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The orientational-ordering transition in single crystals of selected C_{60} complexes with organic donors followed by infrared spectroscopy

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Abstract

Investigations of infrared spectra of single crystals of the complex of fullerene C_{60} with dianthracene (DAN) and C_{60} grown from CS_2 solution (clathrate) versus temperature, between 4 and ca. 430 K, have been performed. A phase transition for the complex and the clathrate accompanied by a splitting of the $F_{1u}(4)$ band into at least two components was detected at temperatures higher than 260 K. The line splitting was attributed to C_{60} symmetry lowering as a result of suppression of its rotation. Phase transitions at 80, 160 and 305 K have been observed for DAN C_{60} $(C_6H_6)_3$; the nature of the transitions has been suggested. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The charge transfer complexes of the fullerene C_{60} with organic donors are especially interesting as potential objects for doping with alkali metal atoms. It seems that these materials should be new molecular superconductors [1] with relatively high critical temperatures. Pristine C_{60} undergoes a first-order phase transition from a high temperature orientationally disordered phase to a low temperature orientationally ordered phase at ca. 260 K [2]. Investigations of the orientational phase transition by infrared (IR) spectroscopy were performed by several authors (e.g., Refs. [3–5]). A broad jump in the width of the F_{1u} modes as well as a splitting of the $F_{1u}(4)$ mode was found. Detailed IR reflectivity and transmission measurements in large spectral and temperature ranges, for various crystallographic planes of C_{60} single crystals, were reported by Kuzmany et al. [7]. It was shown that the orientational phase transition is accompanied by a dramatic jump in the linewidth and frequency of the four F_{1u} modes within a fraction of a degree; the splitting of the $F_{1u}(4)$ mode was also observed. Apart from the first-order phase transition at 260 K, a second phase transition of the fullerene at ca. 90 K and a small structural anomaly

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at 155 K have been reported by David et al. [8]. In the lowest temperature phase ($T < 90$ K), the rotational motion of C_{60} is frozen although a small amount of static disorder still persists. IR spectral studies [3,6] support a model of orientational freezing below 90 K.

In contrast with the IR spectra of C_{60}, the spectra of the fullerene complexes are rich. Apart from the F_{1u} modes vibrational features, which are symmetry forbidden in the I_h point group of C_{60}, have been observed [9–12]. Characteristic bands of the donors (in complexes) and solvents (in C_{60} clathrates) have been also detected. A detailed analysis of the IR transmission spectra of the molecular C_{60} complex with chloro(triphenylphosphine)gold [12] and complexes of fullerene with planar donors of the tetrathiafulvalene, dithiadiazafulvalene and pyranylidene families [13] revealed that the majority of the donor and enclathrated solvent bands in the spectra of the complexes are perturbed or shifted insensibly, by 1–2 cm^{-1} with respect to the bands observed in the spectra of the pure donor and solvent. Some of the bands show anomalies in their temperature dependencies near the C_{60} phase transition temperature [10–12]. The observed changes in IR spectra versus temperature have been correlated with steric hindrances and a competition between effects caused by rotational–vibrational coupling and ‘normal’ temperature behaviour of the vibrational bands described by the Maxwell–Boltzmann distribution law [10].

In this Letter we report the temperature dependencies of the frequency, linewidth, amplitude and integral absorbance of selected vibrational modes of C_{60} molecular complexes and clathrate, mainly in the region of their phase transitions. The data presented in this Letter have been obtained for the single crystals of the fullerene derivatives.

2. Experimental

The C_{60} clathrate containing molecules of carbon disulfide and the molecular complex of the fullerene C_{60} with an organic donor: dianthracene (DAN) were chosen for detailed IR spectral investigations versus temperature from 4 K up to 420–450 K, depending on the thermal stability of the compounds.

The single crystals of C_{60} grown from CS_2 solution have been prepared by a method described elsewhere [14]. The samples of $C_{60}(CS_2)_{0.4}$ clathrate are grown as elongated plates of typical size $4 \times 1 \times 0.2$ mm^3; the crystal surface was smooth and shiny. The clathrate belongs to an orthorhombic lattice but packing of the molecules has not been determined. It seems that the crystals are loosely packed structures [15]. The Hartree–Fock calculations of the system of one C_{60} molecule and one CS_2 show that there are two local stationary points of the CS_2 molecule above hexagonal and pentagonal rings of the C_{60} molecule. CS_2 molecules change their dihedral angles and are displaced by approximately 7 Å above the surface of C_{60} [16].

