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Exploring the push-back effect at organic/metal interfaces

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Local contact(s):

Dr. J. Duvernay, Dr. B. Detlefs

*Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):**

J. Niederhausen*, N. Koch

Humboldt-Universität zu Berlin, Institut für Physik, Newtonstr. 15, 12489 Berlin, Germany

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

Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany

S. Duhm*

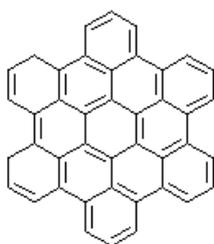
*Chiba University, Graduate School of Advanced Integration Science, Japan***Report:****1. Introduction**

Figure 1: Chemical structure of hexabenzocoronene

As described in the proposal, the purpose of the experiments at ID32 was to correlate the bonding distance of hexabenzocoronene (HBC) on Au(111) to the magnitude of the interface dipole between Au(111) and HBC. For such physisorbed systems, this interface dipole is commonly believed to be mainly due to a push-back of the electron tail spilling out of the bare metal surface. Therefore different bonding distances should result in a different magnitude of the push-back effect and therefore an altered interface dipole. We used the sample temperature as handle in order to tune the bonding distance: Due to a freezing out of molecular vibrational modes, a reduced sample temperature should give a smaller bonding distance.

After controlled sample preparation we were able to acquire high quality XSW data at different temperatures. Additionally, we determined the surface dipole by measuring the secondary electron cut-off (SECO) of photoemission. In the following we will present a short summary of the experimental results.

2. Temperature dependent XPS measurements of HBC on Au(111)

A sub-monolayer coverage of HBC on Au(111) was prepared by thermal evaporation and characterized by XPS. Spectra of the C(1s) peak are shown in figure 2 a). As can be seen by comparing the measurements before and after the XSW scan, there is no visible change of the peak shape. We therefore exclude a significant X-ray-beam induced molecular decomposition on the timescale of a single XSW measurement. The sample was then measured at two different temperatures, room temperature (RT, 293 K) and the minimum temperature achievable with the experimental setup (LT, approximately 75 K). The SECOs for the system measured at RT and LT are shown in figure 2 b). Apparently, there is no resolvable shift.

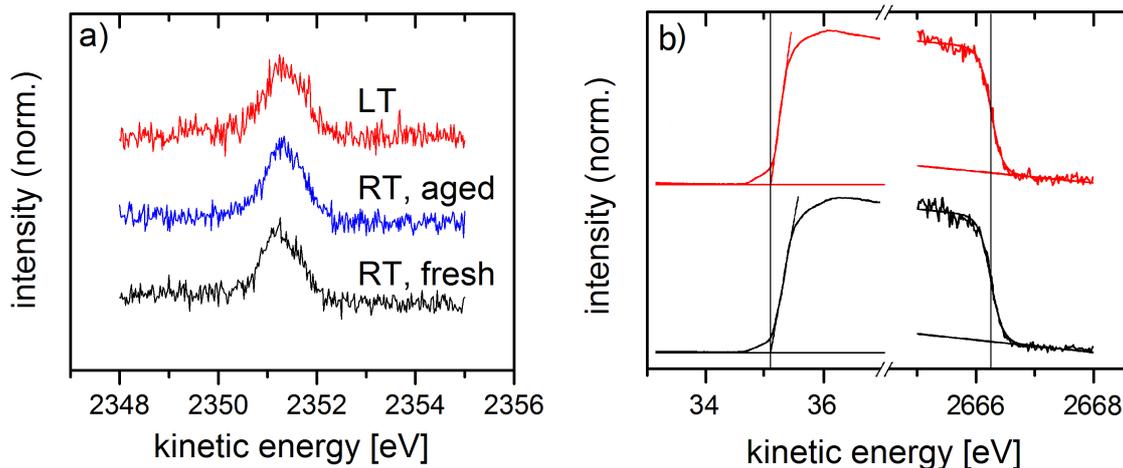


Figure 2: XPS spectra measured on a sub-monolayer of HBC on Au(111). a) C(1s) spectra at RT on a fresh spot (lower, black line) and a spot which had been used for an XSW scan (middle, blue). Also shown is a fresh spot at LT (upper, red line). b) SECO and Fermi edge for RT (lower, black line) and LT (upper, red line).

