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## INFRARED ABSORPTION IN SINGLE CRYSTALS OF $(\text{ET})_2\text{C}_{60}$ GROWN FROM $\text{CS}_2$ SOLUTION

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Fourier transform IR absorption spectra of single crystals of the  $(\text{ET})_2\text{C}_{60}$  complex grown from the  $\text{CS}_2$  solution as well as its components:  $\text{C}_{60}$  and ET, also grown from  $\text{CS}_2$  solution, are presented and discussed. It is shown that the rotation of  $\text{C}_{60}$  is strongly hindered and ET molecules are bent in the crystal structure of the complex. The arguments for the domination of the van der Waals interactions are given.

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### 1. Introduction

The recent development of macroscopic preparation of carbon clusters,  $\text{C}_{60}$ , has stimulated a variety of studies of its compounds and their solid state properties. Several attempts have been made to obtain a conducting, charge-transfer (CT) complex crystal of  $\text{C}_{60}$  since most organic conductors are either CT complexes or ion-radical salts. So far, only a few solid-state complexes, based on  $\text{C}_{60}$  have been synthesized [1-9].

On the other hand, commonly known metallic and superconducting properties of cation-radical salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) with various acceptor molecules [10, 11] have focused the attention on the preparation and investigation into the properties of CT complexes of this donor with  $\text{C}_{60}$  [5, 6, 12].

The efficient complexation of BEDT-TTF (abbreviation ET) with  $\text{C}_{60}$  can be achieved not only due to the strong CT interaction but also because of the fact that the flexible ET molecules can surround the  $\text{C}_{60}$ . It was mentioned by Izuoka et al. [5] that the single crystals of  $(\text{ET})_2\text{C}_{60}$  without  $\text{CS}_2$  inclusions could be obtained. The X-ray analysis revealed that each  $\text{C}_{60}$  molecule is sandwiched between a pair of largely concave ET molecules and that the rotational motion of

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C<sub>60</sub> is quenched completely [5]. Modified methods of preparation of the CT complex (ET)<sub>2</sub>C<sub>60</sub> and its UV-VIS-NIR-IR spectra have been reported and analysed by us previously [12]. It was concluded that the CT between electron donor and acceptor is small.

The present paper offers the detailed IR absorption studies of the single crystals of (ET)<sub>2</sub>C<sub>60</sub> grown from CS<sub>2</sub> solution ((ET)<sub>2</sub>C<sub>60</sub>/CS<sub>2</sub>). A comparison with the spectra of pristine C<sub>60</sub> and ET as well as crystals of C<sub>60</sub> and ET grown from CS<sub>2</sub> solution (C<sub>60</sub>/CS<sub>2</sub> and ET/CS<sub>2</sub>, respectively) is used in the discussion and the assignment of the absorption peaks observed in the single crystal spectra.

## 2. Experimental

The single crystals of (ET)<sub>2</sub>C<sub>60</sub> were grown from a solution of stoichiometric amounts of C<sub>60</sub> and ET in carbon disulfide, according to procedure of Izuoka et al. [5]. The solvent was freshly distilled, dried and degassed with argon atmosphere. The solution was cooled slowly in a Dewar vessel down to room temperature. By slow evaporation of the solvent (7–8 days) in the dark, at room temperature small, black crystals of the form of elongated parallelepiped with typical dimensions up to 5 × 1 × 1 mm<sup>3</sup> have been obtained. The crystals were filtered off, washed with ethanol and dried under vacuum at room temperature. Elemental analysis of the crystals (calculated: C, 64.52; H, 1.08; S, 34.41; found: C, 65.03; H, 1.02; S, 35.62) suggests the compound formula (ET)<sub>2</sub>C<sub>60</sub> but our spectral study reveals small addition of CS<sub>2</sub>. Thus, we propose the formula (ET)<sub>2</sub>C<sub>60</sub>·(CS<sub>2</sub>)<sub>x</sub> where  $x \ll 1$ . X-ray crystallographic measurements on the single crystal were performed at room temperature (RT), with Mo K<sub>α</sub> radiation (graphite monochromator  $\lambda = 0.71079$  Å). The compound is monoclinic with  $a = 26.28(1)$  Å,  $b = 21.79(1)$  Å,  $c = 9.989(4)$  Å and  $\beta = 105.21(3)^\circ$ . Unit cell parameters are very close to that found by Izuoka et al. [5] for (ET)<sub>2</sub>C<sub>60</sub> crystals. They did not detect CS<sub>2</sub> inclusions, however, because of a very low CS<sub>2</sub> concentration.

