

## O 77: Focused Session: Towards a Quantitative Understanding of Complex Adsorption Structures: Surface Science goes Organic III

Time: Thursday 16:00–19:00

Location: TRE Phy

### Topical Talk

O 77.1 Thu 16:00 TRE Phy  
**Infrared-Spectroscopy applied to ultrathin organic films.** — ●PETER JAKOB — Physics Department, Philipps-University Marburg, 35032 Marburg, Germany

IR-spectroscopy is commonly referred to as a fingerprint technique to identify molecular species. However, this method can do better! The high spectral resolution and polarization dependence of vibrational modes allows to distinguish between different local environments ( $\rightarrow$  lateral interactions), bonding configurations ( $\rightarrow$  adsorption site and orientation), and phases (monolayer, bilayer, bulk) of large organic molecules with high selectivity. Thereby IR spectroscopy is non-invasive/destructive, obeys strict selection rules, and provides adequate sensitivity to detect even slight differential changes within grown films. Selected examples of various effects and curiosities associated with ultra-thin molecular layers will be presented, demonstrating the excellent quality and potential of infrared spectroscopy in studying such systems. Notably, for molecular species exhibiting a partially filled (former) LUMO, IR spectra are influenced by interfacial dynamical charge transfer (IDCT) between molecule and metal substrate [1]. By means of line-shape analysis of the associated Fano-like absorption profiles the electron dynamics (electron transfer time) between contact primer layer and metal substrate can be estimated.

[1] F.S. Tautz, *Progress in Surface Science* 82 (2007) 479-520.

O 77.2 Thu 16:30 TRE Phy

**Diffusion and site selection of PTCDA on KCl(100) studied by fluorescence spectroscopy and STM** — ALEXANDER PAULHEIM, CHRISTIAN MARQUARDT, QINMIN GUO, and ●MORITZ SOKOLOWSKI — Institut für Physikalische und Theoretische Chemie der Universität Bonn Wegelerstraße 12, 53115 Bonn, Germany

We report an investigation on the optical properties of the model molecule PTCDA at very low coverages (below 1% of a monolayer) on thin epitaxial KCl(100) films. From STM data we derive a statistical adsorption of isolated molecules at low temperature. Upon thermal activation, diffusion to steps edge sites occurs, comparable to that on other alkali halide surfaces [1]. This scenario was investigated also by fluorescence spectroscopy (FL) and FL excitation spectroscopy, exploiting its high sensitivity. Different adsorption sites lead to different optical transition energies due to differences in the molecule substrate interactions [2]. In addition, from the external vibronic modes we conclude that the PTCDA molecule is distorted from its planar geometry by the interaction with the KCl surface. [1] H. Karacuban et al., *Nanotech.*, 2011, 22, 295305; [2] Paulheim et al., *Phys. Chem. Chem. Phys.*, 2013, 15, 4906.

O 77.3 Thu 16:45 TRE Phy

**Site specific mobility boost of caged bisphenol A trimers on Ag(111)** — ●ÖZGE SAĞLAM, JULIAN A. LLOYD, ANTHOULA C. PAPAGEORGIOU, SYBILLE FISCHER, SEUNG CHEOL OH, KATHARINA DILLER, DAVID A. DUNCAN, FRANCESCO ALLEGRETTI, FLORIAN KLAPPENBERGER, JOACHIM REICHERT, and JOHANNES V. BARTH — Physik Department E20, Technische Universität München, Garching, Germany

Artificial molecular rotors, which have been a focus of attention in the last decade of nanoscience, are fascinating subjects not only in terms of fundamental understanding of molecular motion but also due to their promising potential in the context of molecular scale machinery. The construction of regularly oriented two-dimensional arrays of molecular rotors, rather than isolated single rotors, is a key requirement to demonstrate and miniaturize functional systems for signal processing or sensing. Such a molecular system of regular arrays of molecular rotors has been achieved by utilizing a single layer of bisphenol A (BPA) molecules on the weakly corrugated Ag(111) surface. We employ a combined experimental approach using STM, XPS and NEXAFS providing complementary insights regarding self-assembled networks built with BPA molecules on the Ag(111) surface under UHV conditions. Our data reveal temperature-dependent polymorphism, where mobile molecules undergo rotational movements when trapped in the cavities of a nanoporous network. We propose molecular models stabilized by intermolecular hydrogen bonding, and explain the rotational motion of the caged species by their specific adsorption sites.