3. Temperature dependent XSW measurements of HBC on Au(111)

Several XSW measurements were performed for the systems described above. The energy dependent C(1s)-photoelectron yield and sample reflectivity are shown in figure 3 for RT and LT. We found a 8.15 eV shift of the Bragg energy when going from RT to LT. Taking into account the linear coefficient of thermal expansion for gold, $\alpha_L = 1.42 \times 10^{-5} \text{ K}^{-1}$, this yields a temperature difference of 218 K, which gives a temperature of 75 K for LT. The sample temperature was also checked by a silicon diode positioned at the sample holder. By this we find a sample holder temperature of 57 K.

A detailed analysis of the data is presently in progress. Estimates of the coherent position give around 3 \AA , which seems to be unchanged within the expected errors when going from RT to LT. We want to note that we find an increase of the coherent fraction when going from RT to LT (from around 0.5 to 0.6). This could suggest, that there indeed is a freezing out of vibrational modes. Assuming a Lennard-Jones like potential shape, the freezing out of vibrational modes should result in a measurable change of the average bonding distance. Yet, the precise shape of the potential in which the HBC molecules reside is unknown. If, for instance, we assume it to be harmonic at this bonding distance, a freezing out of vibrational modes will not give rise to a lowering of the bonding distance.

Our results differ from the ones in [3] and [4], which show indications for smaller bonding distances at low temperatures. Therefore our findings support the reasoning formulated therein, that the origin in these cases is to be found in the strong interaction between adsorbate and substrate.

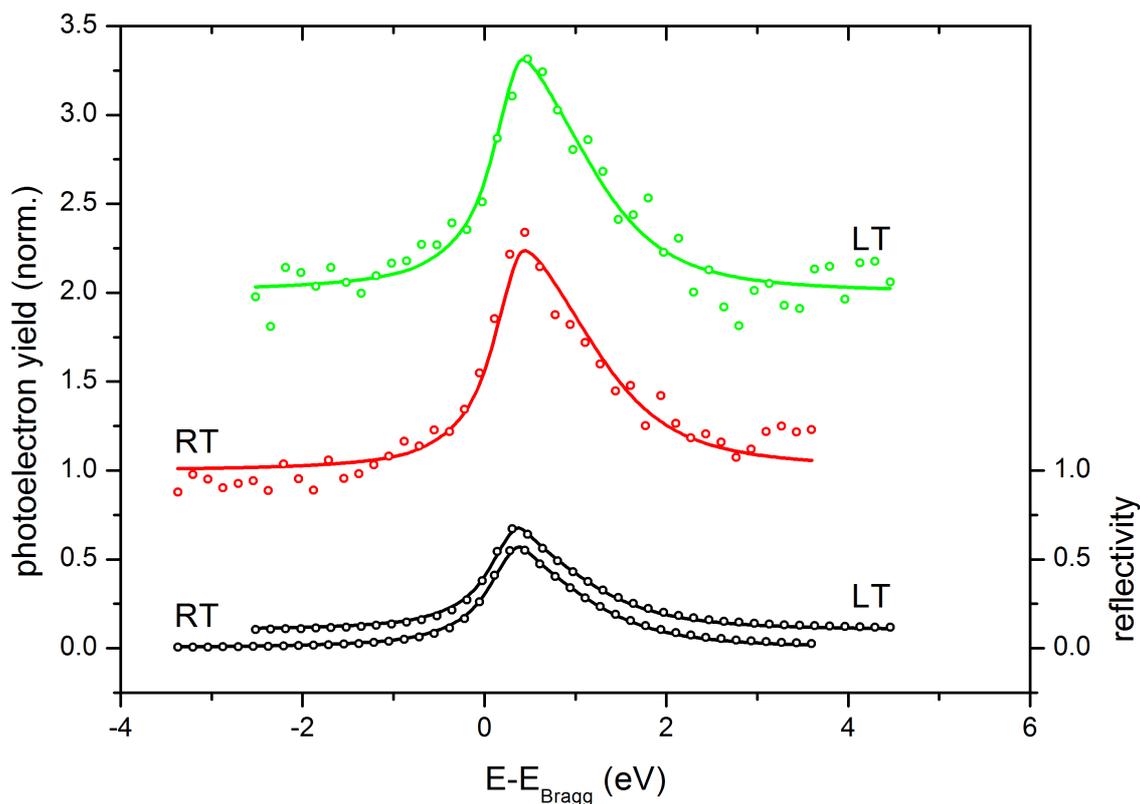


Figure 3: X-ray standing wave scans obtained on HBC on Au(111). The black and the coloured open circles represent the reflectivity data and the photo electron yield, respectively.

In addition to the described experiments we did first tests on ZnO, which is a promising substrate for upcoming experiments. Furthermore we obtained preliminary results for XSW measurements employing the second order reflection of Cu(111) and Au(111).

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

4. References

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