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Soft X-Ray Emission Spectral Analysis of Graphite Fluoride $(CF)_n$ using the DV-Xα Calculations

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ABSTRACT

We measured the soft X-ray emission spectra in the C and F *K* regions of graphite fluoride $(CF)_n$ by suppressing sample decomposition due to synchrotron radiation (SR) excitation, and analyzed the X-ray spectral features using the DV-Xα method. The high-energy peak in the C *K* spectra is assigned to the π peak due to the C 2p orbitals hybridized with the F 2p orbitals. In addition, the X-ray emission spectra can be successfully reproduced by the calculated C and F 2p density of states (DOS) of the stretched C-F bond models in which the C-F bond length is longer than the typical length of 1.397 Å.

INTRODUCTION

Graphite fluoride $(CF)_n$ has unique properties, which include heat-resistance, electrical capabilities, and solid lubrication. Numerous studies on $(CF)_n$ have been performed from the view points of electronic/crystal structures and chemical states/properties [1-5]. For example, Motoyama *et al.* [5] have measured the C *K* X-ray emission spectra of $(CF)_n$ using electron probe microanalysis (EPMA). Their spectra were acquired by moving the sample position during electron-beam irradiation, because electron-beam irradiation easily decomposes $(CF)_n$. The observed C *K* X-ray emission spectral feature has a main peak with a high-energy peak. However, the X-ray spectral features have not been clearly analyzed by theoretical methods.

We have employed soft X-ray emission and absorption spectroscopy for chemical analysis of light-element materials using synchrotron radiation (SR) [6-7]. We have confirmed that soft X-ray spectral measurements by SR excitation have novel advantages for chemical analysis of organic materials, which include less damage to organic material samples by monochromatized-SR-irradiation. In order to obtain reliable soft X-ray emission spectra (XES) of $(CF)_n$ and to investigate its electronic structure, we measured the XES of $(CF)_n$ using a monochromatized SR beam as the excitation probe and analyzed the spectral features using the discrete variational (DV) -Xα molecular orbital (MO) calculations [8].

In the present paper, we describe a reliable XES in the C *K* and F *K* regions of $(CF)_n$, and compare the measured X-ray spectra to their density of states (DOS) calculated by the DV-Xα method.

EXPERIMENTS

The samples were commercially available $(CF)_n$ powder and highly oriented pyrolytic graphite (HOPG) as a reference. Soft X-ray emission spectral measurements in the C and F *K* regions were performed in the beamline BL-8.0.1[9] at the Advanced Light Source (ALS).

XES were obtained using a grating X-ray spectrometer equipped with 10- m curvature radius gratings (for a groove density of 600 lines/mm in the C *K* region and 1500 lines/mm in the F *K* region). The incident SR beam was tuned at 320 eV for the C *K* measurements and at 720 eV for the F *K* measurements. To determine the measurement conditions, the irradiation-time dependence on the C *K* X-ray emission spectra of $(CF)_n$ was measured as shown in Fig. 1. Although the spectral profile in the initial irradiation time of 0-1 min clearly demonstrated a high-energy peak at 282 eV, this peak intensity gradually decreased as the irradiation time increased; the high-energy peak become broader after irradiating between 5- 6 min. To suppress the sample decomposition due to SR-irradiation, we measured each spectrum for 30 s and accumulated ten spectra taken at different sample positions.

3. RESULTS AND DISCUSSION

Figure 2 shows the XES in the C and F *K* regions of $(CF)_n$, compared with the C *K* spectra of HOPG and $(CF)_n$ measured by Motoyama [5] using an EPMA. In the C *K* spectra, $(CF)_n$ exhibits a main peak at 278 eV and a high-energy peak at 282 eV. To compare the spectral features of $(CF)_n$ to HOPG, the high-energy peak is assigned to the π peak. Although the relative intensity of the π-peak to the main peak of $(CF)_n$ excited by SR is slightly lower than that of $(CF)_n$ by an EPMA, the spectral features of the main peak and the π-peak are similar each other. A single peak feature is observed in the F *K* spectrum of $(CF)_n$.

