Investigation of the Electronic Structure of $C_{60}F_{24}$

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The quantum-chemical investigation of $C_{60}F_{24}$ isomers has been carried out by PM3 method. The structures with the various degree of delocalization of carbon π-system have been considered. The theoretical F Kα and C Kα X-ray spectra have been calculated for each isomer and compared with the experimental X-ray spectra of $C_{60}F_{24}$. Satisfactory agreement between the experiment and theory is observed for the isomers, possessing fluorine atoms, situated by the belt around the C_{60} molecule. The structure of the chemical bond in these isomers has been investigated in terms of the fragment analysis. The data of the calculations, considered the charge distribution in $C_{60}F_{24}$ isomers, permitted the successful interpretation of the X-ray photoelectron spectroscopy data. A comparison of IR spectra for $C_{60}F_{24}$ and fluorographite C_2F has demonstrated the similarity of the structure of the chemical bonds in these compounds.

Introduction

The fluorofullerenes are one of the most interesting and curious objects of the fullerene chemistry. The synthesis of these compounds was directly connected with the hope to obtain the unique lubricants and dielectrics, being analogous to the teflons and even better than they are. But unfortunately, the fluorofullerenes have been found to be able to react with nucleophilic agents without any problems.[1]

The direct synthesis of fluorofullerenes by the interaction between C_{60} and fluorinating agent (F_2, XeF_2, BrF_3, BrF_5, etc.) leads to the substance $C_{60}F_x$, being the mixture of fluorofullerenes with the various value of x, as a rule, more than 30.[2] The stepwise synthesis of fluorofullerenes via the intermediate bromation of fullerene led us to obtain the compound with $C_{60}F_{24}$ composition.[3] The stoichiometry of that compound has been confirmed by X-ray photoelectron spectroscopy, using the intensity ratio for C 1s and F 1s bands. The diffraction lines and bands of IR absorption for this fluorofullerene were found to be broadened, indicating the presence of either polymeric forms or structural isomers.

The considered compound was investigated also by the mass spectrometry of positive ions under the thermal activation and ionization by electron impact. No $C_{60}F_{24}^+$ ions have been detected, but their destruction products, C_{60}^+, HF^+, $C_{60}O^+$, etc., have been found. The study of the products of the interaction between the fullerene C_{60} vapor and fluorine[4] also revealed the absence of the compound with $x = 24$ in the obtained spectrum of $C_{60}F_x$. These peculiarities of the physicochemical behavior of $C_{60}F_{24}$ initiated the necessity of further investigation of the chemical and electronic structure of that compound.

The study of the structure of fluorofullerenes $C_{60}F$ and $C_{60}F_2$ has been made by methods of the molecular mechanics.[5,6] A number of quantum-chemical articles, devoted to the investigation of the stability and structure of $C_{60}F_2$ isomers by the semiempirical AM1 method, are known.[7,8] These data show the product of the addition of F_2 to C_{60} to be a mixture of isomers, corresponding to 1,2- and 1,4- addition. The ortho isomer was found to be more stable. The structures and stabilities of 94 isomers of $C_{60}F_{48}$, possessing at least a 3-fold axis, have been calculated using the AM1 method.[9] The structures were shown to be preferable if the double bonds are separated from each other as much as possible. The complete review of the calculations of electronic structure for $C_{60}F_{60}$ by various methods was made in a monograph.[10]

The methods of X-ray and X-ray photoelectron spectroscopy are experimental ones, providing the possibility to investigate the electronic structure of a material and being directly comparable with the results of quantum-chemical calculation. The X-ray emission spectra provide information about the distribution of the electron density of carbon, fluorine etc. in the valence levels of the molecules and solids. The comparison of the spectra with the data of the calculation can be considered as the test on the applicability of the concrete quantum-chemical method to the investigated objects. From the other side, the quantum-chemical modeling itself can explain the many peculiarities existing in the X-ray spectra of the real samples. Recently, the approach, including the complex application of quantum-chemical and X-ray emission methods, was used by us for the investigation of the electronic structure of C_6F_6[11] and C_{60}[12] molecules and stoichiometrical $CF_{1.00}$[13] and superstoichiometrical $CF_{1.33}$[14] polyfluorocarbons.

The results of the quantum-chemical calculation by semiempirical MNDO method for one of $C_{60}F_{24}$ isomers, corresponding to the well-determined structure of $C_{60}Br_{24}$,[15] were presented in ref 3. The substitution of bromine atoms in bromofullerene with fluorine ones was hoped to occur without changes in the symmetry and structure of halogen-substituted fullerene. But the theoretical X-ray spectra of this isomer were found to be in disagreement with the experimental data. So the real structure of the obtained compound was concluded to differ from the calculated one.

The purpose of the present work consists of the modeling of the structure of $C_{60}F_{24}$ isomers by quantum-chemical calculation and in the establishing of the most probable structure of fluorofullerene $C_{60}F_{24}$ by the comparison of theoretical and experimental spectra.

Experimental Section

The compound with the composition $C_{60}F_{24}$ was synthesized at the room temperature by the reaction of BrF_3 vapor with C_{60} fullerene, dissolved in Br_2. The structure of the compound was characterized by the X-ray structural analysis and IR and X-ray photoelectron spectroscopy.[3] IR spectra of $C_{60}F_{24}$ and C_2F were recorded on Specord IR 75 spectrometer for tablets in KBr.

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C Kα and F Kα X-ray fluorescent spectra of $C_{60}F_{24}$ were recorded on X-ray spectrometer Stearat. The sample of the substance was deposited on the copper substrate and cooled up to the liquid nitrogen temperature in the vacuum chamber of X-ray tube. The working regime of X-ray tube with copper anode was $U = 6$ kV, $I = 0.5$ A. The spectra were recorded with ~0.5 eV resolution. Monocrystal NAP was used as a crystal analyzer. The peculiarities of the use of this crystal for recording of C Kα spectra have been described in refs 16 and 17. The accuracy of determination of the energies of X-ray bands was ~0.3 eV.

X-ray photoelectron C 1s and F 1s spectra were recorded by means of VG Microtech spectrometer, using LiF as a standard. The spectra were excited by the Mg Kα line. The electron irradiation of the sample was used to avoid the charging effects.

Calculation Results

In the present work we consider seven isomers with the structures, presented in Figure 1. The series of isomers is designed in order of the increase of the degree of delocalization of the electron density of carbon framework: from isomer **1** with the isolated double bonds up to isomer **7**, possessing all fluorine atoms situated from one side of the fullerene. The cross lines mark the carbon atoms, bonded with fluorine atom. The formal double bonds between carbon atoms are hatched. The carbon atoms, mentioned in the text and tables, are numbered.

The quantum-chemical calculations of isomers were performed by semiempirical PM3 method using GAMESS.[18] All spatial structures of isomers are optimized using the BFGS algorithm. The enthalpies of formation of isomers and ionization potentials of highest occupied molecular orbitals (HOMOs), obtained as a result of calculation, are presented in Table 1.

(a) Isomer 1. Fluorine atoms were bonded to the two carbon atoms of each pentagon of C_{60} molecule in 1,3-position. Such position of fluorine atoms leads to the isolation of double C=C bonds and, hence, the localization of π-electron density. The optimization of geometry for isomer **1** gives the T_h point symmetry group. Carbon atoms with different charges can be joined into three groups, corresponding to the various structural positions (Figure 1a): atoms, participating in hexagon−hexagon (6,6) double bond, e.g., atom 2; atoms, participating in hexagon−pentagon (6,5) double bond, e.g., atom 6; atoms, bonded with fluorine, e.g., atom 1. This isomer contains five nonequivalent bonds. Their lengths and Wiberg indexes, characterizing their order, are presented in Table 2.

C=C and C−C bond lengths, obtained by geometry optimization, are close to those in polyfluorocarbon compound $(C_2F)_n$, 1.33 and 1.54 Å.[19] The average value of C=C bond length in olefins is 1.33 Å, C−C bond length in paraffins − 1.54 Å.[20] The calculated C−F bond length in $C_{60}F_{24}$ molecule (1.36 Å) is shorter than the fluorocarbon bond in $(CF)_n$ (1.41 Å)[21] and fluoroparaffins (1.38 Å).[20] The geometry optimization of $C_{60}F_2$ molecule by molecular mechanics method leads to C−F bond length, equal to 1.36 Å.[22] The optimization of $C_{60}F_{60}$ at I_h symmetry by various quantum-chemical methods results in the different values of the bond lengths.[10] The C−F bond length varies from 1.362 to 1.412 Å as the result of semiempirical calculations. Ab initio calculations with the different basis sets give the C−F bond length from 1.330 to 1.381 Å.

