O 29: Organic-Inorganic Hybrid Systems and Organic Films IV

Time: Tuesday 10:30–13:00 Location: WIL A317

O 29.1 Tue 10:30 WIL A317

Tailoring surface alloys by metal-organic bonds: Adsorption properties of PTCDA on Sn/Ag(111) and Sn/Au(111) surface alloys — •Johannes Seidel[1], Florian Haag[1], Norman Haag[1], Leah Kelly[1], Mahalingam Maniraj[1], Dominik Jungkenn[1], Markus Franke[2], Gerben van Straaten[2], Christian Kumpf[2], Mirko Cinchetti[3], Benjamin Stadtmüller[1], and Martin Aeschlimann[1] — [1]Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schroedinger-Strasse 46, 67663 Kaiserslautern, Germany — [2]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — [3]Experimentelle Physik VI, Technische Universität Dortmund, 44221 Dortmund, Germany

In this work, we extend our new approach [1] of controlling the geometric and electronic interface properties of surface alloys by adsorption of organic molecules. We investigated the PTCDA molecule adsorbed on surface alloys Sn_1Ag_2/Ag(111) and Sn_1Au_2/Au(111) by LEED, NIXSW and momentum photoemission microscopy to reveal changes in the lateral, vertical and electronic structure of the surface alloy caused by the adsorption of PTCDA. In both cases we find a clear vertical relaxation of the Sn atoms upon adsorption of PTCDA, similar to [1], but only in the case of PTCDA on Sn_1Ag_2/Ag(111) a charge transfer into the LUMO is observed. We thus conclude that the driving mechanism for lifting the Sn atoms is not charge transfer rather the formation of local bonds between the oxygen end groups of PTCDA and the Sn atoms. [1] PRL 117, 096805(2016)

O 29.2 Tue 10:45 WIL A317

Adsorbate-Induced Charge Accumulation and Collective Excitations at Metal/Organic Interfaces — •Friedrich Maass, David Gerbert, and Petra Tegeder — Physikalisch-Chemisches Institut; Ruprecht-Karls-Universität Heidelberg, INF 253, 69120 Heidelberg, Germany

The electronic and geometrical structure of organic molecules at metal/organic interfaces have substantial impact on the performance of organic molecule-based devices. We investigated the adsorption geometry and the electronic properties of F_4TCNQ and TCNQ on the Au(111) surface using vibrational and electronic high-resolution electron energy-loss spectroscopy (HREELS), temperature-programmed desorption (TPD), and density functional theory calculations (DFT). With angle-resolved electronic HREELS we characterized a collective excitation of electrons accumulated at the interface[1]. We analyzed the influence of transferred parallel momentum, impinging electron energy, and film thickness. As F_4TCNQ is, in contrast to TCNQ, known to be negativly charged at the Au(111) surface we were also able to investigate the influence of charges in the adsorbate layer on the collective excitation.

[1] Salomon, E., Layet, J. M., and Angot, T. *Phys. Rev. B*, **85**, 125420 (2012).

O 29.3 Tue 11:00 WIL A317

A novel facility for time- and space-resolved molecular dynamics on surfaces — •Bernhard Huber[1], Sebastian Pres[1], Emanuel Wittmann[2], Lysanne Dietrich[1], Julian Lüttig[1], Victor Lisinetskii[1], Matthias Hensen[1], Eberhard Riedle[2], and Tobias Brixner[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — [2]Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität München, Oettingenstraße 67, 80538 München, Germany

How do energy transport processes between individual molecules or inside large heterogeneous structures like light harvesting complexes occur? Is the transport dominated by step-by-step hopping of excitation or do the individual molecules form a strongly coupled system in which the excitation is delocalized over all constituents? How are these transport phenomena influenced by interactions with the substrate, the environment and external light sources? To investigate these questions the measurement signal of the prepared system has to be retrieved with high temporal (femtosecond regime) and spatial resolution far below the optical diffraction limit (several nanometers). The surface spectroscopy facility presented here combines aberration-corrected photoemission electron microscopy (AC-PEEM) with a widely tunable femtosecond laser system down to the UV range rendered by optical parametric amplification. Thus, the surface dynamics can be explored in a time-interferometric scanning scheme with high spectral addressability of sample specific resonances. Here we demonstrate first results of spectrally selective photoemission microscopy.

