

O 55: Focused Session: Towards a Quantitative Understanding of Complex Adsorption Structures: Surface Science goes Organic I

Substantial effort has been devoted within the past few years to develop new experimental and theoretical techniques capable of quantitatively describing the interface between complex molecules and metal surfaces. This includes the determination of precise adsorption structures at sub-Angstrom level and adsorption energies with chemical accuracy, the detailed investigation of interaction potentials, and the unraveling of atomistic bonding mechanisms. This symposium will highlight corresponding studies and discuss current frontiers.

Organizers: Karsten Reuter (TU München), Stefan Tautz (FZ Jülich)

Time: Wednesday 16:00–19:00

Location: TRE Phy

Topical Talk O 55.1 Wed 16:00 TRE Phy
Trends in the energies and entropies of adsorbates on single-crystal surfaces — ●CHARLES CAMPBELL — University of Washington, Seattle, WA, USA

Experimental measurements of the enthalpies and entropies of adsorbed molecules, atoms and molecular fragments on well-defined metal and oxide surfaces will be reviewed. Trends are revealed that show how adsorption energies and adsorbate entropies vary with the molecular structure and the nature of the surface. These results will be discussed in light of relevant theoretical predictions.

O 55.2 Wed 16:30 TRE Phy
Benzene and Its Derivatives Adsorbed on Metal Surfaces: A Bag Full of Surprises — ●WEI LIU, MATTHIAS SCHEFFLER, and ALEXANDRE TKATCHENKO — Fritz-Haber-Institut der MPG, Berlin, Germany

The study of molecule/metal interfaces is important for fundamental and applied surface science, and the electronic properties of these interfaces can be tuned by controlling their geometries. In this regard, a particular challenge for electronic structure theory is to reliably model the structure and stability of such hybrid interfaces. Here, we demonstrate that our recently developed DFT+vdW^{surf} method [1] is able to describe 25 systems [*e.g.*, benzene/Au(111), benzene/Pt(111), naphthalene/Pt(111), thiophene/Ag(111), DIP/Ag(111), and PTCDA/Au(111)] with an accuracy of 0.1 Å in adsorption heights and 0.1 eV in binding energies with respect to reliable experimental data. In addition, our DFT+vdW^{surf} calculations lead to a few peculiar findings: (1) The vdW energy can contribute more to the binding of covalently bonded systems than it does in physisorbed interfaces [2,3]; (2) the binding energies of similar molecules can be identical, despite significantly different adsorption heights; (3) the physically bound (precursor) state for aromatics on Pt(111) can be prominently stabilized and long-lived, making it potentially useful in molecular switches [4].

[1] Ruiz, *et al.*, PRL (2012). [2] Liu, *et al.*, PRB (2012). [3] Liu, *et al.*, NJP (2013). [4] Liu, *et al.*, Nat. Commun. (2013).

O 55.3 Wed 16:45 TRE Phy
Electronic Properties of Surfaces and Interfaces with Self-Consistent van der Waals Density Functional — ●NICOLA FERRI¹, ROBERT A. DISTASIO JR.², ROBERTO CAR², ALEXANDRE TKATCHENKO¹, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Princeton University, Princeton, NJ, USA

The long-range van der Waals (vdW) energy is a tiny part (0.001%) of the total energy, hence it is typically assumed to have a minor influence on the electronic properties. Here, we address this question through a fully self-consistent (SC) implementation of the long-range Tkatchenko-Scheffler (TS) density functional [1]. The effects of TS-vdW^{SC} on electron density *differences* for atomic and molecular dimers are compared with correlated densities obtained from “gold standard” coupled-cluster quantum-chemical calculations finding a qualitatively and quantitatively accordance. In agreement with previous work [2], we find a very small overall contribution from self-consistency in the structure and stability of vdW-bound molecular complexes. However, TS-vdW^{SC} (coupled with PBE functional) significantly affects electronic properties of coinage metal (111) surfaces, leading to an increase of up to 0.3 eV in the workfunction in agreement with experiments. Furthermore, vdW interactions visibly influence workfunctions in hybrid organic/metal interfaces, changing Pauli push-back and charge transfer contributions. [1] A. Tkatchenko and M. Scheffler, PRL

(2009). [2] T. Thonhauser *et al.*, PRB (2007).

O 55.4 Wed 17:00 TRE Phy
XPS and TPD of small molecules adsorbed on metalloporphyrins — ●MATTHIAS FRANKE, MICHAEL RÖCKERT, QURATULAIN TARIQ, OLE LYTKEN, and HANS-PETER STEINRÜCK — Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie II

We are using a surface science approach to study the binding of small molecules to porphyrin metal centers. These interactions are widely encountered in nature, but also provide the basis for many kinds of chemical sensors [1]. Despite the number of theoretical studies on this topic, the results still remain inconsistent [2] and need further experimental data.

