Contribution of edge-carbon atoms and non-benzenoid rings in graphitic carbons to $\pi^*$ peak profiles in CK-XANES spectra

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Abstract In order to analyze the local structure of graphitic carbons by soft X-ray absorption spectroscopy, CK-XANES spectra of polycyclic aromatic compounds having 5-membered pentagonal or 7-membered heptagonal rings were theoretically analyzed by first-principles calculations. Pentagonal rings in the bent graphitic structure take different $\pi^*$ orbital states. Hence, pentagonal rings split the $\pi^*$ peak into two peaks in CK-XANES spectra. Heptagonal rings create electrostatic potential holes in graphitic structures, and the carbon atoms in the heptagonal ring can be regarded as conjugated edge carbon atoms. Hence, heptagonal rings also split the $\pi^*$ peak into two peaks. Edge-carbon atoms split the $\pi^*$ peak into two peaks in CK-XANES spectra. Consequently, carbon atoms in non-benzenoid rings and the edge-carbon atoms in graphitic structures make the $\pi^*$ peak profile wider when compared to graphite.

1. Introduction
Local structure analysis is important in improving the physical/chemical functions of graphitic carbons, which have been utilized for battery electrodes, catalysts, adsorbents, carbon fiber composites, carbon alloys, and nano-carbons. This is because physical/chemical properties of graphitic carbons depend on the electronic states of the graphitic structures. In identifying the local structure, X-ray absorption near-edge structure (XANES) spectroscopy is a powerful tool because XANES spectra can easily and finely provide element- and orbital-selective information based on the selection rule [1]. XANES spectra can also be well simulated by various theoretical calculation methods. Therefore, the combination of XANES measurements and theoretical calculations has been a powerful tool for finely determining the local structure of carbon materials at the atomic scale.

From local structure analysis of graphitic carbons using XANES measurements and the first-principle calculations, we have previously clarified that the $\pi^*$ peak profiles in CK-XANES spectra involve information on the edge carbon atoms in graphitic structures [2-5]. In this study, aiming to further extract the local structure information of non-benzenoid rings from the $\pi^*$ peak profiles, we have calculated the CK-XANES spectra of various graphitic structures having 5-membered pentagonal rings or 7-membered heptagonal rings and compared these results to those for structures with 6-membered hexagonal rings.

2. Methods
2.1. XANES and DOS calculations
CK-XANES spectra were theoretically simulated by the first-principles density-functional theory (DFT) calculation code, CASTEP [6]. An individual molecular model was placed in a sufficiently large super cell. After structure optimization by the Materials Studio code, calculations in the ground state were achieved in CASTEP. Then calculations in an excited state with a C1s$^{-1}$ core hole were performed for each carbon atom. The transition energy of the calculated XANES spectra were corrected by considering the energy differences at the valence and core levels in the ground and excited states [7].
The density of states (DOS), convoluted with a Lorentzian function having a 0.5 eV width, were calculated using the discrete variational (DV)-Xα method \[8\]. To assign the π* and σ* peaks in the calculated XANES spectra, unoccupied C2p- and C2s-DOS profiles were compared with the XANES profiles. Electrostatic potential surface maps were also obtained with the DV-Xα calculations.

2.2. Calculation Models

Three types of polycyclic aromatic hydrocarbon (PAH) models, as shown in Figure 1, were used for calculations: Coronenes, which consist of 6-membered rings; Corannulenes, whose center rings are 5-membered pentagonal rings; and [7]Circulenes, whose center rings are 7-membered heptagonal rings. To elucidate the electronic effects between the edge atoms and center atoms, cluster size was varied to circulenes, circumcirculenes, and circumcircumcirculenes. The smallest models of Coronene (C_{24}H_{12}), Corannulene (C_{20}H_{10}), and [7]Circulene (C_{28}H_{14}) are Circulenes. The larger models of Circumcoronene (C_{34}H_{18}), Circumcorannulene (C_{40}H_{15}), and Circumn[7]circulene (C_{63}H_{31}) are Circumcirculenes. The largest models of Circumcircumcoronene (C_{96}H_{24}), Circumcircumcorannulene (C_{120}H_{20}), and Circumcircum[7]circulene (C_{112}H_{28}) are Circumcircumcirculenes. In the models, CK-XANES spectra of commercially available Coronene and Corannulene were experimentally measured using synchrotron radiation soft X-rays in BL-6.3.2 \[9\] at the Advanced Light Source (ALS).

