

## C *K-V* X-ray Emission Spectra of Fluorinated and Pressure-polymerized Fullerenes

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The carbon *K-V* x-ray emission spectra (XES) of fluorinated and pressure-polymerized fullerenes ( $C_{60}F_{36}$ , *rh*- $C_{60}$ ) have been measured by an electron-probe microanalyzer to investigate the change in the electronic structures of  $C_{60}$  molecule by the introduction of  $sp^3$ -carbons. The XES spectrum of *rh*- $C_{60}$  was almost the same as that of  $C_{60}$ . On the other hand, a remarkable change was observed in the XES spectrum of  $C_{60}F_{36}$ . Discrete-variational Hartree-Fock-Slater calculations elucidated that the  $\pi$ -like electrons in the  $C_{60}$  cage decrease by fluorination but some still remain even in the carbon atoms bonded with a fluorine atom.

Key words: fullerene, high pressure, fluorine, x-ray emission, DV- $X\alpha$

### 1. INTRODUCTION

Owing to the discovery of the macroscopic production method of  $C_{60}$ , many  $C_{60}$  derivatives have been synthesized and the properties of  $C_{60}$  have been well investigated.  $C_{60}$  is a closed cage molecule comprised entirely of quasi- $sp^2$ -hybridized carbons arranged in hexagons and pentagons. For the addition of hydrogen to  $C_{60}$  introduces  $sp^3$  type carbons and changes its electronic structure, hydrogenated fullerenes, (e.g.  $C_{60}H_{36}$ , which is the first derivative to be made), have attracted much interest. However, the material is unstable and the properties have not been well known. On the other hand, new methods for the synthesization of high purity fluorinated fullerenes have been found.<sup>1, 2, 3, 4</sup> Therefore, it has become possible to investigate their structures and the properties. We reported the crystal structures and the phase transformations at high temperature of  $C_{60}F_{36}$  and  $C_{60}F_{48}$ .<sup>5</sup> On the other hand, several crystalline phases possessing two or one-dimensional infinite carbon networks have been synthesized from solid  $C_{60}$  (fcc  $C_{60}$ ) by high pressure treatment.<sup>6, 7</sup> This family of crystalline phases is called fullerene polymers or  $C_{60}$  polymers. Fullerene polymers, as fluorinated fullerenes, are considered to consist of  $sp^2$ -like (threefold coordinated) and  $sp^3$ -like (fourfold coordinated) carbon atoms.<sup>8</sup> These  $sp^2$ - and  $sp^3$ -like carbon coexisting phases are expected to have new properties which are not known for other forms of carbon. In the present study, we observed the carbon *K-V* x-ray emission spectra (XES) of fluori-

nated and pressure-polymerized fullerenes and compared them with that of  $C_{60}$ . In this paper, we also report the results of the DV- $X\alpha$  calculations of fluorinated fullerenes to understand the observed XES spectra.

### 2. EXPERIMENTS

The *K-V* ( $K\alpha$ ) x-rays are emitted by the electric dipole transition of an electron from  $2p$  to  $1s$  atomic orbitals after the photoionization of one of the  $1s$  electrons, where  $V$  denotes valence hole state. The  $2p$  orbitals of boron, carbon, nitrogen, and fluorine form valence molecular orbitals (i.e. a valence band) in compounds. Therefore, the *K-V* x-ray emission (or fluorescence) spectral line shapes represent the local (x-ray emitting atom) and partial ( $2p$ ) electron density of states (DOS) of the compounds. X-ray emission spectra are easily measured by an x-ray fluorescence spectrometer or an electron probe microanalyzer (EPMA) equipped with crystal optics. The x-ray spectra have bulk information because of the long attenuation length of x-rays.

$C_{60}$  powder sample was purchased from Hoechst ("super gold grade" > 99.78 %).  $C_{60}F_{36}$  was provided by Dr. O. V. Boltalina (Moscow State Univ.). Pressure-polymerized fullerenes were synthesized with a split-sphere type high pressure apparatus. The  $C_{60}$  powder sample charged in a Pt capsule was inserted into the center of an MgO octahedron and submitted to high pressure at 5 GPa.

Powder x-ray diffraction (XRD) measurements were performed on a Rigaku RINT-2200 using Cu

$K\alpha$  radiation. Pyrolytic graphite was used as a counter monochromator. The powder was sealed in a 0.2 mm diameter glass capillary. X-ray photoelectron spectroscopic (XPS) experiments were undertaken on an Ulvac-phi model 5600 using non-monochromatic Mg  $K\alpha$  x-rays at 1253.6 eV. The XPS spectra were observed at pressures below  $10^{-9}$  torr.

