

**Experiment title:**

NIXSW study of the vertical adsorption geometry of azobenzene-derived molecular switches on Cu(111) surface

Experiment number:

SI-1898

Beamline:	Date of experiment: from: 03/07/2009 to: 14/07/2009	Date of report: 05/02/2010
Shifts:	Local contact(s): Jorg Zegenhagen (email: zegenhag@esrf.fr), ID32	<i>Received at ESRF:</i>

Names and affiliations of applicants

Prof. Stefan Tautz, Research Center Jülich, Germany

Dr. Petra Tegeder, Freie Universität Berlin, Germany

Prof. Karsten Reuter, Fritz-Haber-Institut, Germany

Report: The aim of the experiment SI-1898 was to continue an ongoing project promoting the detailed and quantitative understanding of the adsorption geometry and electronic structure of azobenzene derived molecular switches at defined noble metal surfaces using normal incidence X-ray standing wave (NIXSW) and density-functional theory (DFT) (cf. progress report on SI-1728, [1]). For the SI-1898 experiment we were planning to study adsorption of azobenzene and 3,3',5,5' tetra-tert-butyl-azobenzene (TBA) on Cu(111) surface.

During preparation of experiment at ID32 we experienced multiple technical problems with the experimental setup including (1) electrical connection failure in the manipulator, namely unstable heater contact and thermocouple contact; (2) water contamination of the argon gas line used for sputter gun. Three times during the beam time the manipulator was disconnected from the UHV chamber and repaired; the chamber was baked three times. Finally, only 80 hours of the X-ray beam (10 shifts) were available, including 8 hours (1 shift) provided additionally, for complete experimental procedure including outgassing after the last successful bake out, setting up the beam, preparing the crystal, on-stage calibration of molecular sources, temperature programmed desorption (TPD) experiments, high resolution XPS, and NIXSW.

In the experiments on azobenzene adsorption, we observed that the N1s core level peak includes three components; two are attributed to the multilayer and one to the molecules in the monolayer state (Fig.1). The multilayer was desorbed in TPD experiments at 360 K. Such prepared well-ordered monolayer of azobenzene on

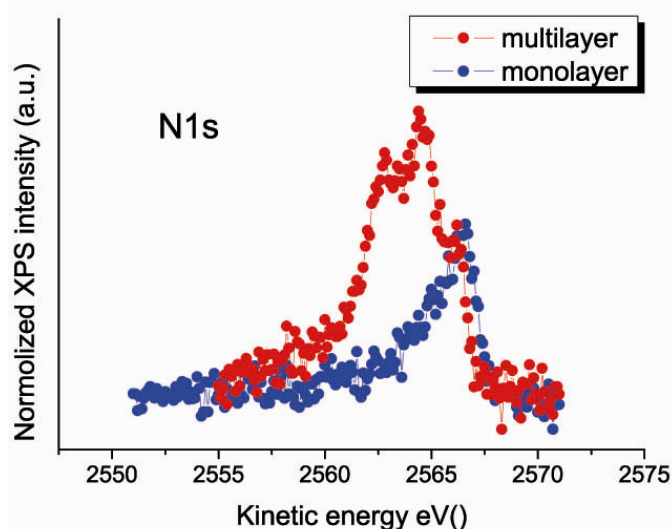


Fig.1 XPS spectra of azobenzene/Cu(111)

Cu(111) was stable at room temperature. High resolution XPS revealed an insignificant beam damage of the molecular layer upon exposure to X-ray. That was observed in a gradual shift of the binding energy of N1s line with exposure time greater than 30 min. However, further analysis of NIXSW data obtained in experiments with 30 and 10 minutes total acquisition time did not exhibit any significant difference in either coherent position CP (height) or coherent fraction CF (vertical distribution) of corresponding peak. In total, two preparation experiments were done, 12 NIXSW data sets were acquired for C1s, 20 data sets for N1s, 4 for Cu2p, and 1 for O1s. The latter was needed because we observed a significant contamination of the sample by oxygen, presumably due to water contamination of the sputter gun or the argon gas line. Additional annealing of the gas line improved the sample cleanliness; however, we could not achieve the completely oxygen-free state of the crystal, which seriously questions the final results of the experiment.

Figure 2 summarizes the results of NIXSW data fits. Appropriate quality of the copper crystal is approved by high values of Cu2p CF and CP. Very low CF of C1s peak is to be interpreted as a result of significant tilt of azobenzene phenyl rings in respect to the nitrogen bridge plane. On the other hand, a relatively high CF of N1s testifies for a good vertical alignment of the layer, which agrees with the high lateral order observed with LEED. However, the average CP of N1s line equals 0.60, which for Cu(111) surface is equivalent to the height of nitrogen atoms of 3.34 Å. This experimental finding contradicts with both the previous theoretical predictions [2] and our experimental data on azobenzene adsorption on Ag(111) [1]. Indeed, we found the height of nitrogen atoms in case of azobenzene/Ag(111) to be 3.07 Å and the monolayer desorption temperature of about 390 K. The monolayer of azobenzene on Cu(111) is more stable; the perfect lateral registry says about a stronger interaction between molecules and substrate as well. Thus one should expect the vertical separation for nitrogen atoms to be at least the same as for Ag(111) surface or even smaller, but not 10% higher as it comes from the NIXSW analysis. The reason for this inconsistency

can be the oxygen detected with XPS for all preparations. If it was accidentally implanted into the sub-surface region of the crystal during sputtering with water contaminated argon gas, it could disturb several upper lattices of copper, efficiently increasing the height of the top-most Cu atomic plane and shifting it up from the Bragg plane. Therefore the measured CP would not provide us the real adsorption height.

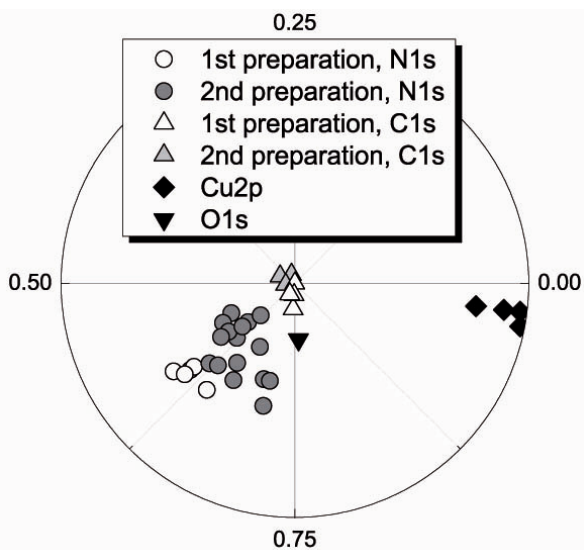


Fig. 2 NIXSW results of azobenzene/Cu(111)

Conclusion: Multiple experimental issues did not allow the successful accomplishing of the proposed experiments. The achieved results are suffering from uncontrolled oxygen contamination of the crystal. Experiments should be repeated.

1. G. Mercurio et al, PRL **104**, 036102 (2010).
2. E. McNellis et al. PRB **80**, 035414 (2009); E.R. McNellis PRB **80**, 205414 (2009).