Spectroscopy of C_{60} and C_{70} Complexes.

Dmitry V. Konarev, Natalia V. Drichko[1], Viktor N. Semkin[1],
Yury M. Shul`ga, Andrzej Graja[2] , Rimma N. Lyubovskaya*.

Institute of Chemical Physics RAS, Chernogolovka, 142432,Russia.
[1] *Ioffe Physical-Technical Institute RAS, St.Peterburg, 194021 ,Russia.*
[2] *Institute of Molecular Physics PAN, Poznan, 60-179 , Poland.*

Abstract. Complexes of C_{60} and C_{70} fullerenes with organic donors were studied by IR-, UV-VIS-NIR- and X-ray photoelectron spectroscopies. The IR spectra of single crystals of some complexes show the $F_{1u}(4)$ C_{60} mode splitting into two components which is attributed to the freezing of the rotation of C_{60} molecule in the coordination with donors. The degree of charge transfer (CT) on C_{60} molecule estimated from the shift of the frequency of the $F_{1u}(4)$ unsplit band shows only weak CT in the complexes. The UV-VIS-NIR- spectra of some complexes show the presence of weak CT bands. A linear dependence of CT absorption energy on vertical ionization potentials of the donors was obtained for C_{60} complexes with tetrathiafulvalenes in solid state. The XP-spectra of the complexes show the changes in the energies of S2p, N1s, Te3d peaks of donors by 0.1-1.6 eV with respect to individual ones.

Introduction. Fullerenes as electron acceptors form compounds varying from molecular complexes [1-3] to ion-radical salts [4] analogously to planar π-acceptors such as tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ). Due to a spherical shape, large size, high symmetry and polarizability [5] of fullerene molecules donor-acceptor complexes of fullerene have some peculiarities: charge transfer from initially planar donors to spherical C_{60} molecules [5], the I_h symmetry breaking [6,7] and the freezing of the rotation of C_{60} molecules in their coordination with donors [7] . In this paper we present some results of IR-, UV-VIS-NIR- and X-ray photoelectron spectroscopic studies of these peculiarities of the fullerene complexes.

Experimental. Complexes of C_{60} and C_{70} fullerenes were obtained by evaporation of fullerenes and donors solutions in carbon disulfide, benzene or pyridine (Py) under argon. The composition of the complexes was determined by elemental, thermogravimetric and X-ray analyses [2,3,8,9].
The IR transmission spectra of single crystals were measured at room temperature by using a FT-IR Perkin-Elmer 1725X spectrometer equipped with a microscope (2 cm^{-1} resolution). KBr pellets were prepared with concentration of complexes 1:2000. UV-VIS-NIR absorption spectra were measured with a Lambda 19 Perkin Elmer UV-VIS-NIR spectrometer at room temperature in KBr pellets with concentration of complexes 1:4000 within 220 -2000 nm range. The CT bands were obtained in 600- 1300 nm range by the subtraction of a normalized spectrum of individual fullerene from that of the complexes. This procedure was possible due to the absence of donors absorption bands in this spectral range. XP -spectra were recorded on a VIEE-15 instrument and were calibrated against the C1s peak (285.0 eV). The spectral data for the complexes are presented in Table.

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Table. The frequencies of the $F_{1u}(4)$ C_{60} mode in the IR spectra of the complexes (single crystals and KBr pellets*), the position of the CT bands in the UV- VIS-NIR-spectra and the shift the binding energy of donor heteroatoms in XP-spectra of the complexes relatively to the individual donors.

N	Complex	Frequency of $F_{1u}(4)$, cm^{-1}		CT band, nm	Energy shift, eV
	C_{60} 250K[6]	1427.5	1430.5	-	-
	293K[6]	1429.4			
1	$BTX \cdot C_{60} \cdot CS_2$	1428	1432	620	(Te) 0.4
2	$BTX \cdot C_{60}$	1427		620	-
3	$DBTTF \cdot C_{60} \cdot C_6H_6$	1430*^{1}		735	(S) 0.3
4	$DBTTF \cdot C_{60} \cdot Py$	1430*^{1}		750	(S) 0.1
5	$(BEDT\text{-}TTF)_2C_{60}\,(Py)_2$	1428		820	
6	$DPhTTF \cdot C_{60} \cdot C_6H_6$	1428*		895	(S) 0.0
7	$(TMDTDM\text{-}TTF)_2C_{60}(CS_2)_3$	1429*^{1}		900	(S) 0.1
8	$(EDT\text{-}TTF)_2C_{60} \cdot CS_2$	1427		900	(S) 0.1
9	$BEDO\text{-}TTF \cdot C_{60} \cdot C_6H_6$	1429		900	-
10	$EDT\text{-}TTF \cdot C_{60} \cdot C_6H_6$	1428*		920	(S) 0.1
11	$(DMDPhTTF)_2C_{60} \cdot C_6H_6$	1429*		940	(S) 0.1
12	$EDY\text{-}BEDT\text{-}DT \cdot C_{60} \cdot C_6H_6$	1428*		935	(S) 0.4
13	$OMTTF \cdot C_{60} \cdot Py$	1428*		980	-
14	$OMTTF \cdot C_{60} \cdot C_6H_6$	1428		1040	-
15	$TPDP(C_{60})_2(CS_2)_4$	1428*		1240	-
16	$(BEDO\text{-}TTF)_2C_{60}$	1428.5	1432	-	(S) 0.7
17	$BNDY \cdot C_{60}$	1429		-	(S) 0.4
18	$(S_4N_4)_{0.8}C_{60}(C_6H_6)_{1.2}$	1430		-	(S) 0.3 (N) 1.6
19	$TPC \cdot C_{60}$	1425	1431	-	-
20	$DAN \cdot C_{60}(C_6H_6)_3$	1426	1430	-	-
21	$BEDT\text{-}TTF \cdot C_{70}\,CS_2$	1428(C_{70})		860	-
22	$(DMDPhTTF)_2C_{70} \cdot C_6H_6$	1430(C_{70})*		1000	-

