

## O 69: Focussed Session: Towards a Quantitative Understanding of Complex Adsorption Structures: Surface Science goes Organic II

Time: Thursday 10:30–13:15

Location: HSZ 01

### Topical Talk

O 69.1 Thu 10:30 HSZ 01  
**Injection/extraction barriers in donor-acceptor blends on metals through core-level spectroscopy** — ●ENRIQUE ORTEGA<sup>1,2</sup>, AFAF EL-SAYED<sup>1</sup>, PATRIZIA BORGHETTI<sup>2</sup>, ELI GOIRI<sup>2</sup>, CELIA ROGERO<sup>2</sup>, LUCA FLOREANO<sup>3</sup>, YUTAKA WAKAYAMA<sup>4</sup>, JOSE LUIS CABELLOS-QUIROZ<sup>2</sup>, DUNCAN MOWBRAY<sup>2</sup>, ANGEL RUBIO<sup>2</sup>, and DIMAS OTEYZA<sup>1,2</sup> — <sup>1</sup>Departamento de Física Aplicada I, UPV/EHU, San Sebastian — <sup>2</sup>Centro de Física de Materiales and DIPIC, San Sebastian — <sup>3</sup>Cons. Naz. Ric.-IOM, L. N. TASC, Trieste — <sup>4</sup>National Institute Material Science, Tsukuba

The active interface in charge injection devices can be generally defined by a monolayer-thick blend of donor/acceptor molecules in contact with a metal surface, where electron and hole injection/extraction barriers are determined by the offset of HOMO/LUMO molecular levels with respect to  $E_F$ . HOMO/LUMO alignment is not easy to elucidate in complex multi-component systems from valence band photoemission. Alternatively, we explored core-level photoemission, as a way to transparently assess molecular level alignment in donor-acceptor/metal interfaces. We performed systematic experiments combining acceptor-like fluorinated phthalocyanine (F16CuPc) and perfluoropentacene (PFP) with pentacene (PEN) and copper phthalocyanine (CuPc), respectively, on Au(111), Ag(111) and Cu(111). We observe, as a function of the donor/acceptor ratio, a characteristic binding energy shift in all core-levels, irrespectively of the donor/acceptor/metal combination. The meaning and the exceptions to such general behavior will be discussed. [See A. El-Sayed et al. ACS Nano 7, 6914 (2013)]

O 69.2 Thu 11:00 HSZ 01  
**Charge Localization at Inorganic/Organic Interfaces** — ●OLIVER T. HOFMANN, PATRICK RINKE, and MATTHIAS SCHEFFLER — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Understanding the mechanism behind level alignment at heterointerfaces is of fundamental importance for a variety of fields, including organicelectronics. Using density functional theory, we investigate the atomistic details of the level alignment of organic acceptors adsorbed on different surfaces. For adsorbates in direct contact with an Ag(111) surface, we observe the formation of hybrid states. This induces density of states at the Fermi energy and all molecules in the layer become partially and uniformly charged. Preventing the hybridization by inserting an NaCl layer between the adsorbate and the metal leads to a drastic change in the charge transfer behaviour. While semi-local density functionals still predict a fractional electron transfer, more sophisticated hybrid functionals break the translational symmetry and result in the integer charging of only a fraction of the molecules. The associated molecular states are found several tenths of an eV below the Fermi energy. This charge localization is accompanied by a distortion of the molecular geometry and can be interpreted as polaron. It affects several observables including core-level shifts or the electrostatic potential in the vicinity of the surface. Furthermore, a qualitatively different dependence of the adsorption-induced work-function change on the coverage is found.

O 69.3 Thu 11:15 HSZ 01  
**Simulating X-ray absorption spectra of large organic adsorbates with DFT: possible pitfalls on the example of free-base porphine on Ag(111) and Cu(111)** — ●KATHARINA DILLER, REINHARD J. MAURER, and KARSTEN REUTER — Technische Universität München, Germany

Near-edge X-ray Absorption Fine-Structure (NEXAFS) spectroscopy is widely used in Surface Science for the characterisation of adsorbate-substrate systems. Especially for large organic molecules, however, the spectral features consist of a set of overlapping peaks and cannot be disentangled easily. For many systems an independent first-principles simulation of the respective spectra is therefore indispensable for the analysis of the experimental data. Particularly for stronger chemisorbed adsorbates the (often applied) approximation to restrict the calculations to the isolated gas-phase molecule is bound to fail. On the other hand, explicit consideration of in particular extended metal surfaces faces multiple challenges that mostly arise from the need to keep the calculations computationally tractable. Using the adsorption

of free-base porphine on Ag(111) and Cu(111) as example we conduct density functional theory (DFT) simulations using both all-electron (FHI-aims) and pseudopotential (CASTEP) based implementations to investigate the efficiency and reliability of prevalent approaches to achieve the actual core-excitation, to ensure the localization of the core-hole, and to properly describe all final states of interest.

