

Multiple Scattering Approach to Polarization Dependence of F K-Edge XANES Spectra for Highly Oriented Polytetrafluoroethylene (PTFE) Thin Film

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Abstract. The polarization dependence of F K-edge X-ray absorption near edge structure (XANES) spectra of highly-oriented thin-film of polytetrafluoroethylene (PTFE) has been analyzed by using multiple scattering theory. The spectra show clear polarization dependence due to the highly-oriented structure. The multiple scattering calculations reflects a local structure around an absorbing atom. The calculated results obtained by considering intermolecular-interactions are in good agreement with the observed polarization-dependence. We have also analyzed structural models of the radiation damaged PTFE films.

Keywords: XANES, multiple scattering theory, polytetrafluoroethylene

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INTRODUCTION

As a photogenerated core-hole is localized at the absorbing atom, the core-level excitation causes Auger decay and sometimes breaks specific chemical-bonds. We can break the specific chemical-bond, if we control photon energy and photon polarization. This technique is called 'molecular scalpel'. In order to discuss the technique, we need to know what kind of structural changes are caused in the irradiation. Historically, in 1983 Eberhardt *et al.* [1] presented the first observation of a site-specific photo-fragmentation for acetone molecules in gas phase. For acetone molecules in gas phase, C^+ and O^+ ions are selectively observed following the carbon 1s to σ^* ($C=O$) excitation. They foresaw the use of energy tunable soft X-rays as 'molecular knife' for breaking large organic molecules at certain atomic sites. Similar experiments have since been conducted for many gaseous molecules and solids [2]. For the solid state, however, less prominent site-specificity has been observed.

Polytetrafluoroethylene (PTFE) $-(CF_2)_n-$ is a fundamental organic material with unique properties such as high chemical-stability, small surface-energy, and excellent electrical-insulation, etc. The ground state structure is not a plane trans-zigzag chain but a three-dimensional helix with symbol '1 $\times$ 13/6' [3]. Highly-oriented thin-films of PTFE on metal substrates can be obtained by the mechanical rubbing method [4]. The screw axis of the helix is oriented parallel to the rubbing direction. Linearly-polarized XANES spectra of an oriented PTFE film at the F and C K-edges show dichroic signals, which depend on the angle between the photon polarization-vector ϵ and the rubbing direction due to

anisotropic chemical bonds. When we irradiate the PTFE with monochromatic photons (the energy is 683eV), C-F bonds are selectively broken by relaxation processes [5]. In this paper, we discuss the F K-edge XANES spectra of the oriented PTFE film by using multiple scattering theory, and give some model structures for the damaged sample caused by photons with excitation energy of the F 1s to C-F σ^* .

EXPERIMENT

Highly-oriented PTFE thin-films were obtained by vacuum evaporation onto Cu substrates, followed by the mechanical rubbing [4]. F K-edge XANES spectra were measured by a total electron yield method at BL-13C, Photon Factory, KEK. We measured the F K-edge spectra by changing the angle α between the rubbing direction and the photon polarization-vector ϵ at normal incidence (see Fig. 1a). The observed polarization dependences are shown in Fig. 1 for the pristine (a) and the damaged (b) films. At $\alpha = 0^\circ$ the ϵ is parallel to the screw axis, and at $\alpha = 90^\circ$ the ϵ is parallel to the C-F bonds. As shown in Fig. 1a the observed main peak in the pristine PTFE at $\alpha = 90^\circ$ is 683 eV, and is ascribed to the transition of F 1s to C-F σ^* [5]. Similar transitions are observed in the case of F K-edge electron-energy-loss near edge structure for the fluoroethylenes and for the 1,3-perfluorobutadienes [6]. While the pristine samples show clear angular dependence (Fig. 1a), the damaged samples do not show the clear photon polarization dependence (Fig. 1b) [7].

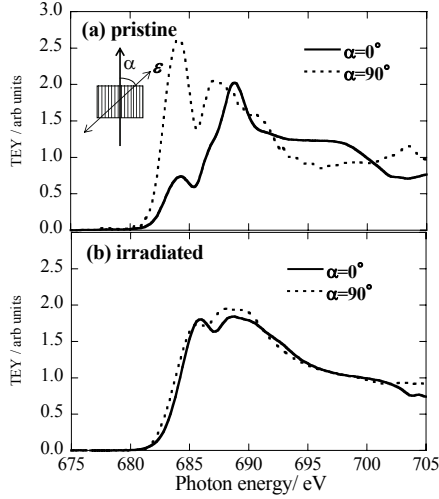


FIGURE 1. Observed polarization dependence of F K-edge XANES spectra for polytetrafluoroethylene (PTFE). Angle α is defined by the photon polarization-vector ϵ and the rubbing direction. (a) is pristine samples. (b) is the observed results after the x-irradiation at energy 683 eV. Irradiation time is 10 h for $\alpha=0^\circ$ and 9 h for $\alpha=90^\circ$.

