

O 28: Organic-Inorganic Systems I: PTCDA

Time: Tuesday 10:30–13:00

Location: S054

Invited Talk

O 28.1 Tue 10:30 S054

Unravelling the structural and electronic properties of organic/metal interfaces with photoemission tomography — ●PETER PUSCHNIG — Institut für Physik, NAWI Graz, Karl-Franzens-Universität Graz, Graz, Austria

In the last years, a renaissance of angle-resolved photoemission spectroscopy (ARPES) for organic/metal interfaces could be observed. This development was mainly driven by the fact that, in opposition to conventional wisdom, the angular dependence of the photoemission current from oriented molecular films can be understood by assuming a plane wave as the final state of the photoemission process. This approximation allows for a simple and intuitive interpretation of the transition matrix element in terms of the Fourier transform of the initial state orbital leading to a combined experimental/theoretical technique, called photoemission tomography (PT).

In this contribution, I will focus on recent experimental and theoretical results obtained by PT. First, on the example of a Cs-doped bilayer of sexiphenyl, I demonstrate how PT enables a layer-resolved picture of the electronic structure thereby revealing the charge transfer processes upon doping. Similarly, for the doping of a monolayer of pentacene on Ag(110), PT unambiguously identifies the electronic states at various doping stages and unravels the processes determining the electronic level alignment. Finally, for the example of a PTCDA monolayer on Ag(110), I will show how ARPES data for a set of photon energies in the range between 20 and 55 eV leads to three-dimensional real-space images of molecular orbitals.

O 28.2 Tue 11:00 S054

Vibronic Modes in Molecular Orbital Imaging — ●ACHIM SCHÖLL¹, MARTIN GRAUS¹, MANUEL GRIMM¹, CHRISTIAN METZGER¹, MATTHIAS DAUTH², CHRISTIAN TUSCHE^{3,4}, JÜRGEN KIRSCHNER⁴, STEPHAN KÜMMEL², and FRIEDRICH REINERT¹ — ¹Universität Würzburg, Experimentelle Physik VII, 97074 Würzburg, Experimentelle Physik 7, 97074 Würzburg — ²Universität Bayreuth, Theoretische Physik IV, 95440 Bayreuth — ³Forschungszentrum Jülich, 52425 Jülich — ⁴Max Planck Institut für Mikrostrukturphysik, 06120 Halle

Photoelectron momentum microscopy with high energy resolution allows imaging of molecular orbitals with resolution of vibronic modes. We demonstrate that the intensity patterns of photoelectrons derived for the vibronic sidebands of molecular states show characteristic changes due to the distortion of the molecular frame in the vibronically excited state. By a comparison to the simulated patterns derived from calculations, an assignment of the specific vibronic mode that preferentially couples to the electronic excitation is possible, which in the example of the HOMO of coronene is a b_{2u} inplane mode with an energy of 0.2 eV. Orbital imaging by photoelectron momentum mapping with vibronic resolution thus provides unique information for the analysis of the coupling between electronic and vibronic excitation, and allows fascinating insight into the properties of molecular materials.

O 28.3 Tue 11:15 S054

Surface crystallography by LEED-IV of large organic adsorbates on Ag — ●INA KRIEGER^{1,3}, GEORG HELD², CHRISTIAN KUMPF³, and MORITZ SOKOLOWSKI¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Bonn, 53115 Bonn, Germany — ²Department of Chemistry, University of Reading and Diamond Light Source, UK — ³Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52428 Jülich, Germany

LEED-IV is a powerful technique for surface crystallography which supplies detailed experimental structure information on the adsorption geometry of large organic molecules on surfaces revealing important insights in inter-atomic interactions and chemical bonding. Using data from different angles of incidence and optimizing the program code we were able to overcome the challenges given by the limitations of the experimental data set and the calculation times required for the complex and large unit cells.