High-quality single crystals of DAN C_{60} $(C_6H_6)_3$ were obtained by a diffusion method [17]. The complex is a Van der Waals compound without noticeable charge transfer. The monoclinic crystals show a layered structure; each C_{60} molecule is sandwiched between two DAN molecules, and the fullerene molecules show some structural disorder at room temperature. The concave shape of the donor molecules allows its efficient packing with the C_{60} spheroids [15]. The complex can be considered as a model system for the study of intermolecular interactions in neutral complexes of the fullerene with organic donors since the concave DAN molecule perfectly encircles the spherical C_{60} molecule.

Temperature dependencies of the $F_{1u}(3)$ and $F_{1u}(4)$ bands of the fullerene molecules in the crystalline complexes with binaphthol [1,6-d,e]-1,3-dithiin-2-ylidene (BDNY), trichloroethylene (TCE), bis(ethylenedioxy)tetrathiafulvalene (BEDO), 9,9′-bis-trans-(telluraxanthenyl) (BTX), tetranitride tetrasulfur (S_4N_4) and ethylenedithio-tetrathiafulvalene (EDT–TTF) were also studied, but only for $T > 300$ K. The details of these complexes preparation, structure and basic physical properties are given elsewhere: for DAN C_{60} $(C_6H_6)_3$ see Ref. [13], for TCE C_{60} see Ref. [18], for $(BEDO)_2$ C_{60} grown from C_6H_6 see Refs. [13,19], for BTX C_{60} CS_2 see Refs. [20,21], for $(S_4N_4)_{0.8}$ $(C_6H_6)_{1.2}$ see Refs. [21,22] and for $(EDT–TTF)_2$ C_{60} CS_2 see Refs. [13,23]. The analysis of IR and electronic absorption/transmission spectra as well as X-ray data shows that the complexes of the fullerene with the above-mentioned donors are involved in polarization interactions of

Van der Waals type. Charge transfer is weak in these compounds and is usually hindered by unfavourable steric factors. As a result, the CT rate approximates to zero and does not correlate with the ionization potential of the donors [13,20].

Non-polarized infrared transmission spectra of the single-crystal samples of the above complexes were recorded with a Perkin–Elmer 1725X spectrometer equipped with an IR microscope and narrow band MCT detector. The spectra were measured for the crystal confined to 0.1 mm in diameter. The crystals were mounted free-standing on a KBr plate and were placed in a temperature-controlled optical device made by Linkam; this system was used for the temperature range from 300 to ca. 450 K. Below the room temperature, down to 4 K the helium cryostat of Oxford Instruments was applied. Although the spectra have been recorded in the 650–5600 cm^{-1} range our interest is confined mainly to two C_{60} modes: $F_{1u}(3)$ at 1182 cm^{-1} and $F_{1u}(4)$ at 1429 cm^{-1}. A standard PEAKFIT program was used for computer separation and decomposition of the bands.

The calorimetric measurements of a small sample of $C_{60}(CS_2)_{0.4}$ were performed using an ac technique with a constantan electric heater and a Cu-constantan thermocouple mounted to the sample. The details of the methodology were similar to those described elsewhere [24].

3. Results and discussion

The Fourier transform IR transmission spectrum of $C_{60}(CS_2)_{0.4}$ clathrate is composed of strong F_{1u} bands of C_{60}, a relatively wide and very strong band of the enclathrated solvent CS_2, at 1509 cm^{-1} and tens of silent and combination modes. The activation of the latter modes points to a lowering of the symmetry of the C_{60} molecule in the clathrate as a result of interactions between the fullerene molecule and the carbon disulfide [11]. The $F_{1u}(3)$ and $F_{1u}(4)$ lines in the pure C_{60} crystal are symmetrical and narrow (the linewidth is ca. 3 cm^{-1}) at room temperature. In the clathrate they are strongly broadened and keep their Lorentzian form; the bandwidth of the $F_{1u}(4)$ line is 6 cm^{-1} (Fig. 1). These lines move towards lower frequency with an increase in temperature (Table 1). Lowering of the temperature leads to a subsequent splitting of the $F_{1u}(4)$ line. The splitting begins near 250 K (Fig. 2a), i.e. near the phase transition temperature [3,7]. At temperatures between 250 and 150 K the frequencies of the components are constant but the bandwidths seem to be weakly temperature dependent; at ca. 150 K they are 5 and 3 cm^{-1}, respectively. The band $F_{1u}(3)$ is insensitive to the temperature variation and for this reason its analysis is not referred to here. The band of CS_2 is only insignificantly broadened.