(b) Isomer 2. The structure of isomer **2**, obtained by geometry optimization, is presented on Figure 1b. This isomer contains two double bonds (between the 18, 20 atoms and between the symmetrical pair of atoms), similar to double bonds in isomer **1**. The other 16 formal double bonds are situated by two in hexagons, e.g. 2, 3, 7, 17, 16, 10 hexagon, and in pentagons, e.g., 3, 4, 9, 8, 7 pentagon. This isomer can be supposed to show the delocalization of the π-electron density in such pentagons and hexagons. The obtained structure (as a result of geometry optimization) can be assigned to D_{2h} point symmetry group. The bond lengths in isomer **2** and degrees of

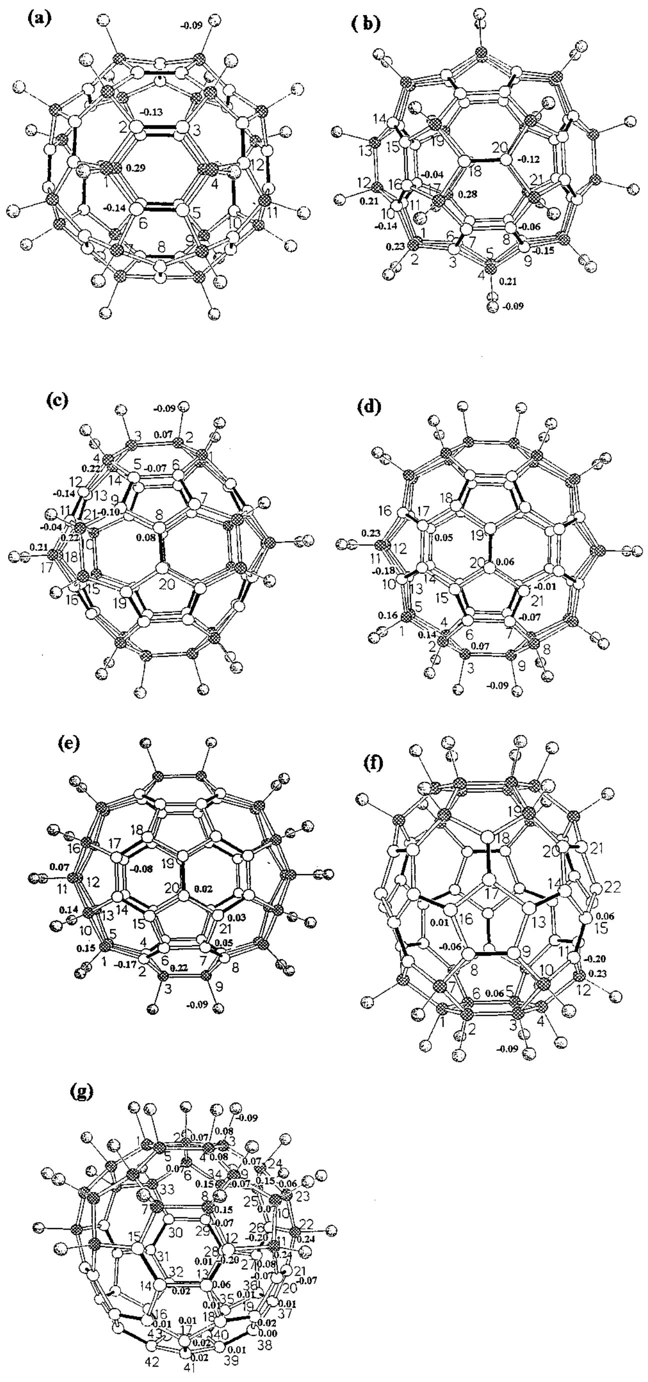

Figure 1. Calculated structures of isomer **1** (a), isomer **2** (b), isomer **3** (c), isomer **4** (d), isomer **5** (e), isomer **6** (f), and isomer **7** (g) for $C_{60}F_{24}$.

TABLE 1: Calculated Heats of Formation (ΔH_f) and HOMO Ionization Potentials (IP) for Isomers 1−7

isomer	ΔH_f (kcal/mol)	IP (eV)
1	−440.75	12.75
2	−433.01	11.61
3	−405.55	11.54
4	−320.13	10.81
5	−382.44	10.71
6	−300.81	10.48
7	−292.46	10.75

TABLE 2: Bond Lengths and Bond Orders for Isomer 1

bond	bond length (Å)	bond order
2−3	1.33	1.92
5−6	1.32	1.90
1−6	1.51	0.95
1−2	1.54	0.94
C−F	1.36	0.99

TABLE 3: Bond Lengths and Bond Orders for Isomer 2

bond	bond length (Å)	bond order
3−7	1.35	1.85
10−16	1.33	1.85
18−20	1.33	1.91
15−16	1.45	1.03
7−8	1.46	1.02
1−2	1.61	0.90
2−3	1.54	0.94
3−4	1.51	0.95
4−5	1.55	0.92
2−10	1.53	0.94
10−12	1.52	0.94
12−13	1.61	0.91
7−17	1.50	0.95
17−16	1.53	0.94
17−18	1.53	0.94
C−F	1.36	0.99

their multiplicity are presented in Table 3. The evaluation of the data of this table permits to conclude that the bonds, hatched in Figure 1b, remain practically the double ones.

Two types of the carbon atoms bonded with fluorine can be separated in isomer **2**. Atoms 17 and 19 and those symmetrical to them have the same environment as the carbon atoms of CF groups in isomer **1**. The charges on these carbon atoms in the isomers are similar. The 16 remaining carbon atoms in isomer **2** have the CF group in the ortho position and are surrounded by only two C═C bonds. The charges on these atoms decrease in respect to the charges on the carbon atoms of CF groups in isomer **1,** up to 0.23e (6,5 bond), 0.21e (6,6 bond). The charges on bonded carbon atoms are the same in localized double bonds and are different for conjugated bonds. The atom, bonded with the carbon atoms of two CF groups, e.g., atom 9 or 10, has more negative charge than the second carbon atom in the considered bond (e.g., atom 8 or 16).

(c) Isomer 3. The structure of isomer **3** is presented on Figure 1c. It has no isolated C═C bonds in respect to isomers **1** and **2**. Two structural units can be separated: hexagon C_6F_2 (e.g., hexagon 13, 12, 11, 17, 18, 21), possessing two conjugated double bonds and C_5-C_5 structure. This structure can be considered as two pentagons C_5, bonded via double bond 8−20 and containing two double bonds (each of pentagons), e.g., between the 7 and 6 and 5 and 9 atoms. Isomer **3** after the geometry optimization was assigned to the D_{2h} point symmetry group. The bond lengths and their orders are presented in Table 4. The bond orders between the 5 and 9 or 8 and 20 atoms in the C_5-C_5 structure are less than that between the 11 and 12 atoms in C_6F_2. It is caused by the greater delocalization of the electron density by carbon atoms of C_5-C_5 system in respect to C_6F_2 hexagon.

In isomer **3** there are the carbon atoms of CF groups (e.g., atoms 2 and 3), bonded with three carbon atoms of another CF groups. The charges on these carbon atoms decrease to 0.07e. The charge distribution for the carbon atoms, bonded by the double bond in C_6F_2 structural unit, is similar to the charge distribution for the carbon atoms of the conjugated bonds in isomer **2**. The charge difference for the pair of carbon atoms (e.g., 5 and 9 atoms) in the conjugated double bonds in nonfluorinated pentagons C_5 is connected with different local surrounding: 5−4, 5−6 bond lengths differ from those for 9−21, 9−8.

TABLE 4: Bond Lengths and Bond Orders for Isomer 3

bond	bond length (Å)	bond order
5−9	1.37	1.75
8−20	1.34	1.67
11−12	1.34	1.85
5−6	1.45	1.06
9−8	1.46	1.03
12−13	1.44	1.04
2−3	1.63	0.92
1−2	1.61	0.92
9−10	1.51	0.96
10−15	1.64	0.90
15−16	1.53	0.94
16−17	1.52	0.95
17−18	1.59	0.92
4−12	1.53	0.94
5−4	1.49	0.96
C−F	1.36	1.00

TABLE 5: Bond Lengths and Bond Orders for Isomer 4

bond	bond length (Å)	bond order
10−14	1.35	1.77
19−20	1.34	1.69
6−15	1.37	1.67
6−7	1.45	1.07
15−14	1.43	1.05
15−20	1.46	1.02
14−17	1.47	1.01
2−6	1.48	0.97
1−10	1.51	0.96
10−11	1.55	0.94
1−5	1.58	0.92
2−3	1.59	0.92
11−12	1.55	0.92
1−2	1.65	0.90
3−9	1.68	0.90
C−F	1.36	1.0

(d) Isomer 4. Isomer **4** (Figure 1d) can be characterized by the addition of four double bonds to the double bond system of C_5-C_5 structure (isomer **3**). The conjugated bonds of hexagons C_6F_2 of isomer **3** are "transferred" to pentagons C_5F_1. The structure of considered isomer is interesting by the presence of two parts with the conjugated double bonds—two "pieces" of fullerene, separated by carbon atoms, bonded with the fluorine atoms. The isomer has D_{2h} symmetry. The bond lengths obtained by geometry optimization and their orders are presented in Table 5. The multiplicity of formal double bonds decreases in respect to that for analogous bonds in isomer 3.

The substantial difference in the charge values for the pair of atoms (e.g., 10 and 14) participating in the conjugated double bonds in pentagons C_5F_1 can be explained by the same reasons, as in the case of isomers **2** and **3**. A further decrease of the absolute charge values for carbon atoms in C_5-C_5 systems is observed for isomer **4**. These carbon structures are similar to the fullerene molecule by such parameters as bond lengths, Wiberg indexes, and charges on atoms.

