ESRF	**Experiment title:** Normal incidence X-ray standing wavefield surface structure determination with chemical-state specificity and high sensitivity	**Experiment number**: SI-638
Beamline: ID32	**Date of experiment**: from: February 2001 to: April 2001	**Date of report**: 12/2/02
Shifts: 2x21	**Local contact(s)**: Bruce Cowie	*Received at ESRF:*

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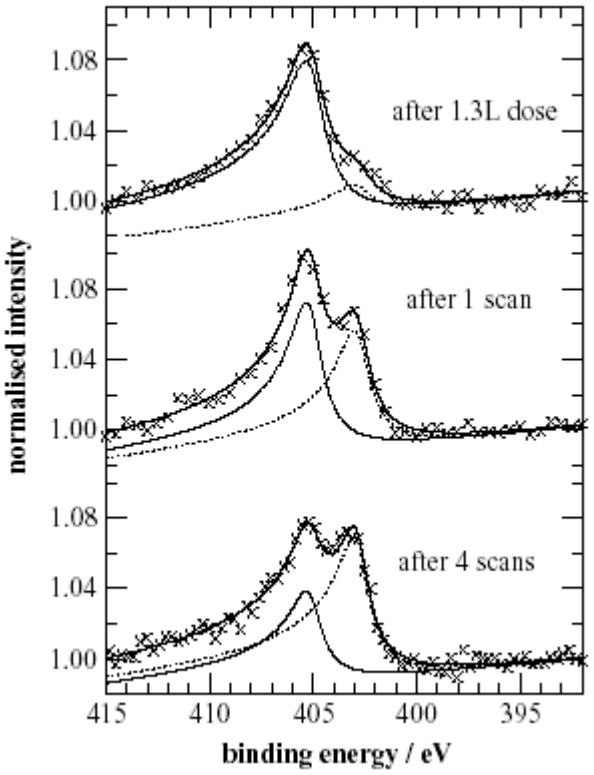
Report: This is an interim report on the first year of operation of a Long Term Project which was awarded from the semesters 2000-II to 2002-I. The award comprised 21 shifts each semester, and the first two such awards were in February and April 2001. The overall objective of the project is to push forward the limits of the application of our NIXSW technique at ID32, exploiting the combination of high flux and relatively high spectral resolution to study systems with intrinsically weak X-ray absorption and/or relatively small photoelectron binding energy chemical shifts, allowing us to determine, with chemical-state specificity, the structure of surface adsorption systems of innate chemical interest.

In order to achieve this we have concentrated on the systems Ni(111)/CO, Ni(111)/NO and these two systems with coadsorbed atomic oxygen. There is a substantial body of literature based on other methods and some controversy concerning key details; for example, can CO occupy sites other than the two inequivalent hollow sites [1] at elevated (e.g. room) temperature [2]? Does O coadsorption displace CO from hollow to atop sites [3, 4]? Are similar effects seen for NO [5]? C, N and O all have very weak X-ray absorption cross-sections, even at the low (≈3 keV) photon energies of NIXSW, so these experimental are only worth considering on a beamline like ID32.

The two runs of 2001 provided with a substantial body of data; data analysis has just been completed. We find clear evidence for mixed hollow site adsorption on CO on clean Ni(111), fcc hollow site adsorption for pure O on Ni(111), and clear evidence of an atop CO species in the presence of coadsorbed O. Chemical-state specific O 1s NIXSW allow these states to be distinguished, although the C 1s chemical shifts for these species are too small to resolve clearly in the NIXSW. In the case of NO the N 1s NIXSW clearly resolves the presence, and local geometry of, coadsorbed intact and dissociated NO. We also, however, see significant incident beam effects; not only do we see beam-induced cracking of adsorbed NO and CO, but also a more surprising site-dependent desorption of CO, with the atop species clearly having a substantially higher desorption cross-section than the hollow species. The figure shows N 1s spectra after NO dosing on Ni(111) and after increasing times in the beam: the lower binding energy state is atomic N arising from dissociation which is clearly enhanced by the beam. These beam effects do have some intrinsic interest, but present some limit on our ability to study complex surface chemistry. Nevertheless, by studying the time-dependence of the data sets it is possible to establish the starting structures quite reliably.



Overall our results from this first year demonstrate clearly that not only NIXSW, but even chemical-shift NIXSW, can be performed using C, N and O 1s photoemission signals for adsorbed molecules on ID32, opening up a far wider range of surface chemical issues to address than those restricted to heavier atoms. Nevertheless, the results also highlight the need for concern over the effects of the incident beam, even for a poorly-focussed beamline.

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