Multiple scattering approach to I K-edge XANES for iodine-doped PVA films

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Abstract. Polarization dependent iodine K-edge XANES spectra of iodine-doped polyvinyl alcohol (PVA) films provide much information on the local structure around iodine anion. The present multiple scattering analyses support that the iodide anions are along to the PVA chain in the films. The difference XANES spectra taken between 0° and 90° and between 45° and 90° are slightly sensitive to the local structure of the PVA film around iodine anions.

1. Introduction
The optical properties of the thin films of Iodine-doped polyvinyl alcohol (I-PVA) have high polarization dependence in the ultraviolet or visible regions [1]-[4]. They are used for various devices, e.g. the polarizers for the liquid crystal display (LCD) monitor. The region of strong absorption and the polarization dependence are sensitive to the concentration of I₃⁻ to I₅⁻, and the orientation of the molecular axis of the polyiodine species in the PVA film. Studies on local structures around iodine species in the PVA film are important for design of devices, e.g. control of absorption bands of the film. Previous study on iodine K-edge EXAFS of I-PVA film reports that the molecular axis of the polyiodine species is parallel to the PVA chain [5]. Detailed analyses of the X-ray Absorption Near Edge Structure (XANES), in particular its polarization dependence, are performed to obtain information on the local structures around the iodine anions.

2. Theory
The real space multiple scattering approach is used for the XANES analyses [6]. The X-ray absorption intensity σ from the core orbital is written by

\[
\sigma = -\frac{8}{3} \text{Im} \left[ \sum_{\ell,\ell'} \rho_{\ell}^* \rho_{\ell'} G(L,10|L)G(L',10|L') (r^{-2})_{\ell\ell'} (1-X)^{-1} t_{\ell L}^{\ell'} \right].
\]  

(1)
where G(LL'|L') is Gaunt integral, is the dipole radial integral between the core and the l-partial photoelectron wave functions, with its phase shift T-matrix tᵢᵢ. Matrix (1-X)⁻¹ = 1+X+X²+… with
which contains the site $T$-matrix $t_\alpha^\alpha$ at site $\alpha$ and the Green's function describing propagation of the photoelectron from site $\beta$ to $\alpha$, accounts for full multiple scattering. Hartree-Fock muffin-tin scattering potential is used in the calculation.

### 3. Results and discussion

#### 3.1 Experimental results

Figure 1 and 2 show the I K-edge spectra of I-PVA films were measured at BL-08, SPring-8 in Japan. The PVA films produced by Kuraray Co. Ltd., Japan are expanded in boric acid solution and the degrees of polymerization are 2400. The saponification of the films is greater than 99.8%. The spectra in figure 1 are for PVA which includes $I_5^-$ and in figure 2 mainly $I_3^-$. The angle $\theta$ between the polarization vector and the PVA chain is varied as $0^\circ$, $45^\circ$ and $90^\circ$. In figure 1 and 2, strong polarization dependence which is observed around 33160 eV (region X) is assigned to the transition from $1s$ orbital of iodine to $\sigma^*$ orbital which is observed both in $I_5^-$ and $I_3^-$. The anisotropy of $I_5^-$ which is stronger than $I_3^-$ suggests that $I_5^-$ is highly oriented along the PVA chain. The region around 33180 eV to 33210 eV (region Y) in figure 1 and 2 is strongly influenced by multiple scattering and contains information about the local structure around the iodine atoms. The polarization dependence is stronger in the film which contains $I_5^-$ than the film which contains $I_3^-$. Figure 3 shows the angular difference spectra of the PVA film obtained from figure 1. The difference spectra are defined as the difference between the XANES spectra taken at $\theta$ and $\theta=90^\circ$.

$$\Delta I(\theta) = I(\theta) - I(\theta=90^\circ).$$  \hspace{1cm} (2)

Figure 1. Observed polarization dependent I K-edge XANES spectra of $I_5^-$-PVA.

Strong polarization dependence is observed in the pre-edge region X and in the continuum region Y.