O 77.4 Thu 17:00 TRE Phy

**Structure and ordering of thin organic layers on silicon surfaces** — ●THOMAS SCHMIDT, CHRISTIAN SCHULZ, TORSTEN WILKENS, and JENS FALTA — Universität Bremen, Germany

The adsorption and growth of organic layers on silicon surfaces offers the opportunity to combine the application potential of organic materials with silicon technology, e.g., for hybrid solar cells, transistors, or biosensors [1–3].

We investigated thin films of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) and copper phthalocyanine (Cu-PC) on Si(111) surfaces that had been passivated with monolayer deposits of either Ag or Bi. Scanning tunneling microscopy and high-resolution low-energy electron diffraction show a drastic improvement of the structural order and morphology as compared to deposition on clean Si(111).

PTCDA forms smooth layers with a herringbone structure on Ag-terminated as well as Bi-terminated Si(111). For the latter case, x-ray photoelectron spectroscopy indicates a charge transfer from the carbonyl oxygen of the anhydride groups to the substrate. Additional structural phases are observed in the initial growth stages, which can be suppressed by deposition at elevated temperatures.

With respect to the structural order of Cu-PC films, Ag turns out to be superior to Bi as passivating agent and leads to well-ordered domains with rhombic (nearly square) unit cells.

[1] D.R.T. Zahn et al., *Solar Energy* 80, 707 (2006).

[2] L. De Stefano et al., *Sensors* 7, 214(2007).

[3] Zhongming Wei et al., *Appl. Phys. Lett.* 95, 033304 (2009).

O 77.5 Thu 17:15 TRE Phy

**Growth of 2D molecular crystals: The role of the substrate topology** — ●DANIEL SCHWARZ<sup>1</sup>, CAROLINE HENNEKE<sup>1</sup>, RAOUL VAN GASTEL<sup>2</sup>, HAROLD ZANDVLIET<sup>2</sup>, BENE POELSEMA<sup>2</sup>, and CHRISTIAN KUMPF<sup>1</sup> — <sup>1</sup>Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich and Jülich Aachen Research Alliance (JARA) – Fundamentals of Future Information Technology, 52428 Jülich, Germany — <sup>2</sup>Physics of Interfaces and Nanomaterials, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, NL-7500 AE Enschede, The Netherlands

We present a LEEM study on the initial growth dynamics and the influence of the substrate topology on 2D molecular crystals. We have selected BDA and PTCDA, which both are elongated flat organic molecules with oxygen atoms at their ends. Deposited on Cu(001) both molecules form well-ordered 2D crystals. However, despite the similarities, the interaction of the molecules with Cu-steps is quite different, resulting in distinct differences in the domain growth dynamics. Steps are permeable for the smaller BDA molecule, which leads to a growth instability of the Mullins-Sekerka type: Domains grow very fast along the steps and much slower perpendicular to the steps. PTCDA, on the other hand, interacts strongly with steps, which makes them impermeable for molecules and hence does not exhibit the Mullins-Sekerka instability.

O 77.6 Thu 17:30 TRE Phy

**Combined 2PPE and photoluminescence study of electron and exciton dynamics at the PTCDA/Ag(111) interface** — ●ANDREAS NAMGALIES, MANUEL MARKS, SANGAM CHATTERJEE, and ULRICH HÖFER — Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität Marburg, D-35032 Marburg

The presence of a metal contact can drastically alter the electron and exciton dynamics of organic semiconductors. For a study of the fundamental processes that govern this dynamics as well as the dynamics of carrier transfer at the metal/organic interface, we combine the advantages of time resolved 2-photon-photoemission (2PPE) and time-resolved photoluminescence in one experiment and investigate well-ordered and characterized thin films of PTCDA/Ag(111). Our luminescence setup enables monolayer sensitivity and a time resolution of approximately 700 fs using a streak camera.