(e) Isomer 5. Isomer **5** has D_{2h} symmetry. Its structure (Figure 1e), similar to the structure of isomer **4**, has two carbon fragments divided by the band of fluorinated carbon atoms. This band includes four completely fluorinated hexagons, differing from the band for isomer **4**, containing four completely fluorinated pentagons. The double carbon−carbon bonds are situated in the hexagons C_6F_2 and C_6. The formation of the formal double bonds in the hexagons, unlike the double bonds in the pentagons of isomer **4**, is more favorable. That is one of the reasons of the higher stability of isomer **5** (Table 1). The

TABLE 6: Bond Lengths and Bond Orders for Isomer 5

bond	bond length (Å)	bond order
2−6	1.34	1.81
15−14	1.37	1.55
19−20	1.39	1.39
14−17	1.42	1.23
15−20	1.44	1.17
6−15	1.46	1.02
6−7	1.47	1.01
10−14	1.51	0.96
1−2	1.53	0.95
2−3	1.52	0.95
11−12	1.57	0.93
1−5	1.59	0.92
1−10	1.61	0.91
10−11	1.62	0.91
3−9	1.64	0.91
C−F	1.36	0.99

TABLE 7: Bond Lengths and Bond Orders for Isomer 6

bond	bond length (Å)	bond order
1−2	1.61	0.92
2−7	1.61	0.91
10−11	1.52	0.95
8−9	1.35	1.77
9−13	1.47	1.02
13−17	1.46	1.02
11−15	1.34	1.78
13−14	1.50	1.69
C−F	1.36	1.00

bond lengths and orders, obtained as a result of geometry optimization, are presented in Table 6.

(f) Isomer 6. The fluorine atoms in isomer **6** are situated on the two opposite sides of the fullerene molecule (Figure 1f). The optimization of geometry indicates D_{3d} symmetry for this isomer. The 3-fold axis goes through the centers of two completely fluorinated hexagons. One of them is numbered as 1, 2, 3, 4, 5, 6 on Figure 1f. The completely fluorinated hexagon is surrounded by three pentagons and three hexagons with the joint (6,5) bonds. Six fluorine atoms were added to these bonds to give the described $C_{60}F_{24}$ isomer.

The structure of the isomer can be divided on two fluorinated and one non-fluorinated fragments. The C−C bonds, being formal double from the calculation results, are hatched on Figure 1f. They include 10 double (6,6) bonds and eight double (6,5) bonds. The described isomer also permits the other position of the formal double bonds on the non-fluorinated fragment of the carbon framework, leading to 12 double (6,5) bonds and six double (6,6) bonds. The obtained result confirms the energetic preference of the double (6,6) bond in respect to (6,5) one.

The interatomic distances and Wiberg indexes for bonds, obtained by the geometry optimization procedure, are presented in Table 7. The weakening and stretching of C−C bonds in all fragments of the molecule containing only C−F bonds (C_6F_6 hexagons) should be noticed. Carbon atoms have the equal charges 0.06e. The bond lengths in the non-fluorinated pentagons C_5 are close to the lengths of the short and long bonds in the fullerene molecule. Only weak delocalization of the electron density on the carbon framework free from fluorine atoms takes place. The carbon atoms of the double bonds and those bonded with one CF group (atom 8) or two CF groups (atom 11), have the negative charge.

(g) Isomer 7. This isomer contains 24 fluorine atoms, located on the one side of the carbon framework (Figure 1g). The isomer has C_s symmetry. The symmetry plane goes through the atom 2 and the middle of the 5−4 bond in the C_5F_5 pentagon. The bond lengths obtained by geometry optimization, are presented in Table 8.

TABLE 8: Bond Lengths and Bond Orders for Isomer 7

bond	bond length (Å)	bond order	bond	bond length (Å)	bond order
20−21	1.35	1.79	27−36	1.47	1.01
12−13	1.34	1.79	29−34	1.51	0.96
26−27	1.34	1.79	11−20	1.50	0.96
18−19	1.36	1.57	22−21	1.50	0.96
36−37	1.36	1.56	25−26	1.51	0.96
28−29	1.37	1.50	8−12	1.50	0.96
35−40	1.38	1.49	26−27	1.51	0.95
17−41	1.39	1.45	11−12	1.51	0.95
38−39	1.39	1.44	2−6	1.57	0.93
13−32	1.39	1.42	24−25	1.59	0.92
29−30	1.41	1.27	3−24	1.58	0.92
13−28	1.43	1.21	10−23	1.59	0.92
35−36	1.45	1.14	8−9	1.59	0.92
17−40	1.45	1.14	4−9	1.57	0.92
17−18	1.45	1.13	3−4	1.59	0.92
39−41	1.45	1.13	2−3	1.59	0.92
37−38	1.45	1.14	4−5	1.60	0.92
19−38	1.45	1.13	22−23	1.61	0.92
40−43	1.47	1.08	7−8	1.59	0.92
13−35	1.46	1.08	9−10	1.61	0.92
27−28	1.46	1.02	10−11	1.60	0.92
21−37	1.48	1.02	25−34	1.59	0.92
13−18	1.47	1.02	34−6	1.61	0.92
19−20	1.48	1.02	C−F	1.36	0.99
13−14	1.46	1.01			

Isomer **7** has only six practically double bonds. These are the bonds between atoms 20 and 21, 12 and 13, 26 and 27 and bonds which are symmetrical to them. The bond between the 20 and 21 atoms is localized. The conjugated double bonds are absent for it. The 12−13 and 26−27 bonds contain one of carbon atoms bonded with two CF groups. This is similar to the bonds of higher multiplicity in isomers **2**−**6**. The parameters of the other hatched C−C bonds in isomer **7** are close to the corresponding values of the short bonds in fullerene (length 1.38 Å,[23] multiplicity 1.46[12]).

Plotting of the Theoretical X-ray Spectra. C Kα and F Kα theoretical spectra were plotted for each $C_{60}F_{24}$ isomer (Figure 2 −8). F Kα spectrum reflects the distribution of 2p(F) electron density in the valence band of the molecule. The height of the separate line in the spectrum is proportional to the sum of squares of coefficients for 2p(F) AOs in the concrete MO of fluorofullerene. The position of the line on the energy scale indicates the value of one-electron energy of MO, obtained by calculation. Each line in the spectrum can be described by Lorenz curve of the determined width. In the present work the width is equal to 0.4 eV for all spectra. The sum of all curves gives the resulting spectrum, which is compared with the experimental F Kα spectrum of $C_{60}F_{24}$.

The plotting of the theoretical C Kα spectrum of molecule included a few stages. Two or three groups of carbon atoms noticeably different by charge value can be separated for each $C_{60}F_{24}$ isomer. For example, the carbon atoms (group 1) participating in the double bonds of isomer **1** have the charges 0.13e or 0.14e, depending on the character of the bond: (6,6) or (6,5) bond. The carbon atoms (group 2), bonded with fluorine atoms, have the charge 0.29e. So the carbon atoms in these groups differ by the charge value on 0.42e, and hence, the energies of 1s levels of carbon atoms from various groups can be expected to be substantially different. Really, X-ray photoelectron spectrum of the considered molecule gives this difference to be equal to ~2 eV. X-ray C Kα spectrum reflects the transitions from the occupied MOs to the inner 1s levels. To model the C Kα spectrum, comparable with the experimental

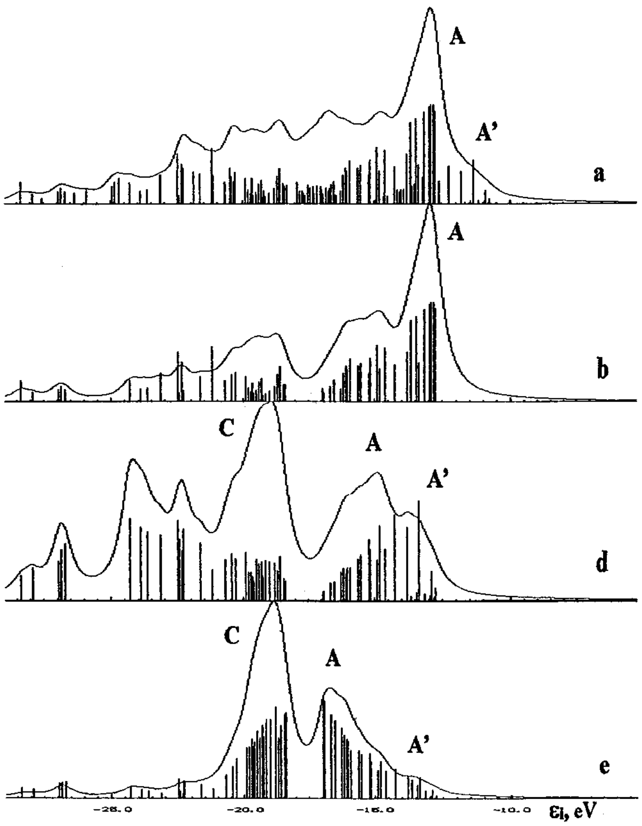

Figure 2. Calculated C Kα (a−d) and F Kα (e) spectra for isomer **1**. (b) X-ray spectrum for carbon atoms in C═C bonds; (d) X-ray spectrum for carbon atoms in CF groups; a, integral spectrum of spectra b and d in the ratio 3/2; spectrum d is shifted on 2 eV toward spectrum b.

spectrum, the C Kα spectra for sp^2-hybridized carbon atoms (C═C bonds, Figure 2b) and sp^3-hybridized carbon atoms (C−F bonds, Figure 2d) should be plotted. The last spectrum must be shifted on 2 eV to short-wave range and summarized with the first one in the ratio 3/2. The summary C Kα spectrum (Figure 2a), reflecting the transitions from all MOs to 1s levels of all carbon atoms in the molecule, can be compared with the experimental data.