The crystals of C<sub>60</sub> grown from a solution of CS<sub>2</sub> were obtained following the procedure of Morosin et al. [13]. C<sub>60</sub>·1.5CS<sub>2</sub> crystal grew in the form of elongated cuboids with typical dimensions up to 4 × 1 × 0.2 mm<sup>3</sup>; the crystal surfaces were smooth and shiny. Commercial ET was purified by a vacuum sublimation and recrystallization from CS<sub>2</sub>. Single crystals of ET/CS<sub>2</sub> of the form of parallelepiped were obtained.

Infrared transmission spectra of single crystal samples were recorded with a Perkin Elmer 1725 X Fourier-transform IR spectrometer equipped with infrared microscope in the range 640–6250 cm<sup>-1</sup>, and narrow-band MCT detector. The crystals were mounted free standing over 0.3 mm aperture. Fourier transform (FT) IR spectra of the single crystals of C<sub>60</sub>/CS<sub>2</sub>, ET/CS<sub>2</sub> and (ET)<sub>2</sub>C<sub>60</sub>/CS<sub>2</sub> and pristine C<sub>60</sub> and ET were recorded at room temperature, with nonpolarized light from the crystal surface confined to 0.1 mm in diameter; the spectra of (ET)<sub>2</sub>C<sub>60</sub>/CS<sub>2</sub> were additionally recorded with polarized light, at two mutually perpendicular polarizations. The FT IR spectra of various samples from the same batch were nearly identical. For the practical reasons the transmission spectra were presented as normalized absorption.

### 3. Results and discussion

The transmission method of spectral investigation of single crystal is significantly more sensitive compared to the reflectivity measurements for very weak modes. The advantage of the IR transmission measurements of single crystals over a powdered sample in KBr pellet techniques is self-evident. Therefore, we present the absorption spectra of the single crystals of  $C_{60}/CS_2$  (a),  $ET/CS_2$  (b) and  $(ET)_2C_{60}/CS_2$  (c) thick enough to produce many weak lines (Fig. 1). To

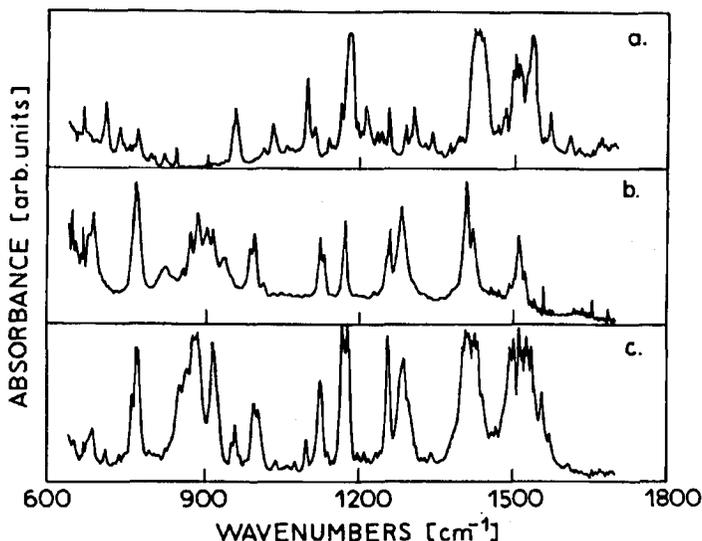


Fig. 1. FT IR absorption spectra of single crystals grown from carbon disulfide solutions: (a)  $C_{60}$ , (b)  $ET$ , and (c)  $(ET)_2C_{60}$ .