It will be shown that a long-lived component of hot electrons in the 2PPE spectrum, whose lifetime and intensity strongly increases as a function of layer thickness, arises at the metal interface as a result of exciton decay of PTCDA. Systematic studies as a function of film thick-

ness reveal, that Foerster-like dipole-dipole coupling is important for the decay in the regime of several monolayers, whereas exciton hopping between PTCDA layers and quenching and the interfaces dominates the decay for thicker films.

O 77.7 Thu 17:45 TRE Phy  
**Molecular Geometry Determination by Atomic Force Microscopy** — ●NIKOLAJ MOLL, LEO GROSS, BRUNO SCHULER, FABIAN MOHN, ALESSANDRO CURIONI, and GERHARD MEYER — IBM Research – Zurich, Säumerstrasse 4, CH-8803 Rüschlikon, Switzerland

Using functionalized tips, the atomic resolution of a single organic molecule can be achieved by atomic force microscopy (AFM) operating in the regime of short-ranged repulsive Pauli forces while the van-der-Waals and electrostatic interactions only add a diffuse attractive background [1]. To theoretically describe the atomic contrast a simple model is introduced in which the Pauli repulsion is assumed to follow a power law as a function of the probed charge density. Even, different bond orders of individual carbon-carbon bonds in organic molecules can be distinguished by AFM [2]. The adsorption geometry of single molecules with intramolecular resolution were measured. The lateral adsorption position was determined with atomic resolution, adsorption height differences, and tilts of the molecular plane with very high precision [3].

[1] L. Gross, F. Mohn, N. Moll, P. Liljeroth, and G. Meyer, *Science* **325**, 1110 (2009).

[2] L. Gross, F. Mohn, N. Moll, B. Schuler, A. Criado, E. Guitián, D. Peña, A. Gourdon, and G. Meyer, *Science* **337**, 1326 (2012).

[3] B. Schuler, W. Liu, A. Tkatchenko, N. Moll, G. Meyer, A. Mistry, D. Fox, and L. Gross, *Phys. Rev. Lett.* **111**, 106103 (2013).

O 77.8 Thu 18:00 TRE Phy  
**Quantifying molecule-surface interactions using AFM-based single-molecule manipulation** — ●CHRISTIAN WAGNER<sup>1,2</sup>, NORMAN FOURNIER<sup>1</sup>, VICTOR G. RUIZ<sup>3</sup>, CHEN LI<sup>4</sup>, MICHAEL ROHLFING<sup>5</sup>, ALEXANDRE TKATCHENKO<sup>3</sup>, F. STEFAN TAUTZ<sup>1</sup>, and RUSLAN TEMIROV<sup>1</sup> — <sup>1</sup>Forschungszentrum Jülich, Jülich, Germany — <sup>2</sup>Universiteit Leiden, Leiden, The Netherlands — <sup>3</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>4</sup>Max-Planck-Institut für Polymerforschung, Mainz, Germany — <sup>5</sup>Universität Münster, Münster, Germany

Scanning probe microscopy plays an important role in the investigation of molecular adsorption. Promising is the possibility to probe the molecule-surface interaction while tuning its strength through AFM tip-induced single-molecule manipulation. Here, we outline a strategy to achieve quantitative understanding of such manipulation experiments [1,2]. The example of qPlus sensor based 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) molecule lifting experiments is used to demonstrate how different aspects of the molecule-surface interaction, namely the short-range adsorption potential [2], the asymptotic van der Waals potential, and local chemical bonds which are the source of the surface corrugation can be quantified by the help of force-field simulations.

[1] N. Fournier et al., *Phys. Rev. B* **84**, 035435 (2011)

[2] C. Wagner et al., *Phys. Rev. Lett.* **109**, 076102 (2012)