To analyze the measured X-ray spectral feature of $(CF)_n$, we calculated the DOS using the DV-Xα method, and compared them to the X-ray spectra. Figure 3 shows the cluster models of $C_{96}H_{24}$ for graphite and $C_{96}F_{96}H_{24}$ for $(CF)_n$ in the DV-Xα calculations. In the DV-Xα calculations for these graphitic-structured materials, it has been confirmed that cluster models with nearly 100-atoms in the backbone were sufficient for spectral analysis [10]. Molecular Mechanics (MM2) methods were used to optimize the structure of these cluster models. In the optimized basal $(CF)_n$ model, the C-F bond-length (denoted by $L_{C\text{-}F}$) is 1.397 Å. The calculation was performed in the ground-states with a basis set of 1s, 2s, and 2p orbitals for C and F atoms. Occupied DOS, which were broadened with a 0.5 eV wide Lorentzian functions, were obtained for the central C and F atoms, which are denoted by asterisks in Fig. 3. Figure 4 shows the calculated DOS of graphite (HOPG) and $(CF)_n$ compared to their X-ray spectra. In graphite, the calculated C 2p-DOS well reproduces the X-ray spectral features. Therefore, the DOS calculation using the 96-atom backbone cluster model is sufficiently reliable for spectral analysis. In $(CF)_n$, the C *K* X-ray spectral features, which consist of a main peak and a high-energy peak, can be roughly reproduced by the C 2p-DOS, while the F 2p-DOS can successfully reproduce the F *K* X-ray spectral features. In addition, the MO energy region of the F 2p-DOS corresponds to the high-energy portion of the C 2p-DOS. Hence, it is confirmed that the high-energy peak in the C *K*-XES is a π peak hybridized with F 2p orbitals.

However, the high-energy peak intensity cannot be sufficiently reproduced by the C 2p-DOS. To reproduce this peak intensity, we performed additional DOS calculations, focusing on the C-F bond-length ($L_{C\text{-}F}$) dependence of the C 2p-DOS. Figure 5 shows the DOS in the C and F atoms of the $C_{96}F_{96}H_{24}$ in which the basal C-F bond length in the center C and F atoms was varied from 0.997 Å (shortened, $\Delta L_{C\text{-}F} = -0.4$ Å) to 2.397 Å (stretched, $\Delta L_{C\text{-}F} = +1.0$ Å). In the shortened $L_{C\text{-}F}$ models, the low-energy portion (σ) of the C 2p-DOS is enhanced as the $L_{C\text{-}F}$ becomes shorter. On the other hand, in the stretched model, the high-energy portion (π) hybridized with F 2p orbitals is enhanced as the $L_{C\text{-}F}$ become longer. The enhanced high-energy peak features of the C 2p-DOS in the stretched C-F bond models ($\Delta L_{C\text{-}F} = +0.4 \sim +0.6$ Å) appear to be consistent with the measured C *K* X-ray spectral features. The F *K* X-ray spectra can also be reproduced by the stretched C-F bond models. It is therefore confirmed that the DOS calculations tuning the C-F bond length can successfully reproduce the X-ray spectra in C and F *K* regions of $(CF)_n$.

4. CONCLUSION

To understand the soft X-ray emission spectral features of graphite fluoride $(CF)_n$, XES in the C and F *K* regions of $(CF)_n$ were carefully measured using the monochromatized synchrotron radiation, and the spectral features were analyzed by the DV-Xα MO calculations. By comparing the measured X-ray spectra to the DOS of a $C_{96}F_{96}H_{24}$ cluster model, the measured high-energy peak in the C *K* spectra is assigned to the π peak due to the hybridized C 2p with F 2p orbitals. However, the DOS of the basal cluster model with a typical C-F bond length of 1.397 Å cannot sufficiently reproduce the peak intensity of the π peak. From the further DOS calculations on the C-F bond length dependence, the X-ray spectral features can be reproduced with the stretched C-F bond models. It is therefore concluded that DOS calculations by the DV-Xα method can successfully reproduce the X-ray emission spectra in the C and F *K* regions of $(CF)_n$, and that the spectral features can be understood by the hybridization of valence orbitals between the C and F atoms.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1 Irradiation-time dependence of the C *K* X-ray emission spectra of $(CF)_n$. Spectra with an irradiation time of 0-1 min, 5-6 min, and 9-10 min were taken with 1-min scans, while the spectrum with 15-18 min was taken with 3-min scans.

Figure 2 Soft X-ray emission spectra in the C (upper panel) and F *K* (lower) regions of $(CF)_n$ and HOPG. C *K* spectrum of $(CF)_n$ measured with an EPMA [5] is also shown under the permissions for the use of the spectral data by Elsevier Ltd.

Figure 3 Cluster models of $C_{96}H_{24}$ for graphite and $C_{96}F_{96}H_{24}$ for $(CF)_n$ used in the DV-Xα calculations. Hydrogen atoms that terminate the carbon atoms at the cluster edges are not shown.