Three groups of carbon atoms, differing by charge value, can be separated in isomers **3**−**7**: (1) the carbon atoms, participating in the π-bond with the charge value, close to zero (spectra b); (2) the carbon atoms, participating in the double bond and possessing the substantial negative charge (spectra c); (3) the carbon atoms bonded with fluorine (spectra d). The integral C Kα spectra (spectra a) for isomers **3**−**7** were plotted as the superposition of three spectra: spectrum b was not shifted, spectrum c was shifted to long-wave range on 1 eV, spectrum d was shifted to short-wave range on 1 eV. The relative contributions of these spectra (b, c, d) in the integral spectra correspond to the distribution of charges in the isomers (Figure 1).

Discussion of Results

The results are discussed in the following subsections: the analysis of the theoretical X-ray spectra, the comparison of theoretical and experimental X-ray spectral data, the structure of chemical bonding in $C_{60}F_{24}$, the interpretation of X-ray photoelectron spectroscopy data, the interpretation of IR spectroscopy data, thermodynamic stability of polyfluorosubstituted fullerenes.

Analysis of the Theoretical X-ray Spectra. The comparison of bond lengths between carbon and fluorine atoms and bond orders for isomers **1**−**7** (Tables 2−8) reveals these parameters to be constant and independent of the isomer structure. The charge on the fluorine atoms (−0.09e) is practically the same. Hence, the similarity of the structure of electronic interactions C−F can be assumed. However, the comparison of the theoretical F Kα spectra (Figure 2−8) shows the state of fluorine atoms to be different in the various isomers. That difference can be seen from the regular appearance of the maximum B and the increase of its intensity. This maximum is absent in the F Kα spectrum of isomer **1**. It can be observed in the F Kα spectrum of isomer **2** and has the maximal intensity in the case of isomer **7**.

Four states of fluorine atoms can be considered for isomers **1**−**7** from the structural point of view: the fluorine atoms in CF group, surrounded by three double bonds (S3), two double bonds (S2), one double bond (S1), and not bonded with any carbon atom, included in the π-system of carbon framework (S0). Table 9 contains the data about the number of the different CF groups in the considered isomers.

In the case of isomer **1** all CF groups are the same possessing three π-bonds in their surroundings. The MOs of ρ- and τ-type can be separated (with some degree of approximation) in the molecule of fluorofullerene $C_{60}F_{24}$, as in the molecule C_{60}. Isomer **1** contains the orbitals of ρ-type (σ-bonding C−F MOs) with the IPs 18−19 eV. The occupied MOs of τ-type can be divided in to two groups in respect to carbon−fluorine interaction. The orbitals with the greater IPs (maximum C in F Kα spectrum, Figure 2e) have the bonding character toward carbon−fluorine pairs, whereas the MOs with lesser IPs (maximum A) can be considered as antibonding in respect to 2p(C)−2p(F) AOs overlap. The energetic gap $\Delta \sim 1.5$ eV is observed between the levels corresponding to these MO groups, seen in X-ray C Kα and F Kα spectra as the splitting of bands.

The appearance of the maximum B in F Kα spectrum of isomer **2** can be connected with the presence of MOs, including 2p(F) AOs with the small participation of 2p(C) AOs. These MOs are almost the lone electron pairs of fluorine atoms, being energetically localized between the bonding and antibonding (in respect to C−F bond) MOs. The quantity of the lone electron pairs of fluorine atoms increases from isomer **2** to isomer **7**, correlated with the stepwise diminishing of the double bonds, surrounding CF groups (Table 9). This leads to the increase of the intensity of maximum B in the theoretical F Kα spectra in the considered series of isomers. At the same time the theoretical C Kα spectra for the carbon atoms of CF groups (Figure 2−8, spectra d) maintain their characteristic two-maximum form, similar to experimental and theoretical C Kα spectra of the stoichiometrical polyfluorocarbon $(CF)_n$.[13] In the latter, each carbon atom is bonded with the fluorine atom.

HOMOs of isomer 1 include 2p(C) AOs of atoms of the double bonds and 2p AOs of atoms of CF groups. The X-ray transitions from these MOs correspond to the maximum A (Figure 2b) and short-wave shoulders A′ (Figure 2d,e) in the C Kα and F Kα spectra for various groups of atoms. The interaction of this type in isomers **2**−**7** is not so effective. It is reflected in the diminishing (isomers **2**, **3**) and disappearance (isomers **4**−**7**) of short-wave shoulders A′ in F Kα spectra and in C Kα spectra of carbon atoms bonded with fluorine. The bandwidth of line A in these C Kα spectra (d) decreases and the bandwidth of line C increases. The relative intensity of these maxima also changes.

To consider the electronic state of carbon atoms not bonded with the fluorine atoms in isomers **3**−**7**, we have separated the theoretical C Kα spectra of carbon atoms possessing the near

TABLE 9: Amount of Different States of Fluorine Atoms in CF Groups for Isomers 1−7

state of fluorine atom in CF group	isomer **1**	isomer **2**	isomer **3**	isomer **4**	isomer **5**	isomer **6**	isomer **7**
S3	24	8					
S2		16	20	4	4	12	4
S1				16	16		6
S0			4	4	4	12	14
total no. of neighboring π-bonds	72	56	40	24	24	24	14

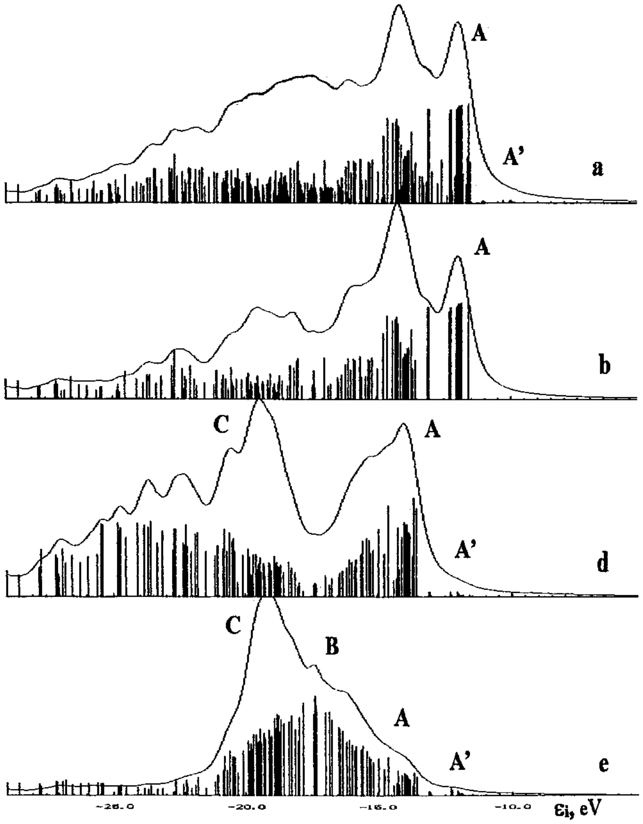

Figure 3. Calculated C Kα (a−d) and F Kα (e) spectra for isomer **2**. The spectra are plotted as in Figure 2.

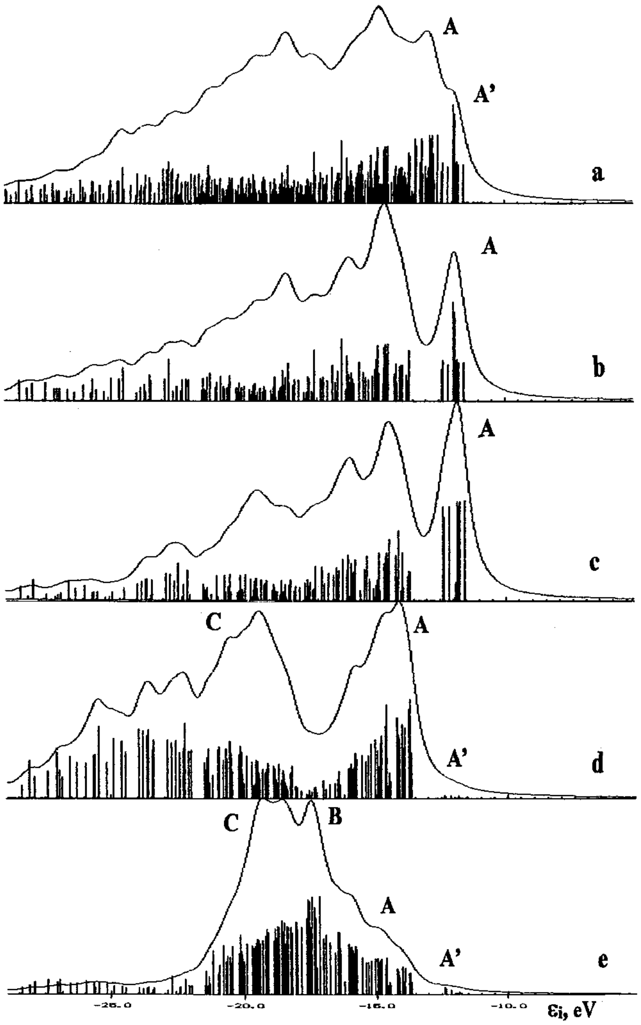

Figure 4. Calculated C Kα (a−d) and F Kα (e) spectra for isomer **3**. Spectrum b is plotted for carbon atoms in C=C bonds and possessing charge close to zero; spectrum c is plotted for carbon atoms in C=C bonds and possessing a substantial negative charge; spectrum d is plotted for carbon atoms in CF groups. Spectrum a is the integral of spectra b, c, and d in the ratio corresponding to the charge distribution on the Figure 1; spectrum c is shifted on 1 eV in the long-wave range and spectrum d is shifted by 1 eV in the short-wave range.