O 77.9 Thu 18:15 TRE Phy  
**Accessing 4f-states in single-molecule spintronics** — ●FRANK MATTHES<sup>1,4</sup>, SARAH FAHRENDORF<sup>1,4</sup>, NICOLAE ATODIRESEI<sup>2,4</sup>, CLAIRE BESSON<sup>3,4</sup>, VASILE CACIUC<sup>2,4</sup>, STEFAN BLÜGEL<sup>2,4</sup>, PAUL KÖGERLER<sup>3,4</sup>, DANIEL E. BÜRGLER<sup>1,4</sup>, and CLAUD M. SCHNEIDER<sup>1,4</sup> — <sup>1</sup>Peter Grünberg Institute, Electronic Properties, Forschungszentrum Jülich, Germany — <sup>2</sup>Peter Grünberg Institute and Institute for Advanced Simulation, Quantum Theory of Materials, Forschungszentrum Jülich, Germany — <sup>3</sup>Institute of Inorganic Chemistry, RWTH Aachen Univer-

sity, Germany — <sup>4</sup>Jülich-Aachen Research Alliance, Fundamentals for Future Information Technology, Forschungszentrum Jülich, Germany

Magnetic molecules are potential functional units for molecular and supramolecular spintronic devices. However, charge transfer and hybridization may modify the electronic structure and thereby influence or even quench the molecular magnetic moment. Yet, detection and manipulation of the molecular spin state by means of charge transport, that is, spintronic functionality, mandates a certain level of hybridization of the magnetic orbitals with electrode states. Here we show how a judicious choice of the molecular spin centres determines these critical molecule-electrode contact characteristics. In contrast to late lanthanide analogues, the 4f-orbitals of single bis(phthalocyaninato)-neodymium(III) molecules adsorbed on Cu(100) can be directly accessed by scanning tunneling microscopy[1]. Hence, they contribute to charge transport, whereas their magnetic moment is sustained as evident from comparing spectroscopic data with ab initio calculations.

[1] S. Fahrenndorf *et al.*, *Nature Commun.* **4**, 2425 (2013)

O 77.10 Thu 18:30 TRE Phy  
**Structure-dependent reactions of tetraphenylporphyrin with Cu(111)** — ●OLE LYTKEN, MICHAEL RÖCKERT, MATTHIAS FRANKE, QURATULAIN TARIQ, MICHAEL STARK, STEFANIE DITZE, HUBERTUS MARBACH, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, 91058 Erlangen, Egerlandstraße 3, Germany

As tetraphenylporphyrin (2HTPP) is deposited on Cu(111) and heated, several distinct reactions happen: First the porphyrin molecule picks up a copper atom from the surface and metalates forming copper(II)tetraphenylporphyrin (CuTPP), which subsequently dehydrogenates, first loosing 8 hydrogen atoms and later the remaining 20. The first dehydrogenation reaction is proposed to link the phenyl rings with the pyrrole rings, and the last dehydrogenation reaction is proposed to be the loss of the remaining hydrogen atoms producing an ill-defined, interlinked, nitrogen-doped carbon network on the surface. The rate of the metalation and the first dehydrogenation both depends strongly on coverage, with an abrupt change as the coverage is increased and the structure of the adsorbed 2HTPP layer changes. Using XPS, STM and TPD (of both deuterated and undeuterated molecules) the reaction rates and the different intermediates on the surface have been investigated in the temperature range from 200-1000 K as a function of the structure of the initial 2HTPP layer.

O 77.11 Thu 18:45 TRE Phy  
**DFT calculations addressing a possible imaging mechanism in the Scanning Tunneling Hydrogen Microscope** — ●UWE FRIEDEL and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

The Scanning Tunneling Hydrogen Microscope (STHM) [1] can resolve intramolecular structures of adsorbed organic molecules and even produce intermolecular contrast along lines of expected hydrogen bondings. The method does not only work with hydrogen, which gave the method its name, but also with other molecules such as CO and noble gas atoms. Still, the reasons for the improved contrast in the STHM are not fully understood yet.

This talk will present dispersion corrected DFT calculations (DFT-D3 [2]) addressing the interaction of a CO molecule positioned between a tip and a pentacene molecule. The distance of the CO molecule from the tip has been monitored as a function of its lateral position above the naphthalene molecule. We will discuss whether an explanation based on Tersoff-Hamann theory [3] can be established in order to understand the improved contrast in the STHM.

[1] C. Weiss *et al.*, *J. Am. Chem. Soc.* **132**, 11864 (2010)

[2] S. Grimme *et al.*, *J. Chem. Phys.* **132**, 154104 (2010)

[3] J. Tersoff and D.R. Hamann, *Phys. Rev. Lett.* **50**, 1998 (1983)