Figure 4 Comparison of the calculated DOS of $(CF)_n$ and HOPG with the measured X-ray emission spectra in the C and F *K* regions.

Figure 5 DOS of the C and F atoms in the $C_{96}F_{96}H_{24}$ cluster model where the basal C-F bond length in the center C and F atoms is varied from 0.997 Å (shortened, $\Delta L_{C\text{-}F} = -0.4$ Å) to 2.397 Å (stretched, $\Delta L_{C\text{-}F} = +1.0$ Å).

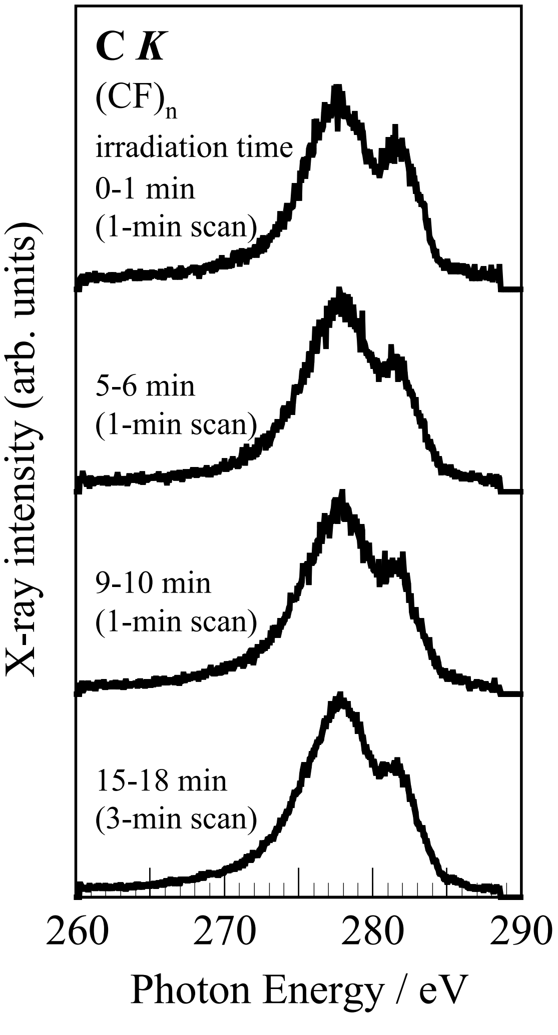
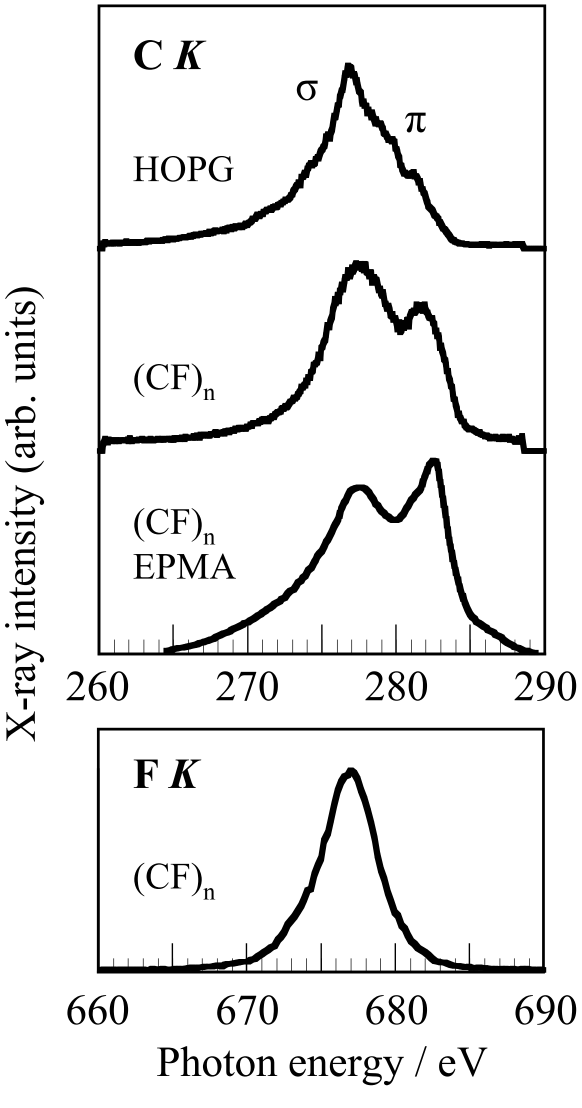


Fig. 1 S. Ueda et al.



