

Highlights

3-1 Observation of a Surface Chemical Reaction with Soft X-ray Energy Dispersive Surface NEXAFS

The near edge X-ray absorption fine structure (NEXAFS) technique is one of the most suitable to trace the structural and chemical changes during a surface reaction, since the NEXAFS spectral features are quite sensitive to the changes in chemical species and the orientation of the molecular adsorbate can be determined by using linearly polarized X-rays. It takes several minutes, however, to record a surface NEXAFS spectrum in the soft X-ray region with the conventional method. In order to obtain the NEXAFS spectrum in one shot, we have recently developed a new technique, energy dispersive surface NEXAFS, by using a position sensitive electron analyzer and a new soft X-ray beamline, BL-7A [1,2].

A schematic diagram for the energy dispersive surface NEXAFS measurements is illustrated in Fig. 1. A sample surface is illuminated by dispersed X-rays, whose energy is spread along the horizontal axis. When X-rays are absorbed, the Auger electrons are emitted from each position, and are separately collected by a position sensitive electron analyzer (GAMMADATA-SCIENTA, SES-2002). An Auger electron yield NEXAFS spectrum is thus obtained in one shot. Typical images on the two-dimensional detector of the electron analyzer are given in Fig. 2, which were taken before and after absorption of CO on Pt(111). The bright line crossing obliquely over the image for clean Pt(111) comes from Pt 4*p* photoemission, and demonstrates the energy dispersion. After CO adsorption, one can find a sharp increase in the intensity

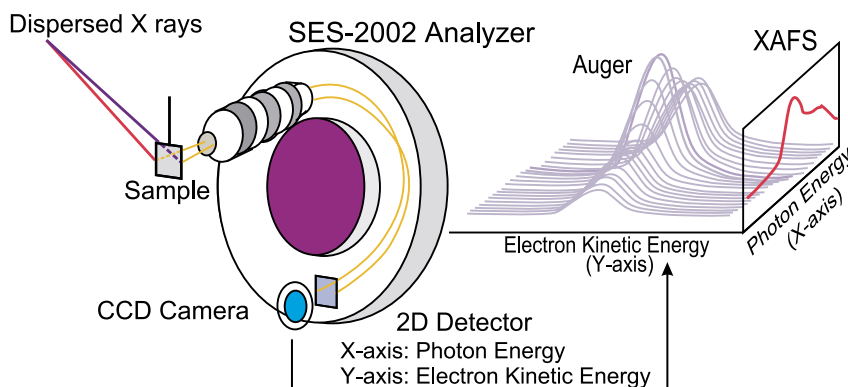


Figure 1
Schematic diagram for the energy dispersive NEXAFS. The horizontal position at the sample surface corresponds to the photon energy.

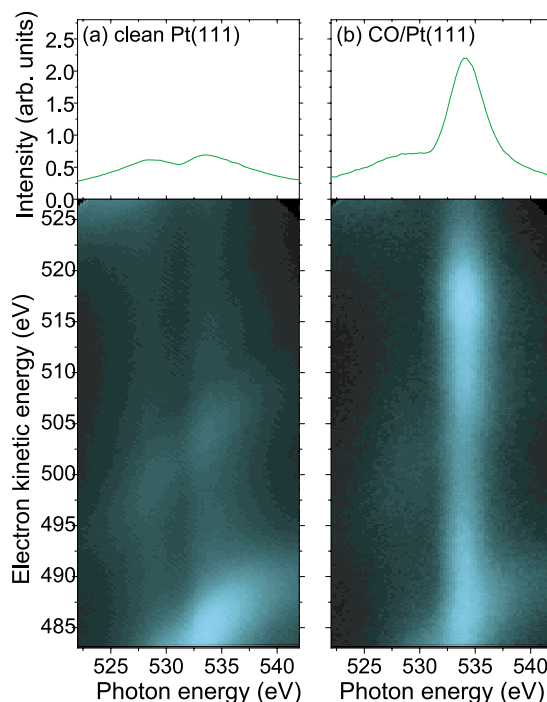


Figure 2
Two-dimensional image on the microchannel plate detector of the electron energy analyzer (bottom) and its integration along the electron kinetic energy (top), taken for a clean (a) and CO adsorbed (b) Pt (111) single crystal. The kinetic energy integration range is 495-527 eV, in order to avoid the Pt 4*p* photoemission.