We have been adsorbing O₂, CO and NO on multilayers of cobalt(II)-tetraphenylporphyrin. Changes in the chemical environment of the metal center were investigated with X-ray Photoelectron Spectroscopy (XPS), while Temperature Programmed Desorption (TPD) was used to measure the strength of the chemical bond between the metal centers and the adsorbed molecules. NO was found to adsorb strongly, with a desorption peak above room temperature, whereas O₂ and CO both adsorb much weaker and desorb already below 150 K.

[1] Di Natale, C; Monti, D.; Paolesse, R.; *materials today*, 2010, 13, 7-8

[2] Shubina, E. T.; *advances in inorganic chemistry*, 2010, 62, 279

Topical Talk O 55.5 Wed 17:15 TRE Phy
Surface crystallography of organic layers — ●GEORG HELD — Department of Chemistry, University of Reading, UK — Diamond Light Source, Harwell, UK

In supramolecular structures of organic molecules on surfaces chemical bonds are formed at different levels, from covalent to Van der Waals. Their interplay determines, both the surface geometry and the electronic structure of these overlayers and, hence, detailed structural characterisation can reveal important information about the balance of the interactions involved. Many organic layers have been well characterized at the molecular level, mostly using scanning probe microscopy and/or spectroscopic methods, but experimental crystallographic information about inter-atomic bonds (intra-molecular, inter-molecular and molecule-substrate) is rare. LEED-IV structural analysis, despite being one of the most powerful techniques for surface crystallography in general, is still facing a number of problems, when applied to organic layers. Current limitations are imposed by the available computer power for large unit cells but also by the size and quality of the experimental data set. We will discuss strategies for improving the data set and modifications to the standard analysis methods that are necessary to make full use of these improvements. The second part of the talk will concentrate on structures of organic layers, such as amino acids on Cu{110}, which have been determined by LEED, and discuss the implications in terms of chemical bond formation and molecular recognition at surfaces.

O 55.6 Wed 17:45 TRE Phy
High-precision LEED measurements of organic monolayers — ●FALKO SOJKA, JULIA PEUKER, TOBIAS HUEMPFNER, MATTHIAS MEISSNER, ROMAN FORKER, and TORSTEN FRITZ — Friedrich Schiller University Jena, Institute of Solid State Physics, Max-Wien-Platz 1, 07743 Jena, Germany

Low energy electron diffraction (LEED) on epitaxial layers is a powerful tool to examine long-range ordering at the interface. Due to limitations like distortion of the LEED images, often additional efforts have to be made in order to derive precise epitaxial relations.[1, 2]

Due to our investigations of compensating geometric distortions and other systematic errors in LEED measurements we are able to perform high-precision determination of epitaxial growth and lattice constants. Therefore we analyzed diverse systems of organic monolayers on different substrates using e.g. coronene, hexa-peri-hexabenzocoronene (HBC), and quaterylene (QT). Our results are partially in contrast to the literature. In our contribution we will also discuss results on organic heterostructures formed from two layers of dissimilar molecules.

In our case we are using two Double-MCP-LEED devices from Omicron and from OCI. These studies are supported by other methods like low temperature scanning tunneling microscopy (LT-STM) and differential reflectance spectroscopy (DRS) [3].

[1] F. Sojka et al., *Rev. Sci. Instrum.* **84**, 015111 (2013).

[2] F. Sojka et al., *Ultramicroscopy* **133**, 35-40 (2013).

[3] R. Forker et al., *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **108**, 34-68 (2012).

O 55.7 Wed 18:00 TRE Phy

Photoelectron diffraction and the organic / inorganic interface — ●DAVID A DUNCAN¹, DAGMAR KREIKEMEYER LORENZO², WERNER UNTERBERGER², FRANCESCO ALLEGRETTI¹, JOHANNES V BARTH¹, and D PHIL WOODRUFF³ — ¹Technische Universität München — ²Fritz-Haber Institut, Berlin — ³University of Warwick, UK

While, there is a growing interest into investigations of biologically-related molecules on surfaces, motivated in part by issues concerned with bio-compatibility and biochemical sensors, very few studies involve quantitative determination of the local adsorption geometries. The technique of scanned-energy mode photoelectron diffraction (PhD) is particularly well-suited to this problem as it allows not only elemental, but chemical state specific local adsorption sites to be determined. Specifically PhD has been utilised to study the building blocks of biological molecules, notably amino acids and nucleobases.

The local adsorption site of the functional groups within these biologically inspired molecules, follows mostly the same pattern as much simpler molecules containing the same groups, retaining mostly the same level of coordination with the substrate, and very similar bond lengths - despite increasing molecular complexity.

