



<b>Experiment title:</b> Non-dipolar corrections in high-energy XPS excited by XSW	<b>Experiment number:</b> SI-2168	
<b>Beamline:</b> ID 32	<b>Date of experiment:</b> from: 19/10/2011 to: 25/10/2011	<b>Date of report:</b> 10/03/2011
<b>Shifts:</b> 18	<b>Local contact(s):</b> J. Zegenhagen	<i>Received at ESRF:</i>

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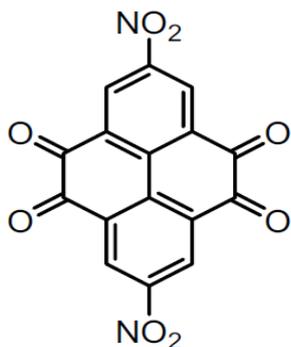
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**Report:**

*Please note: Because of experimental difficulties with the new UHV sample manipulator at ID32 the initial beamtime allocation for SI-2168 (20.1. - 1.2.2011) could not be used by our collaboration. As a result of that and the imminent closure of ID32 in 2012 the proposed study on non-dipole corrections in XSW measurement was not pursued. In agreement with the beamline scientist, the re-scheduled beamtime SI-2168 (19.-25.10.2011), i.e. our last beamtime at ID32, was used to complement earlier XSW measurements of organic molecules on single crystal surfaces.*

**1. Introduction**



The adsorption of Pyrenetetraone (PyT) on Ag(111), which we studied before using the XSW technique (SI-2002), results in surprisingly small bonding distances  $d_0$  and a significant distortion of the molecule. We chose this system to study whether chemical substitution changes the adsorption geometry and/or the interaction strength between the molecule and the substrate. NO<sub>2</sub>-derivatives of PyT (Fig. 1), synthesized within the group of K. Müllen (MPI Mainz), were deposited on Ag(111) to measure the influence of the two functional groups attached to the PyT molecule.

Figure 1: Chemical structure of NO<sub>2</sub>-Pyrene-tetraone (NO<sub>2</sub>-PyT).

## 2. XPS analysis of NO<sub>2</sub>-PyT on Ag(111): C1s and O1s

Controlled by a quartz microbalance we prepared films with increasing coverage of NO<sub>2</sub>-PyT on a clean Ag(111) substrate, i.e. from a submonolayer to one monolayer. We acquired several high quality XSW measurements using the C1s and O1s core-levels. It turned out that the N1s XPS signal was too weak to

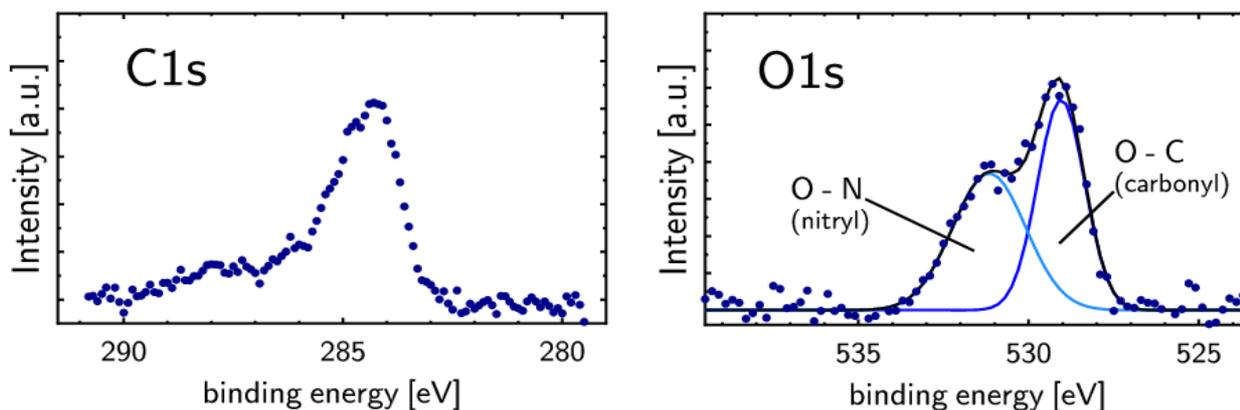


Figure 2: C1s (left) and of O1s (right) core-level spectra from a submonolayer of NO<sub>2</sub>-PyT on Ag(111) after background subtraction. The oxygen spectrum was fitted with two Gaussian peaks, one representing the oxygen atoms which are bound to carbon (carbonyl), the other the oxygen atoms bound to nitrogen (nitryl).