THEORY

According to multiple scattering theory of K-edge XANES [8], the absorption cross section σ with the linearly polarized photon is written by

$$\sigma = -\frac{2}{\pi} \text{Im} \left[\rho_1(k)_c^2 e^{2i\delta_1^A} [t^{-1}(1-X)^{-1}]_{10,10}^{A,A} \right], \quad (1)$$

where A indicates the excited atom site, δ_l^A is the scattering phaseshift of the l th partial wave at site A obtained by the conventional non-local Hartree-Fock method. The $\rho_l(k)$ is the radial dipole integral of wave number k , and l_c is the angular momentum of the initial core state. In eq. (1), the $(1-X)^{-1}$ describes a renormalized infinite-order multiple scattering processes. The operator t is in an angular-momentum representation of the t -matrix. The photon polarization-vector is chosen parallel to the z -axis in eq. (1).

RESULTS AND DISCUSSION

First, we discuss effects of intermolecular interactions for PTFE molecules on F K-edge XANES spectra by comparing those of the crystalline state and of the isolated molecule.

Figure 2b shows the schematic of the PTFE molecule, $\text{CF}_3(\text{CF}_2)_{24}\text{CF}_3$. Intermolecular distances in the crystalline state are $a = 0.968$ nm and $b = 0.559$ nm [3] (Fig. 2a). In the following calculations, we excite the F

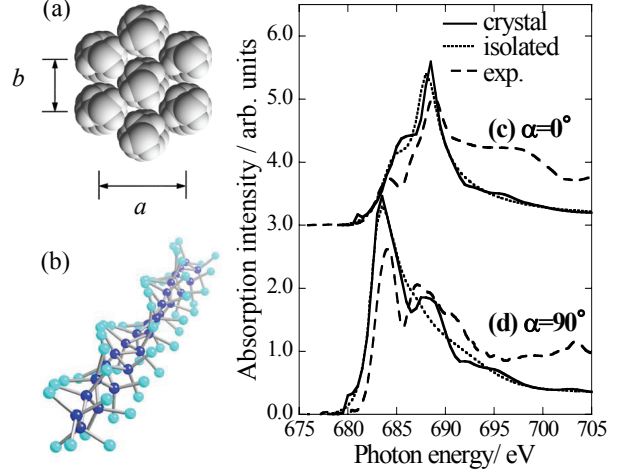


FIGURE 2. (a) and (b) are a schematic of a condensed phase of PTFE and an isolated PTFE chain, respectively. Comparison of the calculated F K-edge spectra of crystal PTFE (solid line), the isolated molecule (dotted line), and the observed spectra (dashed line). (c) and (d) are the case of $\alpha = 0^\circ$ and the case of $\alpha = 90^\circ$, respectively.

atom at the middle of this chain, and converged spectra are obtained by use of an atomic cluster with radius 0.6 nm. In the case of the crystalline PTFE (see Fig. 2a), the atomic cluster includes 78 atoms (25 carbon and 53 fluorine atoms). Figures 2c, d show the comparison of the crystalline state and the isolated molecule. Both $\alpha = 0^\circ$ (Fig. 2c) and $\alpha = 90^\circ$ (Fig. 2d) give characteristic structure in the observed spectra. The comparison between the observed spectrum and the calculated results shows different background in high photon-energy (Fig. 2c,d). The difference would be caused by the muffin-tin approximation in the calculations.

In Fig. 2c, the most intense peak of the calculated result for the crystal is positioned at a slightly higher energy than that of the calculated result of the isolated molecule. The difference between the calculated results of the crystal and the isolated molecule is small. Generally, the photoelectron tends to be emitted along the axis of the photon polarization-vector ϵ . At $\alpha = 0^\circ$ the ϵ is parallel to the screw axis, intramolecular scattering of the photoelectron dominates the spectra. At $\alpha = 90^\circ$ the calculated XANES of the isolated molecule (dotted line) does not have any peak structure near 688 eV, whereas the calculated result for the crystalline state and the observed spectrum have the peak (Fig. 2d). Because the direction of ϵ is perpendicular to the screw axis, the photoelectron is easily accessible to the nearest neighbor molecule. We thus conclude that the intermolecular scattering paths contribute to the peak. The multiple scattering approach thus can describe the angular dependence of F K-edge XANES spectra of PTFE. Next, we consider

