FT-IR Absorption Spectra of Polycrystalline Pressed Samples of the Organic Metals and Superconductors α-, β-$(BEDT\text{-}TTF)_2I_3$ and $(BEDT\text{-}TTF)_2Cu(NCS)_2$

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IR absorption spectra of polycrystalline pressed samples of the organic metals α-$(BEDT\text{-}TTF)_2I_3$, β-$(BEDT\text{-}TTF)_2I_3$ and $(BEDT\text{-}TTF)_2Cu(NCS)_2$ are presented and discussed. Normal protonated as well as deuterated materials were studied. The spectra range from 400 cm^{-1} to 5000 cm^{-1} and are similar to the IR reflectance spectra reported ealier. The data are of special interest in view of the fact that recently bulk superconductivity was observed in such polycrystalline samples of organic metals, and therefore the application of organic superconductors for the preparation of electronic devices seems possible.

Introduction

Since the discovery of a new class of organic superconductors [1, 2] based on the donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), many new materials have been prepared by electrochemical methods with this donor, and many spectroscopic investigations of these materials appeared in the literature. Especially vibrational spectroscopy proved to be a very powerful tool in the study of one dimensional [3–6] and two dimensional [7–12] organic charge transfer compounds.

Many reflectance measurements have been published, but only very few absorption data are reported [9, 12, 13]. The main advantage of absorption spectroscopy is its giving information on the bulk phonons without interference of possible defects and impurities at the surface. However, absorption measurements on single crystals require the preparation of very thin crystals, which is not always possible. Therefore often only measurements on pulverized materials diluted in pressed pellets of CsI are possible. In such cases the question arises, whether those measurements are valid for single crystals as well due to the fact that such organic metals often undergo a phase transition during the preparation of the pellets under pressure [14].

Nevertheless, the recent discovery of superconductivity in polycrystalline pressed samples of organic metals [14] makes the study of such pressed pellets very interesting. In this paper we report on the Fourier transformed infrared (FT-IR) absorption spectra in pressed pellets of protonated as well as of deuterated α-$(BEDT\text{-}TTF)_2I_3$, β-$(BEDT\text{-}TTF)_2I_3$ and $(BEDT\text{-}TTF)_2Cu(NCS)_2$ at 300 K.

Experimental and Results

The materials studied in this work have been prepared by electrochemical methods as previously described [15–17]. It should be emphasized that the starting single crystals are of very high quality and are well characterized [16]. The samples were prepared by grinding the single crystals in an agata mortar together with dry CsI. The weight concentration of the organic metals in the pellet was 0.5%. Special care was taken to achieve homogeneous pellets of good optical quality. The diameters (d) of the $(BEDT\text{-}TTF)_2X$ par-

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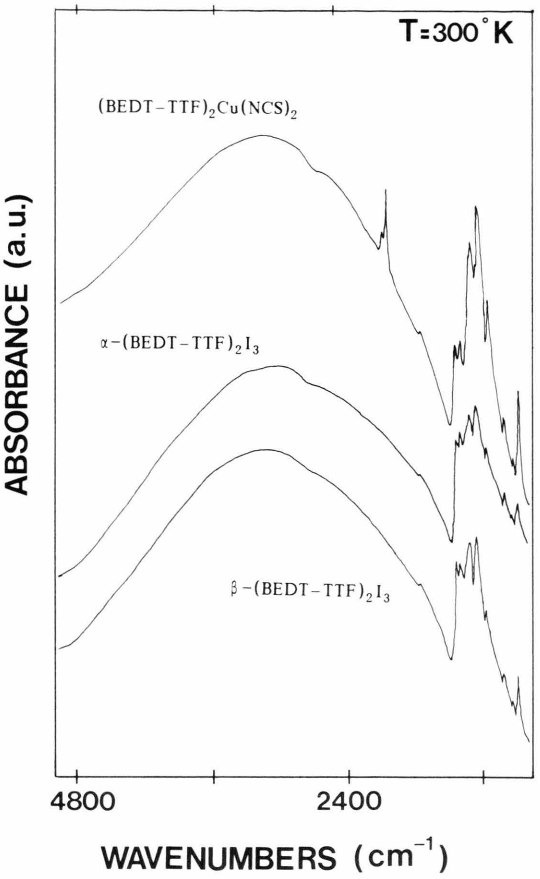

Fig. 1. Infrared absorption spectra of pressed pellets (CsI +0.5% material) of α-(BEDT-TTF)$_2$I$_3$, β-(BEDT-TTF)$_2$I$_3$ and (BEDT-TTF)$_2$Cu(NCS)$_2$.

