cm^{-1} .

Figure 2 presents an enlarged view of the spectral range from 2750 cm^{-1} to 3050 cm^{-1} . The spectra of the neutral donor as well as those of α^- , α_{t}^- and $\beta^-(\text{BEDT-TTF})_2\text{I}_3$, which were all baseline corrected, clearly reveal four peaks (three in the case of the α -phase) between 2900 cm^{-1} and 3000 cm^{-1} . They can be identified as the CH_2 stretching modes of the BEDT-TTF molecule as will be discussed later. Additional weak features appear around approx. 2820 cm^{-1} and 2850 cm^{-1} for the neutral donor and the radical cation salts, respectively. The signal-to-noise ratio in the pure insulating donor is obviously much higher because of the missing plasma band.

A further enlarged view of $\beta^-(\text{BEDT-TTF})_2\text{I}_3$ and $\alpha_{\text{t}}^-(\text{BEDT-TTF})_2\text{I}_3$ is shown in fig. 3. It clearly demonstrates that there is a small but distinct difference of 5 cm^{-1} between α_{t}^- and $\beta^-(\text{BEDT-TTF})_2\text{I}_3$ in the positions of the peak occurring at the highest wavenumber.

DISCUSSION

The infrared spectra of charge transfer salts based on BEDT-TTF are characterized by a broad absorption band around 3000 cm^{-1} together with a vibrational structure caused by coupling of the intramolecular vibrations to the conduction electrons [7-11]. The first feature has been generally ascribed to inter- and intramolecular electronic transitions of the donor

molecule, particularly to transitions between split bands where the splitting arises from strong interactions between donors which are arranged as dimers [11-13]. This broad band, usually designated as the plasma spectrum, can be seen in fig. 1. As all investigated BEDT-TTF radical cation salts show a very similar behaviour, only this example is presented here.

In this kind of materials the vibronic region starts with a sharp increase in absorption just below 1500 cm^{-1} . This feature has been observed in a number of experiments under various conditions [8,9,11-16] and could also be found in the samples investigated here but will not be pursued further in this work. Aside from possible overtones and combinations which, however, are much weaker, the only other lines above 1500 cm^{-1} in these materials are the CH_2 stretch vibrations which generally occur around 2900 cm^{-1} . This view is theoretically supported by Kozlov et al [15,16] who calculated the molecular normal modes of BEDT-TTF and obtained a wavenumber of 2912 cm^{-1} for the $\nu_1(a_g)$ vibration. Furthermore, all lines which are not degenerated, unresolved, or heavily damped should appear as quartets as there exist four variations of the BEDT-TTF molecules vibrating in and out of phase together [7].

Figure 2 confirms this expected behaviour. In the neutral donor BEDT-TTF as well as in α^- , α_t^- and β^- -(BEDT-TTF) $_2$ I $_3$ four different lines (three in the case of the α^- phase where two lines must be degenerate) can be detected in the range from 2900 cm^{-1} to 3000 cm^{-1} . Another proof for this assignment is the observation that in the completely deuterated pure donor these four lines are shifted by an average amount of 750 cm^{-1} to lower frequencies which agrees well with the calculated value [15] of 772 cm^{-1} .

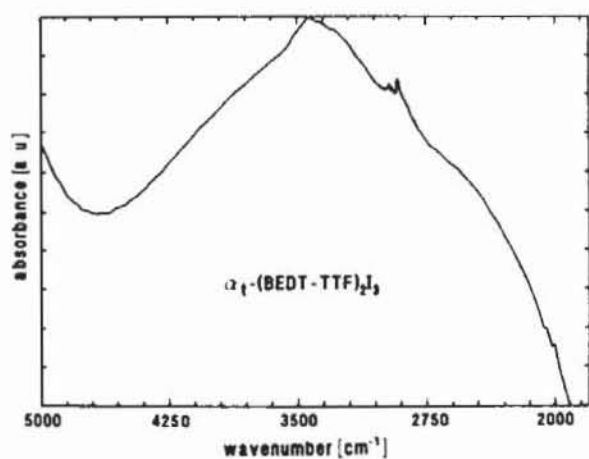


Fig.1: Mid infrared absorption spectrum of a pressed pellet diluted in dry KBr of α_t^- -(BEDT-TTF) $_2$ I $_3$ in the range from 1800 cm^{-1} to 5000 cm^{-1} at room temperature.

