Real-Time Observation of Molecular Orientation during the Adsorption Process by Means of Wavelength-Dispersive X-Ray Absorption Spectroscopy with Polarization Switching

A novel technique has been developed by combining wavelength-dispersive X-ray absorption spectroscopy with switching between the vertical and horizontal linear polarizations, and the molecular orientation of NO and N_2O during adsorption on Ir(111) is observed. It is revealed that NO adsorbs keeping its molecular axis at ~20° from the surface normal during the whole adsorption process. In contrast, the adsorption process of N_2O consists of three periods according to its coverage. Up to 2/3 of the saturation coverage, the orientation angle of N_2O is almost constant at ~35°. Then the average orientation angle gradually increases to ~40° until the N_2O coverage reaches ~4/5 of its saturation, and very slowly increases to ~45° at the saturation coverage. Such a complicated behavior is interpreted by assuming different adsorption sites.

X-ray absorption spectroscopy (XAS) is one of the most powerful techniques to distinguish chemical species on the surface and to determine the orientation as well as the amount of adsorbed molecules. It is necessary to measure at least two XAS data with two different linear polarizations, or to rotate the sample at a fixed polarization, in order to determine the molecular orientation. Therefore, real-time observation of the molecular orientation during an unrepeatable process, e.g., a surface chemical reaction, is quite difficult by using the conventional step-by-step energy scan. We have achieved real-time observation of the molecular orientation by combining two experimental techniques: polarization switching and wavelength-dispersive XAS [1]. The technique for switching between vertical and horizontal linear polarizations, as well as between right and left circular polarizations, had been developed at BL-16A, by installing two APPLE-II type undulators in the

tandem configuration and by modulating the electron orbit through the undulators [2]. On the other hand, the time resolution of the wavelength-dispersive XAS technique in the soft X-ray region, by which the XAS data is recorded without the energy scan, had been improved to 33 ms/spectrum [3]. We have applied this novel technique to the adsorption process of NO and N_2O on an Ir(111) surface.

Figure 1 shows series of N K-edge XAS data for the vertical and horizontal linear polarizations taken during the adsorption process, which were obtained by using 1-Hz switching. Here, the vertical polarization corresponds to the *s* polarization, in which the electric vector of the X-rays lies in the surface plane, while the angle between the electric vector and the surface normal is 55° for the horizontal polarization, which is called the "magic angle".
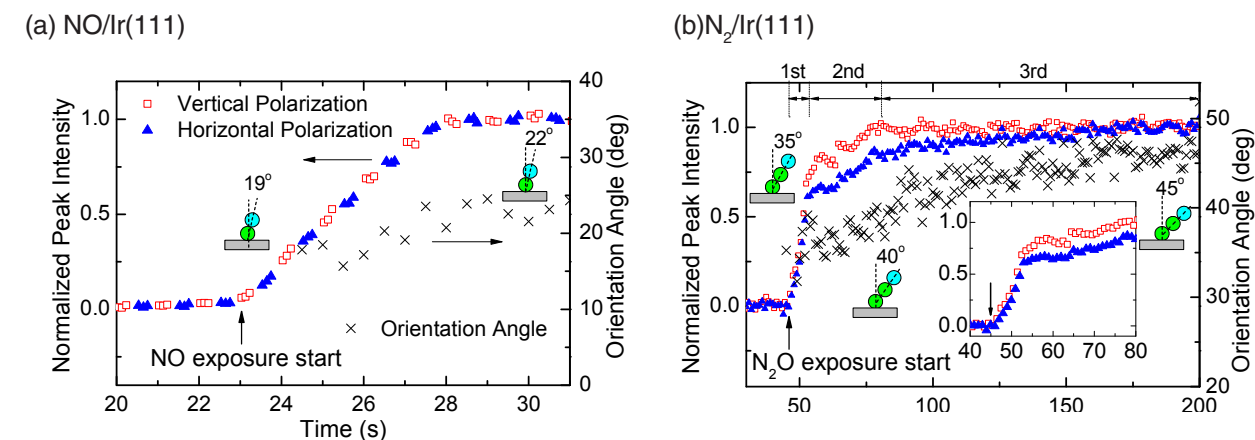
To quantitatively estimate the molecular orientation, the time (*t*) evolution of the normalized peak intensity for the vertical and horizontal polarizations is plotted in Fig. 2. The averaged orientation angle is estimated from the ratio between the peak intensities for the two polarizations. The peak-intensity ratio remains almost constant in the case of NO adsorption, as shown in Fig. 2(a), which directly shows that the orientation angle of NO is unchanged during the whole adsorption process. The estimated molecular orientation angle at each *t* is also plotted in Fig. 2.

