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IR-Fourier Spectroscopic Studies of Structural Changes in Fullerenes C₆₀ and C₇₀-Toluene Systems

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Abstract—The C_{60} -toluene and C_{70} -toluene complexes were studied by IR–Fourier spectroscopy. The complexes were obtained by crystallization from a toluene solution at room temperature. The changes in the IR spectra caused by the deformation of toluene molecules in the complexes allowed us to study the phase transitions in the fullerene–aromatic solvent systems.

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INTRODUCTION

The arc method developed by P. Kretschmer and D. Huffman in 1990 afforded C_{60} and C_{70} in gram amounts and thus led to a new level of fullerene research. It is being actively developed, while remaining the most effective procedure compared with alternative methods. Isolation of fullerenes from soot, however, suggests using organic solvents. When crystallized from solutions, fullerene crystals readily adsorb various atomic and molecular impurities (solvent molecules, oxygen, and other gases), which markedly affect the physicochemical properties of fullerites. Fullerenes are occasionally bound with solvents, forming molecular complexes with polarization van der Waals interactions [1]. These complexes of fullerene with nonpolar molecules (also called mixed or van der Waals crystals) form an extensive class of fullerenes [2]. The clathrate and crystal solvate molecular complexes of fullerenes are extremely unstable in air, degrading within a few days after their removal from the mother solution [3]. On the other hand, they can be surprisingly stable, retaining the crystal structure of solvates for long periods of time (up to 8 years) [4]. Instability is generally exhibited by C_{60} crystal solvates (C_{70} was less studied in this respect).

Crystallization of C_{60} from a toluene solution [5] afforded crystal solvates of two types: $(C_{60} \cdot 2C_6H_5CH_3)$ I and $(C_{60} \cdot C_6H_5CH_3)$ II. Calorimetric studies revealed that crystal solvate I melted incongruently at 12°C, forming crystal solvate II and a saturated solution of C_{60} in toluene; crystal solvate II degraded at 48°C [6]. Storage of the solution at room temperature for 1 day, however, led to a disappearance of both peaks from the DSC curve (i.e., at room temperature, C_{60} and the saturated solution were equilibrium phases).

X-ray diffraction and electron microscopy studies [7] showed that fullerite C_{70} that crystallized from the toluene solution had a hexagonal close-packed (HCP) structure containing a substantial amount of residual solvent, which persisted even after prolonged annealing. At the same time, fullerite C_{70} obtained by vacuum sublimation contained no solvent and had a face-centered cubic (FCC) lattice with a ~21% admixture of the HCP phase. The relative volume of the HCP phase could be decreased by further heating. The cubic phase had a considerable concentration of packing defects in the [111] direction.

Slow evaporation of the solvent at room temperature gave a crystal solvate $C_{70} \cdot C_6H_5CH_3$ with an orthorhombic structure (space group *Pbca* (a = 21.075 Å, b = 32.990 Å, and c = 10.844 Å) [8]. The solvent removal and storage (250°C) of the sample under dynamic vacuum conditions for 1 week gave a mixture of polymorphic phases of C₇₀: FCC phase with $a \approx$ 15 Å and hexagonal phase with a = 10.2 Å and c =18.4 Å [7]. The X-ray diffraction studies of fullerite C_{70} containing no solvent [9] and crystallized from a toluene solution at 110°C also revealed an HCP structure (space group $P6_3/mmc$, a = 10.53(1) Å, c = 17.24(1) Å) with ~5% packing defects. A certain portion of the sample was assumed to be microcrystalline or amorphous. According to [9], the calculations and analysis of the XRD pattern of fullerite C70 obtained at room temperature indicated that the structure could not be described as a two-phase (HCP + FCC) one.

Crystallization of C_{70} from a toluene solution at 25–30°C gave a crystal solvate $C_{70} \cdot C_6H_5CH_3$. The *Amm2* orthorhombic structure (a = 1.086(2) nm, b = 1.055(6) nm, and c = 3.309(8) nm) was attributed by the authors directly to the pure FCC phase of C_{70} . Modification of the FCC lattice to *Amm2* was accompanied by volume expansion because of the intercalation of toluene molecules. The calculations based on the hard sphere packing principle allowed the authors to locate the toluene molecules in the lattice in the following way: the aromatic rings were perpendicular to the *b* axis and the methyl (CH₃) groups were orientated oppositely.

