J. Phys. Chem. A **1999,** *103,* 9921−9924

Electronic Structure of the Fluorinated Fullerene $C_{60}F_{48}$

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Received: June 18, 1999; In Final Form: September 17, 1999

The electronic structure of the fluorinated fullerene $C_{60}F_{48}$ has been studied by X-ray fluorescence spectroscopy. The C Kα spectrum of the compound has the double-humped profile with the well-defined high-energy shoulder. To interpret the C Kα spectrum and investigate the chemical bonding of $C_{60}F_{48}$, a chiral structure of D_3 symmetry was calculated at the ab initio Hartree−Fock (HF) level using the 6-31G basis set. The electron density from the highest occupied molecular orbitals (HOMOs) of the D_3 isomer is mainly localized on the carbon double bonds, and the contribution of 2p electrons of the fluorinated carbon atoms to these orbitals is also noticeable. The high-energy shoulder on the C Kα spectrum was shown to correspond to the electron transitions from HOMOs of $C_{60}F_{48}$ to 1s orbital vacancies of the carbon atoms attached to the fluorine atoms, and therefore the occurrence of this shoulder does not relate to the number of π electrons in the molecule. The molecular orbital structure of $C_{60}F_{48}$ was schematized as a set of blocks; the MOs were distinguished by the type of the chemical bonding between the atoms. Such orbital separation allowed a successful interpretation of the main features of the ultraviolet photoelectron spectrum of the fluorinated fullerene $C_{60}F_{48}$.

Introduction

Fluorination of the solid C_{60} with fluorine gas has been reported to result in a mixture of $C_{60}F_x$, where $x \leq 48$.[1−3] Predominant formation of $C_{60}F_{48}$ was reported for the reaction of F_2 with C_{60} in the NaF matrix.[4] A systematic study of the effect of the reaction time and temperature in the direct fluorination on the fluorine content in the product was carried out and optimal conditions for the preparation of the individual compound $C_{60}F_{48}$ were found.[5] Furthermore, application of the transition metal fluorides (K_2PtF_6, MnF_3) as fluorinating agents has led to the selective preparation of $C_{60}F_x$ with $x = 18$, 36, respectively.[6,7]

To date, $C_{60}F_{48}$ is the fluorinated fullerene with the highest number of fluorine atoms attached to the carbon cage. The ^{19}F NMR studies of $C_{60}F_{48}$ have provided the structure of D_3 symmetry existing as an enantiomer pair.[4] The semiempirical AM1 calculation of all possible isomers of $C_{60}F_{48}$ with a 3-fold axis has revealed two most stable structures of D_3 and S_6 symmetries.[8] Using the MNDO Hamiltonian, the D_3 and S_6 structures were also chosen among the nine isomers whose structures satisfy the observed number of peaks in the ^{19}F NMR spectrum and their integral intensities.[9]

The electronic structure of $C_{60}F_{48}$ has been studied by X-ray photoelectron, ultraviolet photoelectron, and X-ray absorption spectroscopy methods (XPS, UPS, XANES).[10] The spectra were interpreted with the use of the discrete-variational Xα calculation of the D_3 isomer.[11] The sharp peak in the low-energy region of the XANES spectrum was shown to correspond to the π antibonding states of $C_{60}F_{48}$, with the π and σ unoccupied bands of the compound being energetically separated.[10] However, the high-energy part in the UPS spectrum of $C_{60}F_{48}$ was not reproduced in the calculated electron density of states,[11] which may be due to the experimental peculiarities or the limitations of the calculation scheme.

The goal of the present contribution is to study the electronic structure of the fluorinated fullerene $C_{60}F_{48}$ using X-ray fluorescence spectroscopy. In contrast to UPS, this method gives information on the partial electron density distribution of an individual element in the valence band of the chemical compound. The results of the ab initio calculation of the D_3 isomer of $C_{60}F_{48}$ were used for the interpretation of the high-resolution C Kα spectrum of the $C_{60}F_{48}$ sample and investigation of the chemical bonding.