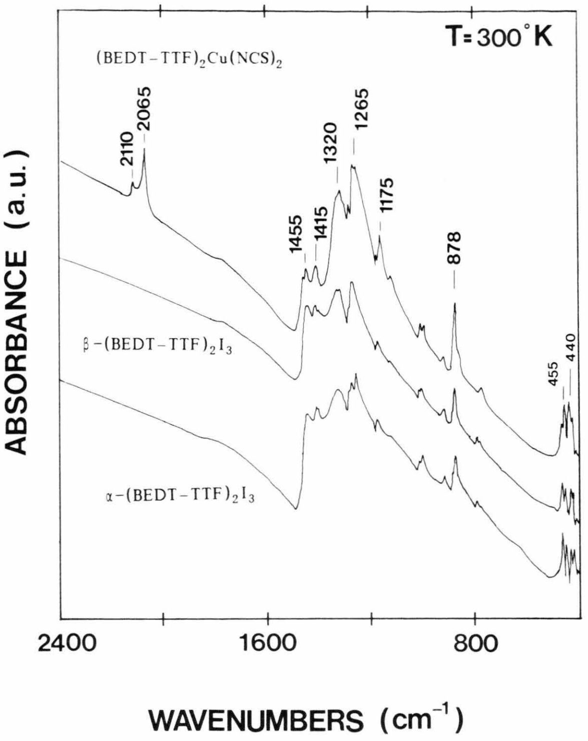

Fig. 2. Enlarged view of the spectra shown in Fig. 1 (range from 400 cm^{-1} to 2400 cm^{-1}) of α-(BEDT-TTF)$_2$I$_3$, β-(BEDT-TTF)$_2$I$_3$ and (BEDT-TTF)$_2$Cu(NCS)$_2$.

ticles were in the range $0.1 < d < 10$ μm. The pressed pellets were prepared with a pressure of 10^4 kg/cm^2. Spectra in the range from 5000 cm^{-1} to 400 cm^{-1} were obtained by using an FT-IR interferometer (Bruker 113 V), DTGS (KBr) and fast MCT (cut off at 750 cm^{-1}) detectors, at a resolution of 1 cm^{-1}. With the DTGS detector 5000 cumulative interferograms were stored in order to obtain a good signal-to-noise ratio.

In Fig. 1 a wide range view of the infrared absorption spectra of α-(BEDT-TTF)$_2$I$_3$, β-(BEDT-TTF)$_2$I$_3$ and (BEDT-TTF)$_2$Cu(NCS)$_2$ is plotted. Figure 2 shows an enlarged view of the range between 2400 and 400 cm^{-1}, while in Fig. 3 the analogue spectra of the deuterated materials are plotted (in the case of the deuterated materials the spectral range from 5000 cm^{-1} to 2400 cm^{-1} is not shown since the spectra are identical with the protonated materials). As can be seen from the figures, the spectra of the three investigated materials are very similar and the spectral range can be roughly devided into two areas: The first one from 5000 cm^{-1} to the sharp increase in absorption at about 1500 cm^{-1} and the second one from 1500 cm^{-1} to 400 cm^{-1}. In the first area, for all materials a very broad absorption peak with the maximum at around 3000 cm^{-1} is observed. In addition, in the spectrum of (BEDT-TTF)$_2$Cu(NCS)$_2$ there exists a sharp doublet at 2065 cm^{-1} and 2110 cm^{-1}. The second area, starting at about 1500 cm^{-1} (see Fig. 2) shows a very rich pattern of bands of asymmetrical shape. The bands are for all protonated samples located nearly at the same frequencies but with different relative intensities. The same is true for the deuterated materials. This is the range of the vibronic bands.

Discussion

A characteristic feature in the infrared spectra of charge transfer systems is the appearance of a broad

