Soft X-ray emission and absorption spectroscopy of hydrofullerene

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Abstract

High-resolution soft X-ray emission and absorption spectra in the C K region of hydrofullerene, which probably consists mainly of C_{60}H_{36}, were measured using highly brilliant synchrotron radiation to identify its molecular structure and electronic structure. Comparison with the C2p-DOS spectra, calculated by discrete variational (DV) Xα molecular orbital calculations, of three possible C_{60}H_{36} isomers, showed that the measured X-ray spectra approximately agreed with the calculated C2p-DOS spectra of the T-symmetry isomer. The X-ray spectral features were explained by the electronic structure hybridized between the sp² and sp³ carbon atoms of the T-symmetry C_{60}H_{36}. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrofullerenes have recently been considered to be interesting materials particularly in relation to carbon nanotubes that may be able to store hydrogen [1]. Several hydrofullerenes have been predicted by theoretical studies [2,3], and synthesis and spectroscopic studies of them have been intensively conducted. Among hydrofullerenes, C_{60}H_{36} in particular has been studied by various spectroscopic methods, such as IR, NMR, UV, and electron/X-ray/neutron diffractions, to identify its molecular structure and electronic structure [4–7]. Various isomers of C_{60}H_{36} were predicted: the most symmetric one, having a double bond on each pentagon, belongs to the Tₕ point-group symmetry, and the T- and D-isomers are the most thermodynamically stable ones. Okotrub et al. [8] have recently studied C_{60}H_{36} using conventional X-ray emission and photoelectron spectroscopy, 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 [9], have been performed yet.

From the X-ray emission spectra, we can clarify the partial density of states (pDOS) in occupied valence orbitals, because the X-ray emission process
is governed by the selection rule in dipole transition. Soft X-ray emission spectroscopy is especially useful for characterizing carbon materials because carbon contamination on the sample surface can be negligible due to the longer mean free path of soft X-rays in matter. In addition, both conducting and insulating materials can be analyzed because the soft X-ray emission process is not affected by the electrical charge of the samples. From the X-ray absorption spectra, we can obtain electronic structural information about unoccupied orbitals, which are strongly related to the occupied valence orbitals. Therefore, the combination of the soft X-ray emission and absorption spectral measurements provides significant information about the electronic structure and chemical bonding states, and can be utilized for characterizing materials.

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. In this paper, we describe the high-resolution C K X-ray emission and absorption spectra of the hydrofullerene, and discuss the spectral features revealed by molecular orbital calculations in relation to the molecular and electronic structures.

2. Spectroscopic measurements and molecular orbital calculations

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} [10–14]. The purity of the C_{60} as the starting material was at least 99.5%. The C_{60} was placed in a high-pressure reactor equipped with resistive heating. The sample was heated to about 200°C under vacuum to dry and purify it. The reactor was then pressurized with high-purity hydrogen to ~9000 psi and slowly heated to 400°C in about 30 min, then held at around 400°C for several hours. 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_{36} was 36.8. Therefore, the hydrofullerene sample may be considered to consist mainly of C_{60}H_{36}. However, its molecular structure was unclear. 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 [15]. The resolving power (E/ΔE) of the spectrometer was estimated to be higher than 500 in the C K region, using a 50-μm 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 [16]. 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-μm exit slit. In these TEY absorption measurements, a photodiode detector which had negligible carbon contamination was used as an incident-beam-intensity monitor to eliminate the effect of carbon contamination on the beamline optics.