to zero charge (Figures 4−8, spectra b) and the substantial negative charge ∼−0.2 e (Figures 4−8, spectra c). The latter charge value is characteristic for carbon atoms bonded with CF groups. In isomers **1** and **2,** all carbon atoms of the π-system are bonded with CF groups, and therefore, the charge values for them are practically equal (Figure 1a,b).

The considered structures of $C_{60}F_{24}$ isomers can be divided in to two groups: isomers **1**−**3**, possessing one band in the short-wave range of C Kα spectrum (maximum A in the spectra of carbon atoms of double bonds), corresponding to π-orbitals of carbon framework, and isomers **4**−**7**, possessing π-levels, distributed in the wide energy range and corresponding to a number of bands in the short-wave range of the C Kα spectrum. The value of the energy range of the π-system depends on the degree of the aromaticity of system. The series of presented isomers $C_{60}F_{24}$ was constructed so that isomers **1** and **2** have almost no interaction between the formal double bonds, while the structures **3**−**7** save (in various degree) the parts of aromatic system of fullerene molecule C_{60}. The increase of the degree of delocalization of the carbon π-system in the series of isomers **3**−**7** can be confirmed by the data on decrease of IP of HOMO, presented in Table 1.

Comparison of Theoretical and Experimental X-ray Spectral Data. The best agreement between the theoretical and experimental spectra (both C Kα and F Kα) has been obtained for isomers **4** and **5**. The theoretical and experimental spectra of fullerene C_{60} are also presented in Figure 9. Quantum-chemical calculation of C_{60} molecule has been carried out by PM3 method with full geometry optimization. The obtained bond lengths are equal to 1.384 and 1.457 Å. The satisfactory agreement between the theoretical and experimental spectra indicates the possibility of the application of the mentioned quantum-chemical method for the investigation of the electronic structure and interpretation of X-ray spectra of fullerene compounds. The good coincidence of the experimental X-ray spectra of $C_{60}F_{24}$ with the spectra plotted on the basis of PM3 calculation of isomers **4** and **5** isomers lets us suppose the structure of these isomers. The synthesized compound also can be the mixture of isomers with the structures close to the proposed structures **4**, **5**, and **6**. The existence of substantially

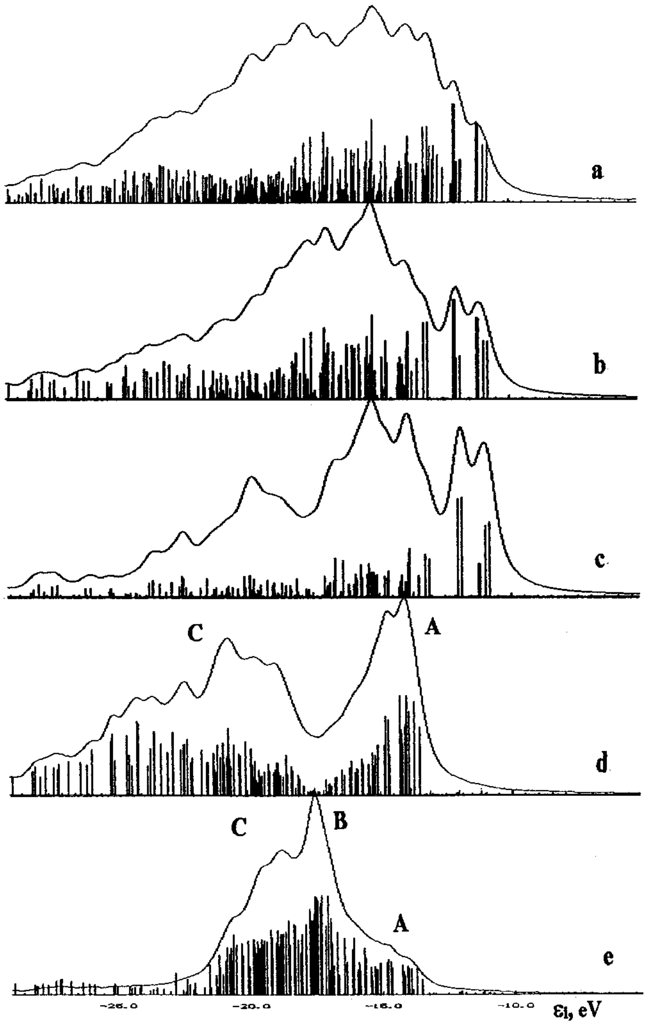

Figure 5. Calculated C Kα (a−d) and F Kα (e) spectra for isomer **4**. The spectra are plotted as in Figure 4.

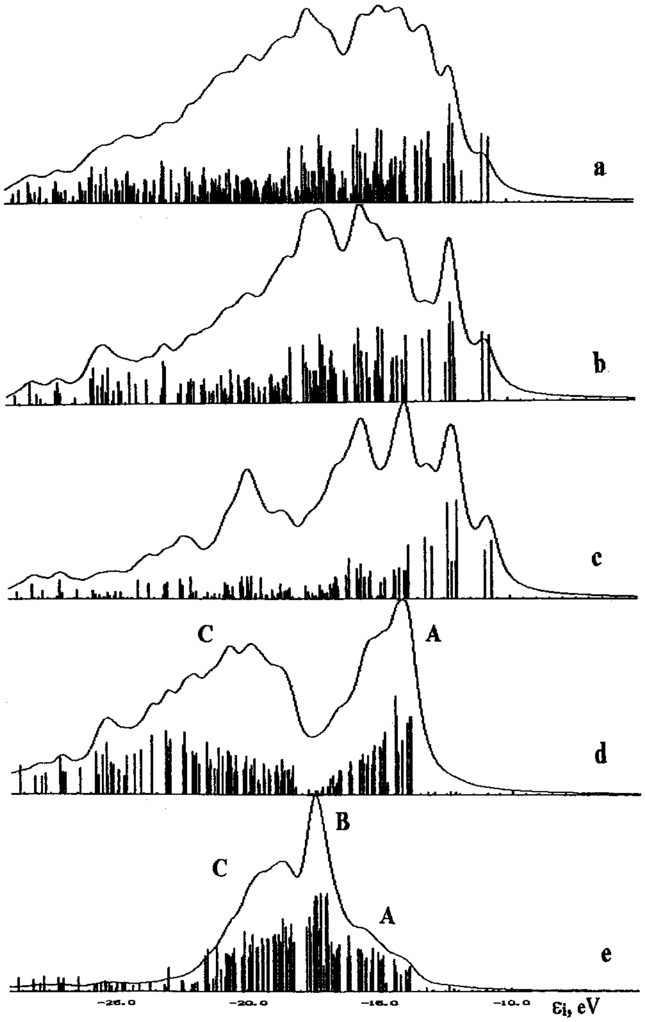

Figure 6. Calculated C Kα (a−d) and F Kα (e) spectra for isomer **5**. The spectra are plotted as in Figure 4.

large carbon surface with conjugated π-system can be expected for the obtained compound.

Structure of Chemical Bonding in $C_{60}F_{24}$. The structure of chemical bonding in $C_{60}F_{24}$ has been investigated for isomers **4** and **5**. The geometry of the carbon framework in $C_{60}F_{24}$ is distorted in comparison with the highly symmetrical fullerene molecule. We have carried out the quantum-chemical calculation of C_{60} with the structural parameters, obtained as a result of geometry optimization for isomers **4** and **5**. The charge values on the carbon atoms of fullerene molecule are equal to zero and each hexagon or pentagon is planar. The distortion of structure leads to the deflection of some carbon atoms out of the polyhedral planes. These atoms, as follows from the calculations, become positively charged (0.01−0.05e). The addition of 24 fluorine atoms to these carbon atoms leads to the isomers with the aromatic systems, separated by the band of CF groups (Figure 1d,e). To clear the peculiarities of interaction of the aromatic carbon system with CF groups in these isomers, the quantum-chemical calculations of hydrocarbon analogues of aromatic structures have been performed (Figure 10). The charge distribution on the carbon atoms of calculated clusters is similar to the charge distribution for the carbon atoms of the aromatic system of isomers. The frontier carbon atoms have the substantial negative charge. The maximal value of it is on the atoms, which are not included in the cycles.