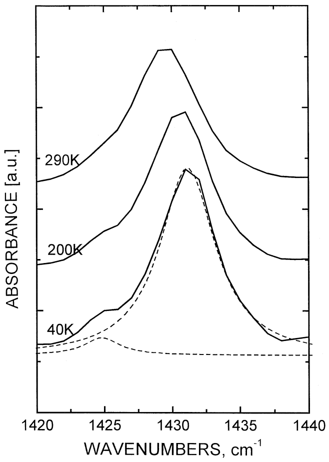

Fig. 1. Evolution of the $F_{1u}(4)$ line shape of the clathrate $C_{60}(CS_2)_{0.4}$. Dashed lines show components of the band at low temperature.

The spectrum of the DAN C_{60} $(C_6H_6)_3$ single crystal shows numerous, well-separated bands attributed to normal vibrations of the fullerene, the donor and the solvent. We will discuss a temperature evolution of the $F_{1u}(4)$ line, which is especially sensitive to the intermolecular interactions and rotational states of the C_{60} (Fig. 3). This line is broad and single at high temperatures (ca. 8 cm^{-1} at 410 K) and becomes trapezium-like at room temperature. For temperatures below 305 K the band can be decomposed into two gaussian lines. The positions of these lines are temperature dependent; at room temperature their maxima are located at 1425 and 1429 cm^{-1}. In Fig. 2b the temperature dependence of the frequency of the $F_{1u}(4)$ line decomposed into two components is shown. Similar anomalies are present for the linewidth. For the high temperatures (between 420 and 305 K) the single line is broad (ca. 8.3 cm^{-1}) and its linewidth is not temperature depen-

Table 1
The position of the $F_{1u}(3)$ and $F_{1u}(4)$ lines in wavenumber for selected temperatures

Compound	$F_{1u}(3)$ line frequency (cm^{-1}) at				$F_{1u}(4)$ line frequency (cm^{-1}) at			
	300 K	360 K	400 K	430 K	300 K	360 K	400 K	430 K
C_{60} $(CS_2)_{0.4}$	1182.5	1181.2	–	–	1429.1	1428.3	–	–
DAN C_{60} $(C_6H_6)_3$	1183.0	1182.4	1182.0	1181.8	1425.9	1426.7	1425.8	1425.6
					1430.0			
BNDY C_{60}	1182.7	1182.1	1181.6	1181.2	1428.4	1427.1	1426.7	1426.3
TCE C_{60}	1182.7	1182.0	1181.7	–	1429.8	1428.3	1427.9	–
$(BEDO)_2$ C_{60}	1182.7	1182.0	1181.5		1431.3	1429.0	1428.3	
$BTXC_{60}$ CS_2	1182.1	1181.9	1181.2	1180.8	1431.0	1431.0	1430.9	1430.4
					1428.0	1428.0	1425.9	1425.1
$(S_4N_4)_{0.8}C_{60}(C_6H_6)_{1.2}$	1182.6	1181.9	1181.4		1429.9	1428.7	1427.7	
(EDT–TTF) C_6 CS_2	1181.9	1181.2	1180.9	1180.3	1427.7	1426.1	1425.4	1424.8

dent. At ca. 310–300 K the linewidth drops down to 6.2 cm^{-1} and its further decrease with temperature is observed down to 80 K. At this temperature a jump from 4.2 to 5.3 cm^{-1} is observed; the latter value is preserved down to helium temperature. The second component does not show anomalies in the temperature region between 305 and 5 K. Both components of the $F_{1u}(4)$ line show a gaussian form down to 5 K. Similar anomalies were observed in both the intensity and integral intensity of the components of the investigated mode of the fullerene in the complex DAN C_{60} $(C_6H_6)_3$. In contrast to the distinct changes of the vibrations of the fullerene and insignificant deformations of the normal vibrations of the donor, the vibrations of the benzene are not disturbed. It

