



ESRF

**Experiment title:**  
ADSORBATE STRUCTURES ON Ni(111)  
USING NORMAL INCIDENCE  
X-RAY STANDING WAVES

**Experiment  
number:**  
SI-149

**Beamline:**  
BL13/ID32

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27

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## Report:

The technique of X-ray standing waves (XSW), when conducted at normal incidence to the appropriate Bragg scatterer planes (NIXSW), has the advantage that it can be applied with equal success for adsorbate structure determination not only on highly perfect crystals such as Si, but also on standard metal single crystals having a mosaicity of as much as tenths of a degree. This normal incidence condition leads to Bragg energies in the low keV region, well-matched to first harmonic undulator radiation from the ESRF.

Although we have had considerable success in developing and exploiting this approach using the Daresbury SRS (beamline 6.3), the ESRF offers some very special advantages as a result of the combined increases in both flux and spectral resolution. This experimental run, the first of its kind at the ESRF, sought to explore this potential of the ESRF for UHV NIXSW in two specific areas;

1. to study low atomic number adsorbates on transition metal surfaces (in this case O on Ni(111)) for which the low X-ray absorption cross-section of the shallow (but deepest) core level of the adsorbate places high demands on the required flux, coupled with a need for good spectral resolution to improve the signal-to-background ratio of the adsorbate photoemission signal (O 1s) on the inelastically scattered electron emission background.
2. to use the high spectral resolution combined with photoelectron detection to investigate the X-ray absorption in adsorbate atoms of the same element but different local states through their core level binding energy 'chemical shifts'. The specific example studied as

a model system was coadsorbed  $\text{PF}_x$  species on  $\text{Ni}(111)$  with  $x=1,2,3$ , a system for which large chemical shifts in the P 2p binding energy have been seen recently, indicating similar shifts in the P 1s level could be expected.

The experiments involved installing on BL13 for the first time the complete UHV spectrometer system with full in situ surface science preparation and characterisation facilities, and required the use of a high through-put and reasonably high resolution electron spectrometer which could be run under computer control synchronously with the X-ray monochromator. The narrow photon energy range to be scanned meant that no undulator scanning was necessary during an NIXSW measurement. Major problems of power supply stability were experienced on the VSW HA100 electron energy analyser, but eventually a mode of operation which was relatively tolerant to this problem was established in order that preliminary data could be collected to evaluate the true potential of the method.

Although the many instrumental problems precluded a full and reliable determination of all the structural parameters of the systems studied, the data provided a very clear proof of principle, and showed that the combined gains in flux and resolution over the Daresbury beamline 6.3 were essentially close to the values estimated before the run. We were also able to collect NIXSW data from chemisorbed O on  $\text{Ni}(111)$  in both (111) and  $(\bar{1}\bar{1}\bar{1})$  reflections and to show that these results are compatible with adsorption in the 'fcc' hollow sites as previously found in LEED studies of the (2x2) phase. Preliminary results for adsorbed CO even indicated that some measurements on C adsorbates are possible.

Most interestingly, we did collect data, again from both {111} reflections, for NIXSW from coadsorbed PF, on  $\text{Ni}(111)$ . The method of preparation of the different  $\text{PF}_x$  fragments used in the past has been electron beam impact, or 'white' synchrotron radiation (zero order) impact onto  $\text{PF}_3$  adsorbed on the surface. At the ESRF we found that the monochromated undulator radiation alone was sufficient to produce very significant photo-fragmentation over a period of tens of minutes to hours. The rate of damage was sufficiently high to produce the species of interest in reasonable quantities, yet slow enough to allow NIXSW studies with limited state conversion within a single run. One particularly interesting observation was a marked temperature dependence in the fragmentation rates. In particular, the  $\text{PF}_2$  species appeared to be very unstable at room temperature and converted rapidly to PF; at room temperature, therefore, only these two species were seen on the surface. By contrast, cooling with liquid nitrogen led to a surface on which- slow conversion of  $\text{PF}_3$  to  $\text{PF}_2$  and  $\text{PF}_2$  to PF could both be followed.

The results of these first NIXSW commissioning experiments on BL13 indicate that, with improvements to the electron spectroscopy hardware and/or software (already in hand at the ESRF) and some modifications to the sample cooling, full structural analyses of molecular adsorbates, including chemically shifted coadsorbed species and low atomic-number-containing molecules will become possible. Further experiments are planned to exploit this potential.