

**Experiment title:**

Interplay between lateral and vertical adsorption structure, studied by NIXSW on PTCDA monolayers adsorbed on Ag(100), Ag(110) and Ag(111)

Experiment number:

SI-1645

Beamline:	Date of experiment: from: 08/04/2008 to: 15/04/2008	Date of report: 05/04/2011
Shifts:	Local contact(s): Yanyu Mi (email: yanyu.mi@cea.fr), ID32	<i>Received at ESRF:</i>
Names and affiliations of applicants: Prof. Stefan Tautz, Forschungszentrum Jülich GmbH, Germany Prof. Moritz Sokolowski, Bonn University, Germany		

Report: The purpose of the SI-1645 experiment was to investigate the adsorption height and molecular distortion of PTCDA molecule on Ag(100) and Ag(110) surfaces using normal incidence X-ray standing wave (NIXSW) technique. This experiment was a continuation of an ongoing NIXSW project (SI-916, SI-979, SI-1117, SI-1208, SI-1451 [1-7]) promoting the detailed and quantitative understanding of geometric and electronic aspects related to the bonding of large, π -conjugated molecules on metal surfaces. The adsorption height of PTCDA on Ag(111), Au(111), and Cu(111) has been investigated earlier [1,2,4-6,9]. Comparing these data with PTCDA behaviour on the other surface orientations of silver is interesting with respect to the interplay between lateral and vertical adsorption structure. The bonding distances and vertical distortions are an extremely sensitive indicator of the location and strength of the molecule-substrate bond on these three chemically identical but structurally different substrates.

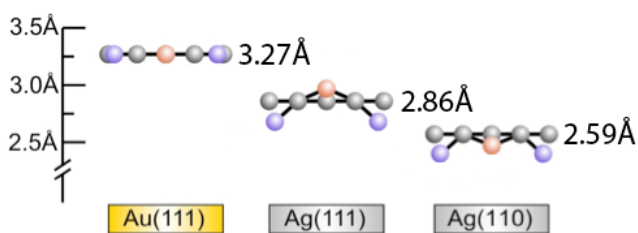


Fig. 1 Vertical geometry of PTCDA on Au(111), Ag(111) and Ag(110)

During the SI-1645 experiments, the full set of NIXSW data was acquired for Ag(110) surface. Measurements on Ag(100) surface failed due to unstable conditions of the electron analyser (Investigation of PTCDA adsorption on Ag(100) was repeated during experiment SI-2186

(February 2011) using recently installed SPECS Phoibos 225 electron analyser; obtained experimental data are under evaluation currently). Evaluation of experimental results gives the following adsorption heights for PTCDA/Ag(110): carbon backbone – 2.59Å, anhydride oxygen – 2.41 Å, carboxylic oxygen – 2.32 Å. The results of NIXSW study of PTCDA adsorption on Au(111), Ag(111) and Ag(110) are summarized in Fig. 1. One clearly observes a general trend of decreasing adsorption height with increasing chemical reactivity of receiving surface. This conclusion about geometrical structure of molecule/metal interface is in mutual accord with experimental (ultraviolet photoemission and scanning tunnelling spectroscopies) finding about its electronic properties: Lowest unoccupied molecular orbital (LUMO) of the adsorbed PTCDA molecule remains unpopulated on Au(111) revealing weak electronic interaction, while on Ag(111) it becomes partially and on Ag(110) fully occupied indicating chemical interaction.

To explain this effect we note that the PTCDA height on different surfaces (Au(111),

Ag(111), Ag(110), Cu(111)[9]), corrected for the different van-der-Waals sizes of the substrate atoms, depends linearly on the surface work function (Fig. 2). This empirical finding indicates that the substrate work-function to first order determines the adsorption height: For charge-accepting molecules, the work function controls the amount of charge transfer from the metal and thus the attractive "one-electron image potential", which in turn governs (1) the bonding height of the molecule above the surface and (2) the energy of the LUMO relative to the chemical potential of the substrate.

Manuscript on the experimental results of SI-1645 experiment and the model discussed above is in preparation.

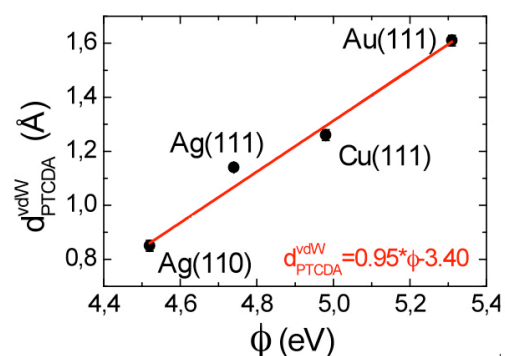


Fig. 2 Adsorption height of PTCDA above the van der Waals surface vs. work-function on different surfaces

References:

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