perform XSW measurements because of a high substrate background at the binding energy of the N1s peak. In the O1s signal (Fig. 2, right) two different peaks could be resolved that can be assigned to the two different chemical surroundings of the oxygen atoms: The peak at lower binding energies (529.0 eV) corresponds to the four oxygen atoms of the carbonyl group, while the peak at higher binding energy (531.3 eV) is related to the four oxygen atoms of the nitryl group. By fitting two Gaussian peaks to the XPS signal of oxygen we could evaluate the intensity variation of the two oxygen species for the subsequent XSW analysis. The carbon XPS signal (Fig. 2, left) is composed of at least four individual peaks corresponding to C-H, C=O, C-N, and C-C bonds. Since also shake-up peaks may contribute to the spectrum, we do not try to fit the relatively complicated C1s signal.

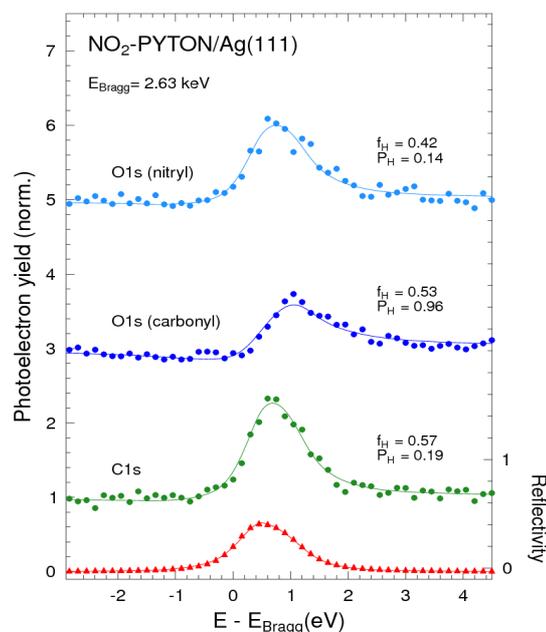


Figure 3: X-ray standing wave scans measured for NO<sub>2</sub>-PyT on Ag(111). The red triangle and the coloured circles represent the reflectivity data and the photoelectron yield, respectively.

## 3. XSW measurement of NO<sub>2</sub>-PyT on Ag(111)

XSW measurements were performed for carbon and oxygen. By fitting each O1s spectrum with the method described above we were able to distinguish the two different oxygen species in the molecule. A preliminary analysis of the XSW scans is shown in Fig. 3. As for the plain PyT molecule (with two hydrogen atoms instead of nitryl groups) the oxygen atoms of the carbonyl group are bent down towards the Ag(111) substrate, resulting in a similar bonding distance as for the PyT molecule. Such an adsorption geometry would indicate that the NO<sub>2</sub>-PyT molecules chemisorb on Ag(111). Additional spectroscopic measurements might be used clarify this issue.

In contrast, for NO<sub>2</sub>-PyT the average carbon bonding distance is significantly larger than for PyT molecules on Ag(111). This remarkable behavior may be attributed to the two nitryl groups which – at least their oxygen atoms – are nearly at the same bonding distance

as the carbon core of the NO<sub>2</sub>-PyT. (As was mentioned before, we were not able to measure the bonding distance of the nitrogen atom.) Whether the NO<sub>2</sub>-groups directly or indirectly cause a 'repulsion' of the carbon core might be studied via advanced DFT calculations.

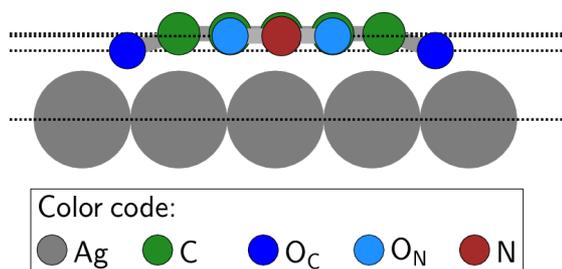


Figure 4: Sketch showing the adsorption geometry of NO<sub>2</sub>-PyT on Ag(111). Please note: For nitrogen no XSW scans could be taken. The bonding distance was therefore assumed to be the same as the nitryl oxygen.

We wish to thank our local contact for the excellent support on ID32.