

O 43: Inorganic/Organic Interfaces: Electronic Properties I

Time: Wednesday 10:30–13:15

Location: MA 005

Invited Talk

O 43.1 Wed 10:30 MA 005

Electronic Interactions and Ultrafast Carrier Dynamics at Hybrid Organic / Inorganic Interfaces — ●OLIVER L.A. MONTI — Department of Chemistry and Biochemistry, The University of Arizona, Tucson, AZ 85721, USA

Hybrid organic / inorganic interfaces play a central role in efficient carrier collection and extraction in next-generation organic optoelectronics. Here, I will discuss the consequences of electronic coupling at hybrid interfaces on electronic structure and ultrafast carrier dynamics for the prototypical case of highly conductive ZnO films. The presence of shallow donor states near the conduction band minimum leads to strong coupling across interfaces with organic acceptors such as C₆₀ and PTCDA, unambiguously manifested by both charge-transfer and hybridization at the interface. Such interactions have dramatic effects on ultrafast carrier dynamics at the interface, lengthening times for escape from the interface by at least two orders of magnitude. I will show how interfacial coupling can be controlled readily with the chemical potential and further discuss the nature of relevant gap states, as revealed by two-photon photoemission spectroscopy. The results have broad implications for efficient charge harvesting and injection at hybrid interfaces.

O 43.2 Wed 11:00 MA 005

Can three-dimensional orbitals of adsorbed molecules be measured? — ●SIMON WEISS^{1,2}, DANIEL LÜFTNER³, EVA-MARIA REINISCH³, THOMAS ULES³, GEORG KOLLER³, SERGEY SOUBATCH^{1,2}, PETER PUSCHNIG³, MICHAEL RAMSEY³, and F. STEFAN TAUTZ^{1,2} — ¹Peter Grünberg Institute (PGI-3), Forschungszentrum Jülich, Germany — ²JARA - Fundamentals of Future Information Technology, Germany — ³Institute of Physics, Karl-Franzens University Graz, 8010 Graz, Austria

Chemical and physical properties of atoms and molecules are determined by their electron wave functions i.e. orbitals. Therefore there is much interest to measure these orbitals, although they are not quantum-mechanical observables. Experimentally only the electron density and energy levels are accessible, the phase information is lost. Using angle resolved photoemission spectroscopy (ARPES) electron density can be measured. Additionally it has been shown that a plane wave final state interpretation of experimental ARPES data allows the retrieval of real space images of molecular orbitals in two dimensions including also phase information. For a complete reconstruction of the molecule it is necessary to introduce the energy dependence to gain the third dimension in momentum space. Here the position of the intensity maximum is of particular importance. As a model system we used the brick-wall monolayer of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) on Ag(110) and measured HOMO and LUMO in a wide energy range. This data we used to reconstruct the orbitals and compare the result with theoretical predictions.

O 43.3 Wed 11:15 MA 005

Orbital tomography: beyond the plane wave final state approximation — ●PETER PUSCHNIG — University of Graz, Institute of Physics, Austria

In recent years it has been shown that the angle-resolved photoelectron cross section from organic molecular films can be accounted for by approximating the final state of the photoemission process by a plane wave. This simple approach, sometimes termed "orbital tomography", has led to a number of interesting applications for organic molecules adsorbed on metal surfaces, such as the unambiguous identification of molecular orbitals [1], the determination of molecular orientations [2], or even the reconstruction of real space molecular orbitals [3]. However, this technique has also been criticized since it relies on a crude approximation for the final state whose accuracy and range of validity has been questioned by many.

In this contribution, I will present theoretical results ranging from small molecules, such as benzene, up to extended two-dimensional structures, such as graphene. By comparing to available experimental data, I will identify the limitations of the plane wave approximation and discuss approaches to improve upon it. In particular, a simple modification to take into account the free mean path of photoelectrons and a modification of the final state which allows to account for shape resonances and scattering effects will be demonstrated.

[1] Puschnig et al., Phys. Rev. B 84, 235427 (2011)

[2] Puschnig et al., Science 326, 702-706 (2009)

[3] Lüftner et al., Proc. Nat. Acad. Sci. U. S. A. 111, 605-610 (2014).

O 43.4 Wed 11:30 MA 005

Many-body transitions in a single molecule visualized by scanning tunneling microscopy — ●FABIAN SCHULZ¹, MARI IJÄS¹, ROBERT DROST¹, SAMPSA K. HÄMÄLÄINEN¹, ARI P. SEITSONEN², ARI HARJU¹, and PETER LILJEROTH¹ — ¹Aalto University School of Science, Department of Applied Physics, Espoo, Finland — ²École Normale Supérieure, Département de Chimie, Paris, France

Scanning tunneling spectroscopy (STS) of molecular systems is usually interpreted in terms of single-particle electronic transitions. A prominent exception is the Kondo effect [1], a many-body state resulting from the interaction of an unpaired molecular spin with the conduction electrons of a metallic substrate. Probing excited states in single molecules by STS, we demonstrate many-body effects arising purely from electronic states confined in the molecule.