Experimental Details

The sample of $C_{60}F_{48}$ was prepared using the synthetic procedure described elsewhere.[5] A C_{60} sample was fluorinated by the fluorine gas at 625 K in the flow tube reactor. The product had no traces of the unreacted fullerene as it followed from the IR and electron impact mass spectra. The stoichiometry derived from the chemical analysis corresponded to $C/F = 60/48 \pm 1$, while the careful examination of the molecular composition by means of the Knudsen cell and electrospray mass spectrometry techniques showed the presence of ca. 3% of $C_{60}F_{46}$ and traces of oxygenated fluorofullerene $C_{60}F_{48}O$.

The X-ray fluorescence spectrum of $C_{60}F_{48}$ was recorded with a “Stearat” spectrometer using an ammonium biphthalate (NAP) single crystal as a crystal analyzer. This crystal has nonlinear reflection efficiency, which is corrected by the procedure described elsewhere.[12] The sample was deposited on the copper supports and cooled to liquid nitrogen temperature in the vacuum chamber of the X-ray tube with the copper anode ($U = 6$ kV, $I = 0.5$ A). The accuracy of determination of the X-ray band energy was ±0.15 eV with the spectral resolution of 0.4 eV.

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10.1021/jp992037f CCC: $18.00

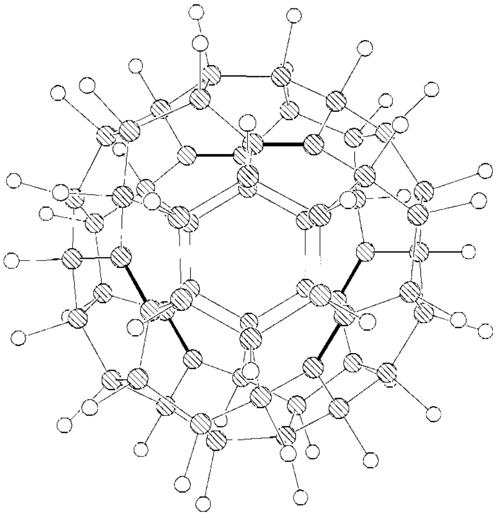

Figure 1. Molecular structure of the D_3 isomer of $C_{60}F_{48}$ relaxed by the semiempirical PM3 method. The double bonds are indicated by bold lines.

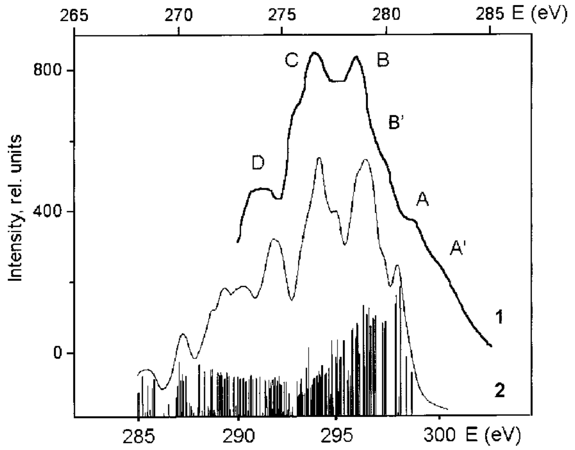

Figure 2. C Kα spectra of $C_{60}F_{48}$; experimental (1) and calculated by the ab initio method (2). The top scale corresponds to the measured photon energy; the bottom scale corresponds to the difference of ab initio eigenvalues.

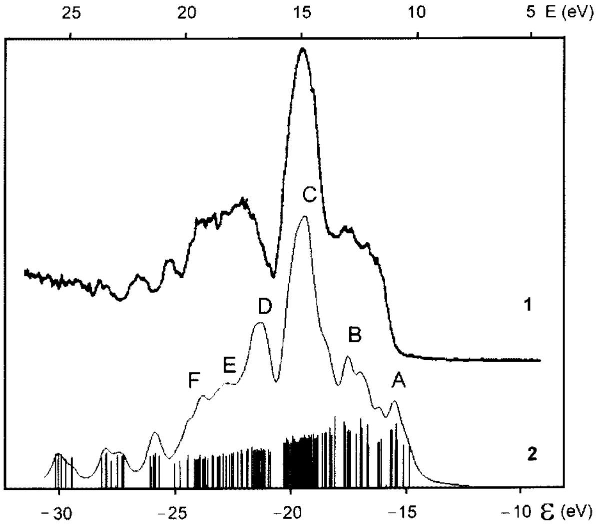

Figure 3. The reproduced from ref 10 ultraviolet photoelectron spectrum of $C_{60}F_{48}$ (1) and the calculated valence electron density of states for the D_3 isomer (2). The top scale is the binding energy; the bottom scale indicates the one-electron energies of the valence levels.