our knowledge, the transmission spectra of the single crystals of  $ET/CS_2$  and  $(ET)_2C_{60}/CS_2$  are published for the first time; the spectra of  $C_{60}/CS_2$  have been reported by us recently [14]. According to Martin et al. [15] the 46 vibrational modes of  $C_{60}$  lie below  $1600\text{ cm}^{-1}$ ; above this frequency, only the higher order vibrations occur. This is why we confine our discussion to the spectral region between  $640$  and  $1600\text{ cm}^{-1}$ .

The FT IR spectra of  $C_{60}/CS_2$  (Fig. 1a) and its complex  $(ET)_2C_{60}/CS_2$  (Fig. 1c) are very rich and consist of tens of weak and very weak bands. The two  $F_{1u}$  modes, which are IR active in  $C_{60}$  molecule of  $I_h$  point group appear to be so strong that they saturate easily around the usual  $1182\text{ cm}^{-1}$  and  $1429\text{ cm}^{-1}$  absorption peaks. Apart from the saturated absorptions, strong and very broad absorption peaked at  $1508\text{ cm}^{-1}$ , characteristic of the solvent can be seen. The frequencies of the observed lines of  $C_{60}/CS_2$ ,  $ET/CS_2$  and  $(ET)_2C_{60}/CS_2$  single crystals, and for comparison the frequencies of the pristine  $ET$  KBr pellet recorded by Kozlov et al. [16] are listed in Table.

TABLE

Vibrational modes ( $\omega$ , in  $[\text{cm}^{-1}]$ ) of  $(\text{ET})_2\text{C}_{60}$  complex grown from  $\text{CS}_2$  solution and its components.

$\text{C}_{60}$ , from $\text{CS}_2$		ET, from $\text{CS}_2$	ET pristine [16]		$(\text{ET})_2\text{C}_{60}$ , from $\text{CS}_2$
$\omega$	Assignment [14]	$\omega$	$\omega$	Assignment	$\omega$
669	$H_u(3)$	668			669
		688	687	$B_{3u}$	686
710	$H_g(3)$				711
740	$G_u(2)$	735			738
757	$G_u(3)$				762
		769	772	$B_{1u}$	771
774	$H_g(4)$				797
795	$F_{2u}(3)$				827
825	$H_u(4)$	826			853
		861	860	$B_{3g}$	865
		875	875	$B_{2u}$	
		890	890	$B_{2u}$	890
908	$F_{1g}(1) \otimes H_u(1)$	906	905	$B_{1u}$	918
		919	917	$B_{2u}$	928
		940	938	$B_{1g}$	
957	$H_g(2) \otimes F_{1u}(1)$				956
965	$G_g(2)$				962
		990	987	$A_g$	
		999	996	$B_{1u}$	998
1019	$H_g(1) \otimes G_u(3)$				1007
1040	$F_{2u}(4)$				1041
1078	$G_u(4)$				1078
1100	$H_g(5)$				1100
1116	$H_g(4) \otimes H_u(1)$				
		1126	1125	$B_{3u}$	1127
1143	$H_g(2) \otimes F_{2u}(2)$				1142
1165	$H_g(2) \otimes G_u(2)$	1174	1173	$B_{1g}$	1170
1183	$F_{1u}(3)$				1182
1198	$G_g(3)$				1198

TABLE (contd.)