For N_2O adsorption, in contrast, a different behavior between two polarizations is observed, suggesting some changes in the molecular orientation during the adsorption process. The adsorption process consists of three periods as indicated in Fig. 2(b). Since the coverage of the adsorbate is proportional to the peak intensity at the magic angle condition, it is revealed that N_2O rapidly adsorbs up to ~2/3 of the saturation coverage in the first period, *t* = ~45–52 s, then the adsorption rate drastically decreases in the second period and the coverage reaches ~4/5 of the saturation at *t* = ~80 s, and the coverage further increases very slowly in the third period, *t* = ~80-200 s.

As for the molecular orientation, the orientation angle in the first period is almost constant at ~35° from the surface normal, then it gradually increases in the second period and reaches ~40° at *t* = ~80 s. Since the

observed angle is an average over all adsorbed molecules, it seems reasonable to suppose that N_2O starts to occupy a different adsorption site with larger orientation angle than that in the first period. In the third period, the orientation angle very slowly approaches ~45°. This technique can be applied to the real-time observation of the molecular orientation of reaction intermediates, which is essential to understand the mechanism of surface chemical reactions.

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K. Amemiya[1], M. Sakamaki[1], S. Nakamoto[2], M. Yoshida[2], K. Suzuki[2], H. Kondoh[2], T. Koide[1], K. Ito[1], K. Tsuchiya[3], K. Harada[3], H. Sasaki[3], T. Aoto[3], T. Shioya[3], T. Obina[3], S. Yamamoto[1] and Y. Kobayashi[3] ([1]KEK-IMSS, [2]Keio Univ., [3]KEK-ACCL)

(a) NO/Ir(111)

(b) N_2/Ir(111)

Figure 2: Normalized peak intensity for vertical and horizontal polarizations in the (a) NO and (b) N_2O adsorption process. Estimated molecular orientation angle is also plotted.

(a) NO/Ir(111)
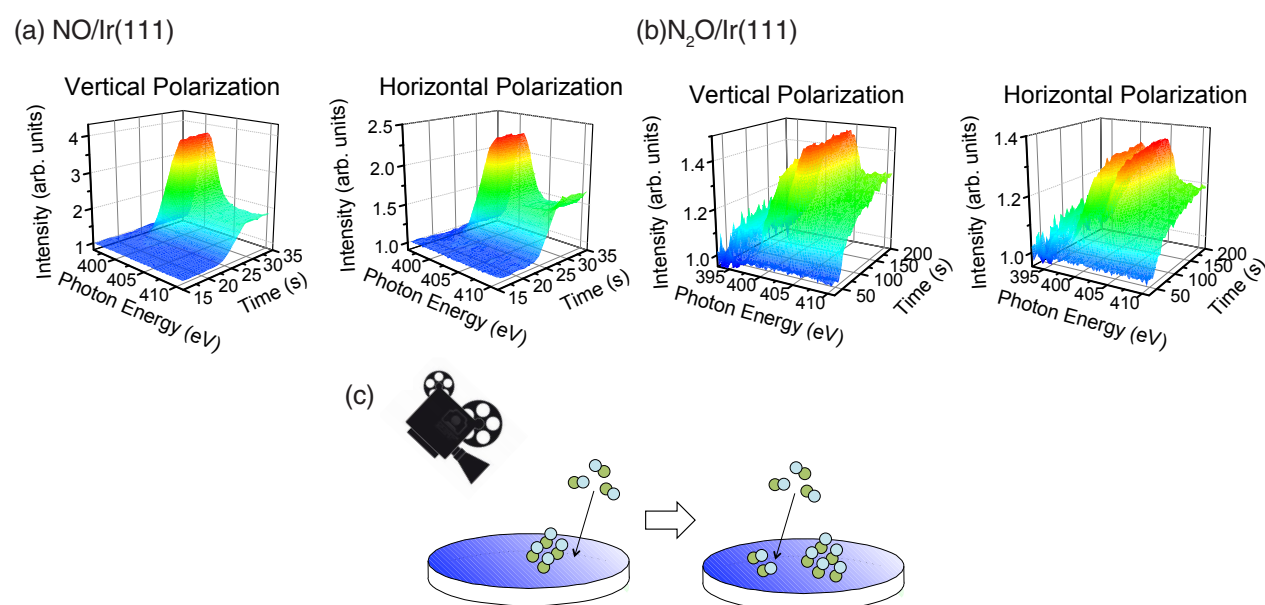
(b) N_2O/Ir(111)

(c)

Figure 1: Series of N K-edge XAS data for vertical and horizontal polarizations simultaneously taken by using 1-Hz polarization switching during exposure of the Ir(111) surface to (a) 5×10⁻⁸ Torr NO and (b) 1×10⁻⁷ Torr N_2O, and (c) schematic illustration of the real-time observation of the molecular orientation.