Calculations

The molecular structure of the D_3 isomer, optimized by the semiempirical PM3 method,[13] is shown in Figure 1. For this method, the geometry optimization of the C_{60} molecule gives bond lengths equal to 1.384 and 1.457 Å, which agree satisfactorily with the measured values of 1.401 and 1.458 Å.[14] Therefore, we expect to obtain the correct geometric parameters for the fluorinated derivative of the fullerene. The electronic structure of $C_{60}F_{48}$ was calculated in the framework of a Hartree–Fock self-consistent field (HF-SCF) using the 6-31G basis set within GAMESS package.[15]

Two kinds of carbon atoms, i.e., the fluorinated atoms and the bare ones, are separated in the $C_{60}F_{48}$ molecule. As it follows from our calculations, the binding energy of 1s electrons of the former kind is higher than that of the latter kind by 1.8 eV (the experimentally measured values are 2.0[10] and 2.2 eV[11]). As a result, the transitions from the same valence orbital to a C 1s vacancy in the X-ray spectrum differ in the energy of the emitted photon. Nonequivalency in these energies was taken into account in the theoretical spectrum by a separate calculation of transition intensities and energies for chemically different carbon atoms. The X-ray transition energy was computed as the difference between the eigenvalues of the valence and the core C 1s orbitals. The X-ray transition intensity was obtained by summing the squared coefficients of the carbon 2p atomic orbitals (AOs) participating in the construction of the concrete molecular orbital (MO). Such an approach for the simulation of an X-ray spectrum was previously shown to be useful for the C Kα spectra of the fullerenes C_{60} and C_{70}.[16–18] The total theoretical C Kα spectrum of $C_{60}F_{48}$ is the sum of the partial spectra for the fluorinated and nonfluorinated carbon atoms. The calculated intensities were normalized by the maximal value and broadened by convolution of the Lorenzian functions with a half-width at half-maximum (HWHM) of 0.3 eV.

Results and Discussion

The C Kα spectrum of the fluorinated fullerene $C_{60}F_{48}$ and the calculated spectrum of the D_3 isomer are given in Figure 2. The experimental spectrum has two main maxima B and C and two less intense features A and D. Comparison of the theoretical spectrum with the experimental one reveals a reasonably good agreement. However, the intensity of the short-wave shoulder A′ in the theoretical spectrum is noticeably less than that in the experimental one. The appearance of this shoulder in the experimental C Kα spectrum of $C_{60}F_{48}$ may be caused by at least two processes. The main process is the X-ray transitions from upper valence levels to core levels of the molecule. Furthermore, during the experiment the inner electrons may be resonantly excited to the unoccupied levels of the molecule and then ones return (so-called “reemission” process). Actually, from the XANES measurements of the highly fluorinated fullerenes, the excitation energy of the C 1s electrons to the lowest unoccupied orbitals is equal to 284.1 eV.[10] Due to the relaxation, the reemission of these electrons is at a somewhat lower energy. The observed difference between the calculated and measured values of the X-ray transition energies is caused by neglecting the relaxation processes in the ionized states of the compound.

To check whether the reduced intensity of the line A′ in the theoretical spectrum is connected with the multielectron processes rather than with the restriction of the used quantum-chemical method, we compared the calculated valence electron density of states (DOS) for $C_{60}F_{48}$ with the UPS spectrum reproduced from ref 10 (Figure 3). The DOS exhibits an excellent agreement with the experimental spectrum for the

