

One-Dimensional Hydrogen Bond of Water on the Pt(211) Stepped Surface Studied by O K-NEXAFS Spectroscopy

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Introduction

The formation of the hydrogen bond of water molecules on solid surfaces is one of the fundamental processes in surface chemistry including electrochemistry, fuel cell catalysis, and corrosion chemistry. The undissociated water molecules form small clusters on a flat surface such as Pt(111) at an early stage of the adsorption. In contrast, the water molecules are preferentially adsorbed on the step sites to form one-dimensional zigzag chains on the Pt(211) surface [1]. In this study, we measured X-ray absorption fine structure spectra at the O K-edge (O K-NEXAFS) to observe the hydrogen bond direction of the D₂O at the step sites.

Experimental

A mechanically polished Pt(211) single crystal (MaTeck, Inc.) was cleaned under ultrahigh vacuum condition by repeated cycles of Ar⁺ sputtering (1 keV), O₂ treatment at 700 K, and flush annealing at 1000 K. The (1x1) structure was confirmed with the low energy electron diffraction. After the substrate was cooled to 110 K, 10 L of D₂O gas was introduced into the chamber by 5 x 10⁻⁸ Torr x 200 s. The sample was heated at 160 K to leave molecules on the step sites. O K-NEXAFS spectra were measured at BL-7A (KEK-PF) by the partial electron yield method at 110 K.

Results & Discussion

Fig. 1 shows the O K-NEXAFS spectra of the D₂O multilayer on Pt(211). In the NI and MI spectra, the broad band at 537.0 eV and 540.5 eV are observed, which are typical for the spectra of bulk ice and correspond to the 1s → σ_{OH}^{*} transition along and perpendicular to the DOD direction, respectively[2]. On the other hand, there is only a small hump at 535.0 eV in the GI spectrum, which represents the free OD of the broken hydrogen bond of the ice. The lack of the spectral features attributable to ice in the GI spectrum suggests that the DOD direction is laid on the surface in this multilayer film. It is noted that in other multilayer films, a GI spectrum which shows almost the same spectral shape as those of NI and MI spectra were obtained.

Fig. 2 shows the O K-NEXAFS spectra of the D₂O adsorbed on the step sites. The band at 540.5 eV observed dominantly in the NI_{||} spectrum (the notation || and ⊥ represent the direction of the electric vector of the

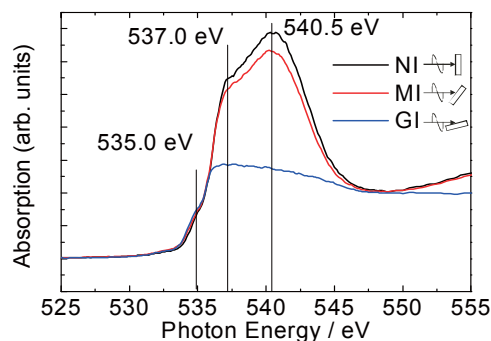


Fig. 1. O K-NEXAFS spectra of D₂O multilayer on Pt(211).

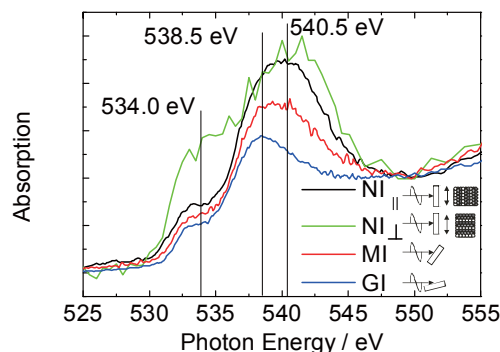


Fig. 2. O K-NEXAFS spectra of D₂O on the step sites of Pt(211).

incidence X-ray with respect to the step line). On the other hand, the pre-edge band at 534.0 eV in the NI_⊥ spectrum is assigned to the free OD of the D₂O molecule. The band at 538.5 eV in the GI spectrum is assigned to the OD bond directed to the surface Pt. These assignments are consistent with the one-dimensional hydrogen bond formation along the step, which was supported by the DFT calculation.

References

- [1] M. Nakamura, et al., J. Phys. Chem. C 2009, 113,4538.
- [2] T. Schiros, et al., J. Phys. Chem. C 2007, 111, 15003.

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