Discrete variational (DV) Xα molecular orbital calculations [17] were performed to identify the measured X-ray emission and absorption spectra. In the X-ray emission process, the core-hole states in inner orbitals are the initial states and the ionization states in the valence orbitals, resulting from the transition of valence electrons to the inner core holes with X-ray emission, are the final states. However, DV-Xα molecular orbital calculations have been successfully applied on the basis of the ground state electronic structure, because cancellation of the relaxation and correlation effects causes the calculated spectra to agree with the measured X-ray emission spectra, in particular with the K-V X-ray emission spectra [18]. Therefore, DV-Xα molecular orbital calculations for identifying the C K X-ray emission and absorption spectra of the hydrofullerene were made on the basis of the ground state electronic structure. Cluster model structures, as input data for the calculations, were optimized by the molecular mechanics method [19] using commercially obtained MM2 software. The calculations were accomplished using the SCAT program [17] in
commercially obtained DV-Xα software on a DOS/V computer having a 400-MHz Pentium II processor. The calculated DOS spectra were obtained by broadening the DOS with the appropriate energy-width Lorentzian functions to fit the measured X-ray spectral features.

3. Results and discussion

Fig. 1 shows X-ray emission and TEY absorption spectra in the C K region of the hydrofullerene and C_{60}. Both X-ray emission and absorption spectra of C_{60} are in good agreement with the previously published data [20,21]. 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). These spectral features had a broader structure than those of C_{60}. This is reasonable because C_{60} consists of only sp^3 carbon atoms with a highly symmetric molecular structure resulting in a highly degenerated valence electronic structure, whereashydrofullerene consists of sp^3 and sp\(^3\) carbon atoms in a less-symmetric molecular structure, resulting in a less-degenerated electronic structure. The absorption spectrum of the hydrofullerene at the C K threshold exhibited peaks at 285 eV (denoted by 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 hydrofullerene, we calculated C2p- and C2s-DOS spectra of C_{60}H_{36} isomers using DV-Xα molecular orbital calculations. Fig. 2 shows the molecular structure of the three most likely isomers: T-, T\(^+_x\)-, and D\(^+_x\)-point-group symmetry C\(_{60}\)H\(_{36}\) [4]. In these isomers, 36 of the carbon atoms bonding to hydrogen atoms take the sp^3 configuration, and the remaining 24 carbon atoms take sp^2, forming double bonds and benzenoid rings. T- C_{60}H_{36} has four benzenoid rings located at tetrahedral positions, T\(^+_x\)-C_{60}H_{36} has 12 isolated double bonds, and D\(^+_x\)-C_{60}H_{36} has two benzenoid rings located at the poles and six isolated double bonds.

Fig. 3 shows the occupied and unoccupied DOS spectra of T-, T\(^+_x\)-, and D\(^+_x\)-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, their 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\(^+_x\)-isomer, and a broader peak in the D\(^+_x\)-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\(^+_x\)-isomer and a broader structure in D\(^+_x\)-isomer.
From the viewpoint of molecular structure identification, the similarity of the occupied C2p-DOS spectra among the three isomers shows that it is difficult to identify the molecular structure of C_{60}H_{15} isomers from C K X-ray emission spectral measurements. However, 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 \( \text{C}_{60} \) \( \text{H}_{36} \) 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; peaks C–F in the measured spectrum in Fig. 1 correspond to the peaks c–f, respectively, in the calculated spectrum of the T-isomer in Fig. 3.