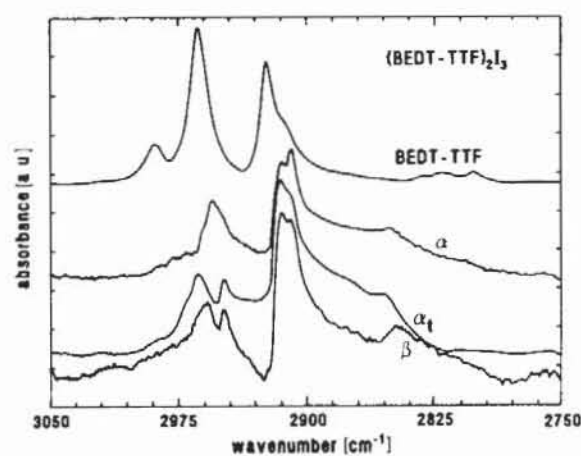


Fig.2: IR absorption spectra of BEDT-TTF, α^- , α_t^- , and β^- -(BEDT-TTF) $_2$ I $_3$. Baseline correction is applied.

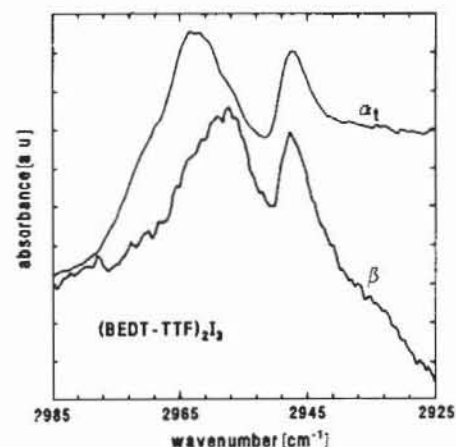


Fig.3: Enlarged view of the infrared spectra of α_t^- and β^- -(BEDT-TTF) $_2$ I $_3$ from Fig.2.

It should be noted that all CH_2 stretch vibrations in the radical cation salts are shifted to lower wavenumbers with respect to the crystalline neutral donor compound. It is well known [10,11] that this phenomenon arises from the electron molecular vibration coupling which obviously does not exist in pure insulating BEDT-TTF.

The infrared spectrum of α -(BEDT-TTF) $_2$ I $_3$ in the range 2900...3000 cm^{-1} shows the same overall behaviour than those of α - and β -(BEDT-TTF) $_2$ I $_3$ together with distinct differences. Whereas in the α - and β -phase the peak appearing at 2913 cm^{-1} is always higher than the one at 2908 cm^{-1} , in the α -phase the relative intensities of these two lines are reversed but at the same positions. Unlike in the case of α - and β -(BEDT-TTF) $_2$ I $_3$ where two different peaks occur around 2950 cm^{-1} , only a single line appears at 2954 cm^{-1} in α -(BEDT-TTF) $_2$ I $_3$. The origin of these findings is not clear in detail yet although we expect a strong correlation between the positions and intensities of these features and the conformations of the BEDT-TTF molecule. A given $(\text{CH}_2)_2$ -group which can occupy the eclipsed or staggered position is involved in short C-H...donor and C-H...anion contacts depending on the local surroundings in the crystal [3]. Thus the detailed structure in the immediate neighbourhood of every CH_2 -group will determine the exact frequency and intensity of the observable vibrations. As the crystal structures of the investigated materials are not simple and because a high degree of overlap between atoms can be found, it was not possible to assign the detected lines to certain CH_2 -group positions at the present stage.

Fig. 3 demonstrates that there exists a small but distinct difference between α - and β -(BEDT-TTF) $_2$ I $_3$. The highly enlarged view from 2935 cm^{-1} to 2985 cm^{-1} shows a shift of 5 cm^{-1} in the highest energetical peak between the two phases. This observation is very remarkable since it indicates indeed a different ordering of the terminal CH_2 -groups in α - and β -(BEDT-TTF) $_2$ I $_3$, which to our knowledge is the first experimental evidence. So it seems clear that the terminal CH_2 -groups in α -(BEDT-TTF) $_2$ I $_3$ do not have the staggered ordering.

LITERATURE

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