1215	$F_{2g}(3)$				1214
1235	$F_{1g}(1) \otimes H_u(3)$				1235
1250	$H_u(6)$				1243
1259	$H_g(2) \otimes H_u(4)$	1261	1259	$B_{2u}$	1258
1291	$G_u(5)$	1284	1282	$B_{1u}$	1289
1307	$H_g(1) \otimes F_{2u}(4)$				1307
1343	$G_g(5)$				1341
1376	$H_g(3) \otimes H_u(3)$				1375
1400	$F_{1g}(1) \otimes H_u(4)$				1404
		1410	1406	$B_{2u}$	1409
		1423	1420	$B_{1u}$	1415
1429	$F_{1u}$				1426
					1428
					1433
1460	$A_g(2)$	1458			1460
1469		1466			1468
		1473			1474
		1491			1493
		1497			1502
		1504			1504
1507	$H_g(1) \otimes H_u(6)$	1508			1510
		1510			1512
					1519
		1522			1523
1530	$H_g(4) \otimes G_u(3)$				1529
1539	$G_g(2) \otimes H_u(2)$	1534			1537
		1541			1542
1555	$F_{2g}(3) \otimes H_u(10)$	1555			1556
1560	$H_g(1) \otimes G_u(5)$	1559			1559
1570	$H_g(4) \otimes F_{2u}(3)$	1570			1571
1577	$H_g(8)$	1577			1577
1610	$H_g(2) \otimes F_{1u}(3)$				1609
		1618			1618
		1624			1625
		1636			1637
		1648			1648

The spectrum of  $C_{60}/CS_2$  clathrate is very rich and exhibits strong bands typical of the broken  $I_h$  symmetry of the genuine, original fullerene. The carbon disulfide is a very good solvent of fullerene and the occurrence of numerous  $CS_2$  molecules in the clathrate structure seems normal. The presence of  $CS_2$  strongly influences the crystal structure of  $C_{60}/CS_2$ . The lowering of the molecular symmetry leads to the activation of many silent modes and appearance of a large number of higher order combination modes in the crystal — it was observed by us recently for clathrates of  $C_{60}$  with various solvents [14] and is again confirmed in the present studies.

Apart from the absorption bands, characteristic of pristine ET molecule, the spectrum of  $ET/CS_2$  shows broad absorption around  $1508\text{ cm}^{-1}$  believed to origin from some inclusion of the solvent molecule into the crystal structure of the ET. These inclusions displace the bending vibrations of the ethylene groups and stretching vibration of the terminal C-C bond by  $3\text{--}4\text{ cm}^{-1}$  and  $3\text{ cm}^{-1}$ , respectively, in the direction of higher frequencies. The bands sensitive to ionization of the molecule are not shifted in the  $ET/CS_2$ . It testifies that the interaction between the solvent molecule and the host structure of ET is very weak, rather of the van der Waals type. The inclusions hinder the bending vibrations of the  $CH_2$  groups of the ET molecules.

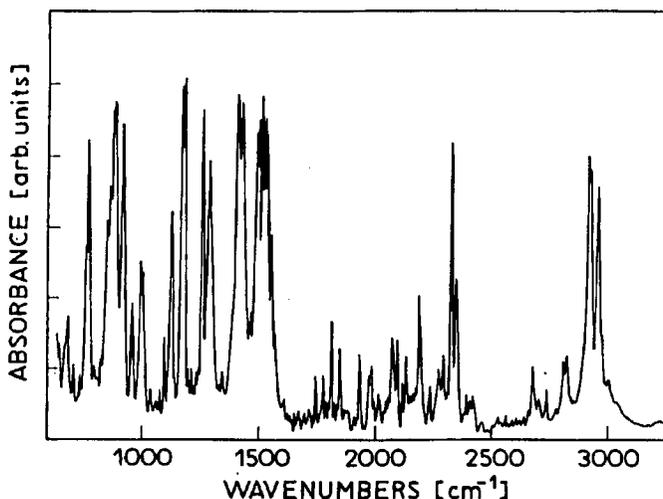


Fig. 2. FT IR absorption spectrum of the single crystal  $(ET)_2C_{60}$  complex grown from  $CS_2$  solution.

