ESRF	**Experiment title:** Interplay between Charge Transfer, Molecular Distortion and Interface Energetics in Hybrid Organic/Inorganic Systems	**Experiment number**: SI-2002
Beamline: ID 32	**Date of experiment**: from: 20/11/2009 to: 1/12/2009	**Date of report**: 16/08/2010
Shifts: 18	**Local contact(s)**: Dr. P. Rajput, Dr. J. Zegenhagen	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

A. Gerlach*, T. Hosokai*, C. Bürker*, F. Schreiber

Institut für Angewandte Physik, Universität Tübingen, Tübingen, Germany

J. Niederhausen*, I. Salzmann*, N. Koch

Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany

S. Duhm*

Chiba University, Graduate School of Advanced Integration Science, Chiba, Japan

Report:

1. Introduction

As described in the proposal, the purpose of the experiments at ID32 was to measure the bonding distances and possible conformation changes of pyrenetetraone (PYTON) and coronenehexaone (COHON) [chemical structures shown in Fig. 2] on Cu(111) and Ag(111). The x-ray standing wave (XSW) measurements were performed to complement existing experimental and theoretical studies on the electronic structure of these conjugated molecules and to establish a fundamental understanding of the four different systems. In particular we were interested in the interplay between the observed charge transfer and adsorption geometry of the molecules [1]. After preparation of the UHV chamber for our X-ray standing wave experiments we were able to take high quality XSW data on Cu(111) of both molecules and XSW data of sufficient quality for PYTON on Ag(111). Below we give a short summary of results from the beamtime (SI-2002) at ID32.

2. XSW measurements on monolayers of COHON and PYTON on Ag(111) and Cu(111)

Several films of COHON and PYTON with coverages between the sub-monolayer and monolayer were prepared and characterized in detail by x-ray photoelectron spectroscopy (XPS) and XSW. Exemplary XSW photoelectron yield curves and reflectivity signals are displayed in Figure 1. On Cu(111) we could measure the averaged bonding distances of carbon and oxygen atoms with coherent fractions of around 0.3 and 0.5, respectively, for both, COHON and PYTON. The relatively low coherent fractions for carbon are expected due to carbon atoms in various different chemical environments in both molecules, which may lead to slightly different bonding distances. In each case the oxygen atoms are a little bit closer to the substrate surface as the carbon atoms [Fig. 2].

