



Electronic Structure of Unoccupied States of Fluorinated Fullerenes $C_{60}F_{18}$ and $C_{60}F_{36}$

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Abstract: Comparative study of near edge X-ray absorption fine structure spectra (NEXAFS) of fluorinated fullerenes $C_{60}F_x$ ($x = 0, 18, 36$) has been implemented. Local density of unoccupied states was obtained and an accurate boundary between π^* and $(\pi+\sigma)^*$ states was determined. The experimental evidence was found that unoccupied π^* - states of $C_{60}F_x$ are delocalized ones and form cluster shells that sequentially disappear in fluorination starting from the highest state. As a result, the density of the lowest π^* - state (LUMO) was revealed to remain being constant in fluorination despite the π -electron subsystem exhaustion.

Keywords: Fluorinated fullerenes, Fluorination, NEXAFS, Electronic structure, Synchrotron radiation

INTRODUCTION

Fluorination of fullerenes seems to be interesting from the fundamental point of view, as this process makes it possible to clarify the role of different electron subsystems, π and $\pi+\sigma$, in forming the electronic structure of the cluster. During the last decade, electronic structure of different fluorinated fullerenes $C_{60}F_x$ have been extensively studied by UV photoemission spectroscopy (UPS) (1) and X-ray photoelectron spectroscopy (XPS) (2–4) by UV-visible absorption spectroscopy (2, 5) and by

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reflection electron-energy-loss (EEL) spectroscopy (6). Of particular interest is the comprehensive research of the dependence of electronic structure of fluorinated fullerenes $C_{60}F_x$ and $C_{70}F_x$ on the number of fluorine atoms in molecule ($x = 11 \div 48$) (2). Correlation of the intensities of π^* and $(\pi^*+\sigma^*)$ conjugated states in the spectra of unoccupied states with the number of fluorine atoms has been revealed: higher number (x) resulted in lowering intensities of the π^* and enhancement of the $(\pi+\sigma)^*$ conjugated states. To clarify details of this correlation, near edge X-ray absorption fine structure (NEXAFS) spectra of fluorinated fullerenes $C_{60}F_x$ with well defined number of fluorine atoms ($x = 18, 36$) and well known atomic structure have been studied (7, 8).

EXPERIMENTAL DETAILS

The experiment was performed at BESSY II storage ring (Berlin) on the Russian-German synchrotron radiation (SR) beamline equipped with the plane-grating monochromator (PGM) and the experimental station of the Russian-German laboratory (9). NEXAFS spectra were measured with the energy resolution $\Delta h\nu \sim 100$ meV. Thin (~ 10 monolayers) films of C_{60} , $C_{60}F_{18}$, and $C_{60}F_{36}$ were grown on SiO_2/Si substrate in preparation chamber of the spectrometer by evaporation of high-purity soot onto substrates just before measurements. Thin SiO_2 layer was used to prevent chemical interaction of adsorbates with the substrate. The vacuum during deposition falls up to $\sim 5 \cdot 10^{-9}$ Torr. Powders of $C_{60}F_{18}$ and $C_{60}F_{36}$ were synthesized by the technology described earlier (7, 8). The rate of the film growth was estimated by controlling the weakening of the substrate photoelectron lines. Heating SiO_2/Si substrates up to $700^\circ C$ enabled purifying of the substrate surface.

RESULTS AND DISCUSSION

Figure 1 shows the C 1s edge NEXAFS spectra of $C_{60}F_{18}$ and $C_{60}F_{36}$ measured at the photon incidence angle $\alpha \sim 45^\circ$ in comparison with C_{60} spectrum. The spectra correspond to the dependence of probability of photoadsorption due to excitation of C1s core-level electron into unoccupied π^* (sharp peaks) or σ^* (broad peak) states on the photon energy. The spectra were corrected to the dependence of the photon flux on the photon energy by normalization of experimental data to the adsorption spectrum of silicon measured in the same photon energy range. In addition, all the spectra were normalized to the intensity of high energy background at $h\nu = 320$ eV. Intensities of broad σ^* peaks of the spectra proved to be close to each other after these normalizations.

Positions of the lowest energy π^* - peak (state 1 or lower unoccupied molecular orbital (LUMO) state) of all the spectra coincide just as in Ref. (2), though the energy of the LUMO (284.5 eV) proved to be 0.4 eV higher. Figure 1 illustrates the transformation of the electronic structure of unoccupied states due to fluorination. Creation of C-F bond must modify the bonding states of carbons from sp^2 to sp^3 hybridization type. As a result, the number of π -electrons and the density of π^* -states should diminish in molecule proportional to the fluorine content, and the density of σ^* -states should increase. Such a transformation was reported in Ref. (2), in which the increase of σ^* -peak and drastic reduction of the relative intensity of LUMO - peak were observed. However, Figure 1 shows a somewhat different behavior. Relative intensity of LUMO peak (1) diminished by only 20% in attachment of 18 fluorine atoms by C_{60} and remains the same after attachment of additional 18 fluorine atoms, which results in 60% exhaustion of the π - conjugated system. To explain the observed NEXAFS spectra transformation, the following assumption was made. The π^* - states of fluofullerenes are delocalized at large extent