Studies of crystallization of C₇₀ from benzene, hexane, and toluene solutions [11] led the authors to conclude that the amount of the intercalated solvent depended on the rate of crystal growth (solvent evaporation). Fullerite C₇₀ obtained as a result of solvent removal on heating was considered to be a mixture of two phases: FCC (a = 14.93 Å) and HCP (a = 10.57 Å and c = 17.27 Å).

The removal of toluene corresponding to the endothermal peak at 430 K on the DSC curve was attributed [12] to the decomposition of the C_{70} -toluene crystal solvates. Two endothermal peaks (at 156 and 179°C) were recorded on the DSC curve in a thermal study [13] of the C_{70} -toluene system. According to XRD data, the authors supposed there were two crystal solvate structures of C_{70} - $C_6H_5CH_3$: orthorhombic *A* and monoclinic *B*.

Investigating a series of polycrystalline samples of C_{60} prepared by crystallization from toluene solutions by different methods, the authors of [14] concluded that (1) the solvent molecules were adsorbed on the microcrystal surfaces rather than incorporated in the crystal lattice of C_{60} and (2) the "sealing" of microcrystals on heating explained why a certain number of solvent molecules were trapped by the sample. The second conclusion was drawn in view of the fact that the solvent could be completely removed only by sublimation.

To remove the residual solvent, fullerite is subjected to prolonged annealing in dynamic vacuum or to sublimation. As a result of annealing, the solvent can be "sealed" in the crystal lattice of C_{60} [15]. After this, its removal becomes still more difficult in view of the fact that heating fullerite above 150–200°C can lead to its oxidation. Fullerite always contains molecular oxygen intercalated in its octa- and tetrapores. According to ¹³C NMR estimations, molecular oxygen occupies around 1% voids of the crystal lattice of C_{60} under normal conditions [16]. Thus certification of samples is important for unambiguous evaluation of experimental data in studies of fullerenes.

X-ray diffraction and thermal analysis are traditionally the main structural methods for investigating crystal solvates. Infrared spectroscopy is mainly used for sample identification. Nevertheless, vibrational spectroscopy allows the observation of changes in symmetry and electron density distribution, determination of the character of interactions between molecules, etc. There are few studies in which IR spectroscopy was used for investigating crystal solvates. The authors of [17] found that the planar aromatic molecules intercalated in the crystal lattice of spheroidal C₆₀ and C₇₀ experienced deformation. In IR studies of the charge transfer complexes (CTCs) of fullerenes with some planar donors [18, 19], approximate relations were obtained for evaluating the low degree of charge transfer ($0 < \delta < 1$) in C260 and C₇₀ CTCs. The force constants of bonds were shown to depend on the electron density on the molecule, and the charge transfer was correlated with the linear shifts of the main vibrational modes 1429 cm^{-1} (C₆₀) and $1430 \text{ cm}^{-1} (\text{C}_{70}).$

The goal of this work was to study the character of interactions of fullerene and toluene molecules in the samples obtained by crystallization of fullerenes C_{60} and C_{70} from toluene solutions at room temperature by IR spectroscopy.

EXPERIMENTAL

The C₆₀ (99.95 wt %) and C₇₀ (98 wt %) powder samples obtained at the Institute of Organometal Chemistry, Russian Academy of Sciences, and ZAO Fullerene Center (Nizhni Novgorod) and recrystallized at room temperature for 1 day from a C₆H₅CH₃ solution ("os.ch." (extrapure) grade) were used.

The fullerites were annealed in air in series: (1) at 50-350°C with step of 50 K and storage for 2 h at each temperature for pelletized KBr samples and (2) at 160, 250, and 350°C with 15 min storage for powders in closed corundum crucibles. The IR spectral studies of both series of samples were performed on an FSM 1202 IR-Fourier spectrometer at a resolution of 1 cm⁻¹ (14 scans). KBr pellets were prepared (in a ratio of 1:250) for IR spectrum recording. X-ray diffraction patterns of fullerite powder samples were simultaneously recorded for the second series of annealings. The structural phase state and the composition of the samples were analyzed by XRD and differential scanning calorimetry (DSC). The XRD patterns were obtained on a Bruker D8 Advance θ/θ diffractometer in parallel beam geometry (parabolic Goebel mirror, CuK_{α} radiation). The X-ray beam was monochromated with a Sol-XE Si(Li) solid detector. The DSC studies were performed on a Diamond DSC (Perkin-Elmer) instrument in Al crucibles at a rate of 40 K/min in an argon flow for \sim 2 mg samples.