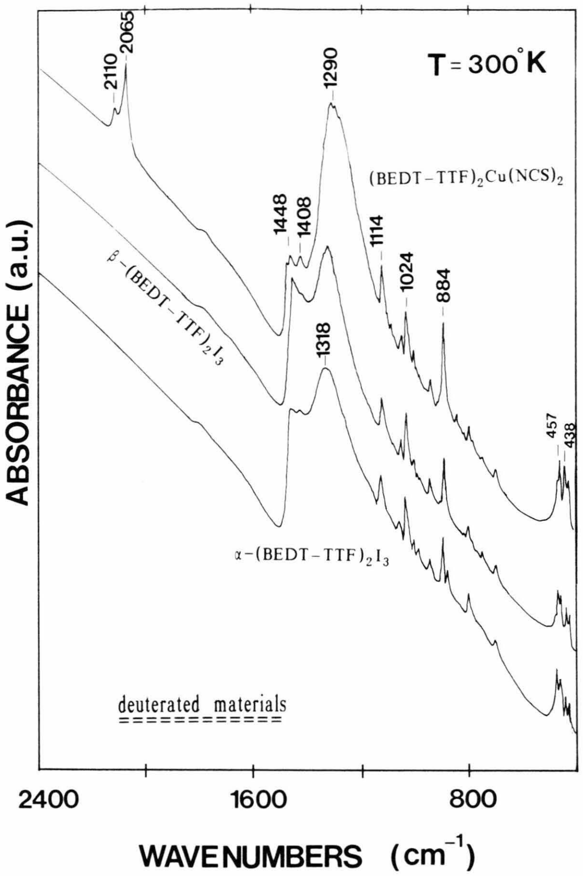

Fig. 3. Infrared absorption spectra of pressed pellets (CsI +0.5% material of *deuterated* α-$(BEDT\text{-}TTF)_2I_3$, *deuterated* β-$(BEDT\text{-}TTF)_2I_3$ and *deuterated* $(BEDT\text{-}TTF)_2Cu(NCS)_2$. Conditions as in Figure 2.

absorption band around 3000 cm^{-1} together with a strong vibrational structure induced by an electron molecular vibration (EMV) coupling [4, 7]. It is well known [5] that in such systems the totally symmetric modes (a_g) of the intramolecular vibrations give rise to a coupling to the conduction electrons. As can be seen in our spectra (see Fig. 1), the investigated compounds show a large broad absorption band at 3000 cm^{-1} and a very rich vibronic pattern. We emphasize the fact that all materials show nearly the same infrared behaviour at the chosen experimental conditions. The broad peak at 3000 cm^{-1} is generally assigned to electronic interband transitions between split bands, whereby the splitting is due to strong intermolecular interactions between the donors and dimers [9, 18, 19].

The sharp doublet appearing at 2065 cm^{-1} and 2110 cm^{-1} in the spectrum of the protonated as well as the deuterated $(BEDT\text{-}TTF)_2Cu(NCS)_2$ is like a finger-print and can be assigned according to reflectance data [20] to a CN stretching mode of the $Cu(NCS)_2$ anions. This assignment is supported by the crystal structure [21], which shows two kinds of isothiocyanate groups in the crystals: A chain along the *b*-axis (CN stretching vibration at 2110 cm^{-1}) and a second type in the form of $[-Cu(NCS)-(NCS)-]_n$ chains (CN stretching at 2065 cm^{-1}). The sharp increase in absorption at around 1500 cm^{-1} marks the beginning of the vibronic pattern. A similar sharp absorption at nearly the same frequency was found in the absorption of single crystals of α-$(BEDT\text{-}TTF)_2I_3$ [9], in pressed pellets of α-$(BEDT\text{-}TTF)_2(NO)_3$ and α-$(BEDT\text{-}TTF)_2(ClO_4)_2$ [13], in reflectance data on α-$(BEDT\text{-}TTF)_2I_3$ [22, 23] and β-$(BEDT\text{-}TTF)_2I_3$ [24, 25], as well as in reflectance data with polarization along the *a*-axis [18] and *b*- and *c*-axis [19, 20] in $(BEDT\text{-}TTF)_2Cu(NCS)_2$ and in IR-absorption measurements in powder of α-$(BEDT\text{-}TTF)_2I_3$ [12].

From Raman measurements of the donor molecule BEDT-TTF [9, 11] as well as of the organic metals $(BEDT\text{-}TTF)_2Br$ [12], β-$(BEDT\text{-}TTF)_2I_3$ [26] and $(BEDT\text{-}TTF)_2Cu(NCS)_2$ [27] it is known which modes are located in the range between 1500 and 1400 cm^{-1} and that they are related to the totally symmetric vibrations of the rings and the central C=C bonds. It was further observed that in all the organic metals a shift to lower energies with respect to the neutral donor BEDT-TTF appears. In the case of β-$(BEDT\text{-}TTF)_2I_3$ [26] the shift is smaller than in $(BEDT\text{-}TTF)_2Cu(NCS)_2$ [27] or even in $(BEDT\text{-}TTF)_2Br$ [12]. It is well known from the theory [4, 7, 9] that in the IR vibronic spectra the shift to lower energies with respect to Raman data is determined by the strength of the EMV coupling and that the shift can be of the order of 200 cm^{-1} [12, 28]. Therefore we account – in agreement with [12] – the band at 1320 cm^{-1} (Fig. 2) as due to coupling of electrons with the C=C stretching mode of the central carbons of the BEDT-TTF cations. In the case of the deuterated α- and β-$(BEDT\text{-}TTF)_2I_3$ the band appears at nearly the same position, while in the deuterated $(BEDT\text{-}TTF)_2Cu(NCS)_2$ the band is shifted by 30 cm^{-1} to lower energies (see Fig. 3), indicating a somewhat stronger EMV coupling. This is of some interest because the deuterated $(BEDT\text{-}TTF)_2Cu(NCS)_2$ has a higher transition temperature ($T_c = 11$ K) into the superconducting state with respect to the protonated samples [29, 30], in contrast to theoretical expectations. The reason for the higher T_c in the deuterated crystals is not clear yet. The bands at 1455 cm^{-1} and 1415 cm^{-1} (see Fig. 2) can be related in the same way to the C=C stretching mode of the ring carbons.