^{1}-A superposition of the $F_{1u}(4)$ C_{60} mode and the donor absorption band.

Abbreviations for donors: BTX - 9,9′-trans-bis(telluraxantenyle); DBTTF - dibenzotetrathiafulvalene (TTF); BEDT-TTF - bis(ethylenedithio)-TTF; DPhTTF - trans-4,4′-diphenyl -TTF; TMDTDM-TTF - tetramethylenedithio-4,5-dimethyl-TTF; EDT-TTF - ethylenedithio-TTF; BEDO-TTF - bis(ethylenedioxo)-TTF; DMDPh-TTF-trans-4,4′-dimethyl-5,5′-diphenyl-TTF; EDY-BEDT-DT- 2,2′-ethanediilidene -bis(4,5-ethylene-1,3-dithiol); OMTTF-octamethylene-TTF; BNDY-binaphto[1,6-d,e]-1,3-ditiin-2-ylidene; TPDP-3,3′,5,5′-tetraphenyldipyranylidene; S_4N_4- tetrasulfur tetranitride; TPC - triptycene; DAN – dianthracene.

Results and discussion. IR spectroscopy was used in the studies of the changes in symmetry and electron densities of donor and acceptor molecules in a complex formation. C_{60} molecule has the four IR active threefold degenerated F_{1u} modes [6,11], the $F_{1u}(4)$ mode at 1429cm^{-1} being the most sensitive to the changes in charge [10] and symmetry [6,11] of C_{60} molecule. Thus only the changes in the $F_{1u}(4)$ mode were considered. It is known [6] that in C_{60} crystals molecules nearly free rotate at room temperature and occupy the sites with T_h symmetry. At $T<260K$ the orientational-ordering phase transition is realized in crystals and only "ratchet" rotation of C_{60} becomes possible, the molecular symmetry of C_{60} being lowered to S_6 one. This results in the double [6] or triple [11] splitting of the $F_{1u}(4)$ mode.

The absorption bands corresponding to the $F_{1u}(4)$ C_{60} mode in the complexes are presented in Fig.1. Donors have no substantial absorption in this range. For the first group of complexes (1a-4a) the $F_{1u}(4)$ band is split into two components. These split bands were fitted by a sum of two Lorentzians with nearly the same bandwidths (~6 cm^{-1}) whose position are given in

Table. The observation of only two components for the threefold degenerated mode can be explained by large bandwidths (~6 cm^{-1}) and a comparatively low resolution of the experiment. The similar splitting of the $F_{1u}(4)$ mode into 3 components at room temperature was also observed in C_{60} complexes with amines [7]. We attributed this effect to the freezing of the rotation of C_{60} molecules at their coordination with donors analogously to the phase transition in C_{60} crystals at T<260K. The absence of free rotation of C_{60} molecules in $DAN{\cdot}C_{60}{\cdot}(C_6H_6)_3$ and $BTX{\cdot}C_{60}{\cdot}CS_2$ complexes at room temperature was confirmed by the data of X-ray analysis [2,12]. The freezing of the rotation lowers the C_{60} symmetry in the complexes relatively to that in C_{60} crystals at T>260K and results in the splitting of the $F_{1u}(4)$ mode. For the second group of complexes (1b-4b) the $F_{1u}(4)$ mode remains unsplit indicating free rotation of C_{60} molecules in these complexes at room temperature.

