

# Soft X-ray Emission and Absorption Spectra of Hydrofullerene

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## INTRODUCTION

Several hydrofullerenes have been predicted by theoretical studies [1, 2], and synthesis and spectroscopy studies of them have intensively conducted. Among hydrofullerenes, various isomers of  $C_{60}H_{36}$  were predicted: the most symmetric one, having a double bond on each pentagon, belongs to the  $T_h$ -point-group symmetry; the most thermodynamically stable ones are the  $T$ - and  $D_{3d}$ -isomers. Okotrub *et al.* [3] have recently studied  $C_{60}H_{36}$  using conventional x-ray emission and photoelectron spectroscopies, and they confirmed that the experimental spectra closely agreed with the theoretical spectra of the  $T$ -symmetry structure. However, no high-resolution soft x-ray emission or absorption spectroscopic studies using highly brilliant synchrotron radiation, which is regarded as a powerful tool for materials characterization, have been performed yet. We therefore measured the high-resolution soft x-ray emission and absorption spectra of hydrofullerene, which probably consists mainly of  $C_{60}H_{36}$ , to identify the molecular and electronic structures, and to evaluate the feasibility of using soft x-ray emission and absorption spectroscopy to identify hydrofullerenes.

## EXPERIMENT

Powder samples of hydrofullerene, whose color was orange yellow, and buckminsterfullerene ( $C_{60}$ ) as a reference were commercially obtained from Materials and Electrochemical Research Corporation (MER). The hydrofullerene was made by hydrogenation of  $C_{60}$ . The hydrogenated  $C_{60}$  was tested by elemental analysis to determine the degree of hydrogenation; the concentration of carbon was 95.1% and that of hydrogen was 4.9%, so the stoichiometry of hydrogen in  $C_{60}H_x$  was 36.8. Therefore, the hydrofullerene sample may be considered to consist mainly of  $C_{60}H_{36}$ .

Spectroscopic measurements of x-ray emission and absorption in the C K region were made at the Advanced Light Source (ALS). X-ray emission spectra were measured using a grating x-ray spectrometer installed in beamline (BL) 8.0 [4]. The resolving power ( $E/\Delta E$ ) of the spectrometer was estimated to be higher than 500 in the C K region, using a 50- $\mu$ m entrance slit and a 600-lines/mm spherical grating having a 10-m radius. The total-electron-yield (TEY) absorption spectra were measured by monitoring the sample photocurrent in BL-6.3.2 [5]. The resolving power of the TEY absorption measurements was estimated to be about 1600 using a 600-lines/mm variable-line-spacing grating and a 20- $\mu$ m exit slit.

## RESULTS AND DISCUSSION

Figure 1 shows x-ray emission and TEY absorption spectra in the C K region of the hydrofullerene and  $C_{60}$  as a reference. The emission spectrum of hydrofullerene exhibited a broad main peak around 279 eV (denoted by A) and a high-energy shoulder peak near 283 eV (B). The absorption spectrum of the hydrofullerene at the C K threshold exhibited peaks at 285 eV (C), 289 eV (E), and 293 eV (F), and a shoulder at 287 eV (D). These absorption-spectral features, which differ from those of  $C_{60}$ , also directly reflect the molecular-structural difference between hydrofullerene and  $C_{60}$ . To identify the x-ray emission and absorption spectral features of the

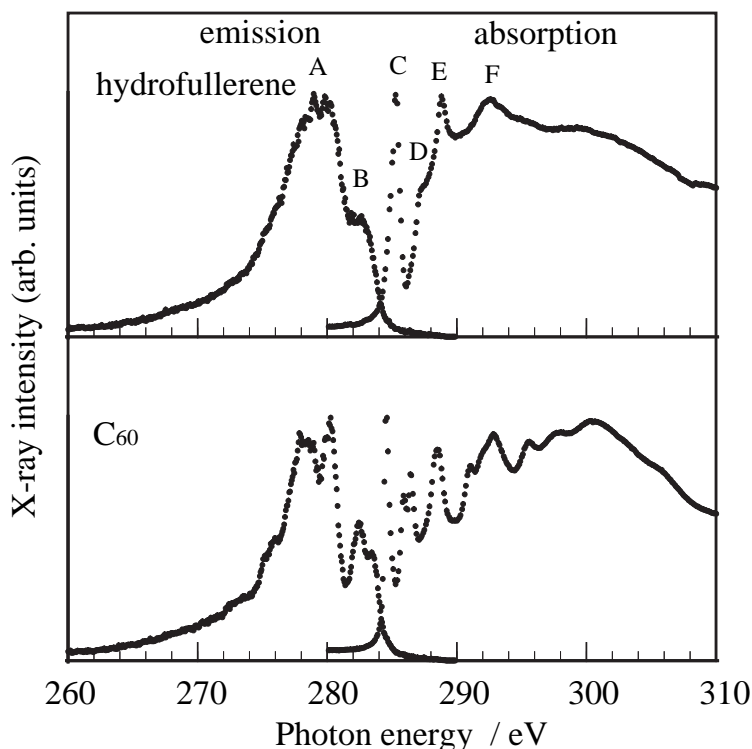


Figure 1 C K x-ray emission and absorption spectra of hydrofullerene (upper panel) and  $C_{60}$  (lower panel) as a reference. Distinctive spectral features in the x-ray emission spectrum of the hydrofullerene are denoted by A and B, and those in the absorption spectrum by C-F.

