



Experiment title: Photoemission and chemical shift NIXSW determination of adsorption structures on Ni and Cu surfaces

Experiment number: SI-368

Beamline:

ID32

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Shifts: 32

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Report:

The X-ray standing wavefield (XSW) method allows adsorbate sites to be obtained in an element-specific fashion by monitoring the X-ray fluorescence, Auger electron emission or photoemission from the adsorbate as one scans through an X-ray Bragg reflection of the substrate. In the normal incidence XSW (NIXSW) method one not only has the advantage of being insensitive to significant mosaicity in the substrate, but the lower photon energies also make photoemission detection easier [1]. A particular potential virtue of photoelectron detection is the ability to monitor the XSW not only with element specificity, but also with chemical state specificity, exploiting the well-known 'chemical shifts' in the photoelectron binding energy associated with different local bonding environments of the same atom. To exploit this potential, however, one requires a combination of high photon flux and high spectral resolution only available from an undulator on an electron storage ring. Typical NIXSW Bragg energies are in the 2.5-3.5 keV photon energy range, perfectly matched to the first harmonic of the ID32 insertion device.

We have therefore initiated a series of experiments to explore and exploit this potential. The initial test experiment was on the model system of PF, on Ni(111) which has been shown to fragment in an electron or photon beam of appropriate characteristics to coadsorbed PF_x species with x=3, 2, 1 and possibly also 0. For fcc (111) surfaces, site identification is especially easy because NIXSW measurements at the (111) and (-111) reflections, which occur at the same energy, provide site triangulation.

A previous chemical-shift photoelectron diffraction (CSPHD) study of Ni(111)/PF_x [2] showed the P 2p state to have clearly resolved chemical shifts for these different species, so we anticipate similar effects in the P 1s photoemission peak. Preliminary investigations of this system at ID32 were made by us in 1997, but the data set was completed in a more convincing way in the most recent run, having solved a number of instrumental problems associated with the UHV end-station and associated electron spectrometer. Further measurements were made of coadsorbed SO_x species and coadsorbed CH₃SH, CH₃S and S on Cu(111) and these data are being analysed, but we concentrate in this report on the more complete PF_x data and its interpretation.

At ID32 the monochromatic synchrotron radiation beam proved sufficiently intense to crack the adsorbed PF₃ at a significant rate, although within a single NIXSW scan the changes in relative occupation of the states are sufficiently small to be accommodated by a suitable background. The **fragmentation** at room temperature (RT) and low temperature (140 K) is quite different; at RT the photoemission spectra show just two peaks assigned to PF₃ and PF. At 140 K four distinct states are seen (see fig. 1) initially assigned to PF₃, PF₂, PF and P. Each peak shows distinctly different XSW profiles (the (111) profiles are shown in fig. 1), with the nominal PF peak, in particular, being inverted in such a way as to indicate a (111) layer spacing roughly midway between two extended Ni atom planes. This cannot be assigned to any simple P site on the surface, and we propose that this state corresponds to the 'upper' P atom of a P₂F_x surface species. Both this and the PF₂ are only stable at low temperature, the latter disproportionating to PF₃ and PF on heating.

The local adsorption sites found for the PF₃, PF₂ and true PF (room temperature-formed) species are in general agreement with the previous CSPHD study. In particular the PF₃ molecules occupy atop sites and the PF₂ species appear to occupy bridge sites, although there is an ambiguity in this assignment. PF (and the surface bonding P in the P₂F_x) appear to occupy only 'fcc' hollow sites.

References

1. D.P Woodruff, Prog.Surf.Sci. 57 (1998) 1
2. K-U.Weiss, R.Dippel, K.M.Schindler, P.Gardner, V.Fritsche, A.M.Bradshaw, D.P. Woodruff, M.C.Asensio and A.R.González-Elipse, Phys.Rev. Lett. 71(1993) 581

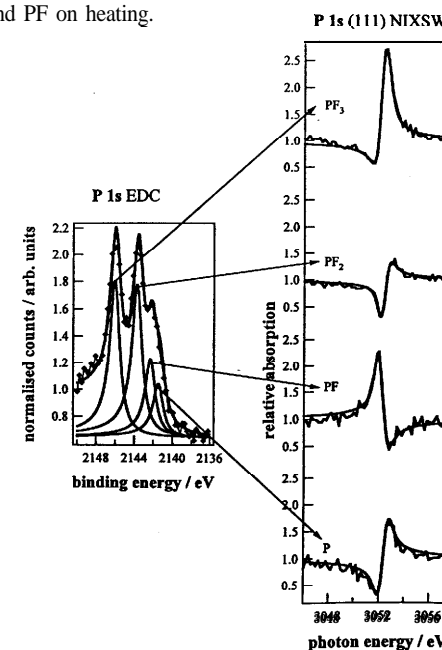


Fig. 1 P 1 s Photoelectron energy spectrum and XSW profiles of the individual components for coadsorbed PF_x formed on Ni(111) at 140 K.