Here we will report on a recent LEED-IV analysis of PTCDA on Ag(100), at present yielding a good Pendry R-factor of about 0.23. The calculation is based on a unit cell containing 156 atoms and experimental curves for five angles of incidence with an energy-to-parameter ratio over 200 eV. We were able to derive structural information about

the surface geometry, in particular with regards to vertical distortions of the molecule core and the buckling of the substrate surface, which could so far not be obtained by other structure methods and are in good agreement with results from DFT and NIXSW studies. Supported by the DFG.

O 28.4 Tue 11:30 S054

Structure and thermal stability of organic heterostructures on Ag(111) — ●SEBASTIAN THUSSING, LAURA FERNANDEZ, and PETER JAKOB — Fachbereich Physik, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany

The growth of highly ordered molecular films exceeding the first few monolayers represents a challenge as these layers are inherently unstable and susceptible to dewetting processes. Understanding the kinetics of associated phase transformations and proper characterization tools are therefore crucial in such studies. We have investigated the thermal stability and intermixing of various heterolayer model systems (stacked CuPc/PTCDA and TiOPc/PTCDA layers grown on Ag(111)) by means of analyzing the characteristic vibrational modes of these molecules using IR spectroscopy. In addition, SPA-LEED provided information regarding the lateral ordering of these layers. We find that the growth of TiOPc layers on Ag(111) leads to the formation of a stable bilayer where the first layer is oriented with "Ti=O up" and the second layer with "Ti=O down". This particular structural arrangement is attributed to a minimization of dipole-dipole interaction within this stacked Ti=O assembly. Considering the stability of this configuration, bilayers of TiOPc (and CuPc for comparison) have been combined with PTCDA contact primer layers. Again the TiOPc-bilayer exhibits exceptional thermal stability with minimal intermixing with underlying PTCDA/Ag(111) up to about 450K. This is in contrast to the growth of a CuPc bilayer on PTCDA/Ag(111) which shows negligible intermixing but CuPc cluster formation already at T = 250K.

O 28.5 Tue 11:45 S054

Perylene derivatives adsorbed on O-terminated ZnO. An X-ray standing wave study — ●ANTONI FRANCO-CAÑELLAS¹, JENS NIEDERHAUSEN², ALEXANDER HINDERHOFER¹, TIEN-LIN LEE³, ALEXANDER GERLACH¹, NORBERT KOCH^{2,4}, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, Germany — ²Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany — ³Diamond Light Source, UK — ⁴Institut für Physik, Humboldt-Universität zu Berlin, Germany

Adsorption-induced conformational changes of large organic molecules have been extensively studied in the past for metal-organic interfaces employing the X-ray standing wave (XSW) technique [1], which provides an element-specific measurement of the adsorption distance of the molecule. Here, we show that the same method can be applied to inorganic-organic semiconductor interfaces. In particular, perylene, PTCDA and PTCDI adsorbed on O-terminated ZnO were studied with XSW. Our results shed light on how the ZnO affects the adsorption geometry of the molecule and how different functional groups distort and modify the overall adsorption distance, which is crucial to properly understand the substrate-molecule energy-level alignment within the context of hybrid inorganic-organic systems for optoelectronic applications [2,3].

[1] A. Gerlach et al., in *The Molecule-Metal Interface* (eds N. Koch, N. Ueno and A. T. S. Wee), Wiley-VCH, Weinheim, Germany (2013).

[2] R. Schlesinger et al. *Phys. Rev. B* 2013, 87, 155311.

[3] M. Gruenewald et al. *J. Phys. Chem. C* 2015, 119, 4865.

O 28.6 Tue 12:00 S054

Tracing structural and electronic changes in the first metal layer of metal-organic hybrid interfaces — ●JOHANNES SEIDEL¹, NORMAN HAAG¹, LISA GRAD¹, GERBEN VAN STRAATEN³, MARKUS FRANKE³, CHRISTIAN TUSCHE², JÜRGEN KIRSCHNER², CHRISTIAN KUMPF³, BENJAMIN STADTMÜLLER¹, MIRKO CINCHETTI¹, and MARTIN AESCHLIMANN¹ — ¹Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schrödinger-Strasse 46, 67663 Kaiserslautern, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle, Germany — ³Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany

In this work, we show how the geometric and electronic properties of metal surfaces can be altered by the molecule-substrate interaction. As a model system, we chose a Ag(111) surface and embed Pb tracer atoms into the topmost Ag(111)-layer by surface alloying.

