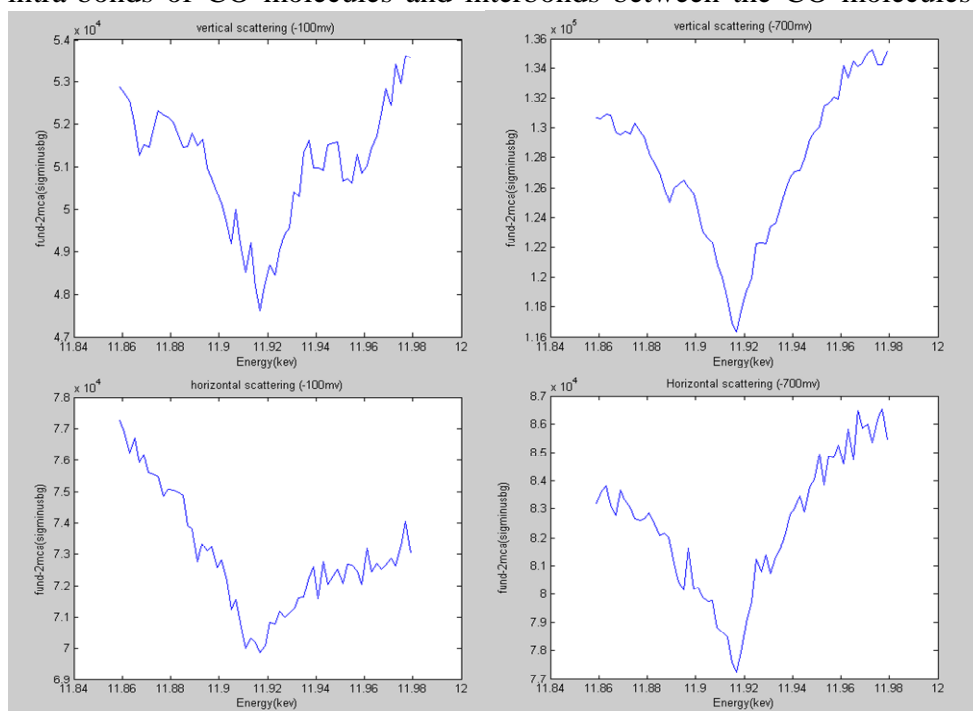
	<b>Experiment title: Charge transfer at the electrochemical interface</b>	<b>Experiment number:</b> 28-01-727
<b>Beamline:</b> BM28	<b>Date of experiment:</b> from: 27/9/06 to: 3/10/06	<b>Date of report:</b> 7/5/2008
<b>Shifts:</b> 18	<b>Local contact(s): David Paul</b>	<i>Received at ESRF:</i>
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## Report:

In the last decade, the *in-situ* surface x-ray diffraction technique has been a critical tool for determining the potential stability of specific surface structures in electrolyte under reaction conditions. Central to all electrochemical reactions is the issue of charge transfer at the interface between a metal electrode and the electrolyte solution. In fact, charge transfer at interfaces is a phenomenon common to many scientific disciplines ranging from chemical technology to biomaterials and biophysics. In the case of the specific adsorption of anions it is known that by tuning the electrode potential it is possible to change the character of the atomic bonding from ionic to covalent up to the onset of anion desorption. For halide adlayers on Au(111), e.g. chloride, bromide and iodide it has been determined that, in the ordered adsorbed layers that are formed, the adsorbed species is almost completely discharged, i.e. the electrosorption valency,  $\gamma$ , is  $-1$ . At lower potentials, however, where the anion adlayer is disordered, electrochemical results indicate that  $\gamma$  is considerably lower.

In this experiment we completed our resonant x-ray scattering study of the adsorption of iodine onto Au(111) in the electrochemical environment and extended the measurements to probe the charge transfer in the CO/Au system. The data complemented two previous experiments; one at the ESRF on BM28 in December 2004 (28-01-710) and one at the Advanced Photon Source, Argonne in January 2005 (beamline BESSRC-CAT-12BM). Iodine forms an incommensurate hexagonal monolayer on the Au(111) surface that

becomes disordered as the potential is swept cathodically prior to desorption. The first experiment on BM28 focussed on the use of resonant x-ray scattering at the iodine  $L_I$  edge (5188 eV) as the electrode potential was stepped over the region of the order-disorder transition and the desorption process. The experiment at the APS also probed the Au/I system but resonant x-ray scattering measurements in this case were performed in the region of the Au  $L_{III}$  adsorption edge (11919 eV) and a detector was used which allowed the separation of the elastically scattered and fluorescent x-ray signal. In both experiments the scattered x-ray intensity at a reciprocal lattice position sensitive to the iodine monolayer and topmost Au atomic layer was measured as a function of the energy of the incident x-ray beam over a particular adsorption edge. This was particularly challenging for the experiments at 5188 eV as there is considerable adsorption of the x-rays in the liquid layer and polypropylene films that cover the electrode surface. Preliminary analysis of the data had indicated that there was a dramatic change in the near-edge resonant region for iodine as the electrode potential was varied over the order-disorder transition in the iodine monolayer whereas the electronic state of the surface Au atoms remained relatively unperturbed (perhaps due to screening in the Au surface). Recent studies of Pt(111)/CO have indicated that the resonant x-ray diffraction measurements can be very sensitive to the polarization of the incident x-ray beam. Menzel *et al.* [1] demonstrated that when CO is adsorbed onto Pt, the excited Pt core electron experiences a strong anisotropic environment due to the empty states present in the intra-bonds of CO molecules and interbonds between the CO molecules and the surface Pt atoms, which



leads to a dramatic dependence of the resonant scattering on the polarization of the incident x-ray beam. Similar results were obtained for the adsorption of sulphate molecules onto Pt(111). We attempted to probe this effect both on the I/Au(111) system but also for the adsorption of CO onto Au(001), the latter system being possible only in the electrochemical

environment. Results for the I/Au(111) system are shown in the figure above which shows the background-corrected elastic resonant x-ray signal measured through the Au  $L_{III}$  adsorption edge at a reciprocal lattice position (0, 0, 1.55) for a  $\sigma$ -polarized and  $\pi$ -polarized incident x-ray beam at applied electrode potentials of -100 mV (when iodine is adsorbed onto the Au(111) surface and at -700 mV (when the surface is free of adsorbed iodine). This reciprocal lattice position is very close to the 'anti-Bragg' condition on the specular crystal truncation rod (CTR) where the scattering is due only to the surface Au atomic layers. Extraction of this data was rather difficult due to the strong inelastic fluorescent scattering that overlapped with the elastic

signal at energies close to the adsorption edge. Visual analysis of the data indicates that there are some polarization effects and attempts are currently being made to clean up this data set and apply the relevant correction factors so that the polarization dependence can be examined in detail. Part of the problem with this analysis is due to the fact that the MCA spectra measured at each energy were not recorded and the data analysis relies on approximate methods for the subtraction of the inelastic scattering. This was only realized towards the end of the experiment and the data measured for CO adsorption onto Au(100) includes the accompanying MCA files with the result that the corrected data are much cleaner. All of the data from the I/Au(111) and CO/Au(001) experiments are currently being analyzed to identify the effects due to adsorption and x-ray beam polarization. In collaboration with the group of Hoydoo You at Argonne National Laboratory the data will then be analysed using the currently available theoretical models [1].

[1] A. Menzel *et al.*, Rad. Phys. Chem., **75**, 1651 (2006).