O 37: Metal substrates: Adsorption of organic / bio molecules IV

Time: Tuesday 15:00–16:30 Location: H36

O 37.1 Tue 15:00 H36

Structural dependence of metal organic interface state dynamics studied with 2PPE — •Manuel Marks[1], Christian H. Schwalb[1], Andreas Namgalies[1], Sönke Sachs[2], Achim Schöll[2], Friedrich Reinert[2], Eberhard Umbach[2], and Ulrich Höfer[1] — [1]Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität Marburg, D-35032 Marburg — [2]Universität Würzburg, Experimentelle Physik II, D-97074 Würzburg

Time- and angle-resolved 2-photon photoemission (2PPE) has proven to be a powerful experimental approach to study the electron dynamics at metal organic interfaces. With adsorption of the first monolayer (ML) PTCDA on Ag(111) an unoccupied strongly dispersing interface state (IS) emerges at 0.6 eV above the Fermi Level E_F [1]. Also for 1 ML NTCDA/Ag(111) a similar unoccupied state arises at 0.37 eV above E_F. The respective inelastic electron lifetimes of 54 fs and 110 fs indicate that the states have a significant overlap with the metal substrate and mainly originate from an upshifted Shockley surface state. We systematically studied the disordered precursor phase of the PTCDA monolayer [2]. For this interface a non-dispersing unoccupied state at 0.45 eV above E_F can be observed that has an electron lifetime of 63 fs. The influence of the adsorbate morphology and the origin of this non-dispersing feature will be discussed. Either the disorder leads to a localization of the surface state or the signal stems from a molecular state shifted in energy due to the chemical interaction.

[1] C. H. Schwalb *et al.*, Phys. Rev. Lett. **101**, 146801 (2008)

[2] L. Kilian *et al.*, Phys. Rev. Lett. **100**, 136103 (2008)

O 37.2 Tue 15:15 H36

A FT-IRAS study on the adsorption and growth of ultrathin films of PTCDA on Au(111) and Ag(111) surfaces — •Gregor Öhl, Carolin R. Braatz, and Peter Jakob — Surface Spectroscopy Group, Philipps-University, Marburg, Germany

The vibrational properties of ultrathin films of 3,4,9,10 perylene tetracarboxylic dianhydride (PTCDA) adsorbed on Au(111) and Ag(111) as investigated by means of Fourier-transform infrared absorption spectroscopy (FT-IRAS) will be presented. The films were grown by organic molecular beam deposition (OMBD) in an UHV environment and analyzed *in situ*. Our excellent spectral resolution accompanied by a formidable sensitivity allows us to clearly distinguish the various phases encountered during the growth and follow the thermal evolution of the layers from cryogenic up to elevated temperatures. Results will be presented for coverages from the sub-monolayer to the lower multilayer regime. Furthermore, the effects of preadsorbed spacer layers of rare gases will be discussed.

O 37.3 Tue 15:30 H36

DFT study of PTCDA on Ag(111) including a STM tip — •Andreas Greuling, Marcin Kaczmarski, and Michael Rohlfing — Universität Osnabrück, Fachbereich Physik, Barbarastraße 7, 49069 Osnabrück

Any progress in the field of molecular electronics requires a detailed knowledge of conduction through molecules. As a prerequisite, detailed knowledge of the geometrical structure of a model system like the system 'PTCDA on Ag(111) probed with a STM tip' is of big importance. In experiment it is possible to peel the PTCDA from the surface by using a STM tip above a corner oxygen atom. Furthermore, the molecule flips from the surface to the tip and back under certain tip-surface distance and voltage conditions. Here, we investigate these mechanisms by employing ab initio calculations applying the widely used SIESTA code. Using Density Functional Theory (DFT) in the Local Density Approximation (LDA) we present calculated geometries for the process of peeling of the molecule. Additionally we show tip-surface interaction potentials also considering the influence of a homogen electrical field.

O 37.4 Tue 15:45 H36

Island decay studies of PTCDA on Ag(100) — •Julian Ikonomov, Christoph H. Schmitz, and Moritz Sokolowski — Institut für Physikalische und Theoretische Chemie, Universität Bonn, Germany

We have studied two-dimensional islands of perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) deposited on the Ag(100) surface. For submonolayers, the attractive interactions between the molecules lead to two-dimensional islands with a quadratic equilibrium shape. The ordered PTCDA islands are surrounded by a disordered two-dimensional gas-like phase, consisting of highly mobile molecules [1]. The island ripening and decay were investigated with scanning tunneling microscopy (STM) at room temperature. The decay curves follow the classical continuum model for time evolution of clusters (Ostwald theory). The island area changes with a power low t^α with an exponent α of about 2/3 which clearly reveals that the decay of the PTCDA islands is diffusion limited. For an ensemble of more closely to each other located PTCDA islands, a mass transport from the smaller to the larger islands has been observed. We have performed numerical simulations of the decay curves of the islands in this ensemble and obtained values for relevant parameters, e.g., the step line tension of the PTCDA islands, the attachment-detachment rate, and the equilibrium density of the two-dimensional gas-phase.

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[1] J. Ikonomov, O. Bauer, and M. Sokolowski, Surface Science **602**, 2061 (2008).

O 37.5 Tue 16:00 H36

The orbital structure of π-conjugated organic molecules on metal surfaces probed by angle-resolved photoemission — Johannes Ziroff[1], •Michael Wiessner[1], Frank Forster[1], Peter Puschnig[2], Achim Schöll[1], and Friedrich Reinert[1,3] — [1]Universität Würzburg, Experimentelle Physik VII, D-97074 Würzburg — [2]University of Leoben, Chair of Atomistic Modelling and Design of Materials, A-8700 Leoben — [3]FZ Karlsruhe, Gemeinschaftslabor für Nanoanalytik, D-76021 Karlsruhe

We present angle resolved photoemission spectra of monolayers of π-conjugated molecules adsorbed on single-crystalline metal surfaces. Comparing the experimental k-dependant intensity distribution of the molecular states to DFT calculations for the free molecule allows to detect sophisticated modifications of the molecular orbitals at the interface.

In case of the single-domain system PTCDA on Ag(110) the 2D emission pattern confirms that the now occupied interface state is mainly derived from the former LUMO-orbital. Moreover, a clear contribution of metal states is evident from additional intensity in normal emission. In the contrary, the structure of the molecular HOMO changes only slightly upon chemisorption on Ag surfaces. Additional data on other planar π-conjugated organic molecules such as coronene or NTCDA demonstrates the potential of this approach in analysing the interaction at metal-organic interfaces in great detail.

O 37.6 Tue 16:15 H36

Observing free-electron-like states in a Ferrocene layer — •Mircea V. Rastei, Benjamin W. Heinrich, Cristian Iacovita, Mauro Boero, Laurent Limot, and Jean-Pierre Bucher — Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Université de Strasbourg, France

We use low-temperature scanning tunneling microscopy and spectroscopy to study Ferrocene on Cu(111). Unlike the decomposition observed on Au(111), here the molecules are preserved upon adsorption and form ordered layers. Differential conductance spectra and maps reveal the existence of interface states of free-electron-like character in the HOMO-LUMO gap. Similar states were reported for other adlayers (NaCl, Xe, PTCDA), but this is the first interface state observed by STM at an organometallic layer. Additionally, we show that these states can be localized by depositing Cu atoms onto the Ferrocene layer, while for other metal atoms (Co, Au) a complex behavior is observed.