DISCUSSION OF RESULTS

The fullerite C_{60} and C_{70} samples were obtained by crystallization form a toluene solution at room temperature. Both samples contained toluene, as confirmed by IR spectroscopy (Fig. 1). The C_{60} crystal solvates, however, were unstable at room temperature,



Fig. 1. IR spectra of the starting C_{60} and C_{70} crystallized from a toluene solution at room temperature.



Fig. 2. DSC curves of the C₆₀ and C₇₀ samples crystallized from a toluene solution; the heating rate was 40 K/min.

the residual toluene remaining in small amounts in intercrystallite voids. At the same time, fullerite C_{70} under these conditions was a completely solvated crystal with a high content of the solvent. According to our estimates (IR spectroscopy,¹ the toluene content was ~1.5 wt % in C_{70} and ~0.1 wt % in C_{60} . The crystal structure of the $C_{70} \cdot C_6H_5CH_3$ complex was layered, with fullerene spheres lying in deformed hexagonal layers and with solvent molecules lying in the trigonal prismatic voids between layers [5]. The positions of the absorption bands of toluene (~690 and ~725 cm⁻¹) in the spectrum of fullerite C_{60} differ from those for C_{70} (Fig. 1). Some part of toluene is not involved in the crystal solvate (see below).

Figure 2 shows the thermograms of fullerites C_{60} and C_{70} obtained at a heating rate of 40 K/min in the range 50–200°C. The DSC curve of the C_{70} crystal solvate contains an endothermal peak, starting at ~160 and ending at ~185°C and corresponding to disintegration of the crystal solvate. The basic endothermal decomposition of the orthorhombic crystal solvate $C_{70} \cdot C_6H_5CH_3$ can overlap with the endothermal excess solvent desorption and exothermal oxidation.

Let us consider the XRD data of the C_{70} crystal solvate sample after heating it in air for 15 min (Fig. 3). The starting fullerite C_{70} (after crystallization from a toluene solution) is orthorhombic crystal solvate. After heating to 160°C followed by cooling to room temper-

¹ The reference sample was fullerite with 1.1 wt% residual toluene (according to TGA data obtained by E.V. Skokan, Moscow State University).



Fig. 3. X-ray diffraction patterns of (1) the starting $C_{70}-C_6H_5CH_3$ complex and (2–4) the same complex after heating at (2) 160, (3) 250, and (4) 350°C for 15 min in air. X-ray diffraction diagrams of $C_{70} \cdot C_6H_5CH_3$ [10]; HCP C_{70} no. 00-048-1206 and FCC C_{70} no. 00-055-1908 (PDF-2 database, ICDD).

ature before diffractometry, the sample was evidently a two-phase mixture of the orthorhombic (crystal solvate crystallized again at room temperature) and HCP phases. After heating to 250°C and then to 350°C, the structure of fullerite corresponded to the HCP phase of C_{70} . It was impossible to evaluate the small amount of the FCC phase because the main peaks of both phases coincided (Fig. 3). According to the IR data, toluene was removed from the corresponding fullerite C_{70} samples above 250°C, and insignificant oxidation (epoxide absorption band at 1017 cm⁻¹), forming a C–O–C bond, was observed after heating at 350°C for 15 min.

To examine the peculiarities of structure and intermolecular interactions in the C_{70} -toluene complex, we analyzed the IR spectrum of fullerite C_{70} . The formation of molecular complexes of fullerenes with organic solvent molecules leads to electron density redistribution from donor to fullerene and lowers the symmetry of the fullerene molecule, which is reflected in the IR spectrum as a shift of the fundamental absorption bands and the appearance of additional (symmetry-forbidden) bands. It is impossible to evaluate the degree of charge transfer from the shift of the $T_{1u}(4)$ mode which is most sensitive to electron density transfer in this case because the absorption band of the $T_{1\nu}(4)$ mode (1430 cm⁻¹) is split as a result of the formation of the $C_{70}-C_6H_5CH_3$ complex (Fig. 4a). The low-frequency shoulder owes its origin to frozen rotation of C_{70} molecules in the complex because of the interactions of fullerene and toluene molecules. The planar toluene molecule is orientated in parallel to the hexagons of C₇₀ molecules, hindering their rotation. Moreover, the half-width and position of absorption bands in the IR spectra are affected by the lowering of symmetry because of the disordering of C₇₀ in the solvate phase and the distortion of the molecular shape of C_{70} in its interaction with the solvent molecule. The charge transfer is very weak and hindered by unfavorable steric factors. The large planar donor molecule cannot be accommodated at a close distance in parallel to the planes of the penta- and hexagons of spheric C_{70} molecules.