The structure of electronic interactions in $C_{60}F_{24}$ can be considered as a result of interaction of MOs of carbon framework with fluorine AOs. Therefore, we have performed the fragmentary analysis[24,25] of fluorofullerene molecules in respect to C_{60} fragments ($C_{60}^{\ddagger}$) with the same positions of carbon atoms as in isomers **4** and **5**. This approach allows to determine the nature of fragment MOs, participating in the formation of MOs of the whole system and the degree of such participation. The results of the fragmentary decomposition of the occupied MOs of $C_{60}F_{24}$ by the system of all MOs of $C_{60}^{\ddagger}$ is presented schematically in Figure 11. The valence band of $C_{60}F_{24}$ molecule consists of 204 occupied levels, which can be divided into a few blocks by the character of MOs.

HOMOs of $C_{60}F_{24}$ are the combination of ρ-type orbitals of fullerene molecule. The vacant MOs of $C_{60}^{\ddagger}$ (ρ^*) participate in these MOs in substantial degree (up to 40%). This fact leads to the increase of IPs for MOs of $C_{60}F_{24}$ in respect to the corresponding IPs of $C_{60}^{\ddagger}$. The high occupied MOs of fluorofullerene (IP $\sim$ 10.8−12.1 eV) are the analogy to the π-type MOs of aromatic molecules. The lower levels are two energetically overlapping blocks of MOs with the substantial contribution of 2p(F) AOs. The values of IPs $\sim$ 13.1−14.7 eV can be assigned to the MOs, which are the combination of the fragment MOs of ρ- and τ-type. The carbon atoms of CF groups are interacting with π-bonds of carbon fragments by means of orbitals directed tangential to the sphere, where the carbon framework could be included. These orbitals are the orbitals of τ-type in the MO system of fullerene molecule. 2p(F) AOs are also directed tangential, leading to the formation of antibonding π-orbitals between carbon and fluorine AOs of CF

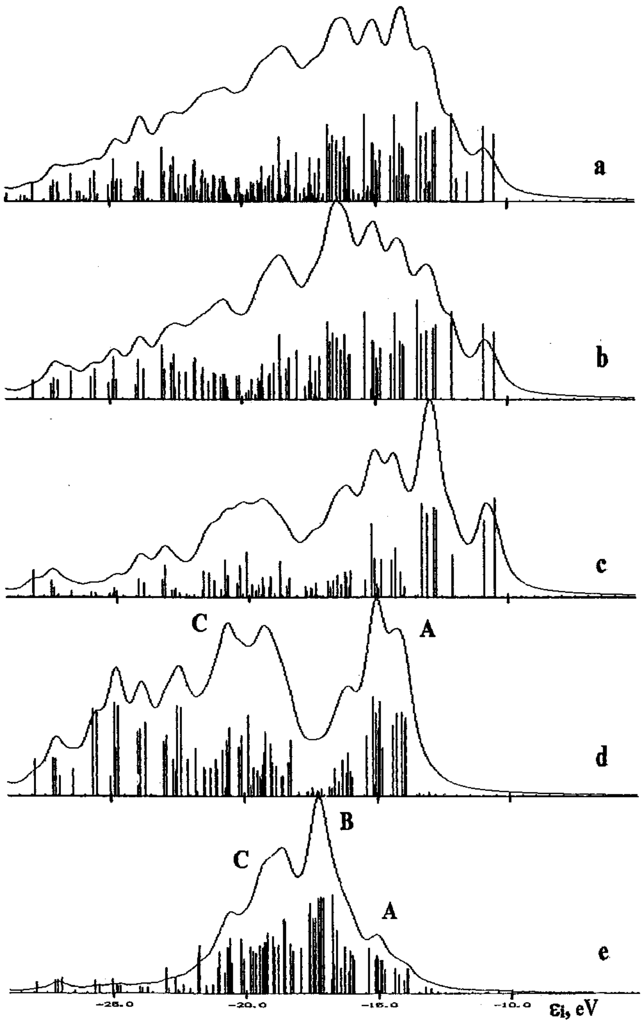

Figure 7. Calculated C Kα (a−d) and F Kα (e) spectra for isomer **6**. The spectra are plotted as in Figure 4.

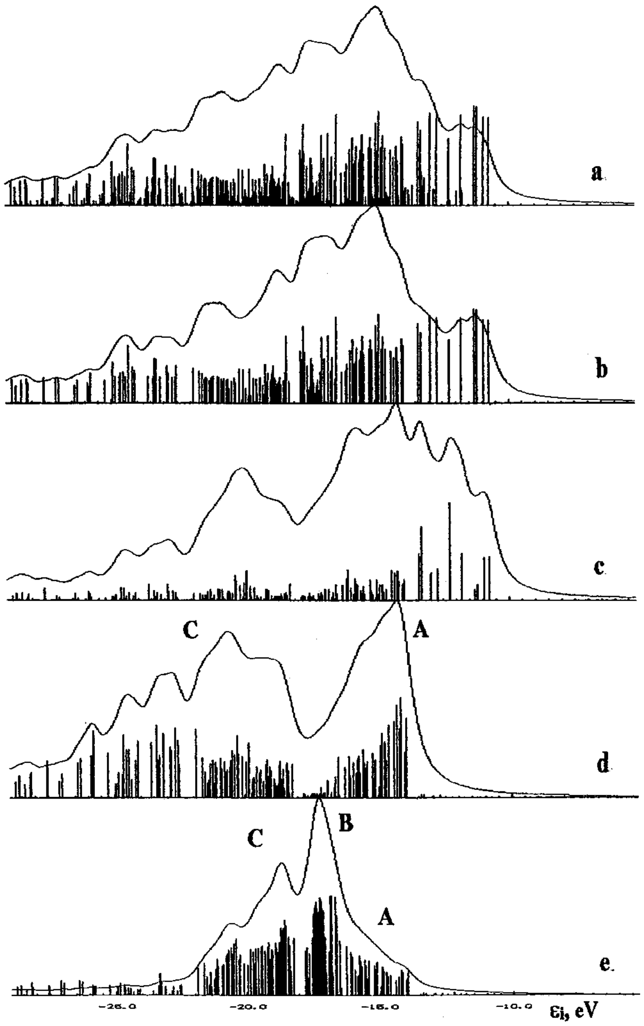

Figure 8. Calculated C Kα (a−d) and F Kα (e) spectra for isomer **7**. The spectra are plotted as in Figure 4.

group. The fragment orbitals of τ-type and 2p(F) AOs, in our terms also τ-type orbitals, are participating in MOs with the IPs in the range ~13.7−16.9 eV. MOs of this block realize the σ-interaction between carbon atoms; the interaction between atoms in CF groups has π^*-character.

MOs of fluorofullerene, being the "lone" electron pairs of fluorine atoms (tangential to the sphere), are in the narrow energetically range ~0.4 eV. Their IPs (17.3−17.7 eV) are close to the energies of 2p(F) AOs. Two overlapping blocks of MOs, which are different by the character of bonding in CF groups, are in the lower energy range. The higher block (17.9−19.4 eV) consists of MOs, which are the combination of fragment MOs of ρ- and τ-type and 2p(F) AOs. These blocks differ by the character of bonding in CF groups. The presence of the orbitals of ρ-type with the combinations of 2p(C) AOs of carbon atoms in CF groups and radial directed 2p(F) AOs provides the σ-bonding between carbon and fluorine atoms. The next MO block (IPs ~ 19.2−22.4 eV) is the combination of the fragment MOs of τ-type and "tangential" 2p(F) AOs. The system of these MOs provides the bonding interaction between the atoms of CF groups. Finally, the lowest (by energy) of considered blocks (IP > 21.5 eV) consists of MOs, providing the σ-bonding between all atoms of fluorofullerene molecule with the substantial contribution of 2s(C) and 2s(F) AOs.

Interpretation of X-ray Photoelectron Spectroscopy Data. The method of X-ray photoelectron spectroscopy permits determination of the energy of the electron bonding for inner atomic levels and its change as a result of redistribution of electron density at the formation of chemical bond in molecules. The calculated charge distribution for **1**−**7** isomers (Figure 1) can be compared with the data on the shift of C 1s level in $C_{60}F_{24}$.[3]

X-ray photoelectron spectroscopy method has been used earlier to characterize the structure of fluorofullerenes $C_{60}F_x$ (x ~ 40).[26] Unlike this interpretation of C 1s spectra, we think the two most intensive maxima in the spectra belong to the carbon atoms bonded with fluorine atoms (the band with the greatest energy shift) and to the carbon atoms, not bonded with fluorine (the band with the lesser shift). The different interpretation of the experimental data can be connected with certain experimental difficulties, arising as a result of charging of these dielectric samples.