Cobalt phthalocyanine adsorbed on the moiré pattern of monolayer hexagonal boron nitride on Ir(111) [2] allows to carry out STS on molecules that are initially in different charge states [3]. The observed resonances are inconsistent with the single-particle interpretation of tunneling spectroscopy. Instead, these resonances can be understood as a series of many-body excitations of the different ground states of the molecule [4].

[1] I. Fernandez-Torrente *et al.*, Phys. Rev. Lett. **101**, 217203 (2008).[2] F. Schulz *et al.*, Phys. Rev. B **89**, 235429 (2014).[3] F. Schulz *et al.*, ACS Nano **7**, 11121 (2013).[4] F. Schulz *et al.*, Nature Phys., accepted.

O 43.5 Wed 11:45 MA 005

Electronic structure of organic monolayer films on a Pb/Ag(111) surface alloy — ●JOHANNES SEIDEL¹, NORMAN HAAG¹, BENJAMIN STADTMÜLLER¹, CHRISTIAN TUSCHKE², MIRKO CINCHETTI¹, JÜRGEN KIRSCHNER², and MARTIN AESCHLIMANN¹ — ¹Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schrodinger-Strasse 46, 67663 Kaiserslautern, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle, Germany

The ability to control the electronic properties of organic semiconductors at metal-organic hybrid interfaces is crucial for their applicability in future electronic and spintronic devices. Hence, many studies so far focused on tailoring such interfaces by tuning either the properties of the molecular film or of the organic adsorbates. In this study we will extend this concept by altering properties of the metal substrate, i.e., by tuning the metal-organic interface "from the bottom".

We have studied the electronic valence structure of the interface formed by prototypical organic molecules adsorbed on a Pb/Ag(111) surface alloy by ARPES using a k-space microscope. The Pb/Ag(111) surface alloy shows a distinct spin-texture due to the Rashba-Bychkov effect. Our ARPES data reveals almost identical molecular features in the valence band for molecular monolayer films on Ag(111) and the Pb/Ag(111) surface alloy. However, the band structure of the clean Pb/Ag(111) surface alloy is significantly modified by the molecular adsorption which we attribute to a change in the vertical relaxation of the atomic positions of the surface alloy.

O 43.6 Wed 12:00 MA 005

Strong Interaction between Subphthalocyanines and Copper (111): A computational study — ●SHASHANK S. HARIVYASI¹, ELISABETH WRUSS¹, OLIVER T. HOFMANN¹, OLIVER L. A. MONTI², and EGBERT ZOJER¹ — ¹Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Graz, Austria — ²Department of Chemistry & Biochemistry, University of Arizona, Tucson, Tucson, AZ, United States

The detailed energetics of a metal-organic interface is influenced by multiple factors. These include: the nature of the interaction between the metal and the molecules, the geometric conformation of each of those adsorbed molecules on the surface, and the packing arrangement and coverage density of the monolayer.

In this work, we use DFT calculations to analyze adsorption

of Chloroboron-Subphthalocyanine (SubPc) on a Cu (111) surface. SubPc is an interesting candidate for elucidating the interplay of the above-mentioned aspects given the molecule's cone-shaped geometry in gas-phase, the extended conjugated electron system and the significant dipole moment. We studied the adsorption energetics and electronic structure for various conformations and simulated STM results. In our findings, we highlight the role of van der Waals forces in adsorption and how they result in an unusually strong interaction between the metal and the molecule that, in turn, leads to planarization of the molecules on the surface and a pronounced hybridization of molecular and metal states. The latter is analyzed on the basis of charge rearrangements and the densities of states projected onto the molecular orbitals.

O 43.7 Wed 12:15 MA 005

Modeling geometry and electronic structure of flat-lying phthalocyanines on metal surfaces — ●ELISABETH WRUSS¹, DAVID EGGER^{1,2}, YU LI HUANG³, TOMÁŠ BUČKO⁴, WISSAM SAIDI⁵, SATOSHI KERA³, and EGBERT ZOJER¹ — ¹Institute of Solid State Physics, Graz University of Technology, Graz, Austria — ²Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel — ³Graduate School of Advanced Integration Science, Chiba University, Chiba, Japan — ⁴Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Bratislava, Slovakia — ⁵Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, United States

The adsorption behavior of metal-phthalocyanine (MPc) molecules on coinage metal surfaces is investigated using density functional theory. To take van der Waals (vdW) interactions into account, the geometry optimization is done using the PBE+vdW-surf [1] approach. The resulting adsorption heights are in excellent agreement with experimental XSW measurements, while in calculations without a vdW correction only a repulsive interaction potential between the metal and the adsorbate is observed. The electronic structure is investigated using generalized gradient (GGA) and hybrid functionals. We find that both approaches provide a highly reliable description of the adsorption-induced work-function modifications, but predict different alignments of the electronic states. This is due to spurious orbital self-interaction error present in GGA calculations, which is strongly mitigated by the use of hybrid functionals. [1] Ruiz et al., PRL. 108, (2012).