O 69.4 Thu 11:30 HSZ 01  
**Topical Talk**  
**Core and valence spectroscopy of physisorbed molecules: Role of substrate** — ●CLAUDIA DRAXL — Humboldt-Universität zu Berlin, Berlin

The interplay between weak intermolecular bonding and molecule-substrate interaction governs orientation, alignment, conformation, and packing of molecules. These geometrical aspects, in turn, determine the electronic and optical properties of the molecular layer(s). The substrate can, however, play an even more important role. It may affect the electronic structure in terms of charge transfer, polarization, and vibrational effects. To this extent, theoretical results obtained by density-functional theory and many-body perturbation theory will be analyzed and confronted with various microscopic and spectroscopic experimental probes. I will show how, for example, the molecular HOMO and LUMO levels are shifted by image-charge effects induced by a metal surface, and how small amounts of transferred charge can alter the molecular orbitals. Finally, the impact of electron-phonon coupling on x-ray absorption spectra of low-dimensional systems will be discussed.

O 69.5 Thu 12:00 HSZ 01  
**Substrate induced intermolecular dispersion and observed hybridisation: Pentacene on Cu(110)** — ●THOMAS ULES<sup>1</sup>, EVA REINISCH<sup>1</sup>, MARKUS OSTLER<sup>2</sup>, GEORG KOLLER<sup>1</sup>, DANIEL LÜFTNER<sup>1</sup>, PETER PUSCHNIG<sup>1</sup>, and MICHAEL RAMSEY<sup>1</sup> — <sup>1</sup>Institute of Physics, Karl-Franzens University Graz, 8010 Graz, Austria — <sup>2</sup>University of Erlangen-Nürnberg, Erlangen, Germany

The 5Å monolayer on Cu(110) has been studied by Angle Resolved UPS (ARUPS). The tomographic analysis of the ARUPS data cube into band (E vs. k) and momentum (kx vs. ky) maps reveal changes in both the substrate and molecule electronic structure upon the formation of the monolayer. In the region down to 1eV below the Fermi edge the momentum maps clearly show a 5Å LUMO intensity distribution with a remarkably large dispersion of ~ 0.7eV in the direction of the long molecular axes. This contrasts to the calculated dispersion of a free standing 5Å monolayer of only 20 meV and a truly significant enhancement of intermolecular dispersion is claimed. The strong periodic potential of the 5Å overlayer leads to an apparent opening of a band gap in the Cu sp band which will be argued to be the result of the change of Cu sp states to molecular LUMO character.

O 69.6 Thu 12:15 HSZ 01  
**Time-resolved simulation of angular resolved photoemission** — ●MATTHIAS DAUTH and STEPHAN KÜMMEL — University of Bayreuth, Germany

We present an approach for calculating angular resolved photoemission spectra (ARPES) by explicit simulation of the photoemission process in real-time. This allows us to go beyond the frequently employed molecular-orbital and eigenvalue-based interpretation of photoemission. In the latter, electrons are assumed to be emitted from single particle orbitals and final states are implicitly assumed to be plane waves. Our approach lifts these approximations. We use the framework of time dependent density functional theory to propagate the electronic system under the influence of an external ionizing laser field. Electron interaction and dynamical effects such as internal relaxation are thus explicitly taken into account. We simulate the energy and angular resolved photoelectron detection by evaluating the kinetic energy spectrum of the outgoing time-dependent electron density. The dynamic ionization process is analyzed in detail and compared to results that are obtained from the molecular orbital picture in combination with the plane wave approximation.

O 69.7 Thu 12:30 HSZ 01  
**Adsorption geometry and electronic structure of iron ph-**

**thalocyanine on Ag surfaces revealed by photoelectron momentum mapping** — ●VITALIY FEYER<sup>1,2</sup>, MARTIN GRAUS<sup>3,4</sup>, PASCAL NIGGE<sup>3,4</sup>, MICHAEL WIESSNER<sup>3,4</sup>, ROBERT G. ACRES<sup>2</sup>, CARSTEN WIEMANN<sup>1</sup>, CLAUS M. SCHNEIDER<sup>1,5</sup>, ACHIM SCHÖLL<sup>3,4</sup>, and FRIEDRICH REINERT<sup>3,4</sup> — <sup>1</sup>Research Center Jülich, 52425 Jülich, Germany — <sup>2</sup>Sincrotrone Trieste, 34012 Basovizza, Trieste, Italy — <sup>3</sup>Universität Würzburg, 97074 Würzburg, Germany — <sup>4</sup>Karlsruher Institut für Technologie KIT, 76021 Karlsruhe, Germany — <sup>5</sup>Universität Duisburg-Essen, D-47048 Duisburg, Germany