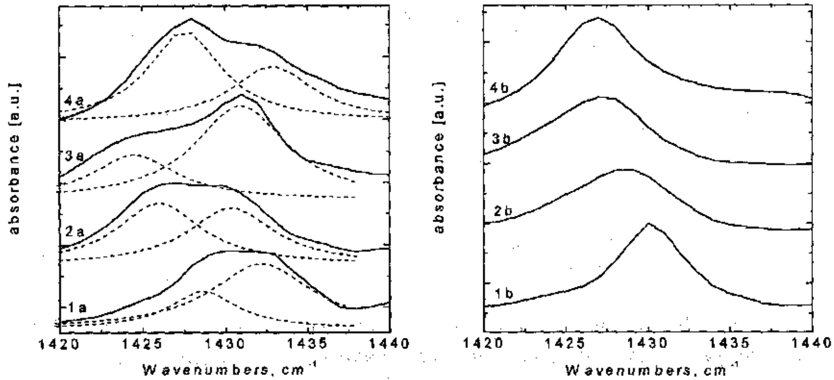

FIGURE 1. IR specrta of single crystals of the complexes in 1420-1440 cm^{-1} range at room temperature:
1a- $(BEDO)_2C_{60}$; 2a- $DAN{\cdot}C_{60}{\cdot}(C_6H_6)_3$; 3a- $TPC{\cdot}C_{60}$; 4a- $BTX{\cdot}C_{60}{\cdot}CS_2$
1b- $(S_4N_4)_{0.8}\,C_{60}\,(C_6H_6)_{1.2}$; 2b- $BNDY{\cdot}C_{60}$; 3b-$(EDT\text{-}TTF)_2C_{60}{\cdot}CS_2$; 4b- $BTX{\cdot}C_{60}$

The dependence of the position of the unsplit $F_{1u}(4)$ mode on the degree of C_{60} reduction is almost linear [10]. The following relationship for the estimation of the CT degree (δ) on C_{60} molecule is derived from this dependence [5] : $\delta \cong 0.03\ \Delta\nu$, where $\Delta\nu$ is the shift of the $F_{1u}(4)$ mode position in the complexes (Table) relatively to that in individual C_{60}. The maximal shifts do not exceed 2 cm^{-1} and are within the experimental accuracy. The values of δ estimated from this relationship are close to zero for all complexes (δ<0.05). Thus the compounds obtained are neutral complexes in a ground state.

UV-VIS-NIR spectroscopy shows the presence of CT bands of weak intensity in 600-1300 nm range in some complexes. The CT absorption energy ($h\nu_{CT}$) in neutral complexes is defined by $h\nu_{CT} = I_P^v - E_A^v - E_c$, where E_A^v is electron affinity of the acceptor, I_P^v is vertical ionization potentials of the donor and E_c is the energy of electrostatic interaction in excited ionic state. Therefore for one acceptor with a series of donors the $h\nu_{CT}$ values depend linearly on donor I_P^v. It is seen in Fig.2 (circles) that this dependence for C_{60} complexes with OMTTF, BEDO-TTF, BEDT-TTF and DBTTF donors (I_p^v - 6.30, 6.46, 6.70, 6.81 eV, respectively [13]) is really quite linear and is approximated by $h\nu_{CT} = 0.82\ I_p^v - 3.93$. This dependence enables the estimation of I_P^v values for other donors from the $h\nu_{CT}$ values in C_{60} complexes (Fig.2, crosses). The $h\nu_{CT}$ values for C_{70} complexes (Fig.2, stars) are ~0.08 eV lower than those for C_{60} ones with identical donors.

For the donors with equal I_P^V the $h\nu_{CT}$ values are ~0.6 eV higher in C_{60} complexes in solid state than those in TCNE ones [14]. This fact can be explained by two reasons. C_{60} is a weaker acceptor than TCNE. The E_c values in complexes depend on the distances between ions in excited state therefore the delocalization of the radical anion charge over a large C_{60} sphere results in the decrease of E_c values in C_{60} complexes relatively to TCNE ones.

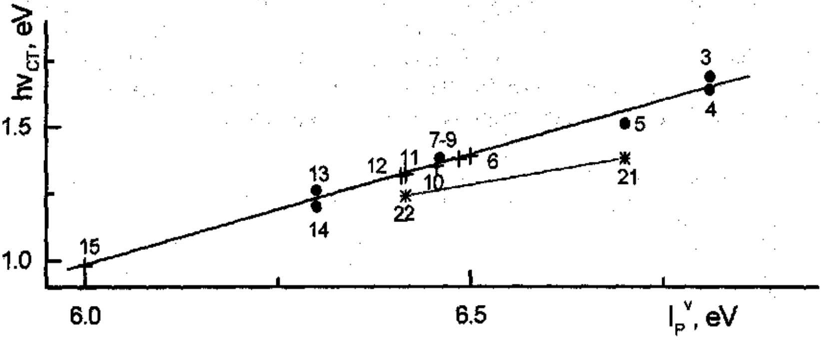

FIGURE 2. The dependence of $h\nu_{CT}$ vs. I_p^V of the donors for C_{60} and C_{70} complexes (the numeration of the complexes is given according to Table).

XP-spectroscopy shows that the energy of S2p, N1s, Te3d peaks of the donors changes by 0.1-1.6 eV relatively to the individual ones. These shifts can be caused not only by CT from the donor to C_{60} but the calibration against the C1s peak since the position of this peak can be different for the donor and the corresponding complex.

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