O 43.8 Wed 12:30 MA 005

First-Principles Simulation of Near-Edge X-Ray Absorption Fine-Structure (NEXAFS): Comparison of Core-Level Constraining Approaches — ●GEORG S. MICHELITSCH, KATHARINA DILLER, REINHARD J. MAURER, TOM BÄRWINKEL, and KARSTEN REUTER — Technische Universität München, Germany

NEXAFS allows to directly probe the electronic structure of a surface-adsorbate system by excitation of core electrons to unoccupied states. The interpretation of the experimental signatures is greatly facilitated by independent first-principles calculations. For this, ground-state density-functional theory (DFT) based approaches explicitly constraining the occupation of core-levels constitute a numerically particularly efficient approach suited to tackle large adsorbate systems. Notwithstanding, their approximate treatment of core-hole relaxation and hole-excited electron interaction needs to be carefully assessed. Using experimental K-edge spectra for common building blocks of organic adsorbates like benzene and porphine as a reference, we perform such an assessment specifically within the context of the numeric atomic orbital

basis sets of the all-electron DFT-package FHI-aims. We find relative peak positions to be quickly converged with basis set size and already at the level of semi-local DFT functionals. While this favors the use of these approaches for the simulation of large adsorbate systems, we critically discuss differences in the core hole occupation strategy and their consequences for the simulation of higher-lying core hole excitations and spin-anisotropic systems.

O 43.9 Wed 12:45 MA 005

Heteromolecular CuPc-C60 monolayer films on the Co(1000) surface — ●NORMAN HAAG, JOHANNES SEIDEL, JOHANNES STÖCKEL, BENJAMIN STADTMÜLLER, MIRKO CINCHETTI, and MARTIN AESCHLI-MANN — Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schroedinger-Strasse 46, 67663 Kaiserslautern, Germany

Heteromolecular monolayer films consisting of two different types of molecules are promising candidates for tailoring the geometric and electronic properties at metal-organic hybrid interfaces. So far, this approach has only been demonstrated on noble metal surfaces where the molecules show a weak chemical molecule-substrate interaction [B. Stadtmüller, Nat. Commun. 5, 3685 (2014)]. In this study, we extend this concept to ferromagnetic surfaces by investigating the formation of heteromolecular CuPc-C60 structures on the Co(1000) surface. On such transition metal surfaces, the strong molecule-substrate interaction usually prevents the formation of long-range ordered molecular structures. We have studied the electronic and structural properties of the heteromolecular CuPc-C60/Co(1000) system using a k-space photoemission microscope. Analyzing the angular dependent photoemission pattern allows us to assign spectroscopic features to molecular orbitals and to determine the orientation of corresponding molecules on the surface. A comparison of these results to the CuPc and C60 homomolecular films on Co(1000) reveals that the formation of ordered heteromolecular films is mainly caused by a site-specific interaction of C60 with Co.

O 43.10 Wed 13:00 MA 005

Excitation processes in Copper-porphyrin aggregates studied by multi-photon Photoemission Electron Microscopy (PEEM) — ●HANNES HARTMANN¹, INGO BARKE¹, MOHAMMADREZA BAHRAMI¹, LUKAS RATHJE¹, TAMAM BOHAMMUD¹, PER-ARNO PLÖTZ¹, J.A.A.W. ELEMANS², OLIVER KÜHN¹, KARL-HEINZ MEIWES-BROER¹, and SYLVIA SPELLER¹ — ¹Institute of Physics, University of Rostock, Germany — ²Institute of Molecules and Materials, Radboud University Nijmegen, Netherlands

Hybrid systems composed of nanoparticles and molecular aggregates are subject to intense research due to potential applications in organic electronics and for photovoltaics. We are interested in the role of the local environment on the various types of excitations in such systems and in their transport. Copper-porphyrin aggregates are prepared on Si(111) covered by native oxide and on highly ordered pyrolytic graphite (HOPG) by self-organized growth. Multi-photon excitation with a tunable fs-laser system leads to emission of photoelectrons that are analyzed in a Photoemission Electron Microscopy (PEEM). Beside the electronic structure, correlative mapping including scanning probe microscopy (AFM) at the same location can help to identify contributing processes and to elaborate the role of structural features and transport properties on the emission intensity and energy.