We report a comprehensive study of the adsorption behavior of iron phthalocyanine on the low-index crystal faces of silver. Experiments were carried out at the NanoESCA beamline of the Elettra synchrotron. The experimental setup includes a non-magnetic, electrostatic photoelectron emission microscope and a double-pass hemispherical analyzer that directly images a parallel momentum component of photoelectron at a fixed binding energy. A combination of photoelectron momentum mapping (PMM) and low-energy electron diffraction (LEED) provides access to the superstructure unit cell and the arrangement of the molecules within the unit cell. Additionally, momentum patterns give information about the electronic structure at the interface and the symmetry of molecular orbitals. Comparative analysis of the PMM of the lowest unoccupied molecular orbitals (LUMO) of FePc on the substrates with different symmetry indicates that both degenerate LUMOs receive charge transfer from the substrate.

O 69.8 Thu 12:45 HSZ 01

**Phase Determination of Electronic Wavefunctions utilizing the Circular Dichroism in the Angular Distribution of Photoelectrons** — ●MARTIN GRAUS<sup>1,2</sup>, MICHAEL WIESSNER<sup>1,2</sup>, PASCAL NIGGE<sup>1,2</sup>, ACHIM SCHÖLL<sup>1,2</sup>, and FRIEDRICH REINERT<sup>1,2</sup> — <sup>1</sup>Universität Würzburg, 97074 Würzburg, Germany — <sup>2</sup>Karlsruher Institut für Technologie KIT, 76021 Karlsruhe, Germany

The experimental measurement of molecular orbitals by angle resolved photoelectron spectroscopy (ARPES) respectively photoemission electron microscopy (PEEM) is on the edge of providing three dimensional images of the respective electronic density distribution. This provides unprecedented insight into the structural, electronic and chemical properties of molecular materials, which are of practical relevance for future molecular electronics. A challenge in gathering the full or-

bit information lies in the determination of the quantum mechanical phase since it is usually lost by the conventional process of measuring solely the square of the wave function's absolute value. However, the phase is highly desired as the key parameter for the backwards Fourier Transform, which is necessary to create real space images out of the measured k-space data. We demonstrate an experimental approach to solve the phase problem taking advantage of interference patterns in the circular dichroism angular distribution (CDAD), whereby the handedness is introduced by the experimental geometry. This key experiment evidently shows that the determination of the full quantum mechanical wave function is possible by simultaneous measurement of intensity and phase.

O 69.9 Thu 13:00 HSZ 01

**3D Tomographic Imaging of Molecular Orbitals in Real Space** — ●PASCAL NIGGE<sup>1,2</sup>, MARTIN GRAUS<sup>1,2</sup>, VITALIY FEYER<sup>3,4</sup>, MICHAEL WIESSNER<sup>1,2</sup>, ACHIM SCHÖLL<sup>1,2</sup>, and FRIEDRICH REINERT<sup>1,2</sup> — <sup>1</sup>Universität Würzburg, 97074 Würzburg, Germany — <sup>2</sup>Karlsruher Institut für Technologie KIT, 76021 Karlsruhe, Germany — <sup>3</sup>Research Center Jülich, 52425 Jülich, Germany — <sup>4</sup>Sincrotrone Trieste, 34012 Basovizza, Trieste, Italy

The imaging of molecular orbitals by angle resolved photoelectron spectroscopy (ARPES) or photoemission electron microscopy (PEEM) has shown to be a very powerful tool for the investigation of molecular materials. By mapping the angle dependent intensity patterns of photoelectrons this technique provides tomographic images of the density distribution of the orbitals in k-space. The full potential of the tomographic mapping of molecular orbitals becomes obvious by providing three-dimensional images of orbitals in real space. While this has already been proposed theoretically, the practical realization requires access to variable photon energies at a synchrotron. We present first experimental data that demonstrates how 3D-imaging of molecular orbitals is feasible with a PEEM, which allows reconstruction of the molecular orbital in momentum space from the hemispherical k-space tomograms. Utilizing the additional phase information derived from experiments with circular light polarization, the full molecular orbital can be uncovered in 3D in real space by a Fourier transformation, thus providing unprecedented insight into the electronic structure of molecules.