Three bands A, B, and C can be separated in X-ray photoelectron C 1s spectrum of $C_{60}F_{24}$ (Figure 12). The band A can be assigned to the carbon atoms of CF groups. The maximum B corresponds to the carbon atoms nonbonded with fluorine atoms and possessing near zero charge. The appearance of the negative charge on carbon atoms leads to the shift of inner levels toward diminishing of IP. Therefore, the maximum C in X-ray photoelectron C 1s spectrum of $C_{60}F_{24}$ can be directly assigned to the carbon atoms of the ρ-system, bonded with CF groups. The ratio of maxima intensities $I_A/I_B/I_C$ corresponds to the relative quantities of the various types of carbon atoms in $C_{60}F_{24}$ and can be used in the consideration of structure models. Table 10 contains the quantities of atoms with the charges in the following ranges: A +0.29 to +0.14e; B +0.08

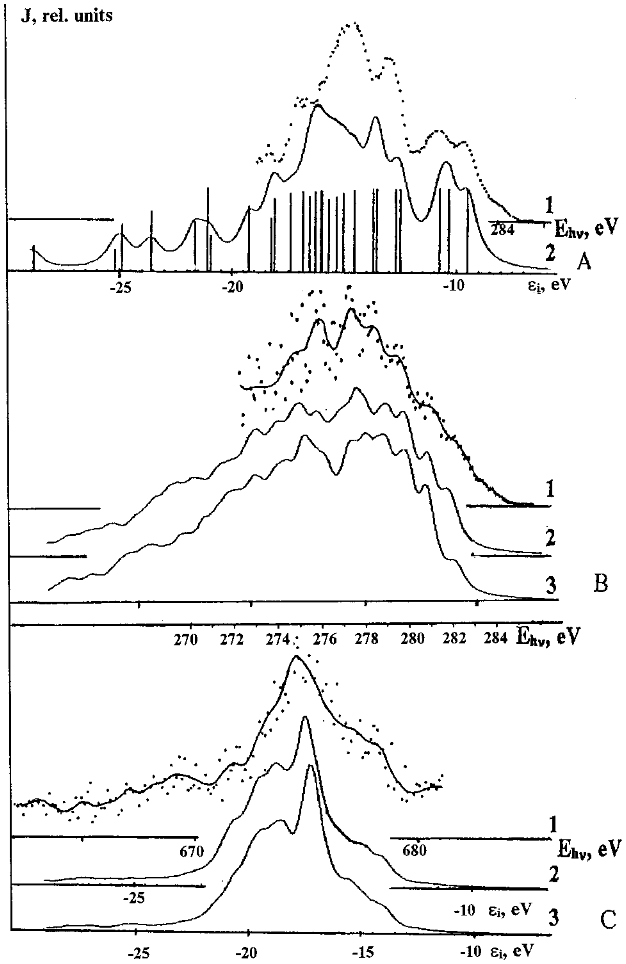

Figure 9. Experimental (A, 1) and theoretical (A, 2) X-ray spectra for fullerite C_{60}. C Kα (B, 1) and F Kα (C, 1) experimental spectra of $C_{60}F_{24}$, theoretical C Kα (B, 2, 3) and F Kα (C, 2, 3) spectra for isomers **4** and **5**.

to $-0.07e$; C -0.12 to $-0.20e$ and their ratio for each isomer. The quantity of atoms in the interval A is taken as 1. The experimental data is given in accordance with the $C_{60}F_{24}$ composition. The ratio of the various types of atoms is equal for isomers **4** and **5,** and is in better agreement with the experimental data, contrasting with the data for other isomers.

Interpretation of IR Spectroscopy Data. Additional confirmation of the existence of the proposed $C_{60}F_{24}$ model can be obtained from the analysis of IR absorption spectra. IR spectra of fullerene fluoride $C_{60}F_{24}$ and graphite fluoride C_2F in the 400−1600 cm^{-1} absorption range are presented in Figure 13. The most intensive bands in these spectra are assigned to the CF bonds (cm^{-1}): 1120 ($C_{60}F_{24}$), 1120 and 1250 (C_2F). Two bands in the IR spectrum of C_2F correspond, as assumed in ref 27, to the presence of fluorine atoms in two various structural positions. The structure of each layer of C_2F is supposed to be presented as parallel strips of completely fluorinated carbon hexagons and areas of the aromatic system. Only one band for the C−F bond (1120 cm^{-1}) is observed for $C_{60}F_{24}$, coinciding with the most intensive band in IR spectrum of C_2F. The observed shoulder at 1250 cm^{-1} for $C_{60}F_{24}$ can correspond to the vibrations of CF groups, bonded with three other CF groups, as in C_2F.

The band at 1219 cm^{-1} exists in the spectrum of graphite fluoride CF.[19] The presence of this band can indicate the existence of islands of $(CF)_n$ on the surface of $C_{60}F_{24}$. Taking into account the relatively small size of these islands and/or the small amount of isomers, containing such islands, the intensity of the corresponding vibrational band is expected to be weak and it is observed as a shoulder of the stronger band. The numerical differentiation of IR spectra permits observation

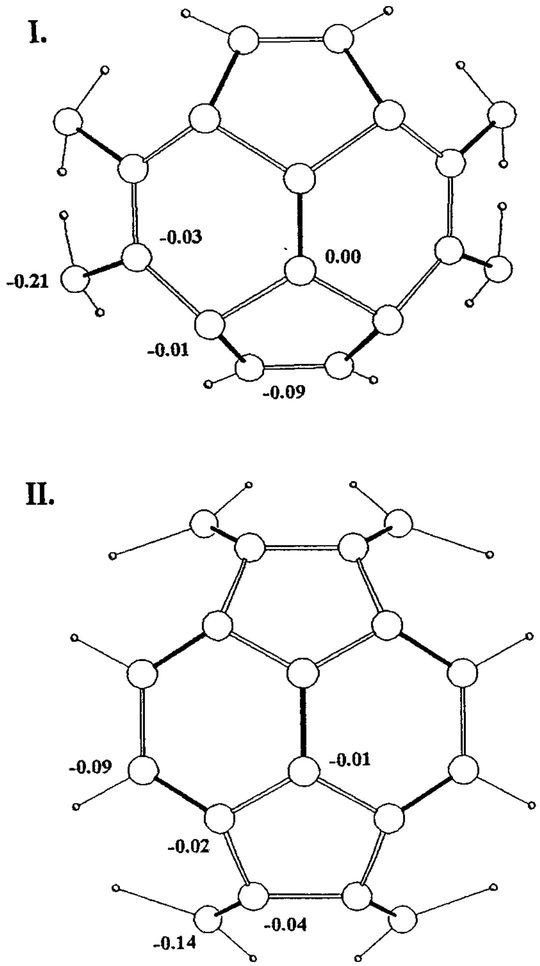

Figure 10. Calculated hydrocarbon analogues of aromatic fragments for isomer **4** (I) and isomer **5** (II).

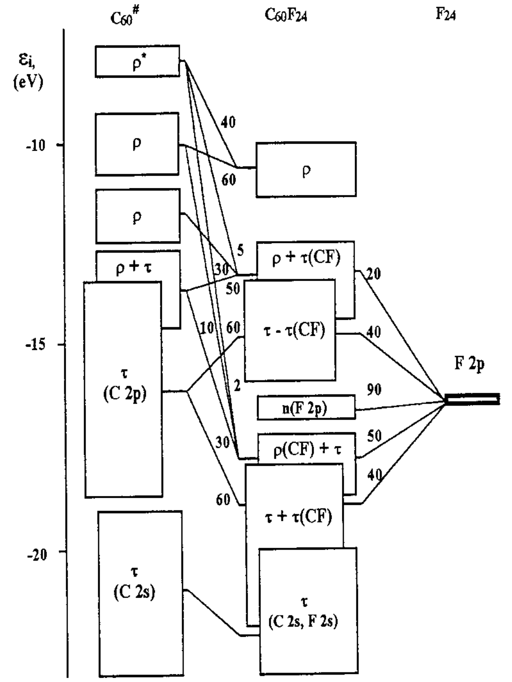

Figure 11. Correlation between levels of distorted $C_{60}^{\ddagger}$, levels of isomer **4** of $C_{60}F_{24}$, and 2p(F) AOs. The numbers indicate the contribution of $C_{60}^{\ddagger}$ MOs and 2p(F) AOs in the formation of MOs of isomer.

TABLE 10: Theoretical and Experimental Relative Intensities for *A*, *B*, *C* Maxima (*A* = 1,0) in X-ray Photoelectron Spectrum of $C_{60}F_{24}$[a]

maximum	isomer **1**	isomer **2**	isomer **3**	isomer **4**	isomer **5**	isomer **6**	isomer **7**	expt
A	1,0 (24)	1,0 (24)	1,0 (24)	1,0 (20)	1,0 (20)	1,0 (12)	1,0 (10)	1,0
B		0,67 (16)	0,83 (20)	1,6 (32)	1,6 (32)	3,5 (42)	4,6 (46)	1,6
C	1,5 (36)	0,83 (20)	0,67 (16)	0,4 (8)	0,4 (8)	0,5 (6)	0,4 (4)	0,3

[a] Numbers in parentheses are equal to quantities of carbon atoms, possessing different charges.

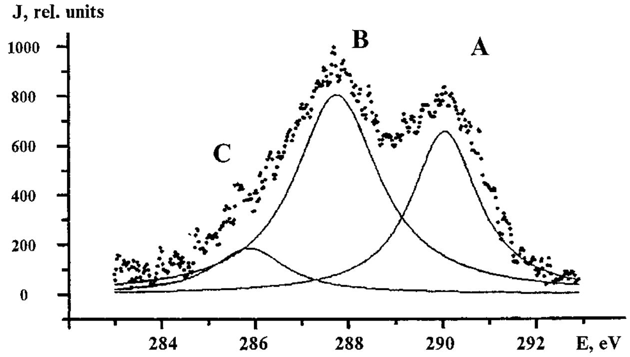

Figure 12. X-ray photoelectron C 1s spectrum of $C_{60}F_{24}$.