We have studied the electronic valence structure of interfaces formed by prototypical organic molecules adsorbed on the Pb/Ag(111) surface alloy by momentum microscopy. While the adsorption of PTCDA significantly alters the alloy band structure, no changes are observed for CuPc. The changes in the valence band of the PTCDA/Pb/Ag(111) interface can be explained by vertical relaxation of the Pb tracer atoms as determined by x-ray standing waves method. Such relaxation occurs only at the interface formed with PTCDA, not with CuPc. We thus propose that the modifications of the Pb/Ag(111) surface alloy can be attributed to the formation of local bonds between PTCDA and the surface alloy which are absent in case of CuPc.

O 28.7 Tue 12:15 S054

Determination of the adsorption geometry of the PTCDA on the Cu(110) surface by NIXSW triangulation —

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The normal incidence x-ray standing wave (NIXSW) technique is frequently used to determine the adsorption height of atoms or molecules adsorbed on surfaces. Moreover it is possible to identify the adsorption site as well using several Bragg reflections and the triangulation approach.

We applied this method to a ordered layer of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) on the Cu(100) surface. This molecular phase contains two differently orientated PTCDA molecules, equivalent from structure point of view, which are found to be located at bridge sites. Compared to PTCDA adsorbed on the low index Ag surfaces, the bending of the PTCDA molecule on Cu(100) is different. The carboxylic oxygens are no longer located below the perylene backbone. Nevertheless the tendency that the oxygen atoms adsorb close to on top positions relative to the surface atoms is conserved.

O 28.8 Tue 12:30 S054

Controlling the electronic properties of heteromolecular monolayers without affecting their structure through exchange of the phthalocyanine central metal atom —

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Planar aromatic molecules in a mixed monolayer can indirectly influence each other leading to charge transfer from one molecule to the other via the substrate[1]. This effect provides new ways to tailor the properties of metal-organic interfaces but it's application is complicated by the fact that exchanging the molecular species can change the lateral ordering. This can be avoided when phthalocyanine molecules are used since their interaction with neighboring molecules is largely independent of the central metal atom. Taking advantage of this we prepared mixed monolayers of SnPC and PTCDA on Ag(111) and compared them with known CuPC + PTCDA monolayers exhibiting the same lateral structure[1]. We observed a shift of the PTCDA FLUMO and surprising changes in the vertical adsorption structure, proving that this technique allows tuning of the organic-metal interface properties independently of the lateral structure.

[1] Benjamin Stadtmüller et al., Nature Communications 5 (2014)

O 28.9 Tue 12:45 S054

Understanding the planarization of shuttle-cock shaped subphthalocyanine molecule on Cu(111) surface —

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The structure of an organic semiconductor plays a determining role in its adsorption on a metal surface. Large planar molecules like planar phthalocyanines, pentacene and PTCDA typically lie completely flat on most metal surfaces. The situation becomes more complex in case of non-planar molecules. They generally show a tendency to planarize upon adsorption but the extent of this planarization varies from negligible to almost complete for various metal-molecule combinations.

Here, we try to understand the reasons for this planarization by studying an extreme example exhibiting almost complete planarization: adsorption of shuttle-cock shaped Chloroboron subphthalocyanine on Cu (111). Using DFT, we study the steps of the adsorption process by gradually increasing the van der Waals interaction between the adsorbate and the substrate and following the evolution of the molecule's electronic and geometrical structure. We identify the bonding of the molecule as a two-stage process involving Fermi-level pinning followed by a rehybridization of the molecule's frontier orbitals. Especially the observed evolution of charge rearrangements help us to explain why we see an almost complete planarization.