EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Unrevealing the surface chemistry of the thiolate ($\sqrt{3}\times\sqrt{3}$)-R30° lattice on Au(111)	**Experiment number**: CH-4428
Beamline:	**Date of experiment**: from: 03/02/2016 to: 09/02/2016	**Date of report**: 02/04/2016
Shifts:	**Local contact(s)**: Maciej Jankowski	*Received at ESRF:*

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Report:

Thiol self-assembled monolayers (SAMs) on gold are the most popular molecular thin films. Oxide-free, clean, flat gold surfaces can be easily obtained which can be modified not only in gas phase but also in liquid media under ambient conditions. However, in spite of considerable theoretical and experimental efforts, the structure and chemical composition of this interface remain elusive. Most of the structural studies involve the ($\sqrt{3}\times\sqrt{3}$)-R30° or c(4×2) lattices on unreconstructed Au(111) surfaces, which are the most stable structures favoured from molecular chemisorption. However, these structural models have been contested since experimental data suggested that thiol chemisorption promotes a strong substrate reconstruction. In this way, recent models based on RS–Au_{ad} species have been proposed in analogy with those found in nanoclusters. According with this trend, a novel ($3\sqrt{3}\times3\sqrt{3}$)-R30º structural model consisting of three RS–Au_{ad}–SR moieties and three (RS-) species with their S atoms at atop positions [1] was prosed which is valid for both Au nanoclusters and Au(111) surfaces.

Consequently, the objective of the present proposal was to perform an X-ray structural study to unravel the interface structure of this system to confirm/disregard the presence of topmost gold adsorbed atoms on the Au(111) surface that agrees with STM experiments and DFT calculations that are the origin of the (RS-) models proposed in the literature.

Before starting the experiment, the experimental conditions were optimized to minimize the exposure and radiation damage on the sample (see proposal CH-4428). During the experiment several sample preparations were performed with the goal to optimize the ($\sqrt{3}\times\sqrt{3}$)-R30° structure. The optimal surface was used to measure a rather extensive data set, CTRs + fractional rods, that was analyzed to probe the presence or not of the gold adatoms on the surface.

The number of independent reflections measured was of 723 from a total of more than 950 reflections. The agreement factor between equivalent reflections was of 12% after correcting and averaging data with substrate symmetry.
Figure 1 shows 3 intensity profiles for reflectivity, (2,-1,L) CTR and the (2,0,L) fractional rod, indexed in the basis of the (√3×√3)-R30° cell.

The preliminar analysis of the data shows the presence of gold vacancies on the topmost surface layer (vacancy layer). The outgoing gold atoms from the vacancy layer form a new layer on top of this layer with same percentage ratio between vacancies and extra atoms (on the new highest layer).

These results fully satisfy the objectives pursuid in the proposal. The analysis and structural characterization procedure is not totally finished yet but it will be soon.

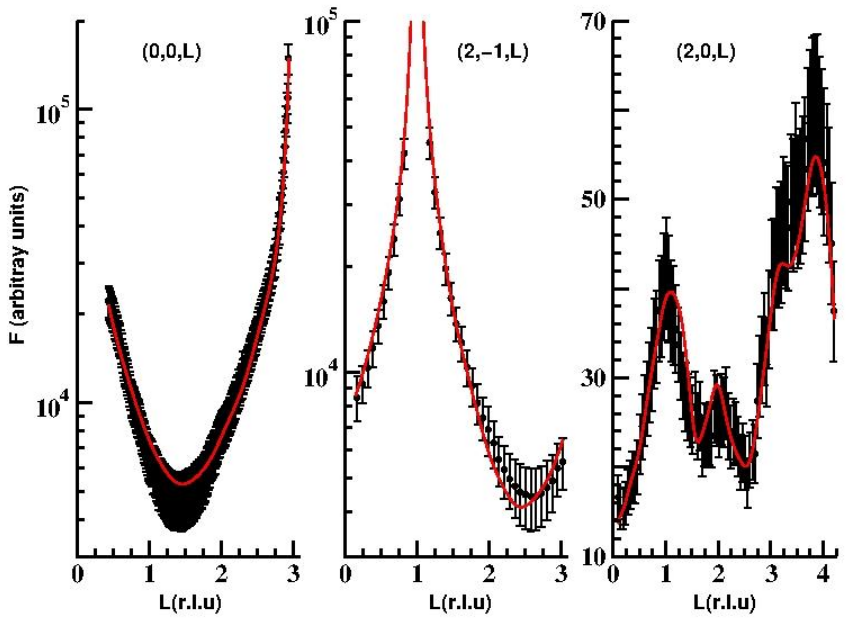

Figure 1. Reflectivity (0,0,L), CTR (2,-1,L) and fractional order (2,0,L) intensity profiles. The fractional order rod (2,0) only contains structural information coming from the (√3×√3)-R30º superstructure. The integer order rods (reflectivity and CTRs) mainly contain information from the bulk and the (1x1) unreconstructed surface, responsibles of the huge intensity difference between them and the superstructure rod.

References:

[1] P. Carro, *Phys.Chem.Chem.Phys.* 16 (2014) 19017 and references therein. [2] P. Carro et al., *J. Phys. Chem.* C 117 (2013) 2160