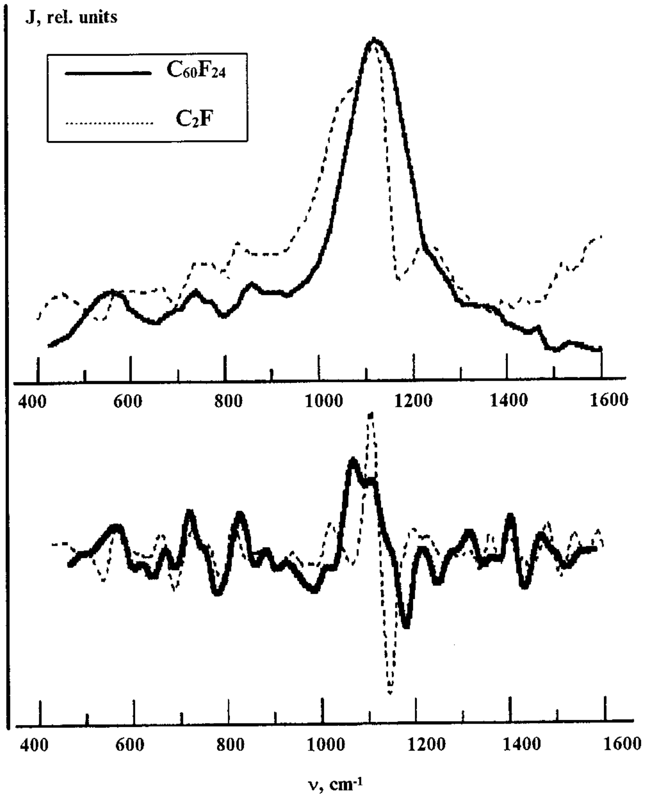

Figure 13. IR absorption spectra and their derivatives for $C_{60}F_{24}$ and graphite fluoride C_2F.

of the obvious similarity between the position and intensities of bands of IR spectra of $C_{60}F_{24}$ and C_2F, being connected with the analogous character of C−C and C−F bonds in both compounds.

Thermodynamic Stability of Polyfluorosubstituted Fullerenes. The values of the heat of formation, calculated by the PM3 method, indicate the possibility of existence of all considered $C_{60}F_{24}$ isomers. The structures with the more uniform distribution of fluorine atoms on the surface of carbon framework are thermodynamically more preferable. But, the data, obtained by us, lead us to conclude that the isomer containing sufficiently large areas of delocalized π-electron density was yielded in the synthesis. The isomers **4** and **5** can be considered as being somewhat optimal between the thermodynamic (the minimal energy of system) and kinetic requirements for the process of fullerene fluorination. The kinetic factors include the preferential ortho, para addition of fluorine atoms[7,8] and maximal conservation of the carbon π-system of the fullerene molecule.[28]

Conclusion

The comparison of the experimental (X-ray emission, X-ray photoelectron, IR spectroscopy) and theoretical (quantum-chemical calculations by the PM3 method) data for various isomers of $C_{60}F_{24}$ permits the conclusion that the appearance of CF groups on the surface of C_{60} molecule takes place with the conservation of substantial areas of the carbon π-system. The redistribution of charges on carbon atoms can be explained in terms of fragmentary analysis by the participation of vacant MOs of C_{60} in the structure of block of HOMOs for fluorofullerene. The substantial negative charges on carbon atoms, bonded with two CF groups, can be explained as the result of destruction of the cyclic π-system and the electronic interactions in the formed structures. The presence of a few CF groups near each other leads to the appearance of MOs, which are in fact lone electron pairs of fluorine atoms. The lone electron pairs of fluorine atoms can interact with σ-orbitals of the carbon framework to give the blocks of bonding and antibonding MOs (in respect to the C−F bond), existing together with MOs of the usual σ-bonds between carbon and fluorine atoms.

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References and Notes

(1) Taylor, R.; Holloway, J. H.; Hope, E. G.; Avent, A. G.; Landgley, G. J.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1992**, *9*, 665.

(2) Kniaz, K.; Fischer, J. E.; Selig, H.; Vaughan, G. B. M.; Romanow, W. J.; Cox, D. M.; Chowdhury, S. K.; McCauiey, J. P.; Strongin, R. M.; Smith III, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 6060.

(3) Yudanov, N. F.; Okotrub, A. V.; Bulusheva, L. G.; Asanov, I. P.; Lisoivan, V. I.; Shevtsov, Yu. V. *Mol. Mater.* **1996**, *7*, 127.

(4) Chilingarov, N. S.; Nikitin, A. V.; Rau, J. V.; Sidorov, L. N. *Book of Abstracts of International Workshop Fullerenes and Atomic Clusters, St. Petersburg, Russia, June 19−24.* **1995**, 147.

(5) D'yachkov, P. N.; Breslavskaya, N. N.; Ippolitov, E. G. *Dokl. Akad. Nauk* **1993**, *331*, 315.

(6) Wang, S−H.; Jansen, S. A. *J. Phys. Chem.* **1995**, *99*, 8556.

(7) Dixon, D. A.; Matsuzawa, N.; Fukunaga, T.; Tebbe, F. N. *J. Phys. Chem.* **1992**, *96*, 6107.

(8) Peel, J. B.; Rothwell, R. G. *Aust. J. Chem.* **1994**, *47*, 131.

(9) Clare, B. W.; Kepert, D. L. *J. Mol. Struct. (THEOCHEM.)* **1997**, *389*, 97.

(10) Cioslowski, J.; *Electronic Structure Calculation on Fullerenes and Their Derivatives*; Oxford University Press: New York, 1995.

(11) Okotrub, A. V.; Yumatov, V. D.; Mazalov, L. N.; Furin, G. G.; Murakhtanov, V. V.; Bulusheva, L. G. *Zh. Strukt. Khim.* **1988**, *29*, 76.

(12) Okotrub, A. V.; Murakhtanov, V. V.; Mazalov, L. N.; Terpugov, N. V.; Nikiforov, A. A.; Lunegov, S. N.; Shevtsov, Yu. V.; Belikova, G. S.; Turskaya, T. N. *Dokl. Akad. Nauk* **1993**, *329*, 752.

(13) Bulusheva, L. G.; Okotrub, A. V.; Mit'kin, V. N.; Murakhtanov, V. V.; Mazalov, L. N. *Zh. Strukt. Khim.* **1995**, *36*, 630.

(14) Bulusheva, L. G.; Okotrub, A. V.; Mit'kin, V. N.; Murakhtanov, V. V.; Mazalov, L. N. *Zh. Strukt. Khim*. **1996**, *37*, 1071.

(15) Birkett, P. R.; Kroto, H. W.; Tayior, R.; Walton, D. R. M.; Grose, R. I.; Hendra, P. J. *Chem. Phys. Lett*. **1993**, *205*, 399.

(16) Yumatov, V. D.; Okotrub, A. V.; Mazalov, L. N. *Zh. Strukt. Khim*. **1985**, *26*, 59.

(17) Mazalov, L. N.; Yumatov, V. D.; Okotrub, A. V. *Izv. Akad. Nauk SSSR* **1985**, *49*, 1483.

(18) Schmidt, M. W.; Baldridge, K. K.; Boatz J. A. *J. Comput. Chem*. **1993**, *14*, 134.

(19) Kita, Y.; Watanabe, N.; Fujii, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3832.

(20) Zonis, S. A., Simonov, G. A., Eds. *Guide for Chemist*; Ì.-L.: Goskhimizdat, 1962; Vol. I.

(21) Mahajan, V. K.; Badachhape, R. B.; Margrave, J. L. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 1103.

(22) Breslavskaya, N. N.; Diyachkov, P. N. *Koord. Khim*. **1994**, *20*, 803.

(23) Sopert, A. K.; David, W. I. F.; Siviat, D. S.; Dennis, T. J. S.; Hare, J. P.; Prassides, K. *J. Phys.: Condens. Matter* **1992**, *4*, 6087.

(24) Murakhtanov, V. V.; Mazalov, L. N.; Bulusheva, L. G. *Zh. Strukt. Khim*. **1989**, *30*, 31.

(25) Murakhtanov, V. V; Mazalov, L. N.; Okotrub, A. V. *Metallophiz. Nov. Tekhnol*. **1994**, *16*, 3.

(26) Cox, D. M.; Cameron, S. D.; Tuinman, A.; Gakh, A.; Adcock, J. L.; Compton, R. N.; Hagaman, E. W.; Kniaz, K.; Fisher, J. E.; Strongin, R. M.; Cichy, M. A.; Smith III, A. B. *J. Am. Chem. Soc*. **1994**, *116*, 1115.

(27) Yudanov, N. F.; Chernyavskii, L. I. *Zh. Struktur. Khim*. **1987**, *28*, 86.

(28) Aihara, J.; Takata, S. *J. Chem. Soc., Perkin Trans. 2* **1994**, 65.