at a photon energy of ~ 534 eV, which is attributed to the O1s CO π^* transition. The Auger electron intensities were then integrated over electron kinetic energy to obtain the NEXAFS spectrum (top panel). A small dip was observed at ~ 532 eV for clean Pt(111), due to the oxygen contamination on the beamline components. The spectrum for CO/Pt(111) was then divided by the one for the clean surface, in order to normalize the spectra with

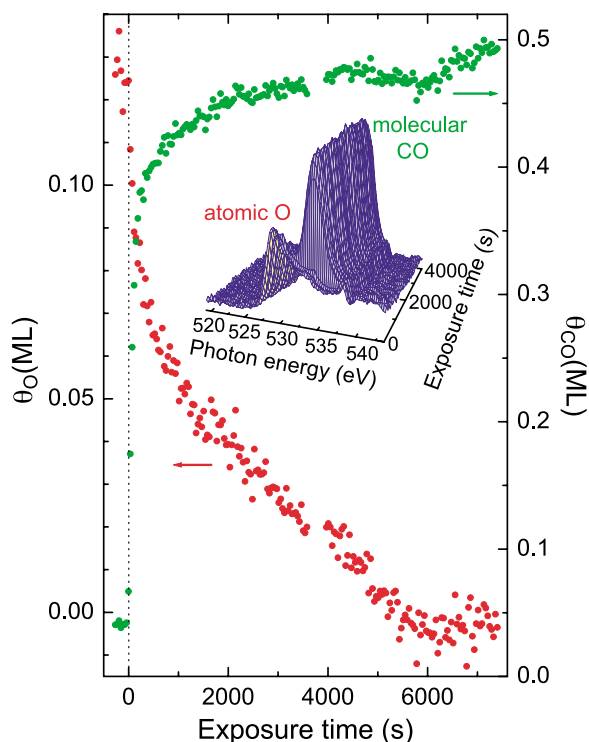


Figure 3 Series of O *K*-edge energy dispersive NEXAFS spectra (inset) taken in situ by exposing O/Pt(111) to 1.3×10^{-6} Pa CO at 240 K, and time dependence of the O and CO coverage (θ_{O} and θ_{CO} , respectively) during exposure. Each spectrum was taken at magic angle (35° from normal) incidence with an accumulation time of 30 s.

the photon flux and detector efficiency.

Figure 3 shows energy dispersive surface NEXAFS spectra taken by exposing the O/Pt(111) surface to CO. Each spectrum was similarly divided by the one for the clean Pt(111). One can clearly see a decrease of a peak at ~ 529 eV (atomic oxygen), as well as evolution of a prominent peak at ~ 534 eV (molecular CO). This is because part of the adsorbed CO is oxidized to CO_2 , which immediately desorbs. The O and CO coverage, also given in Fig. 3, was estimated by a curve-fitting analysis of a series of NEXAFS spectra. It is clearly seen that the O coverage immediately decreases as exposure starts. This apparently contradicts the previous scanning tunneling microscopy (STM) study [3], where no decrease of oxygen was observed during the “induction period” of ~ 300 s. This is probably because STM gives only local information of the surface, or because only a mobile oxygen species, which cannot be seen with STM, reacts in the “induction period”. Thus, we have for the first time observed the entire reaction over the whole surface by means of energy dispersive surface NEXAFS.

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3-2 Spin Reorientation Transitions of Magnetic Thin Films Induced by Chemisorption of Atoms and Molecules

Perpendicular magnetic anisotropy (PMA) is one of the most interesting subjects in magnetic thin films not only from the fundamental aspect of physics but from technological applications. If one considers only classical dipole interactions for the magnetic easy axis, one could conclude that the in-plane magnetization is always favored and PMA cannot be expected. Since the exchange interaction between two spins is isotropic, PMA is ascribed to spin-orbit interaction. For detailed understanding of PMA, information on orbital moments is thus essential, and X-ray magnetic circular dichroism (XMCD) is one of the most suitable methods.