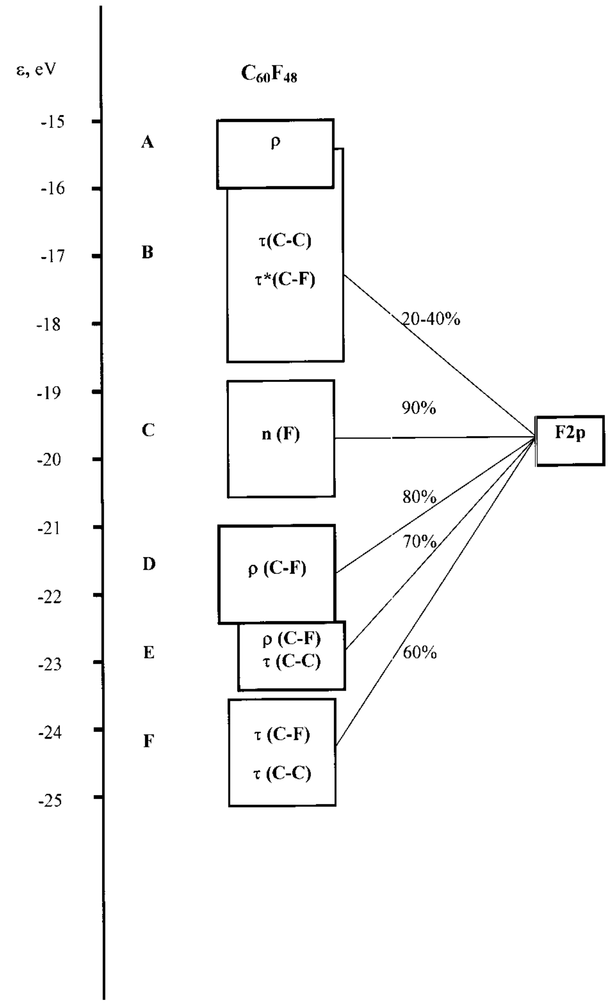

Figure 4. Correlation between levels of $C_{60}F_{48}$ and fluorine 2p-AOs. The numbers indicate the contribution of fluorine orbitals to the MO.

position and intensity of the peaks, with the exception of the high-energy spectral region. The DOS derived from the HOMOs, which occupy the energy interval from −14.97 to −15.78 eV, forms the peak A. This peak is missing from the UPS spectrum of $C_{60}F_{48}$ at photon energy $E_{h\nu} = 40$ eV. Lowering the photon energy to 11.7 eV indicated that the ionization threshold energy of the compound was 8.4 eV[10] and the absence of the contribution from the HOMOs of $C_{60}F_{48}$ in the UPS spectrum was due to the low photoionization cross section of the loosely bound electrons. Therefore, the comparison between the calculation on the D_3 isomer and the C Kα and UPS spectra of $C_{60}F_{48}$ reveals that the accuracy of the quantum-chemical method applied in this work is sufficient for the investigation of the electronic structure of the fluorinated fullerene.

Carbon and fluorine 2p-AOs may be divided into two types: radial *ρ*-orbitals directed toward the center of the carbon cage and tangential *τ*-orbitals aligned with the local normal of the cage surface. The analysis of the valence MOs of $C_{60}F_{48}$ in these terms permits us to present schematically the electronic structure of the molecule as a set of blocks (Figure 4). A number near the thin line corresponds to the percent contribution of the fluorine 2p-AOs to the MOs. Block A includes four MOs ($65a_2$, $67a_1$, 131e, 132e), the electron density from which is sufficiently localized on the double C═C bonds. The carbons 2p-AOs, composing these MOs, are radially directed, forming the *ρ* system of the molecule. The MOs of block A provide *π* bonding between the carbon atoms of the double bonds. The F2p-AOs and 2p-AOs of the fluorinated carbon atoms are also involved in the formation of these MOs—ca. 17 and 22%, respectively. The electrons of the *ρ* system are the major contributors to maximum A of the calculated DOS of the isomer (Figure 3). The MOs composing block B occupy the energy interval from −15.5 to −18.8 eV and form the high-energy structure of the UPS spectrum of $C_{60}F_{48}$. The carbon and fluorine 2p-AOs involved in these MOs are tangentially directed to the C_{60} cage, thus providing *σ* interactions of the carbon atoms, *τ*(C−C) set, and the negative overlapping between the orbitals of different kinds of atoms, *τ**(C−F) set. The contribution of the fluorine electrons to the MOs of block B increases from 20 to 40% as the MO energy is decreased.