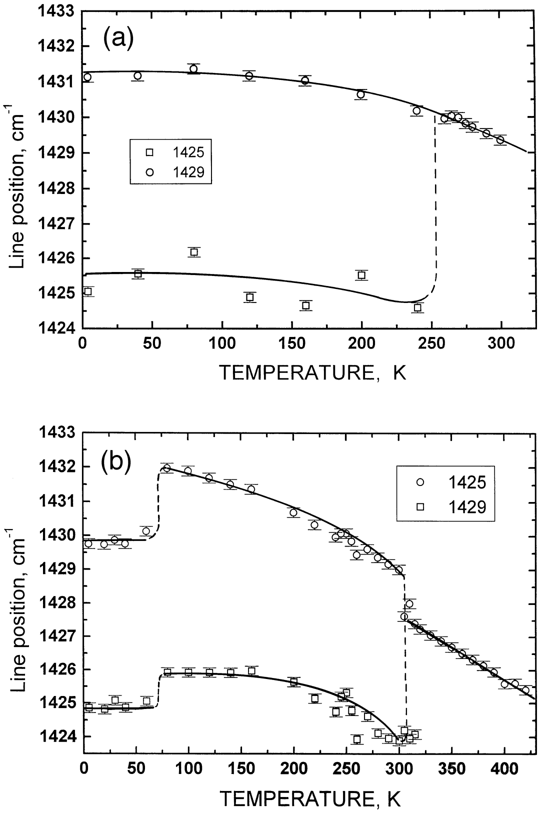

Fig. 2. Temperature dependences of the $F_{1u}(4)$ line frequency of the clathrate $C_{60}(CS_2)_{0.4}$ (a) and the complex DAN C_{60} $(C_6H_6)_3$ (b).

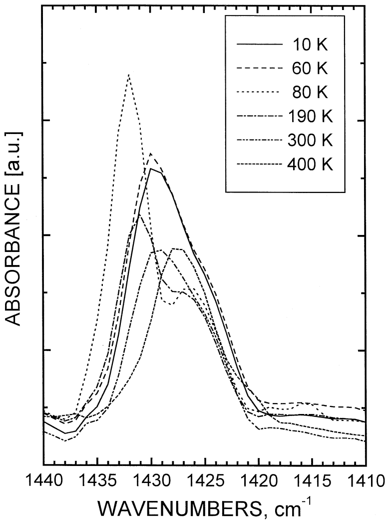

Fig. 3. Thermal evolution of the $F_{1u}(4)$ band of the complex DAN C_{60} $(C_6H_6)_3$; the shape of the band is shown for selected temperatures.

shows that the enclathrated solvent molecules interact very weakly with the fullerene sublattice and donor molecules.

The line splitting observed for the investigated complex at temperatures lower than $T = 305$ K is also given by the phase transition occurring in the fullerene sublattice which leads to suppressing of fullerene rotation, but the linewidth cannot be explained even qualitatively by dissipation processes within librational excitations. There are two differences in the temperature evolutions of the $F_{1u}(4)$ line in the investigated complex and in the C_{60} single crystal. Firstly, its linewidth decreases with a rate of 0.01 cm^{-1} K^{-1} in the complex but only with the rate of 0.003 cm^{-1} K^{-1} in the fullerite, below the phase transition temperature. Secondly, the linewidth of the $F_{1u}(4)$ line is considerable (ca. 8 cm^{-1}) and temperature independent in the complex but much smaller (ca. 2.8 cm^{-1} at $T = 260$ K) and T-dependent in the fullerite, above the critical temperature. In addition, the $F_{1u}(4)$ line of DAN C_{60} $(C_6H_6)_3$ shows the gaussian form in the whole temperature range. We suggest that the large and inhomogeneous broadening of the $F_{1u}(4)$ line can be provoked by structural orientational disorder, which has been detected in the investigated complex [15]. Thus, the strong temperature-dependence of the complex linewidth between 80 and 305 K can be explained as a contribution of two mechanisms: (1) activation of the libration states of the spherical C_{60} molecule and (2) dissipation of the vibrational energy of C_{60} for the donor and solvent molecules.

For an investigation of the influence of the donor–acceptor interactions or steric hindrances introduced by various donor molecules, we also studied the positions of the $F_{1u}(3)$ and $F_{1u}(4)$ modes of some supplementary complexes; the results are shown in Table 1. The data are limited to temperatures above room temperature because the orientational phase transition in the complexes of the fullerene usually occurs at $T > 300$ K. The band frequencies are imperceptibly lower at higher temperatures but there are frequency shifts of the order of 1–2 cm^{-1} for temperature range of 300–430 K. For BTX C_{60} CS_2, the band splitting is observed at room temperature. It seems also that the band frequencies are a little higher for strong complexes (e.g. for C_{60} complexes with BEDO or BTX).