There are four types of carbon atoms in \( \text{T-C}_{69} \text{H}_{36} \), as shown in Fig. 4. Thirty-six carbon atoms bonding to hydrogen atoms take the sp\(^3\) configuration, and the remaining 24 carbon atoms take sp\(^2\), forming six-membered benzene rings. The 24 sp\(^3\)-C atoms (denoted by type I) are all identical, and each of them bonds to two sp\(^2\)-C atoms and one sp\(^1\)-C atom. There are three types of sp\(^3\)-C atoms: 24 of the sp\(^3\)-C atoms (types II and III) each bond to two sp\(^3\)-C atoms, one sp\(^2\)-C atom, and one H atom, while the other 12 sp\(^3\)-C atoms (type IV) each bond to three sp\(^2\)-C atoms and one H atom. Fig. 5 shows (a) occupied and (b) unoccupied C2p- and C2s-DOS spectra of the individual sp\(^2\)- and sp\(^3\)-C atoms. Measured C K X-ray emission and absorption spectra of hydrofullerene are superimposed on the total occupied and unoccupied C2p-DOS spectra, respectively. Spectral features A and B observed in the X-ray emission spectrum were approximately reproduced by the total occupied C2p-DOS spectra, and features C, D, E, and F in the absorption spectrum were also reproduced by the total unoccupied C2p-DOS spectra. By comparing the X-ray emission and absorption spectra of hydrofullerene with the calculated C2p- and C2s-DOS spectra, we were able to assign the peak structure in the measured spectra. In the emission spectrum, the broad main peak A corresponds to the C2p-DOS of sp\(^3\)-C (I), sp\(^2\)-C (II, III), and sp\(^3\)-C (IV), resulting in \( \sigma \) orbitals. The high-energy shoulder B corresponds only to the C2p-DOS of sp\(^3\)-C, and it can be assigned to \( \pi \) orbitals. For the absorption spectrum, the unoccupied orbital populations of the individual carbon atoms are shown in Table 1. Peak C can be assigned mainly to \( \pi^* \) orbitals, because the 2p orbitals of sp\(^3\)-C (I) account for ~90% of the population at peak C. For peaks D, E, and F, their orbital populations are shared by the sp\(^3\)-C (I), sp\(^2\)-C (II, III), and sp\(^3\)-C (IV) with 11–45% of 2p orbitals and up to about 11% of 2s orbitals. In particular, 2p orbitals of both sp\(^3\)-C (I) and sp\(^3\)-C (II, III) account for more than 30% of the population at peak D, and 2p orbitals of both sp\(^2\)-C (II, III) and sp\(^3\)-C (IV)
Fig. 4. Local structure of T-C_{46}H_{126}. Hydrogen atoms bonding to sp^3 carbon atoms are not shown in the figure. Four different types of carbon atoms are denoted by I-IV.

(a) occupied (emission)  (b) unoccupied (absorption)

Fig. 5. Calculated C2p- and C2s-DOS spectra of the four different types of carbon atoms (I-IV) in T-C_{46}H_{126}. The upper panels compare the measured X-ray emission and absorption spectra (dotted lines) with the calculated total C2p-DOS spectra (solid lines) of T-C_{46}H_{126}. 
Table 1
Orbital populations of the four different types of carbon atoms (I-IV) in the unoccupied orbitals corresponding to the measured X-ray absorption peaks denoted by C-F

<table>
<thead>
<tr>
<th>MO energy/eV</th>
<th>Orbital population/%</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>sp²-C (I)</td>
</tr>
<tr>
<td>2s</td>
<td>2p</td>
</tr>
<tr>
<td>(C) 5.2</td>
<td>0.6</td>
</tr>
<tr>
<td>(D) 8.6</td>
<td>3.1</td>
</tr>
<tr>
<td>(E) 10.4</td>
<td>2.3</td>
</tr>
<tr>
<td>(F) 13.2</td>
<td>6.1</td>
</tr>
</tbody>
</table>

account for more than 30% at peak E. This shows that peak D has more sp² character than peak E. Peak F is mainly due to σ* character of sp³-C (II, III) and sp²-C (I).

4. Conclusion

We measured high-resolution soft X-ray emission and absorption spectra in the C K region of hydrofullerene, which probably consists mainly of C_{60}H_{36}, using highly brilliant synchrotron radiation. By comparing the measured X-ray spectra, especially absorption spectra, with the calculated C2p-DOS spectra of three possible C_{60}H_{36} isomers, we showed that the major portion of the measured hydrofullerene may be the T-symmetry isomer. By analogy with the X-ray emission and absorption spectral features of the hydrofullerene assigned by DV-Xα 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 σ and π orbitals, respectively, formed by sp²- and sp³-C atoms. (2) The sharp peak C at 285 eV in the absorption spectra is due to σ* orbitals, and the other fine-structure peaks D-F are due to the hybridized unoccupied molecular orbitals formed by the sp²- and sp³-C atoms. These results show that high-resolution soft X-ray emission and absorption spectroscopy, combined with molecular orbital calculations, will be a useful tool for identifying the molecular and electronic structures of hydrofullerenes.

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References