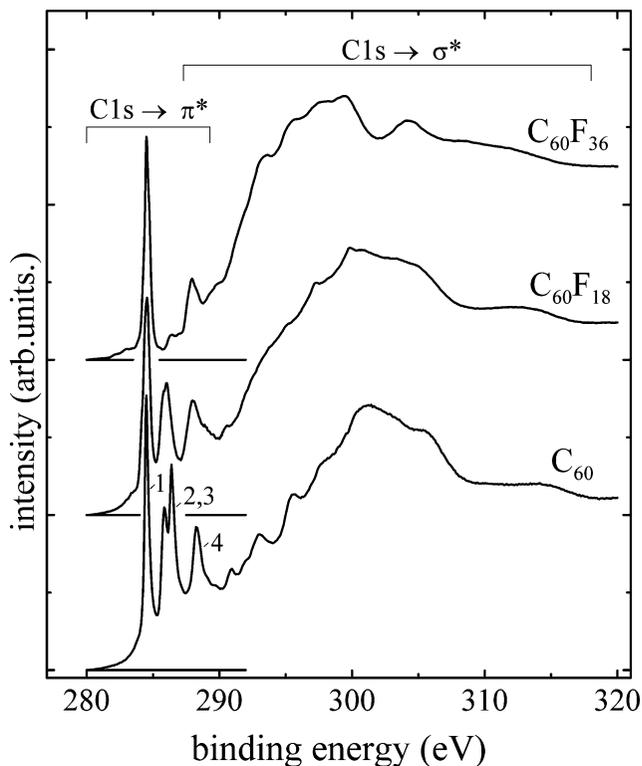


Figure 1. NEXAFS spectra of ordinary fullerene C_{60} and of fluorinated fullerenes $C_{60}F_{18}$ and $C_{60}F_{36}$.

and form cluster shells. These shells are created in the course of enlargement of the π - electron system starting from low energy states and disappear in the course of the π -electron system exhaustion starting from high energy states. Indeed, π^* - high energy states 2 and 3 rapidly disappear when π -electron system is reduced due to fluorination, whereas the intensity of low energy state 1 (LUMO) remains practically constant even at high degree of fluorination. Figure 1 also shows states 1, 2 and 3 are pure π^* - states and state 4 is the mixture of π^* and σ^* orbitals.

In summary, local density of unoccupied states was measured for fluorinated fullerenes $C_{60}F_x$ ($x = 18, 36$) in comparison with that of ordinary fullerenes C_{60} . Accurate boundary between π^* and ($\pi^*+\sigma^*$) states was determined. The conducted study of fluorinated fullerenes with different content of fluorine atoms evidences for relatively simple atomic-like structure of fluorine derived states and for vanishing the π^* -states due to the diminution of the π - electron number in the course of fluorination. The conclusion was made that unoccupied π^* - states of $C_{60}F_x$ are delocalized ones and form cluster shells. These shells sequentially disappear due to π -electron subsystem exhaustion in enlargement of fluorination extent starting from the highest state. This mechanism unexpectedly keeps constant the density of LUMO state in the course of fluorination.

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REFERENCES

1. Benning, P.J., Ohno, T.R., Weaver, J.H., Mukherjee, P., Adcock, J.L., Compton, R.N., and Dunlap, B.I. (1993) Electronic structure of highly fluorinated C_{60} . *Phys. Rev. B*, 47: 1589–1592.
2. Mitsumoto, R., Araki, T., Ito, E., Ouchi, Y., Seki, K., Kikuchi, K., Achiba, Y., Kurosaki, H., Sonoda, T., Kobayashi, H., Boltalina, O.V., Pavlovich, V.K., Sidorov, L.N., Hattori, Y., Liu, N., Yajima, S., Kawasaki, S., Okino, F., and Touhara, H. (1998) Electronic structures and chemical bonding of fluorinated fullerenes studied by NEXAFS, UPS, and vacuum-UV absorption spectroscopies. *J. Phys. Chem. A*, 102(3): 552–560.
3. 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., and Smith, A.B. (1994) X-ray photoelectron and NMR studies of polyfluorinated C_{60} : Evidence that C-C bonds are broken. *J. Am. Chem. Soc.*, 116: 1115–1120.

4. Kawasaki, S., Okino, F., Touhara, H., and Sonoda, T. (1996): Discrete-variational $X\alpha$ calculations of $C_{60}F_x$ with $x=0, 36$, and 48 . *Phys. Rev. B*, 53: 16652–16655.
5. Amarantova, S.V., Bezmelnitsyn, V.N., Boltalina, O.V., Danailov, M., Dudin, P.V., Ryzkov, A.V., and Stankevitch, V.G. (2001) Investigation of fluorinated C_{60} by means of optical spectroscopy. *Nucl. Instrum. Meth. A*, 470: 318–322.
6. Shnitov, V.V., Mikoushkin, V.M., Gordeev, Yu.S., Boltalina, O.V., and Gol'dt, I.V. (2006) Single and collective electron excitations in solid $C_{60}F_{18}$. *Fullerenes, Nanotubes and Carbon Nanostructures*, 14(2–3): 297–301.
7. Boltalina, O.V., Bolshevskii, A.Ya., Sidorov, L.N., Street, J.M., and Taylor, R. (1996) Preparation of $C_{60}F_{36}$ and $C_{70}F_{36/38/40}$. *J. Chem. Soc. Chem. Commun.*, 529–530.
8. Goldt, I.V., Boltalina, O.V., Sidorov, L.N., Kemnitz, E., and Troyanov, S.I. (2002) Preparation and crystal structure of solvent free $C_{60}F_{18}$. *Solid State Sciences*, 4: 1395–1401.
9. Fedoseenko, S.I., Vyalikh, D.V., Iossifov, I.E., Follath, R., Gorovikov, S.A., Püttner, R., Schmidt, J.S., Molodtsov, S.L., Adamchuk, V.K., Gudat, W., and Kaindl, G. (2003) Commissioning results and performance of the high-resolution Russian–German beamline at BESSY II. *Nucl. Instr. and Meth. A*, 505: 718–728.