The spectrum of  $(ET)_2C_{60}/CS_2$  (Figs. 1c and 2) is very rich and exhibits the bands of  $C_{60}$  and ET as well as the strong and broad band at  $1508\text{ cm}^{-1}$  characteristic of  $CS_2$ . It indicates that the solvent molecules are included into the crystal structure of the complex. All the bands of  $C_{60}$  as well the IR active modes of  $F_{1u}$  symmetry as the silent modes are observed in the  $(ET)_2C_{60}$  nearly at the same frequencies as in  $C_{60}/CS_2$  (Table). It means that the symmetry of

the  $C_{60}$  molecules is lowered (the silent and combination modes typical of broken  $I_h$  symmetry are observed); on the other hand — the charge transfer between  $\pi$  donor molecule (ET) and the acceptor ( $C_{60}$ ) is small. Moderate modification of the spectrum is observed in the region of bending and wagging modes of  $CH_2$  groups of the ET molecules (Table). The bands  $1415$  and  $1426\text{ cm}^{-1}$  ( $\delta\text{ CH}_2$ ) and  $1289\text{ cm}^{-1}$  ( $\omega\text{ CH}_2$ ) are shifted by  $6 \div 9\text{ cm}^{-1}$  in relation to frequencies observed for pristine ET [16]. These shifts are higher than those observed for ET single crystals grown from  $CS_2$ . It suggests that the complex formation additionally hinders the bending and wagging vibrations of the  $CH_2$  groups.

Some characteristic changes are observed also in the region of C-S stretching and SCC bending modes of ET (Fig. 3). As mentioned elsewhere [12], the splitting

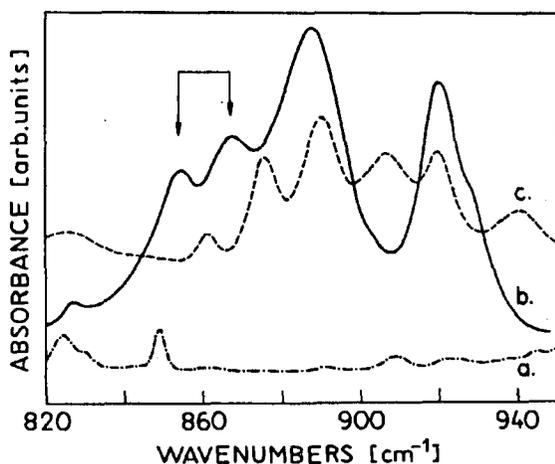


Fig. 3. FT IR absorption spectra of single crystals grown from  $CS_2$  solutions: (a)  $C_{60}$ , (b)  $(ET)_2C_{60}$  and (c) ET in the region of C-S vibrations. The Davydov doublet is marked.

of some bands is observed between  $840$  and  $920\text{ cm}^{-1}$ . In particular, the band at  $861\text{ cm}^{-1}$  is split into the doublet  $853$  and  $865\text{ cm}^{-1}$ . It seems that there are two translationally inequivalent lattice sites in the unit cell of the  $(ET)_2C_{60}/CS_2$ , and the doublet is referred to as Davydov splitting [17]. This hypothesis is confirmed by the transmission spectra of the single crystal of the complex in the polarized light showing a strong angular dependence of the component intensities. Small shifts of other bands of ET donor suggest that the molecule may be bent and some bonds are tightened. The center of interaction between ET and  $C_{60}$  is localized in the vicinity of the peripheric sulfur atoms of the former molecule.

#### 4. Conclusions

For the first time the transmission spectra of single crystals of  $ET/CS_2$  and  $(ET)_2C_{60}/CS_2$  are presented. It is demonstrated that the transmission spectra of the complex contain not only the IR active modes of  $C_{60}$  and ET but also

numerous features arising from isotopic or solid state effects due to the symmetry breaking of the  $C_{60}$  molecule and the higher order vibrations; the bands of  $CS_2$  are also present. It should be mentioned that the rotation of  $C_{60}$  is strongly hindered and ET molecules are bent in the crystal structure of the  $(ET)_2C_{60}/CS_2$ . The splitting of the bands  $861$  and  $919\text{ cm}^{-1}$  is attributed to the inequivalence of the sites in the unit cell. In spite of distinct spectral evidences of the complex formation,  $(ET)_2C_{60}/CS_2$  is a molecular complex of the van der Waals type with some influence of the charge transfer interactions.

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