To study the behavior of toluene molecules in fullerite during annealings below 350°C, we recorded the absorption spectra of the samples annealed directly in KBr pellets. Annealing in KBr pellets precludes the diffusion of oxygen to fullerite, and insignificant oxidation of fullerite occurs only due to the starting intercalated oxygen. In this case, toluene molecules can be observed in both fullerite crystals and intercrystallite voids. Figure 4b shows the fragments of the IR spectra (wavenumbers 700–750 cm⁻¹) of fullerite C₇₀ samples crystallized at room temperature from toluene solution and annealed in air. Despite the weak charge transfer in the complex, the low-frequency shift of the absorption bands corresponding to the C-H symmetric deformation vibrations of the aromatic ring $(\delta_{s}(C-H))$ is quite significant $(729 \rightarrow 723 \text{ cm}^{-1})$; 729 cm^{-1} is the position of the absorption band in the IR spectrum of toluene compacted with KBr (Fig. 4b)). Note that some part of toluene lies outside the crystal solvate, as indicated by the shoulder of the \sim 727 cm⁻¹ band on the side with large wavenumbers.

The electrostatic interaction, whose energy depends on the distance between the donor and acceptor molecules, is mainly determined by the dispersion component. For most effective interaction, the donor molecule should approach the fullerene molecule as closely as possible, adjusting itself to the spherical shape of the latter. This can be attained only as a result of the geometrical distortions of the donor molecule. Consequently, during complexation, the donor molecule adopts a new conformation (other than planar for the toluene molecule) that ensures its maximum approach to fullerene. The inevitable deformation of



Fig. 4. Fragments of the IR spectra of (a, b) C_{70} and (c, d) C_{60} crystallized at room temperature (1) from a toluene solution and (2–6) annealed in air at (2) 150, (3) 200, (4) 250, (5) 300, and (6) 350°C; (7) KBr + toluene.

toluene molecules is reflected in a shift of the IR absorption bands. The annealing of the C_{70} crystal solvate at 150°C led to a more distinct high-frequency shoulder at 725 cm⁻¹, while the annealing at 200°C resulted in a splitting of the absorption band (725 + 727 cm⁻¹); at higher temperatures, the absorption band shifted toward higher frequencies and became weaker (Fig. 4b). The latter was probably caused by the liberation of toluene molecules from fullerite and evaporation of "free" toluene from the KBr pellet. The abrupt shift of the absorption band of toluene suggests that the crystal solvate decomposed in the range 150–200°C. This agrees with the DSC data (Fig. 2) and allows the recording of the $C_{70}-C_6H_5$ complex by IR spectroscopy.

Note that grinding the C_{70} crystal solvate in a mortar for ~5 min led to a shift of the IR absorption band of toluene from 723 to 725 cm⁻¹ because of the disintegration of the crystal solvate, resulting in weaker interactions between toluene and fullerene molecules. A similar shift was recorded after annealing the crystal solvate in a KBr matrix for 2 h (at ~150°C). This suggested that the C_{70} - $C_6H_5CH_3$ complex was transformed from solid solvate to clathrate state.

Let us consider changes in fullerite C_{60} crystallized from a toluene solution after annealings below 350°C. The DSC curve of fullerite C_{60} (Fig. 2) did not exhibit any significant thermal effects, which confirms the known fact of the decomposition of the $C_{60}-C_6H_5CH_3$ crystal solvate after the evaporation of the mother solution [6]. Let us consider the diffraction patterns of fullerite C₆₀ crystallized at room temperature after heating for 15 min in air at 160, 250, and 350°C (Fig. 5). Since the high-temperature (desolvation temperature 48°C) monoclinic $C_{60} \cdot C_6H_5CH_3$ crystal solvate can only exist in a mother solution, the diffraction pattern of the starting sample reflected the FCC phase of fullerite C_{60} and the distortions caused by the weak peaks of the HCP phase. As is known [20], the XRD patterns of FCC-fullerite C₆₀ show distortions in the form of a low-angle shoulder on the (111) line, the complex profile of the (311) line, and broadenings explained by the presence of the unstable (relative to FCC) HCP phase in the form of two-layer inclusions (packing defects) in the three-layer FCC structure.

