	Experiment title: The Au(111)/alkylthiolate interface: where are the gold adatoms?	**Experiment number**:
Beamline: ID32	**Date of experiment**: from: 4 July to: 18 July 2008	**Date of report**:
Shifts: 24	**Local contact(s)**: Jörg Zegenhagen, Blanka Detlefs	*Received at ESRF:*

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Report:

The object of this experiment was to try to resolve a long-standing puzzle concerning the structure of the molecule/metal interface in alkanethiolate SAMs (self assembled monolayers) on Au(111). For many years the wisdom, based on theoretical total-energy calculations, was that the thiolates bond through the S headgroup atoms to hollow or bridging sites on an unreconstructed Au(111) surface. More recently a photoelectron diffraction study from a group in Japan, and NIXSW results from our own group, showed clearly that the true local site of the S atom at the surface is atop an Au atom in a bulk continuation site. It is now generally accepted that the solution to this apparent dilemma is that the Au surface is resonstructed, and the thiolate is actually bonded to an Au adatom on the surface. There are, however, two conflicting models of this reconstruction. One of these, derived from our own NIXSW work, is that a single thiolate is bonded to a single Au adatom that occupies a hollow site on the surface. The alternative model, derived from STM results from the group of John Yates, is that two thiolate atoms, occupying atop sites relative to the underlying surface , are also bonded to a single Au adatom that occupies a bridging site between them.

The specific objective of this experiment at ID32 was to try to distinguish these Au-adatom-monothiolate (AAM) and Au-adatom-dithiolate (AAD) models. The key technique to achieve this was X-ray absorption spectroscopy (XAS). The underlying idea is that, using the polarisation of the SR to produce a 'searchlight' of the outgoing S 1s electrons above the S K-edge, it should be possible to establish whether the S atoms have an Au near neighbour *only* below (as in the AAM model) or whether there are Au atoms both below and adjacent to the S atoms, as in the AAD model. The simplest data to interpret in this way would be surface EXAFS (SEXAFS), but we already knew from experiments at the SRS that achieving adequate signal-to-noise ratio for SEXAFS of S on Au would be extremely challenging due to the many Au shallow core levels of high photoionisation cross-section. This did, indeed, prove to render SEXAFS experiments for this syetm impossible, even at the ESRF. However, the near-edge XAS (NEXAFS) probes the same scattering phenomena, although the interpretation is less straightforward, and meaningful NEXAFS data could be obtained. As a result, measurements were made of NEXAFS at the S K-edge, and NIXSW at both S and C atoms, for both methylthiolate and butylthiolate species on Au(111) at different coverages. Coincidentally, the experiments also highlighted the problems of radiation damage of these sensitive molecules, although this could be suppressed to an acceptable level by using liquid nitrogen cooling of the sample.

In order to interpret the NEXAFS data we exploited a collaboration with Michael Odelius at Stockholm University who provided theoretical simulations. Unfortunately, what these calculations showed is that NEXAFS does not provide a reliable method of distinguishing the AAM and AAD models, because the energy of the σS-Au resonace feature associated with scattering at the adjacent Au atom in the AAD model occurs at the same energy as the σS-C intramolecular resonance, and *not* at the same energy as the σS-Au resonance associated with scattering from the Au atom below the S in both the AAM and AAD models. Nevertheless, the new results provided significant further insight into both the NEXAFS technique and the thiolate structures [1,2], although the core question remains unresolved.

[1] A.Chaudhuri, M. Odelius, R.G. Jones, T.-L. Lee, B. Detlefs, D.P.Woodruff, *'The structure of the Au(111)/methylthiolate interface: new insights from near-edge X-ray absorption spectroscopy and X-ray standing waves'* ***J. Chem. Phys.*** **130** (2009) 124708
[2] A. Chaudhuri, D.C. Jackson, T.J. Lerotholi, Robert G. Jones, T.-L. Lee, B. Detlefs, D.P.Woodruff *'Structural investigation of Au(111)/butylthiolate adsorption phases'* ***Phys. Chem. Chem. Phys.*** **12** (2010) 3229