Figure 2. Observed polarization dependent I K-edge XANES spectra of $I_3^-$-PVA.
In the region X we observe strong polarization dependence, which cannot be explained by multiple scattering calculations. The molecular orbital calculations show that only 5p orbital parallel to the polyanion can accept excited electrons from a deep 1s orbital, which predicts the strongest absorption intensity for the linear polarization. The polarization dependence is much smaller for I$_3^-$-PVA than that for I$_5^-$-PVA. This could be explained by a simple model where I$_3^-$ are not so regularly aligned in comparison with I$_5^-$ in PVA.

3.3 Structural models and calculations

Earlier report of I K-edge EXAFS of I-PVA films suggests that I$_3^-$ and I$_5^-$ should be oriented along the PVA chains [5]. Figure 4 shows the structural model of PVA I$_5^-$, where $d_{12} = d_{14} = 3.244$ Å and $d_{23} = d_{45} = 3.025$ Å. Optimized structural distances of I$_5^-$ are calculated by using Gaussian03 with density functional theory (DFT) calculations (B3LYP/LanL2DZ). These values are 0.1 Å longer than the values reported by Yokoyama et al. [5]. This structural model of I-PVA film is used for the XANES calculations, which contains four PVA chains around the iodine anion. All of the hydroxyl groups in the PVA are directed to chain direction of iodine. The distance between the central iodide anion and the nearest carbon atom (C-I distance) is 5.10 Å (model A). For the model A, we assume that the shortest distances between I and H are the sum of Van der Waals radii. The central iodine in I$_5^-$ is surrounded by eight hydroxyl groups.

Figure 3 shows the difference spectra from the results of the multiple scattering calculation for the I$_5^-$-PVA model and observed result. The vertical lines designate the position of the observed valley (see figure 3). We observe an excellent agreement between the experiment and the theory. We composed other structural model B; C-I distance is the same as the model A, but the central iodine atom is close to four hydroxyl groups.

Figure 6 shows the difference spectra calculated from the model B. The agreement gets poor for this model. We also calculated other models which has different C-I distances, different number of PVA chains, slightly shifted I$_5^-$ and different I-I distances. The model A shows the best result.

3.2 1s→$\sigma^*$ transition

Figure 4 shows the structural model of PVA I$_5^-$, where $d_{12} = d_{14} = 3.244$ Å and $d_{23} = d_{45} = 3.025$ Å. Optimized structural distances of I$_5^-$ are calculated by using Gaussian03 with density functional theory (DFT) calculations (B3LYP/LanL2DZ). These values are 0.1 Å longer than the values reported by Yokoyama et al. [5]. This structural model of I-PVA film is used for the XANES calculations, which contains four PVA chains around the iodine anion. All of the hydroxyl groups in the PVA are directed to chain direction of iodine. The distance between the central iodide anion and the nearest carbon atom (C-I distance) is 5.10 Å (model A). For the model A, we assume that the shortest distances between I and H are the sum of Van der Waals radii. The central iodine in I$_5^-$ is surrounded by eight hydroxyl groups.

Figure 5 shows the difference spectra from the results of the multiple scattering calculation for the I$_5^-$-PVA model and observed result. The vertical lines designate the position of the observed valley (see figure 3). We observe an excellent agreement between the experiment and the theory. We composed other structural model B; C-I distance is the same as the model A, but the central iodine atom is close to four hydroxyl groups.

Figure 6 shows the difference spectra calculated from the model B. The agreement gets poor for this model. We also calculated other models which has different C-I distances, different number of PVA chains, slightly shifted I$_5^-$ and different I-I distances. The model A shows the best result.
4. Conclusion

Detailed polarization dependence of I K-edge XANES spectra for I-PVA films are analyzed using multiple scattering calculations, in order to obtain the information about the local structure around iodide anion. We find the structural model A shown in figure 4 is quite plausible.

These results imply that the hydroxyl groups of PVA are responsible for the stable sites of iodide anion in the PVA film; the preferred position of iodide anion in the PVA film is important in producing films which have well-defined absorption band in visible region of I-PVA film.

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