O 55.8 Wed 18:15 TRE Phy

Adsorption height alignment at heteromolecular hybrid interfaces — ●BENJAMIN STADTMÜLLER, SONJA SCHRÖDER, FRANCOIS C. BOCQUET, CAROLINE HENNEKE, CHRISTOPH KLEIMANN, SERGUEI SOUBATCH, MARTIN WILLENBOCKEL, F. STEFAN TAUTZ, and CHRISTIAN KUMPF — Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany and Jülich Aachen Research Alliance (JARA-FIT)

The future success of organic electronic devices strongly depends on the ability to control the properties of the active organic materials and their interfaces. In this context the formation of the first organic layer adsorbing on a metal surface plays an important role, which in turn is dominated by the interplay between different interaction mechanisms between the molecules and with the surface.

Here, we report on a systematic investigation of metal-heteromolecular interfaces consisting of two different molecules, both in contact with a metal surface: PTCDA or NTCDA act as the charge accepting, CuPc or SnPc as the charge donating molecular species. We concentrate on structural properties like the adsorption heights, and their interplay with charge donation and acceptance. Most importantly, when comparing homo- and heteromolecular layers of these molecules, we have found a systematic trend of adsorption height adjustment be-

tween donor and acceptor molecules. This self alignment goes along with a substrate-mediated charge transfer from the donors to acceptors and a mutual enhancement of the respective characters of the molecules. We propose that this effect is of general validity for π -conjugated molecules adsorbing on noble metal surfaces.

O 55.9 Wed 18:30 TRE Phy

Self-metalation of 2HTPP on Cu(111) studied with XSW: Influence of the central metal atom on the bonding distance

— CHRISTOPH BÜRKER¹, ●ANTONI FRANCO-CAÑELLAS¹, KATHARINA BROCH¹, TIEN-LIN LEE², ALEXANDER GERLACH¹, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, Tübingen, Germany — ²Diamond Light Source, UK

Recently, the self-metalation reaction of 2H-tetraphenylporphyrin (2HTPP) on Cu(111) to copper(II)-tetraphenylporphyrin (CuTPP) induced by annealing to 500 K was reported [1]. We present a systematic X-ray standing wave (XSW) study of both molecules, performed at the Diamond Light Source, to investigate the influence of the central metal atom on the adsorption geometry. The measured small bonding distance of both molecules on Cu(111) indicates strong interaction with the substrate [2]. Comparison between the average bonding distance of the carbon atoms and nitrogen atoms reveal a distorted molecule, as the nitrogen atoms adsorb at lower bonding distances. The two chemically equivalent types of nitrogen atoms (imino and aminic) of 2HTPP exhibit a distorted porphyrin ring. After the chemical reaction to CuTPP no change of the bonding distance of the carbon skeleton is seen, but the entire molecule becomes flattened. The results are compared to a similar scenario for metal-free phthalocyanine H₂Pc and copper-phthalocyanine (CuPc) [3].

[1] J. Xiao et al., *J. Phys. Chem C* **116** (2012), 12275.

[2] G. Heimele et al., *Nature Chem.* **5** (2013) 187.

[3] A. Gerlach et al., *Phys. Rev. B* **71** (2005), 205425.

O 55.10 Wed 18:45 TRE Phy

The complex polymorphism and thermodynamic behavior of a seemingly simple system: naphthalene on Cu(111) —

●ROMAN FORKER¹, JULIA PEUKER¹, MATTHIAS MEISSNER¹, FALKO SOJKA¹, TAKAHIRO UEBA², TAKASHI YAMADA², TOSHIAKI MUNAKATA², and TORSTEN FRITZ¹ — ¹Friedrich Schiller University, Institute of Solid State Physics, Helmholtzweg 5, 07743 Jena, Germany — ²Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

Naphthalene, C₁₀H₈, is the smallest polycyclic aromatic hydrocarbon (PAH). Despite its rather simple, non-chiral chemical structure naphthalene is known to form three different commensurate phases in epitaxial films on Cu(111), including apparently chiral arrangements of molecules in one of them [*J. Phys. Chem. C* **114**, 13334 (2010)]. In an attempt to understand this polymorphism we performed temperature-dependent and surface coverage-dependent in situ low-energy electron diffraction (LEED) measurements revealing an unexpected and extraordinarily complex structural and thermodynamic behavior. At low coverage the molecules form a disordered gas-like phase which is a consequence of effectively repulsive intermolecular interactions. The chiral structure originates from a precursor that exhibits short-range order at intermediate coverage. This precursor undergoes a steady and reversible orientational shift upon variation of coverage or temperature which ultimately yields a long-range ordered stable epitaxial film, thereby resembling a liquid–solid phase transition. At higher coverage a competing point-on-line structure, which has not been reported before, is preferred to the commensurate chiral structure.