O 29.4 Tue 11:15 WIL A317

Electronic and optical properties of Organic/Inorganic Heterostructures from First Principles: PPP@ZnO — •Benjamin Höffling, Dimitri Nabok, Caterina Cocchi, and Claudia Draxl — Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Zum Großen Windkanal 6, 12489 Berlin, Germany

The electronic properties of poly(*para*-phenylene) (PPP) adsorbed on the non-polar (001) surface of rocksalt (*rs*) ZnO are studied by means of all-electron density functional theory (DFT) and many-body perturbation theory within the G_0W_0 approach. We focus in particular on the question of the electronic band discontinuities at the interface and examine the influence of quantum confinement, molecular polarization, and charge redistribution. For our prototypical system, PPP@ZnO, we find a type-I heterostructure.

The band offsets derived from a G_0W_0 treatment of the interface structure are compared to values derived using simpler mesoscopic methods, like the electron-affinity rule or alignment via the electrostatic potential, revealing that these approaches are insufficient to even qualitatively predict the type of heterostructure of this kind of system.

We also explore the optical excitations of the interface system, compare them to the excitonic properties of the pristine PPP and ZnO, and discuss the methodological implications for the theoretical description of interface electronics.

O 29.5 Tue 11:30 WIL A317

Integer charge transfer induced by insulating layer — •Michael Hollerer[1], Daniel Lüftner[1], Philipp Hurdax[1], Thomas Ules[1], Simon Weiss[2,3], Sergey Soubatch[2,3], Frank Stefan Tautz[2,3], Georg Koller[1], Peter Puschnig[1], Martin Sterrer[1], and Mike Ramsey[1] — [1]Insitute of Physics, University of Graz, NAWI Graz, Universitätsplatz 5, 8010 Graz, Austria — [2]Peter Grünberg Insitut (PGI-3), Forschungszentrum Jülich, 52425, Jülich, Germany — [3]Jülich Achen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425, Jülich, Germany

While it is becoming accepted that charge transfer can occur across thin dielectric films on metal substrates, particularly for organic overlayers, the occupancy of the lowest unoccupied molecular orbital (LUMO), whether fractional or integer, and the distribution of the charged molecules within the layer is under debate. Herein we present a comprehensive analysis of the charge transfer phenomena, facilitated by the strong reduction of the work function, in the model system pentacene on thin MgO(001) on Ag(001). Using scanning tunneling microscopy (STM) and angular resolved photoemission supported by density functional theory we are able to unambiguously deduce integer occupation of all molecules in the monolayer film on MgO(001)/Ag(001) compared to fractional occupation on the bare Ag(100) substrate. Moreover, the energy of the peaks observed in scanning tunneling spectroscopy, above and below the Fermi level, can be directly related to those of the singly occupied and singly unoccupied molecular states.

O 29.6 Tue 11:45 WIL A317

Impact of collective electrostatics on XPS Spectra of organic adsorbate layers — •Thomas C. Taucher, Oliver T. Hofmann, and Egbert Zojer — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria

In this contribution we investigate the applicability of slab-type density functional theory-based band structure calculations to quantitatively model XPS core-level shifts at metal-organic interfaces. We compare the performance of the initial state approach (neglecting screening effects) and different variants of the final state approach (inherently considering screening) for the case of self-assembled monolayers of long, upright standing molecules. In particular we here discuss serious artifacts occurring when combining final state approaches with periodic boundary condition based calculations.

Beyond these more technical aspects, we also compare the relative impact of chemical shifts and binding energy shifts caused by collective electrostatic effects. The latter, albeit often overlooked, do play an important role for densely packed adsorbate layers consisting of molecules that bear polar elements.[1] In fact, electrostatic shifts of core-level binding energies pave a way for using XPS as a probe of local changes in the electrostatic energy in a sample.

[1] T. C. Taucher et al., J. Phys. Chem. C., 2016, 120, 6, 3428.

O 29.7 Tue 12:00 WIL A317

Surface-Assisted Diastereoselective Ullmann Coupling of Helicenes — •Christian Wäckerlin[1], Jingyi Li[1], Anaïs Mairena[1], Kévin Martin[2], Narcis Avarvari[2], and Karl-Heinz Ernst[1] — [1]Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland — [2]Laboratoire Moltech Anjou, Université d'Angers, Angers, France

Surfaces functionalized with covalently linked chiral molecules are highly desirable; to name two examples, for stereoselective catalysis or electron spin filtering. However, the way chiral molecules at surfaces interact with each other and assemble is still an open question. Here we report the Ullmann coupling of chiral 2-bromo[4]helicene monomers to helicene dimers on Cu(100). Such dimers can exist as three isomers, the two enantiomers [(P,P) and (M,M)] and the isomer (P,M) which is the diastereomer with respect to the two enantiomers. Using scanning tunneling microscopy (STM), we show that coupling is diastereoselective, i.e. we observe the enantiomers [(P,P) and (M,M)] but not the (P,M)-dimers. Moreover, the (P,P)- and (M,M)-dimers self-assemble and separate into enantiopure domains.