hydrofullerene, we calculated C2p- and C2s-DOS spectra of the three most likely  $C_{60}H_{36}$  isomers ( $T$ -,  $T_h$ -, and  $D_{3d}$ -point-group symmetry  $C_{60}H_{36}$ ) using discrete variational (DV)-X $\alpha$  molecular orbital calculations [6]. In these isomers, thirty-six of the carbon atoms bonding to hydrogen atoms take the  $sp^3$  configuration, and the remaining twenty-four carbon atoms take  $sp^2$ , forming double bonds and benzenoid rings. Figure 2 shows the occupied and unoccupied DOS spectra of  $T$ -,  $T_h$ -, and  $D_{3d}$ - $C_{60}H_{36}$ , and  $C_{60}$  as a reference. These spectra were obtained by broadening the total C2p- and C2s-DOS with 0.5-eV-wide Lorentzian functions. The highest occupied molecular orbital (HOMO) energy was normalized to 0 eV in the molecular orbital (MO) energy. In the occupied C2p-DOS spectra of the  $C_{60}H_{36}$  isomers, the spectral features are similar to each other: a high-energy peak at 0 eV, main broad peaks around -4 eV, and a low-energy tail from -6 eV to -20 eV. The occupied C2s-DOS spectra of these isomers are also similar to each other: main broad peaks around -15 eV and a high-energy tail up to -2 eV. In the unoccupied C2p-DOS spectra, the spectral features are distinctly different among the  $C_{60}H_{36}$  isomers. In the lowest unoccupied molecular orbitals (LUMO) region near 5 eV, a sharp peak was observed in the  $T$ -isomer, a double-peak structure in the  $T_h$ -isomer, and a broader peak in the  $D_{3d}$ -isomer. In the region from 7 to 15 eV, where the C2p orbitals are hybridized with C2s orbitals, three peaks were clearly observed at 7.5, 10.5, and 13 eV in the  $T$ -isomer. However, a finer peak structure was observed in the  $T_h$ -isomer and a broader structure in the  $D_{3d}$ -isomer.

From the viewpoint of molecular structure identification, the differences in the fine structure in the unoccupied C2p-DOS spectra do show potential for identifying the isomers from x-ray absorption spectral measurements. By comparing the unoccupied C2p-DOS spectra of the  $C_{60}H_{36}$  isomers with the measured x-ray absorption spectrum, we may identify the major portion of the

measured hydrofullerene as the *T*-isomer, because the calculated spectrum of the *T*-isomer was most similar to the measured spectrum. By analogy with the x-ray emission and absorption spectral features of the hydrofullerene assigned by DV- $X\alpha$  molecular orbital calculations, we explained the spectral features of the hydrofullerene as follows: (1) The main peak A and high-energy shoulder B in the x-ray emission spectrum are due to  $\sigma$  and  $\pi$  orbitals, respectively, formed by  $sp^2$ - and  $sp^3$ -C atoms. (2) The sharp peak C at 285 eV in the absorption spectra is due to  $\pi^*$  orbitals, and the other fine-structure peaks D–F are due to the hybridized un-occupied molecular orbitals formed by the  $sp^2$ - and  $sp^3$ -C atoms.

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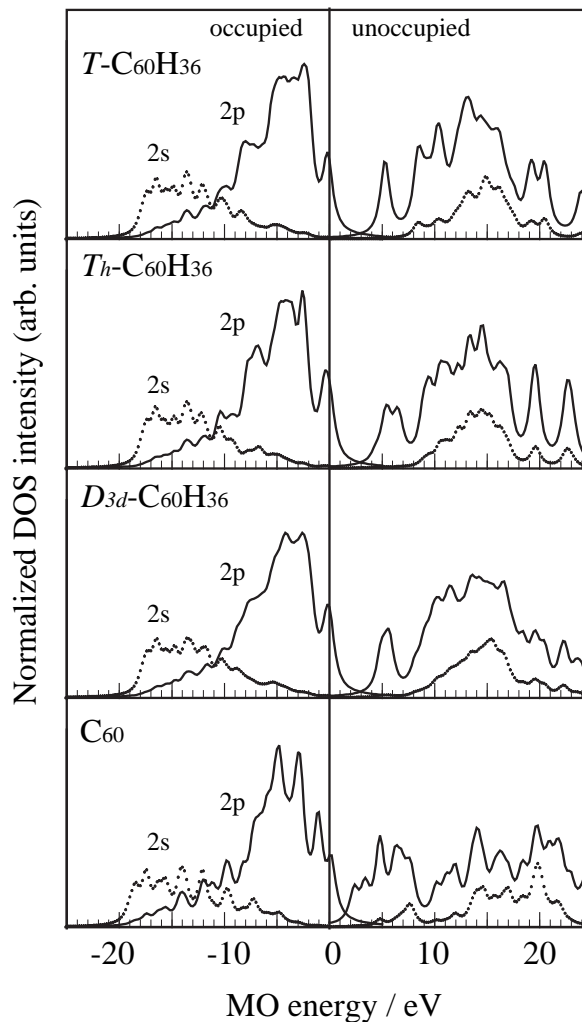


Figure 2 Occupied and unoccupied C2p- (solid lines) and C2s- (dotted lines) DOS spectra of the *T*-, *T<sub>h</sub>*-, and *D<sub>3d</sub>*- $C_{60}H_{36}$  and  $C_{60}$  as a reference, which were obtained by DV- $X\alpha$  molecular orbital calculations. Each spectrum was obtained by broadening the individual DOS with 0.5-eV-wide Lorentzian functions. The highest-occupied-molecular-orbital (HOMO) energy was normalized to 0 eV in the molecular orbital (MO) energy.