The C  $K$ -V emission spectra were measured by an EPMA with the second-order reflection. The typical measurement conditions were as follows. The electron beam size was about 50 - 100  $\mu\text{m}$  in radius. The electron acceleration energy was 8 kV and 15 kV for  $\text{C}_{60}\text{F}_{36}$  and pressure-polymerized fullerenes, respectively. The sample current was about 0.03  $\mu\text{A}$  (for  $\text{C}_{60}\text{F}_{36}$ ), 0.1  $\mu\text{A}$  (for pressure-polymerized fullerenes) to avoid sample decomposition. We made pellet samples by pressing powders. Pellet sample surfaces of  $\text{C}_{60}\text{F}_{36}$  were coated with Pt to give electric conductivity.

### 3. CALCULATIONS

The DV- $X\alpha$  calculation, one of the local density functional methods, has been highly successful in describing electronic structures of a number of molecules and clusters. The advantages of this method are that calculations are essentially free from any adjustable parameters, and that the cluster size necessary to reproduce the fine structure of a spectrum can be very small. The accuracy of the Slater's transition-state technique in calculating optical transition energies and ionization potential is well documented.<sup>9, 10</sup> It has been reported that the electronic structures calculated by the DV- $X\alpha$  method well reproduce observed electronic spectra.<sup>11</sup> For example, the measured C  $K$ -V x-ray line shapes of benzene,  $\text{C}_{60}$  and  $\text{C}_{70}$  have been successfully reproduced by the DV- $X\alpha$  calculations.<sup>12, 13</sup>

In order to determine the atomic coordinates of  $\text{C}_{60}\text{F}_{36}$ , we have assumed  $T$  symmetry and optimized atomic positions of the 60 carbon and 36 fluorine atoms by AM1 calculations. In all DV- $X\alpha$  calculations the number of sampling points was 50,000. The atomic orbitals used as basis set were 1s, 2s,  $2p_x$ ,  $2p_y$  and  $2p_z$  for each atom.

### 4. RESULTS AND DISCUSSION

Figure 1 shows the observed x-ray diffraction patterns of  $\text{C}_{60}$ ,  $\text{C}_{60}\text{F}_{36}$  and pressure-polymerized fullerenes. The diffraction lines of  $\text{C}_{60}\text{F}_{36}$  are indexed by a bcc lattice having the lattice constant  $a=1.302$  nm. Two phases were synthesized by the present high pressure treatment. It was found by the XRD experiments that rhombohedral (hexagonal-system parameters :  $a = 0.917$  nm,  $c = 2.456$  nm) and amorphous phases were produced in the synthesis temperature range of 823 - 903 K and 903 - 1223 K, respectively. For the convenience sake, the rhombohedral and the amorphous phases are abbreviated as  $rh\text{-C}_{60}$  and  $a\text{-C}_{60}$ , respectively.

Figure 2 shows the observed C 1s XPS spectra

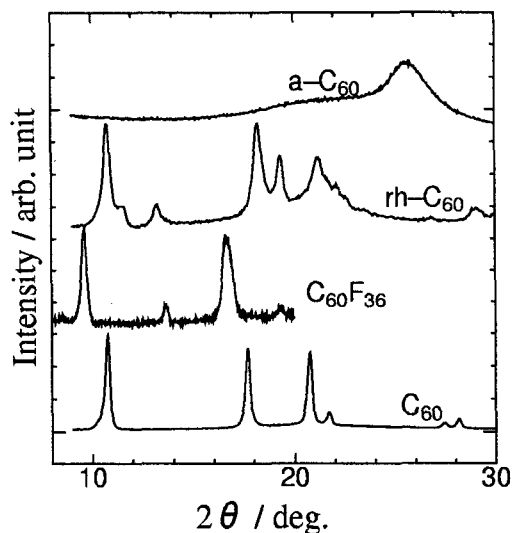


Fig. 1: X-ray diffraction patterns of  $\text{C}_{60}$ ,  $\text{C}_{60}\text{F}_{36}$ ,  $rh\text{-C}_{60}$  and  $a\text{-C}_{60}$ .

of  $\text{C}_{60}$ ,  $\text{C}_{60}\text{F}_{36}$ ,  $rh\text{-C}_{60}$  and  $a\text{-C}_{60}$ . There is no remarkable difference in the spectra of  $\text{C}_{60}$ ,  $a\text{-C}_{60}$  and  $rh\text{-C}_{60}$ . On the other hand, there are two features in the spectrum of  $\text{C}_{60}\text{F}_{36}$ ; the higher and lower energy features correspond to C 1s of carbon atoms attached to a fluorine atom ( $\text{C}^I$ ) and of bare carbon atoms ( $\text{C}^{II}$ ), respectively. The ratio of the integrated intensities of these two features is consistent with the formula  $\text{C}_{60}\text{F}_{36}$ .<sup>5, 14</sup>

