ESRF	Experiment title: Normal-incidence X-ray standing wavefield surface structure determination with chemical-state specificity & high sensitivity (Long Term Project 1998/II to 2000/I)	Experiment number: SI-407
Beamline: ID32	**Date of experiment:** September 98 and June 99	**Date of report:** August 99
Shifts: 2x21	**Local contact(s):** Vincenzo Formoso/ Bruce Cowie	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

This short interim report is intended to provide an update on progress on our long-term project at ID32 in order to provide supplementary information for the new application to pursue a quite distinct programme of work on the same beamline as an extension of an existing Warwick/Berlin collaboration on photoelectron diffraction which has previously been performed only at soft X-ray energies using the BESSY and ALS sources. Normally, no report on the long-term project would be required until the complete 2-year project was completed.

The present project is concerned with the development and application of the normal-incidence X-ray standing wave (NIXSW) method which we originally developed using the SRS at Daresbury. ID32 at the ESRF offers a combined gain in both flux and resolution which opens up entirely new applications of this general method, notably in the exploitation of 'chemical shifts' in core level photoelectron binding energies to allow chemical-state selectively in NIXSW studies, but also offering the possibility to study low coverage adsorbates systems or other adsorption structures involving weak absorbers.

Our efforts have so far focussed on testing and exploiting the chemical-shift NIXSW (CS-NIXSW) method. The experiments involve *in situ* preparation of the sample surface (low index transition and noble metals surfaces 0 so far Ni(111) and Cu(111) plus appropriate

adsorbates) in UHV in the special end-station for this purpose which is equipped with an electron spectrometer to measure the emitted Auger and photoelectrons following X-ray absorption, and which also requires resources for *in situ* surface characterisation. Until early 1999 this work was performed in the orginal UHV system for this purpose, but its very small size was a major limitation and the low energy electron diffraction (LEED) optics never worked satisfactorily. Despite these problems, the early experiments did make great progress in developing the ESRF-specific aspects of the methodology and the software needed to analyse the chemical-state specific raw data. The scientific outcome so far is on four/five adsorption systems:

1. Ni(111)/PF_x: a prior chemical-shift photoelectron diffraction study of this system meant that this was intended to be a 'simple' model system for our first tests. Adsorbed PF_3 fragments in the SR beam, and this previous work indicated PF_3, PF_2 and PF coadsorption in atop, bridge and hollow sites respectively. Our ESRF study has shown that while this may be true at the lowest temperatures, the system in general is much more complex due to a strong temperature dependence in the surface photochemistry. A full report of the reults has just been accepted for publication in *Surface Science*
2. Cu(111)/CH_3SH; methanethiol interacts with Cu(111) through initial deprotonation to form methyl thiolate, CH_3S- in two different forms, one mainly at low temperature, one mainly at high (room) temperature. At higher temperatures further fragmentation to atomic S occurs. The CS-NIXSW results have allowed major advances in understanding this system and a manuscript describing the main findings is currently under review at *Physical Review Letters*
3. Ni(111)/CH_3SH; data for this closely related system (which has also been the subject of controversy in the literature) are currently being analysed
4. (& 5.) Ni(111) and Cu(100) + SO_x; SO_2 is known to interact with these surfaces to form at least one SO_x species in addition to atomic S. Our data suggest that probably x=3 in both cases (although this is rather controversial) and provide extensive local structural information on coadsorbed SO_x/SO_2/S species. This work is currently being prepared for publication

Most recently an entirely new UHV end-station has been commissioned which will allow proper *in situ* characterisation (including LEED) and should permit investigations in which knowledge of the long-range ordered surface phase is known. We had been looking forward to performing the first experiments of this kind in June of this year. Unfortunately, having spent 2 weeks at the beamline helping to commission the new chamber and perform pre-preparation of our samples, the main manipulator bellows sprung a large leak one day before our first day of beamtime; as the manufacturers were unable to complete the repair until after the end of our beamtime, no experiments were performed in this run.