



**Experiment title: CHEMICAL SHIFT NORMAL
INCIDENCE STANDING WAVE STUDY OF
COADSORBATES ON Ni(111)**

**Experiment
number:**
SI-273

Beamline:
ID32

Date of experiment:
from: 15/04/97 to: 28/04/97

Date of report:
18/08/97

Shifts:
30

Local contact(s):
Vincenzo Formoso

Received at ESRF:
22 AOUT 1997

Names and affiliations of applicants (* indicates experimentalists):

G.J.Jackson, D.P.Woodruff (University of Warwick, UK)

R.G.Jones (University of Nottingham, UK)

B.C.C.Cowie (CCLRC Daresbury Laboratory, UK)

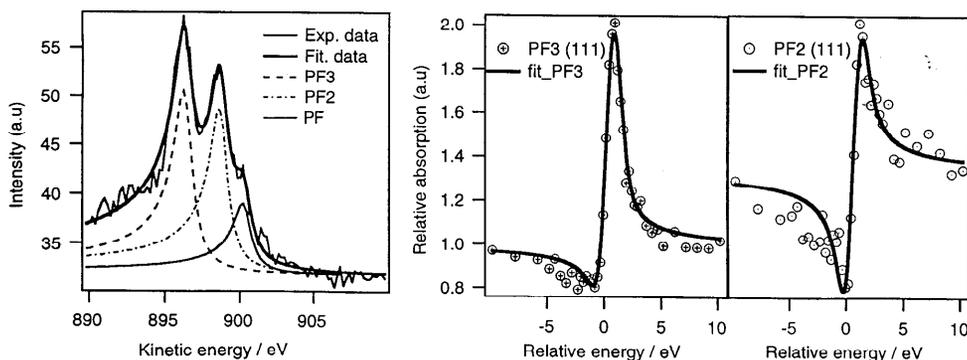
Report

During the last 10 years we have developed, using the SRS at Daresbury, the technique of normal-incidence X-ray standing waves (NIXSW), a variant of the usual XSW technique which retains the basic capabilities of this technique to determine adsorbate structure, but allows the use of standard metal single crystals due to the relaxed constraint on the crystalline perfection of the sample. Working at normal incidence to (111) planes of fcc metals typically fixes the photon energy in the 2.5-3.5 keV range, ideally matched to the first harmonic of a standard ESRF undulator such as that on ID-32.

Our special interest in using the ESRF is to exploit the potential for *chemical shift NIXSW* by using the photoemission signal to detect the photoabsorption. If a particular elemental species is present on the surface in two or more different states, either in different local geometries with respect to the substrate or to other atoms to which it may be bonded in a molecular species, the core-level photoemission from this atom will show different photoelectron binding energies associated with these different states. The ESRF undulator provides the combination of flux and spectral resolution to exploit this effect, allowing chemical-state, as well as elemental specificity in the local structural information.

A model system to demonstrate this potential is coadsorbed PF_x ($x=1,2,3$) species on Ni(111) formed by the photon-induced damage of a layer of adsorbed PF_3 on this surface. A similar application of chemical-shift photoelectron diffraction using the P 2p photoemission has found the PF_3 to occupy atop sites, PF_2 in bridge sites and PF in hollow sites (Weiss et al. PRL, 71 (1993) 2054). Our initial objective was to test this result and the whole idea of the CS-NIXSW method.

Our first attempt to explore this problem was in May 1996. This was the first ever use of the full UHV surface science chamber on ID-32 and was only possible at that time through the use of a borrowed VSW electron energy analyser due to a lack of suitable computer control for the Perkin Elmer analyser which was a part of this system. Not surprisingly, this first test ran into many beamline problems but a small amount of data on the photodissociation reaction of PF_3 in the monochromatic beam of ID-32 was obtained, showing a pronounced difference in behaviour at room temperature and low temperature. In the new experimental run, the Perkin Elmer analyser was used, but while this performed far more reliably the means of computer control remained well short of optimal efficiency. There were also major problems with, for example, electrical shorts on the LEED optics and loss of beam due to a machine vacuum problem. Nevertheless, the rather modest amount of data which were collected do demonstrate the viability of the technique. The figure shows some results from this experiment. On the left is shown the P 1s photoemission spectrum with the PF_3 , PF_2 and PF chemically shifted components fitted. Spectra of this type were collected at each photon energy through the NIXSW scan and curve-resolved to give individual adsorption profiles. The right-hand panels show these profiles for the two major components (the PF signal was weak and thus very noisy) together with the fits obtained to deduce the associated coherent fractions and positions. These parameters are consistent with the adsorption sites obtained from the earlier photoelectron diffraction experiments.



P 1s Photoemission spectrum (left) from partially fragmented PF_x on Ni(111) and (right) the (111) NIXSW profiles obtained from the PF_3 and PF_2 intensities together with theoretical fits.