Here, spin reorientation transitions (SRT) of ultrathin magnetic films induced by chemisorption of atoms and molecules have been investigated for CO-, NO-, H- and O-adsorbed Co/Pd(111) and CO- and H-adsorbed Ni/Cu(001) by means of Co $L_{\text{III,II}}$ - and Ni $L_{\text{III,II}}$ -edge XMCD [1]. The left panel in Fig. 1 shows the Co $L_{\text{III,II}}$ -edge XMCD spectra of 4.5 ML Co/Pd(111) before and after CO adsorption measured at BL-7A. On clean Co/Pd(111), strong XMCD signals appear at grazing X-ray incidence, while no signals are seen in normal incidence, this implying in-plane magnetization. On the contrary, after CO adsorption on Co/Pd(111), the XMCD shows perpendicular magnetization of the film, this

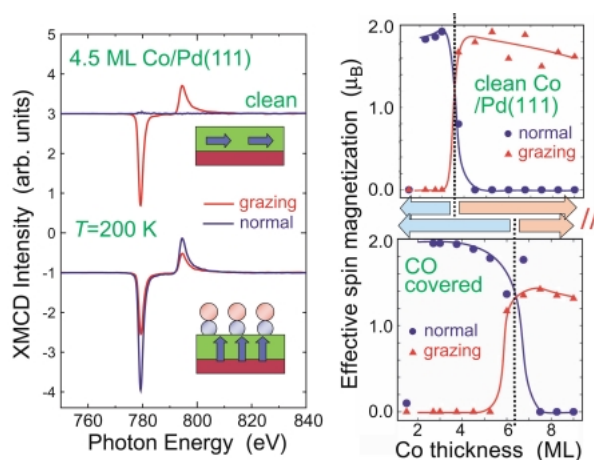


Figure 4 (left) Co $L_{\text{III,II}}$ -edge XMCD spectra of 4.5 ML Co/Pd(111) before and after CO adsorption and (right) the spin magnetization of Co/Pd(111) as a function of Co thickness. Remanent magnetization was examined at 200 K.

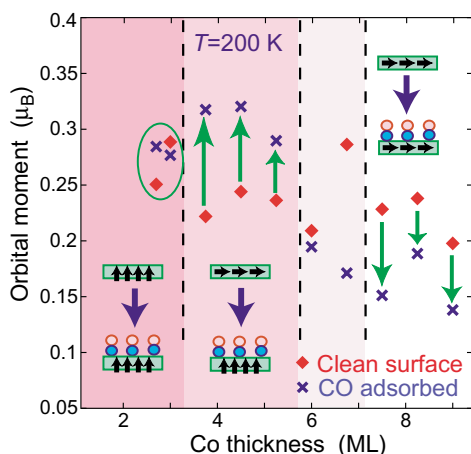


Figure 5
Remanent orbital magnetic moments of Co/Pd(111) before (diamond) and after (cross) CO adsorption at 200 K.

exemplifying the occurrence of SRT to PMA induced by CO adsorption. The right panel in Fig. 4 shows the spin magnetization as a function of Co thickness, estimated from the XMCD spectra and the spin sum rule. The critical thickness, below which PMA appears, is found to be shifted from ~ 3.5 ML on the clean surfaces to ~ 6.5 ML on the CO-adsorbed films. NO gives a similar effect for SRT of Co/Pd(111), while H or O adsorption does not

show any effect. As investigated previously, both CO and H adsorptions on Ni/Cu(001) were found to induce SRT.

By integrating the XMCD spectra and applying the first XMCD sum rule [2], one can consequently evaluate the orbital magnetic moments. Figure 5 shows the orbital moments of the Co 3d levels before and after CO adsorption. It is found that the surface parallel orbital moment is reduced by adsorption, while the surface normal orbital moment is left unchanged. We can thus conclude that the observed stabilization of PMA due to chemisorption is ascribed to quenching of the surface parallel magnetic orbital moment. Similar results are found in CO adsorption on Ni/Cu(001). In the case of H adsorption on Ni/Cu(001), it is concluded that both the in-plane and perpendicular orbital moments are reduced on adsorption, this indicating different mechanisms for the stabilization of PMA in different geometrical structures between CO and H on Ni/Cu(001) surfaces.

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