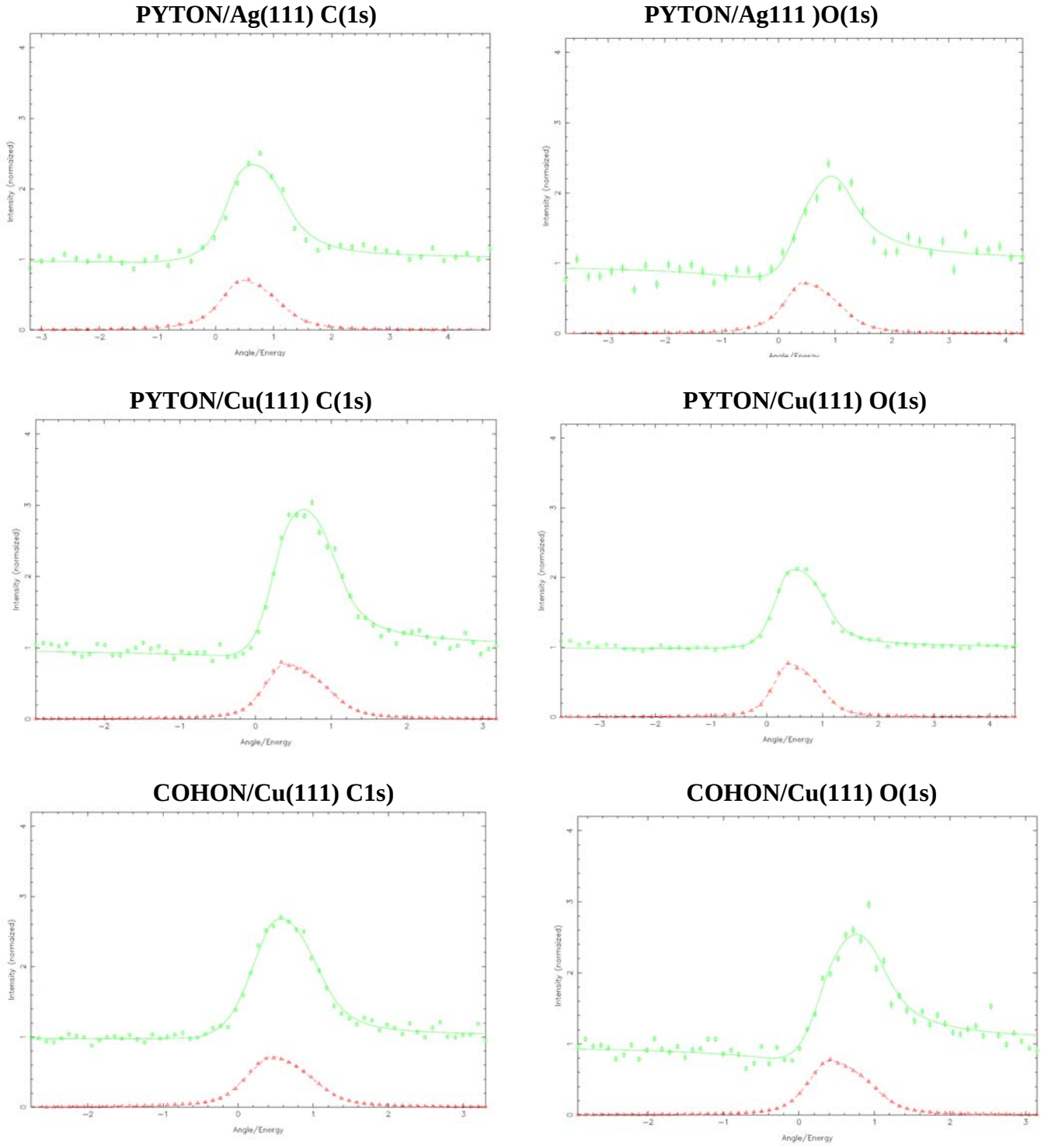

Figure 1:
XSW Yield (green curves) and reflectivity (red curves) of COHON and PYTON on Ag(111) and Cu(111), respectively. Circles and triangles correspond to measured data points and lines to least square fits.

The XSW data measured on the Ag(111) crystal did not show the same excellent quality as the data on the Cu(111) substrate, which is most probably due to insufficient quality of the Ag(111) crystal, which we had brought from our lab to the ESRF. Thus, unfortunately, for COHON/Ag(111) we could not measure any meaningful bonding distances. For PYTON/Ag(111), however, the bonding distances of carbon and oxygen atoms could be obtained with a larger uncertainty compared to PYTON/Cu(111) [Fig. 1] and again the oxygen atoms have a lower bonding distance than the carbon atoms.

The results are summarized in Figure 2. In analogy to 3,4,9,10-perylene tetracarboxyilic dianhydride (PTCDA) on metal surfaces [2], the conformation change of PYTON and COHON, which are both planar in the gas phase, upon adorption on Cu(111) or Ag(111) might be related to an organic/metal charge-transfer

complex formation. The XSW results obtained at the ESRF together with photoemission data obtained in our home laboratories and calculations based on density functional theory will be topic of forthcoming publications. Overall, the results measured at ID 32 match our expectations.

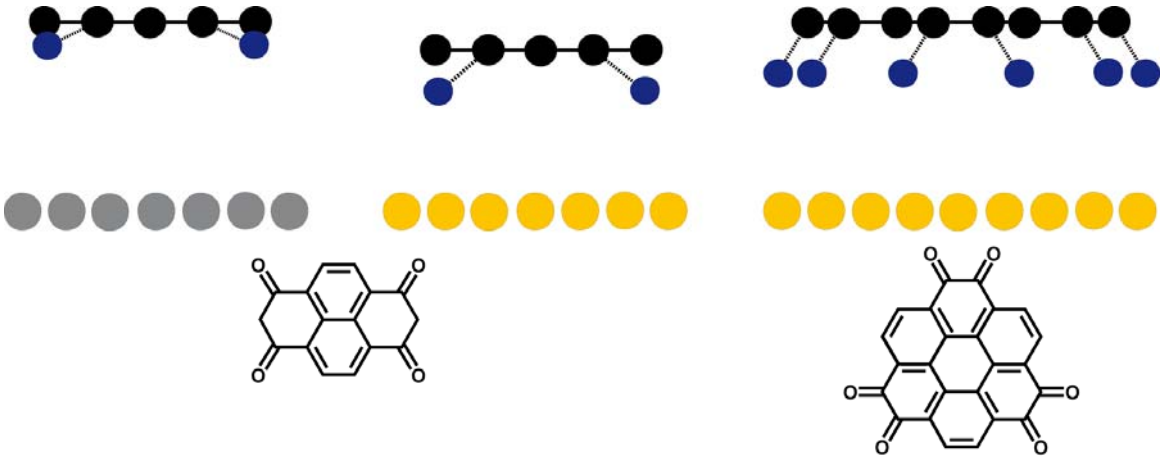

Figure 2:
Sketch of the adsorption distances of PYTON (left) and COHON (right) on Ag(111) (grey) and Cu(111) (yellow). In all cases a view along the molecular plane is displayed, which highlights the smaller bonding distance of oxygen (blue circles) compared to carbon atoms (black circles). In the bottom the chemical structure of PYTON and COHON is displayed.

References

[1] L. Romaner, G. Heimel, J.-L. Brédas, A. Gerlach, F. Schreiber, R. L. Johnson, J. Zegenhagen, S. Duhm, N. Koch, E. Zojer, *Phys. Rev. Lett*. **99** (2007) 256801.

[2] A. Gerlach, S. Sellner, F. Schreiber, N. Koch, J. Zegenhagen, *Phys. Rev. B* **75** (2007) 0454015.
S. Duhm, A. Gerlach, I. Salzmann, B. Bröker, R. L. Johnson, F. Schreiber, N. Koch, *Org. Electron*. **9** (2008) 111.