TABLE 1: Energy Intervals of Short-Wave Features of the Calculated $C_{60}F_{48}$ Spectrum and Assigned to These Features X-ray Transitions from Upper Valence MOs to 1s Carbon Levels[a]

feature	energy interval (eV)	MOs
A′	298.27−298.01	132e, 131e
A	297.73−297.45	$67a_1$, 130e, $65a_2$, 129e, $66a_1$
B′	297.00−296.86	128e, $65a_1$, 127e
B	296.51−295.35	**132e**, $64a_1$, 126e, $64a_2$, **131e**, 125e, $63a_1$, $63a_2$, **$67a_1$**, **130e**, 124e, **$65a_2$**, **129e**, **$66a_1$**, $62a_2$, $62a_1$, 123e, 122e, $61a_2$, 121e

[a] MO marked off by bold indicates transition to 1s levels of nonfluorinated carbon atoms other MO presents transition to 1s levels of fluorinated carbon atoms.

Block C includes MOs that consist of the tangential fluorine 2p-AOs to over 90%. These MOs are practically lone electron pairs of the fluorine atoms and they form the main peak in the UPS spectrum of $C_{60}F_{48}$. The orbitals, bonding with respect to C−F interactions, are divided by a gap of 0.6 eV from the nonbonding MOs. The MOs of block D provide *σ* bonding between the carbon and fluorine atoms; the carbon−carbon interactions are very weak. The MOs responsible for *σ* bonding in the CF groups and between the neighboring carbon atoms compose block E. Finally, the MOs of block F consist of the *τ*-type carbon and fluorine AOs, providing “multicentral” bonds in the molecule.

The peculiarity of the electronic structure of $C_{60}F_{48}$ prohibits experimental indication of the valence *π* band in this compound. First, *π*-like MOs composing the *ρ* system of the molecule are distributed in the narrow energy interval of about 1 eV. Second, block A including these MOs is considerably overlapped with the next block of the occupied orbitals. Therefore, the *π* orbitals cannot appear as a separate maximum in the UPS spectrum of $C_{60}F_{48}$ even at low ionization energies. One would expect that maxima A and A′ of the C Kα spectrum of $C_{60}F_{48}$ are formed by the X-ray transition of *π* electrons and indicate the preservation of the *π* system areas on the carbon cage. The comparison between the C Kα spectrum and the theoretical one shows this is not true. Table 1 presents the correlation between the short-wave features of the spectrum and X-ray transitions of 2p electrons of fluorinated or bare carbon atoms. Maximum A′ is ascribed to the electron transitions from 131e and 132e orbitals (HOMO and HOMO + 1) to the vacancies in 1s levels of carbon atoms attached to fluorine ones. Maximum A on the C Kα spectrum of $C_{60}F_{48}$ indicates the participation of 2p-AOs of the fluorinated carbon atoms in the formation of MOs in the energy interval from −15.51 to −15.78 eV (peak A in the DOS of the D_3 isomer). The X-ray transition energies of *π* electrons correspond to maximum B of the C Kα spectrum.

The *π** states of $C_{60}F_{48}$ mainly form four lowest unoccupied MOs (LUMOs) also distributed in the energy interval of 1 eV, but they are divided from the σ^* states by a gap of 2.4 eV. This permits observation of the π^* states in the XANES spectrum of $C_{60}F_{48}$.[10]

Conclusion

The electronic structure of the highly fluorinated fullerene $C_{60}F_{48}$ was probed by X-ray fluorescence spectroscopy together with the quantum-chemical calculation of the D_3 isomer. Reasonably good agreement between theoretical and experimental data provided an extended study of chemical bonding in the molecule. The electron density from the frontier orbitals is mainly localized on the double C=C bonds conserved in the molecular structure. The valence π-like states distributed in the narrow interval are energetically overlapped with σ-like states of $C_{60}F_{48}$, which prevents their separation in the experimental UPS spectrum. The electronic structure of the considered molecule is characterized by the occurrence of the practically lone electron pairs of the fluorine atoms, which divide the MOs that are bonding and antibonding relative to carbon−fluorine interaction. These peculiarities of the $C_{60}F_{48}$ electronic structure give rise to the double-humped profile of the C Kα spectrum and the strong main maximum in the UPS spectrum.

Acknowledgment. The authors are grateful to the Russian scientific and technical program “Fullerenes and atomic clusters” (Projects No. 5-1-98 and No. 99-15-96044) and the Russian Education Ministry for the Grant in fundamental natural science field.

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