In clathrates and complexes of the fullerene, the C_{60} molecules are in different surroundings and usually show different local symmetry to the pristine C_{60} solid. As was shown for the powdered samples in KBr pellets [10], the temperature of the phase transition can be shifted or the transition is suppressed in the above-mentioned compounds. If the steric factors hinder the transformation, the critical temperature is higher. It was shown for example for a solid fullerene epoxide ($C_{60}O$) [25]. $C_{60}O$ is orientationally disordered at room temperature but upon cooling, an orientational ordering transition at 278 K leads to a low temperature sc phase.

From our spectral study of the clathrate $C_{60}(CS_2)_{0.4}$ it is clear that the phase transition occurs between 250 and 260 K. This was confirmed by heat capacity measurements performed for a single crystal of mass ca. 10^{-6} g. This small crystal of $C_{60}(CS_2)_{0.4}$ clathrate undergoes the phase transition at 250 K (Fig. 4). For comparison, the heat capacity of the complex $(BEDT–TTF)_2$ C_{60} is also shown in the figure. The intermolecular interactions in this complex are so strong that the phase transition is suppressed; it corresponds with our observation that the steric hindrance nearly stops the rotation of the C_{60} at a temperature of ca. 300 K [10,26].

The spectral investigations of the fullerene complex with DAN show that the dynamics of C_{60} molecules in this compound are not the same as in the solid C_{60}. The fullerene sublattice of DAN C_{60} $(C_6H_6)_3$ undergoes an orientational phase transition at ca. 305 K; this transition revealed by $F_{1u}(4)$ mode

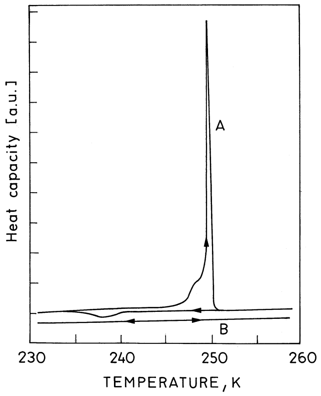

Fig. 4. Temperature dependences of the heat capacity for $C_{60}(CS_2)_{0.4}$ clathrate (A) and $(BEDT–TTF)_2$ C_{60} complex (B), measured for single crystals with a mass of the order of 10^{-6} g.

splitting and deep but narrow anomalies in the linewidth and integral intensities of both components: 1425 and 1429 cm^{-1}. The anomalies are also detected in the temperature dependence of the linewidth and integral intensities of some normal vibrations of the donor. A small anomaly in the IR band intensities was also detected at ca. 160 K. This anomaly is not clearly seen in the temperature dependencies of the $F_{1u}(4)$ mode but is clear for the normal vibration of the donor at 1474 and 1478 cm^{-1}. A similar anomaly has been detected in a single crystal of the fullerene by Shi et al. [27] and David et al. [8]. We suggest that the spectral anomaly at 160 K discovered by us could be attributed to the glass transition in the C_{60} sublattice of the DAN $C_{60}(C_6H_6)_3$ complex. It is also possible that the transition occurs in the donor sublattice. The spectral anomaly observed at ca. 75–80 K should be attributed to the freezing of the rotational motion of the C_{60} molecules. The process occurs progressively and this is why the IR changes are rather washed away, especially in the variation of the donor vibrations.

4. Conclusions

In conclusion, the investigated complexes can be divided into two groups taking into account the shape of the $F_{1u}(4)$ line of C_{60}. The complexes of the first group show a single narrow line. This shape of absorption line is typical for fullerene complexes in which the C_{60} molecules are highly symmetrical and rotate freely in the crystal lattice. The complexes of the second group show an unsymmetrical $F_{1u}(4)$ line at room temperature, which can be decomposed into two components at least. This line splitting remains for temperatures above 300 K. The split $F_{1u}(4)$ line testifies to the fact that the symmetry of C_{60} is lowered by the strong interaction between the donor and the fullerene. The line splitting for the complex DAN $C_{60}(C_6H_6)_3$ was observed at temperatures lower than 305–310 K and it was suggested that this effect is caused by the orientational-ordering phase transition. Other parameters of the $F_{1u}(4)$ line such as the linewidth, amplitude and integral intensity and the parameters of some normal vibrations of the donor (e.g. at 1478 cm^{-1}) show anomalies at phase transitions observed at ca. 80, 160 and 305 K.

The phase transition for the clathrate $C_{60}(CS_2)_{0.4}$ occurs at 250 K, nearly the same temperature as for the pure C_{60} single crystals. We assign these anomalies to the orientational-ordering phase transition typical for fullerites C_{60}.

Acknowledgements

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