It should be mentioned that in [12] in the case of a powder of α-(BEDT-TTF)$_2$I$_3$ a band at 1445 cm^{-1} was assigned to the antisymmetrical (b$_{1u}$) vibration of the C=C stretching mode, and a band at 1410 cm^{-1} tentatively to a CH$_2$ bending mode. We would like to recall that the unit cell of α-(BEDT-TTF)$_2$I$_3$ is triclinic and contains two formula units per cell. In addition, there exist two crystallographically independent types of donor stacks, and the bond lengths of the donors in the two stacks differ significantly [15]. Therefore we suggest that there are two slightly different C=C stretching bands due to the different interactions in the two stacks. In the case of (BEDT-TTF)$_2$Cu(NCS)$_2$ the situation might be similar due to the fact that two different donor dimers exist which show a nearly perpendicular arrangement. More complicated is the situation in the case of β-(BEDT-TTF)$_2$I$_3$, where we observe at least in the protonated case two bands as well. Normally, in the single crystals of β-(BEDT-TTF)$_2$I$_3$ there exists only one type of donor stack and in this stack the cations are dimerized. Here we deal with polycrystalline pressed samples. We know that the β-phase undergoes a phase transition during the preparation of the pressed samples (pressure $\approx 10^4$ kg/cm^2) because Raman measurements clearly show two independent I_3^- anions [31], and temperature dependent conductivity measurements on polycrystalline pressed samples of β-(BEDT-TTF)$_2$I$_3$ show an onset to superconductivity at 9 K, this superconducting state being *stable* [32], in contrast to the usually observed metastable superconducting state observed in single crystals [33]. Therefore there might also exist two types of donor cations with different strengths of interaction to the anion channels in these pressed pellets of β-(BEDT-TTF)$_2$I$_3$. For this reason we tentatively assign the two bands at 1455 cm^{-1} and 1415 cm^{-1} to C=C stretching modes of the ring carbons. This assignment is supported by the spectra of the deuterated compounds where at least in the cases of the α-(BEDT-TTF)$_2$I$_3$ and (BEDT-TTF)$_2$Cu(NCS)$_2$ bands at 1448 cm^{-1} and 1408 cm^{-1} appear (see Figure 3).

In the following the bands at 1265 cm^{-1} and 1175 cm^{-1} (see Fig. 2) shall be discussed. We correlate those bands to CH$_2$, C–C–H and H–C–H vibrations. This attribution is supported by the spectra on the deuterated compounds (see Fig. 3), where those bands disappear and are shifted to lower energies (1114 cm^{-1} and 1024 cm^{-1}) in contrast to the band at 1320 cm^{-1} which appears in the deuterated case in about the same position, supporting the assignment as a C=C stretching mode of the central bond.

In Fig. 2 at 1293 cm^{-1} and 1181 cm^{-1} two small narrow dips can be seen. In [9, 34, 35] these dips are correlated to the methylene vibrations, and here especially to a C–C–H bending mode for the 1293 cm^{-1} band. This seems to agree with the finding in the deuterated compounds (Fig. 3), where such dips cannot be seen. In particular, in the case of (BEDT-TTF)$_2$Cu(NCS)$_2$ (see Fig. 2) a splitting in the dips can be seen which is according to [35] direct evidence for two types of BEDT-TTF anions with slightly different hydrogen–anion interactions.

The bands at 878, 455 and 440 cm^{-1} in Fig. 2 can be assigned to an EMV coupling with C–S modes, in agreement to [9, 12, 22]. In the deuterated materials these bands are shifted a little bit (884, 457 and 438 cm^{-1}). It is interesting to notice how the bands at 455 cm^{-1} and 440 cm^{-1} are split. The hardening of the C–S modes in the deuterated samples supports the fact of a stronger EMV coupling as already accounted for the C=C stretching mode. Recently [22], taking into account a theoretical calculation [12] for the EMV coupling constant, it was proposed that the band at 440 cm^{-1} is due to an out-of-plane deformation of the BEDT-TTF cations. The broken symmetry is presumably also connected with the dimerisation of the stacks in these materials.

In conclusion we can say that the IR absorption spectra of pressed pellets of the organic metals α-(BEDT-TTF)$_2$I$_3$, β-(BEDT-TTF)$_2$I$_3$ and (BEDT-TTF)$_2$Cu(NCS)$_2$ are quite similar to earlier reported IR reflectance spectra on single crystals of the same materials, with some small differences especially in the relative intensities of some EMV bands.

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