Thus, toluene can exist in the structure of fullerite C_{60} in a certain amount "sealed" in the intercrystallite voids. The amount of toluene, as well as the degree of packing disordering, depends on the crystallization conditions. According to IR spectral data, after heating fullerite C_{60} samples in air for 15 min, trace amounts of toluene persisted up to 350°C, while the



Fig. 5. X-Ray diffraction patterns of (1) the starting $C_{60}-C_6H_5CH_3$ complex and (2–4) the same complex after heating at (2) 160, (3) 250, and (4) 350°C in air for 15 min. X-ray diffraction diagrams: FCC C_{60} no. 00-044-0558 and HCP C_{60} no. 00-047-0787 (PDF-2 database, ICDD). The arrows show the reflections of the HCP phase.

oxidation that formed C–O–C bonds (absorption bands at 550, 849, and 1032 cm^{-1}) in the epoxides and dimers was insignificant and observed only after heating at 350°C.

The degree of charge transfer from toluene to C_{60} molecule was evaluated from the shift of the $T_{1u}(4)$ mode (which is most sensitive to the electron density transfer) in the IR spectrum of the starting sample (Fig. 4c). The shift of the 1429 cm⁻¹ absorption band shows nearly linear dependence on the degree of charge transfer [1] and was ~1 cm⁻¹ in our case; thus the degree of charge transfer is $\delta < 0.03$. The accuracy of the charge transfer estimate depends on the accuracy of the experimental positions of absorption bands in the IR spectra (±0.1 cm⁻¹). This estimate ($\delta < 0.03$) characterizes the C_{60} – C_6 H₅CH₃ sample as a molecular complex with van der Waals interactions.

Let us consider changes in the positions of the IR bands of toluene (Fig. 4d) of the samples annealed in the KBr matrix (at $50-350^{\circ}$ C for 2 h). As in the case of C_{70} , the absorption band $\delta_s(C-H)$ in the spectrum of the starting sample shifted toward low wavenumbers $729 \rightarrow 725$ cm⁻¹. The shift can be attributed to the deformation of the planar toluene molecules localized on the boundaries of microcrystals. In the course of the annealing, residual toluene was slowly liberated from fullerite. Changes in the positions of the bands could be visualized only after annealing at 300°C (727 cm^{-1}) and reached maximum $(727 \text{ and } 730 \text{ cm}^{-1})$ at 350°C, considerably weakening, which points to the sequential liberation of toluene from fullerite and KBr pellet. The 725 cm⁻¹ band of toluene shifted slowly as the annealing temperature increased, which suggests the absence of desolvation and agrees well with the DSC data. The band position changed only below 300° C in contrast to the $C_{70} \cdot C_6H_5$ CH₃ crystal solvate, for which the IR band position changed already after annealing at 150°C. This is direct evidence that toluene is not present in the crystal solvate (which decomposes at lower temperatures) and its removal is hindered (in agreement with the conclusions of [14, 15] about toluene "sealing" on the boundaries of crystallites during annealing and possible complete removal of residual toluene only during sublimation).

To summarize, the $C_{70} \cdot C_6H_5CH_3$ crystal solvate and fullerite C_{60} intercalated with toluene obtained by crystallization at room temperature were studied by IR spectroscopy. The differences in the positions of the absorption bands of the aromatic solvent in the IR spectra of C_{60} and C_{70} after annealing at 50–350°C were caused by the deformation of toluene molecules in fullerene complexes. The interactions of fullerene and toluene molecules and the structural changes in the C_{60} – $C_6H_5CH_3$ and C_{70} – $C_6H_5CH_3$ systems can be characterized by the shifts of the 1429 cm⁻¹ (C_{60} and C_{70}) and 725 cm⁻¹ ($C_6H_5CH_3$) absorption bands. Along with differential scanning calorimetry and X-ray diffraction, IR spectroscopy can thus be used for studies of phase transitions in fullerene–aromatic solvent systems.

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