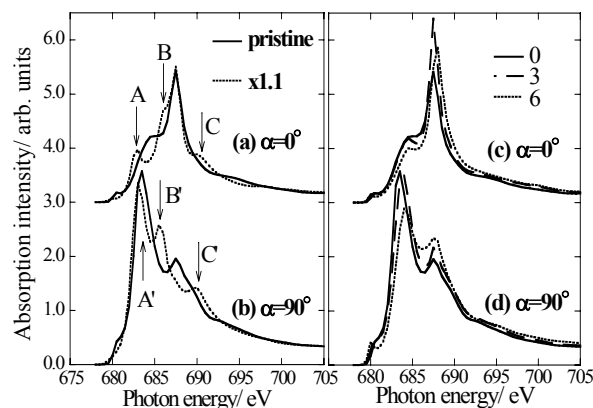


FIGURE 3. Comparison of the intermolecular distance dependence of F K-edge XANES (a and b) and calculated results of F K-edge XANES spectra for PTFE with F-defects (c and d). (a) and (b) are the results of $\alpha = 0^\circ$ and $\alpha = 90^\circ$, respectively. 'pristine' is the results of the intermolecular distance 0.56 nm (same as 'crystal' in Fig. 2). 'x1.1' is the result of the distance 0.56 (nm) $\times 1.1 = 0.62$ (nm). Numbers in (c) and (d) mean the number of F-defects (n_F).

the dependence of the spectra on the intermolecular distance for the analysis of the intermolecular interaction. Figures 3a, b show the comparison between the calculated results for the crystalline state with intermolecular distance 0.56 nm ('pristine') and 0.56 (nm) $\times 1.1 = 0.62$ (nm) (' $\times 1.1$ '). At ' $\alpha = 0^\circ$ ' the calculated result of ' $\times 1.1$ ' has a small shoulder B and new peaks A and C (Fig. 3a). At ' $\alpha = 90^\circ$ ' the calculated result of ' $\times 1.1$ ' has three peaks (A', B' and C') and is different from the result of the pristine spectrum (Fig. 3b). The calculated results of the ' $\times 1.1$ ' are different from the observed spectra (Fig. 1a). Therefore, the intermolecular distance 0.56 nm for the pristine is valid for the system (see Fig. 2c,d). These results demonstrate that the information about the bulk structure is essential to analyze this system.

Now, we can discuss the structural changes due to the radiation damage. As shown in Fig. 1b, the spectra with little polarization dependence observed after the irradiation imply that the radiation damages of the PTFE sample loses the orientation of the chains. We expect that there are serious structural-changes in the carbon chain as well as C-F bond scission. In order to explain how the highly-oriented PTFE film lose the angular dependence, we remove F atoms.

At first, we removed F atoms in distance order from the nearest neighbor atom of the absorbing atom without introducing any structural changes on the carbon chain. Figures 3c,d is the calculated results of the crystalline state as a function of the number of F-defects ($n_F = 0, 3, 6$). At $\alpha = 0^\circ$ the intensity of main peaks depend on that for n_F (Fig. 3c). At $\alpha = 90^\circ$ the main peak

for the model $n_F = 6$ is weaker than that of the other n_F , while the next peak is stronger than the other results (Fig. 3d). Moreover the larger ' n_F ' models change main-peak position to higher photon-energy position. These calculated results show the smaller polarization dependence than that of the observed change (Fig. 1b). Therefore, the simple F-defect models cannot explain the observed changes. In order to explain the observed loss of the polarization dependence, we should consider randomly-oriented molecular assembly caused by introducing structural changes of carbon-chains following the C-F bond scissions.

CONCLUSION

The multiple-scattering calculations can explain the photon-polarization dependence of F K-edge XANES spectra for highly-oriented PTFE film. The F K-edge XANES spectra do not reflect only the structures of the absorbing molecular-chain but also information on the molecular assembly. When we analyze the F K-edge XANES of the bulk PTFE, it is an essential to consider the molecular assembly. After the irradiation, the observed spectra show little polarization-dependence (Fig. 1b). The theoretical XANES analyses have given information on atomic-scale changes by comparing the calculated results of spectra for different model structures. We can thus expect that F-defects would introduce changes to randomly-oriented PTFE structures.

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