O 29.8 Tue 12:15 WIL A317

NEXAFS study of robust ultrathin Fe(II) spin-crossover films on surfaces — •Sebastian Rohlf[1], Matthias Kalläne[1], Simon Jarausch[1], Benedikt Flöser[2], Felix Tuczek[2], and Kai Rossnagel[1] — [1]Institut für Experimentelle und Angewandte Physik, Universität Kiel, 24098 Kiel, Germany — [2]Institut für Anorganische Chemie, Universität Kiel, 24098 Kiel, Germany

The spin-state manipulation of Fe(II) coordination complexes by external stimuli is associated with a change in the electronic, magnetic, and structural properties. In particular, the temperature- and light-induced switching mechanisms may be utilized in future spintronic devices. Both of these switching effects were observed even in monolayers adsorbed on the weakly interacting substrate HOPG [1]. Nevertheless, the dissociation of spin-crossover (SCO) molecules in direct contact to a metal surface is still impeding measurements in device-like environments. A novel approach to overcome this limitation is the electronically stabilized SCO system Fe(pyrpy)$_2$(phen), a recently synthesized derivative of the well-studied complex Fe(H$_2$bpz)$_2$(phen). Here, we present near edge X-ray absorption fine structure (NEXAFS) spectroscopy results of Fe(pyrpy)$_2$(phen), adsorbed in thin films on Au(111) and TiTe$_2$, for different temperatures and laser light irradiation conditions. Our results confirm the preservation of the spin-switching ability in thin films of this derivative. Furthermore, the comparison of the measured switching efficiencies on both substrates provides evidence for an intact interface layer in contact to the Au(111) surface. [1] M. Bernien *et al.*, ACS Nano **9**, 8960-8966 (2015).

O 29.9 Tue 12:30 WIL A317

Atomic and Electronic Structure at Metal-Endohedral Fullerene / Metal Interfaces — •Leah Kelly[1], Johannes Seidel[1], Norman Haag[1], Johannes Stöckl[1], Markus Franke[2], Gerben van Straaten[2], Christian Kumpf[2], Benjamin Stadtmüller[1], Mirko Cinchetti[3], and Martin Aeschlimann[1] — [1]Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, 67663 Kaiserslautern, Germany — [2]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — [3]Experimentelle Physik VI, Technische Universität Dortmund, 44221 Dortmund, Germany

Spin carrying molecules, so called single molecular magnets, are a highly promising class of materials to realize data storage on the nanoscale. Of interest are metal-endohedral fullerenes, with spin centers shielded by a fullerene core.

In this work we studied Sc3:N@C80 on Ag(111). The structural properties were characterized by LEED and NIXSW, the electronic structure by momentum microscopy. In contrast to the gas phase, the N and Sc atoms inside the fullerene cage are vertically displaced due to adsorption of the molecules on the surface. In addition, we find a clear charge redistribution at the metal-organic interface including a transfer into the Sc3:N@C80 LUMO, which has been found to have significant electron density at the metals, yielding a possibility for substrate mediated coupling between spin centers. Our findings provide a basis for studying the cooperative behavior for caged 3 metal spin-systems in contact with a surface.

O 29.10 Tue 12:45 WIL A317

Wavelength sensitivity of the photostationary state of azobenzene-functionalized SAMs — •Wibke Bronsch, Larissa Boie, Cornelius Gahl, and Martin Weinelt — Freie Universität Berlin, Deutschland

Azobenzene is a molecular switch with significantly different static dipole moments in its trans and cis isomer, respectively. Embedded in self-assembled monolayers (SAMs), this property can be used for real-time tuning of the sample work function. A specific work function is hence a measure of a particular photostationary state (PSS) of the SAM. In this contribution we investigate the PSS of azobenzene-functionalized undecane thiol diluted with dodecanethiol on Au(111). Work function variations are monitored by means of two-photon photoelectron spectroscopy. We show that the PSS is very sensitive to the illumination wavelength when tuned across the S$_2$ absorption band of the 2-dimensional molecular aggregate. Due to the interplay of the different absorption cross sections and quantum yields of the two isomers, the PSS changes from mainly trans to mainly cis in the range of 300 to 370 nm.