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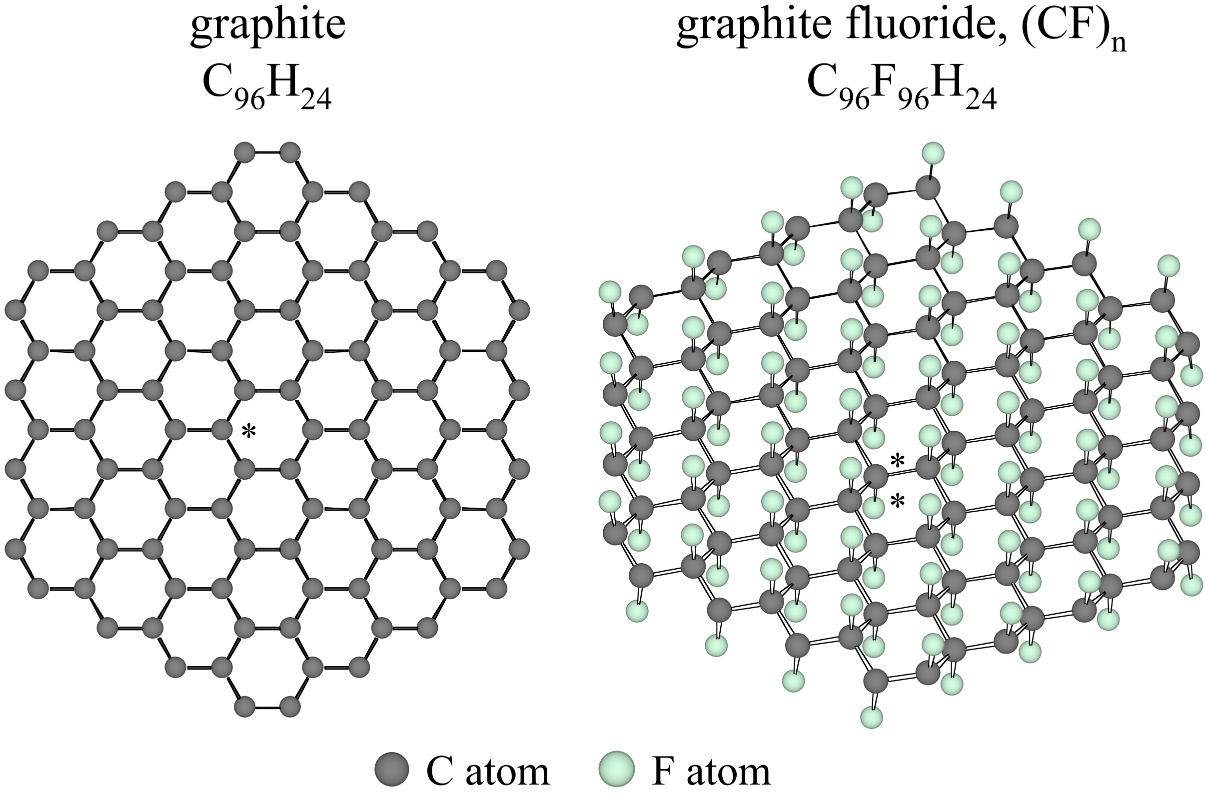
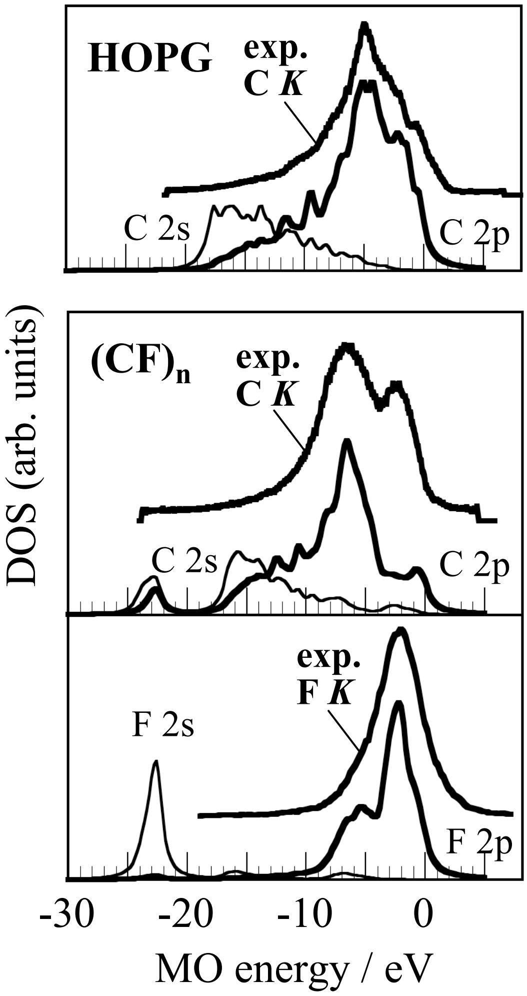

graphite

$C_{96}H_{24}$

graphite fluoride, $(CF)_n$

$C_{96}F_{96}H_{24}$

Fig. 3 S. Ueda et al.