3. Results and discussion

3.1. Coronenes

Figure 2 shows the cluster model, calculated XANES spectra, C-DOS, and electrostatic potential surface map with the cluster model of Coronene (a), Circumcoronene (b), and Circumcircumcoronene (c). For Coronene, the center C atoms are labeled as 1_{C_{hex}}, the conjugated edge C atoms as 2_{C_{ed-C}}, and the H-terminated edge C atoms as 3_{C_{ed-H}}. The measured CK-XANES spectra can be well reproduced by the calculated XANES spectra (total). Therefore, the XANES spectra calculated by CASTEP are confirmed as being reliable for XANES analysis. In the C-DOS, three 2p*-DOS peaks, which are not hybridized with the 2s*-DOS, can be identified as π* peaks.
Corresponding to the three π* peaks, the three threshold peaks in the calculated XANES spectra can be assigned to the π* peaks. In the calculated XANES spectra, the 1C\textsubscript{hex} atoms in the center hexagonal ring exhibit a single π* peak, while the 2C\textsubscript{ed}C\textsubscript{con} conjugated edge C atoms and 3C\textsubscript{ed}H\textsubscript{H-terminated} edge C atoms exhibit the split π* peaks. It can be clarified that such split π* peaks of the edge C atoms make the π* peak profile wider.

For the Circumcoronene and Circumcircumcoronene, similar π* peak splitting can be exhibited at the edge C atoms in the calculated XANES spectra. Such localized electronic states of edge C atoms can be clearly visualized in the electronic potential surface maps; the edge C atoms have a fairly positive potential while inner C atoms have a negative potential. Additionally, electronic states of the π* peak splitting of the edge C atoms cannot affect the inner C atoms, because the 1C\textsubscript{hex}~3C atoms in Circumcoronene and the 1C\textsubscript{hex}~5C atoms in Circumcircumcoronene exhibit the single π* peak profiles. These calculated results agree with those of previous reports [4, 5, 10].

3.2. Corannulenes
Figure 3 shows the results for Corannulene (a), Circumcorannulene (b), and Circumcircumcorannulene (c), which all have a 5-membered pentagonal ring at the cluster center.
Figure 3. Cluster model, electrostatic potential surface, calculated CK-XANES spectra, and C- DOS of Corannulenes. Measured CK-XANES spectrum is compared to the calculated XANES spectra in Corannulene (a). In the calculated XANES spectra, split π* peaks are marked with solid circles.

For Corannulene, the center C atoms of the pentagonal ring are labeled as 1C_{pen}, the conjugated edge C atoms as 2C_{ed-C}, and the H-terminated edge C atoms as 3C_{ed-H}. The measured CK-XANES spectra of corannulene can be well reproduced by the calculated XANES spectra (total). Again, the XANES spectra calculated by CASTEP are confirmed as being reliable for XANES analysis. Corresponding to the three π* peaks of C-DOS, the threshold three peaks in the calculated XANES spectra can be assigned to the π* peaks. In the calculated XANES spectra, the 1C_{pen} atoms in the center pentagonal ring exhibit the split π* peaks, which is different from the 1C_{hex} atoms in Coronene. This difference can be explained by considering the electronic states of π* orbitals in Corannulene. Corannulene takes a bent plane structure due to the center pentagonal ring. The π* orbitals in the convex side and in the concave side take different electronic states. The difference can be visualized in the electrostatic potential maps when viewed from the top and rear sides, which splits the π* peak into two peaks. Hence, C atoms in a pentagonal ring make the π* peak wider. The 2C_{ed-C}, conjugated edge C atoms, and 3C_{ed-H}, H-terminated C atoms, also exhibit the split π* peaks.