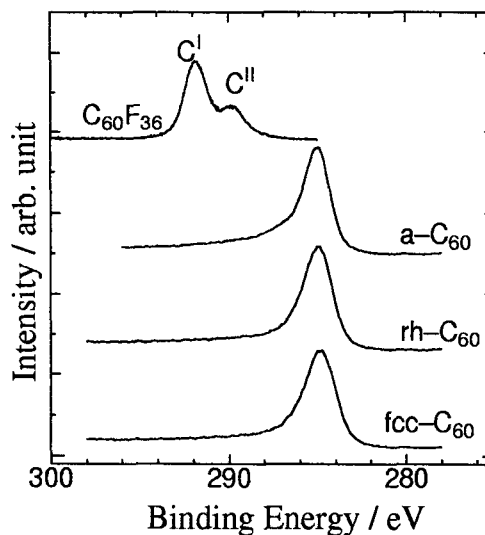
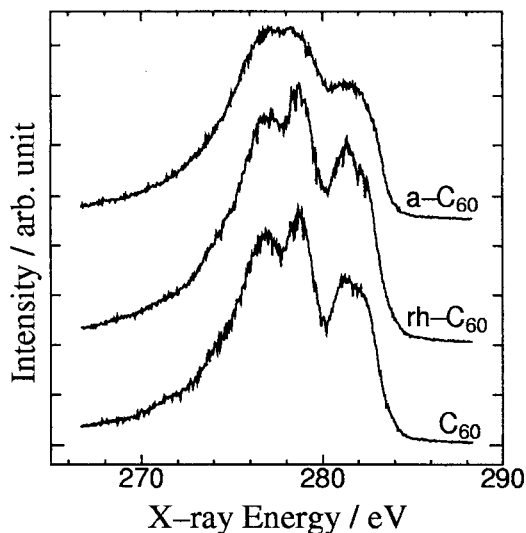
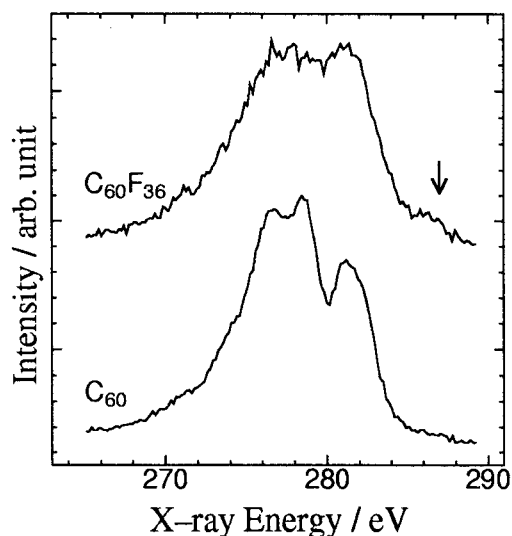


Fig. 2: C 1s XPS spectra of  $\text{C}_{60}$ ,  $a\text{-C}_{60}$ ,  $rh\text{-C}_{60}$  and  $\text{C}_{60}\text{F}_{36}$ .

Figures 3 and 4 show the observed XES spectra of pressure-polymerized and fluorinated fullerenes, respectively. Kawai et al.<sup>12</sup> reported a comparison between the XES spectra of  $\text{C}_{60}$  observed with a

Fig. 3: XES spectra of  $C_{60}$ ,  $a-C_{60}$  and  $rh-C_{60}$ .Fig. 4: XES spectra of  $C_{60}$  and  $C_{60}F_{36}$ .

variety of experimental conditions. Their discussion convinced us that our observed spectrum of  $C_{60}$  is very accurate. It was reported by Okada et al.<sup>8, 15)</sup> that several important features of the band structure of  $rh-C_{60}$  calculated by using the local density approximation are different from those of fcc  $C_{60}$ .<sup>16)</sup> They also discussed that the difference of the band gap energy between  $rh-C_{60}$  and fcc  $C_{60}$  is about 0.7 eV. However, the difference between the valence-band DOS of  $rh-C_{60}$  and fcc  $C_{60}$ <sup>17)</sup> is small and the energy resolution of our XES experiments is not so high. It would be the reason why the observed XES spectrum of  $rh-C_{60}$  is almost the same as that of  $C_{60}$  as shown in Fig. 3. On the other hand, the spectrum of  $a-C_{60}$  does not have such fine structures as that of  $C_{60}$  has. The dis-

ordered local structures of  $a-C_{60}$  result in such a broad profile.