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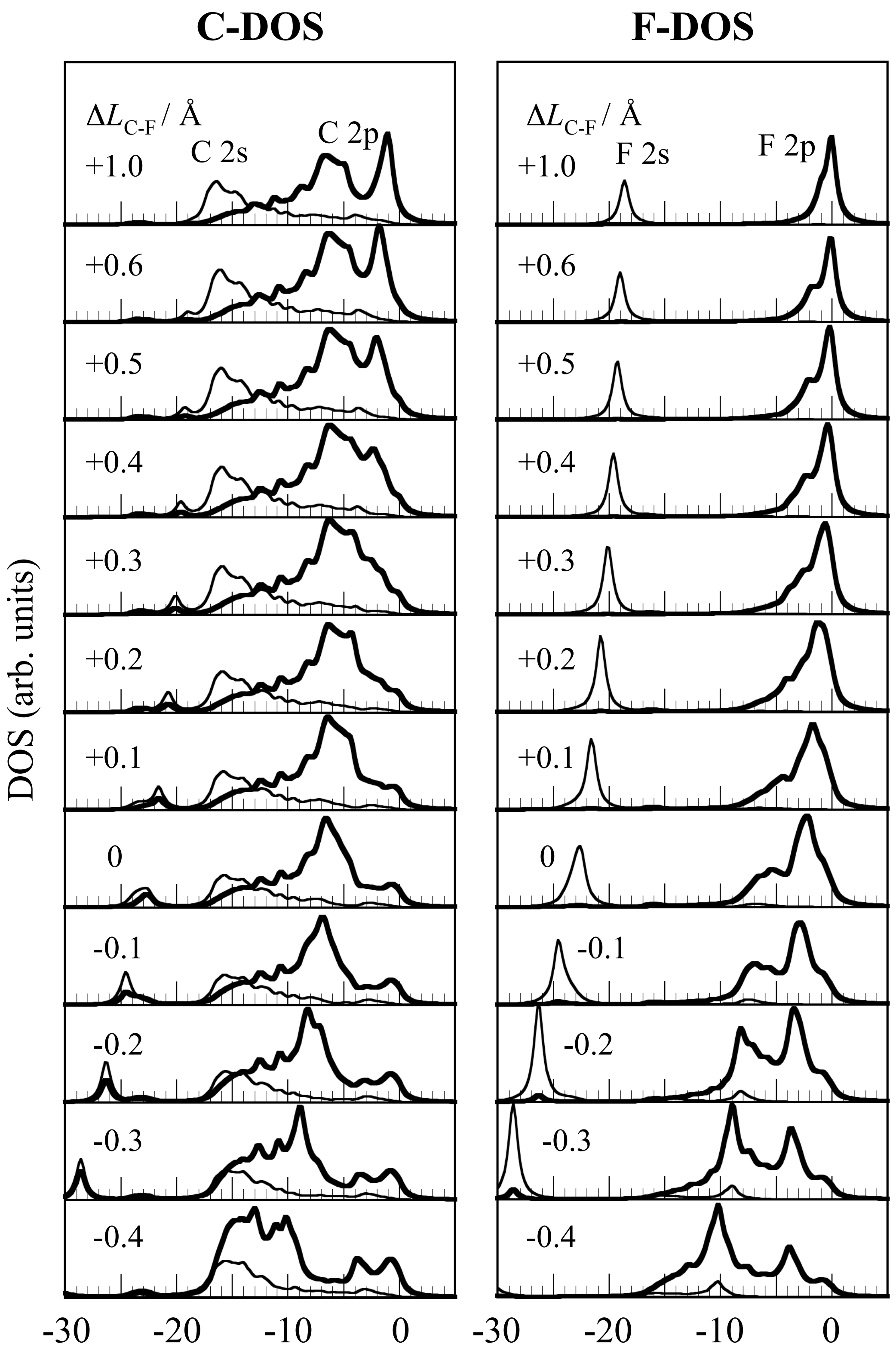

Fig. 5 S. Ueda et al.