In the calculated XANES spectra of Circumcorannulene and Circumcircumcorannulene, similar π* peak splitting can be exhibited in the 1C_{pen} atoms. The conjugated edge C atoms, 4C_{ed-C}, and H-terminated C atoms, 5C_{ed-H}, in Circumcorannulene exhibit the split π* peak profiles. The conjugated edge C atoms, 6C_{ed-C}, and H-terminated C atoms, 7C_{ed-H}, in Circumcircumcorannulene also exhibit the split π* peak profiles. It can also be clarified that such split π* peaks of the edge C atoms make the π* peak profile wider. By contrast, inner 2C–3C atoms in Circumcorannulene and 2C–5C atoms in Circumcircumcorannulene exhibit the single π* peak profiles. It is therefore confirmed that C atoms in the pentagonal ring and the edge C atoms make the π* peak profile wider.
3.3. [7]Circulenes

![Figure 4. Cluster model, electrostatic potential surface, calculated CK-XANES spectra, and C-DOS of [7]Circulenes. In the calculated XANES spectra, split π* peaks are marked with solid circles.](image)

Figure 4 shows the results of [7]Circulene (a), Circum[7]circulene (b), and Circumcircum[7]circulene (c), which all have a 7-membered heptagonal ring at the cluster center.

In [7]Circulene, the center C atoms of the heptagonal ring are labeled as 1C\textsubscript{hep}, the conjugated edge C atoms as 2C\textsubscript{ed-C}, and the H-terminated edge C atoms as 3C\textsubscript{ed-H}. Corresponding to the three π* peaks of C-DOS, the threshold three peaks in the calculated XANES spectra can be assigned to the π* peaks. In the calculated XANES spectra, the 1C\textsubscript{hep} atoms at the center heptagonal ring exhibit the split π* peaks, which is different from the 1C\textsubscript{hex} atoms in Coronene. This difference can be explained by considering the electronic states of π* orbitals in the heptagonal ring. The electrostatic potential map of [7]Circulene shows an electrostatic potential hole at the heptagonal ring. This suggests that the 1C\textsubscript{hep} atoms can be regarded as conjugated edge C atoms. Hence, C atoms in the heptagonal ring exhibit the split π* peak profile. The 2C\textsubscript{ed-C} of conjugated edge C atoms and 3C\textsubscript{ed-H} of H-terminated C atoms also exhibit the split π* peaks.

In the calculated XANES spectra of Circum[7]circulene and Circumcircum[7]circulene, similar π* peak splitting can be exhibited in the 1C\textsubscript{hep} atoms due to the electrostatic potential holes at the heptagonal rings. The conjugated edge C atoms, 4C\textsubscript{ed-C}, and H-terminated C atoms, 5C\textsubscript{ed-H}, in Circum[7]circulene exhibit the split π* peak profiles. The conjugated edge C atoms, 6C\textsubscript{ed-C}, and H-terminated C atoms, 7C\textsubscript{ed-H}, in Circumcircum[7]circulene also exhibit the split π* peak profiles. It can also be clarified that the split π* peaks of the edge C atoms make the π* peak profile wider. By contrast, inner 2C–3C atoms in Circum[7]circulene and 2C–5C atoms in Circumcircum[7]circulene exhibit the single π* peak profiles.

It is therefore confirmed that C atoms in the heptagonal ring and the edge C atoms make the π* peak profile wider.
4. Conclusion

CK-XANES spectra of graphitic structures having non-benzenoid rings were theoretically calculated to analyze the local structure of graphitic carbons. The conjugated and H-terminated edge C atoms in graphitic structures exhibited split π* peak profiles. C atoms in the 5-membered pentagonal rings also exhibited split π* peak profiles, due to the different π* orbital states of the convex and concave sides in the vent structures. C atoms in the 7-membered heptagonal rings also exhibited split π* peak profiles, due to the electrostatic potential hole at the heptagonal ring. It is concluded that edge carbon atoms in the graphitic structures and in non-benzenoid rings make the π* peak profile wider in CK-XANES spectra.

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