As shown in Fig. 4, the change in XES spectra by fluorination was clearly observed. A shoulder peak (marked with an arrow in Fig. 4) in the high energy side of the profile emerges by fluorination. The C  $K-V$  XES spectrum of  $C_{60}$  is in good agreement with the C  $2p$  partial density of states (pDOS) of ground states calculated by DV- $X\alpha$  method.<sup>12)</sup> C  $K-V$  x-ray emission energy corresponds to the energy difference between  $1s$  and  $2p$  orbital energies. If there are some kinds of carbon atoms having different  $1s$  orbital energies, their  $2p$  pDOS should be separately considered to simulate XES spectrum. To simulate the spectrum of  $C_{60}F_{36}$ , DV- $X\alpha$  calculations with the electronic configuration of Slater's transition state on the two kinds of carbon atoms ( $C^I$  and  $C^{II}$ ) having different  $1s$  orbital energies were performed. Although it would be better to perform calculations on all atoms of the molecule, the following method was employed in the present work because the full calculations require a long computation time. Two calculations were done for the two representative  $C^I$  and  $C^{II}$  atoms. The simulated XES spectrum is sum of the two kinds of C  $2p$  pDOS, weighted by multiplying by the number of corresponding atoms of each kind.

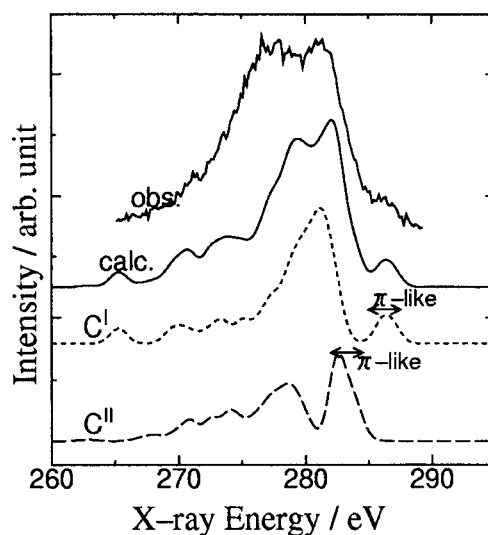


Fig. 5: The observed and calculated XES spectra of  $C_{60}F_{36}$ . Dotted and dashed lines indicate the C  $2p$  pDOS of  $C^I$  and  $C^{II}$ , respectively. The simulated peaks are broadened by a Gaussian function with a half width at half maximum (HWHM) of 0.7 eV to mimic the observed spectrum.

Figure 5 shows the observed and the simulated XES spectra of  $C_{60}F_{36}$ . As shown in Fig. 5, the simulated profile of  $C_{60}F_{36}$  is in good agreement with the observed one and the shoulder peak in the

high energy side which emerges by fluorination is also reproduced well, although the emission energies are slightly overestimated. It was found that the small peak that emerged at higher energy side by fluorination is due to the C<sup>I</sup> atom (Fig. 5).

It is considered that the highest energy peak of C<sub>60</sub> XES spectrum mainly originate from  $2p_{\pi} \rightarrow 1s$  transition. On the other hand, fluorination reduces the  $\pi$ -like electrons of C<sub>60</sub> cage and Fig. 5 indicates that the population of the  $\pi$ -like electron of C<sup>I</sup> is much smaller than that of C<sup>II</sup>. The  $2p_{\pi} \rightarrow 1s$  x-ray transition of C<sup>I</sup> and C<sup>II</sup> are observed in different energy regions (the former as a shoulder and the latter as a component of the main peak of the XES spectrum). This is due not only to the difference between the orbital energies of  $\pi$ -like electrons of C<sup>I</sup> and C<sup>II</sup> but also mainly to the difference of their  $1s$  orbital energies (Figs. 2 and 5).

### 5. SUMMARY

We observed the C  $1s$  XPS and C  $K$ -V XES spectra of the  $sp^2$ - and  $sp^3$ -like carbon coexisting C<sub>60</sub> phases synthesized by fluorination and high-pressure treatments. The spectra of C<sub>60</sub>F<sub>36</sub> are quite different from those of C<sub>60</sub>. However, no remarkable change was observed in the spectra of rh-C<sub>60</sub>. This indicates the weak interaction between two adjacent C<sub>60</sub> clusters in the polymer plane of rh-C<sub>60</sub>. On the other hand, DV-X $\alpha$  calculation for C<sub>60</sub>F<sub>36</sub> gives a good description of the XPS and XES spectra.

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