O 60: Organic Molecules on Inorganic Substrates IV: Electronic Properties, Excitations, Dynamics

Time: Wednesday 15:00–17:30 Location: H24

O 60.1 Wed 15:00 H24

Quantum size oscillations of oligoacene gaps adsorbed on Au(111) — •Richard Korytár — Charles University, Prague, Czech Republic

For gas phase oligoacenes, our recent theoretical work suggests a possibility for oscillations of the excitation gaps with the length of the molecule. In view of the recent experimental progress of on-surface synthesis, we employ the density functional theory to investigate here the fate of these oscillations for oligoacenes adsorbed on a Au(111) surface. Since the long range-nature of the Coulomb interaction is removed on metallic substrates due to screening, correlation effects are weaker and the tendency towards oscillatory behavior is enhanced.

O 60.2 Wed 15:15 H24

Excited state dynamics and transient band structure changes in molecular thin films — •Sebastian Hedwig[1], Sebastian Emmerich[1], Johannes Stöckl[1], Benito Arnoldi[1], Mirko Cinchetti[2], Stefan Mathias[3], Benjamin Stadtmüller[1], and Martin Aeschlimann[1] — [1]Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schrödinger-Straße 46, 67663 Kaiserslautern, Germany — [2]Experimentelle Physik VI, Technische Universität Dortmund, 44221 Dortmund, Germany — [3]Georg-August-Universität Göttingen, Göttingen 37077, Germany

The future success of organic materials in optoelectronic applications relies on our ability to understand and optimize their optical and transport properties. Despite their common origin – the electronic band structure – their interplay in organic materials is far from being understood. In this context, we recently employed time-resolved photoelectron spectroscopy with fs-pulsed XUV-radiation to reveal a direct correlation between the excited state dynamics of a thin C_{60} film on Ag(111) and a transient inhomogeneous broadening of the entire occupied valence states upon optical excitation. Here, we extend our recent study to different C_{60} coverages between one and ten monolayers to determine the role of the Ag(111) substrate for the timescale and the magnitude of the transient band structure broadening. Moreover, additional time- and momentum resolved photoemission data will allow us to reveal possible transient changes in the molecular band dispersion of the C_{60} films upon optical excitation with visible light.

O 60.3 Wed 15:30 H24

Excited Electron Dynamics in Thiophene-based Polymers — •Tobias Reiker[1], Carsten Winter[1], Deb Kumar Bhowmick[1], Nils Fabian Kleimeier[1], Zitong Liu[2], Deqing Zhang[2], and Helmut Zacharias[1] — [1]Center For Soft Nanoscience, Westfälische Wilhelms-Universität Münster — [2]Institute of Chemistry, Chinese Academy of Science, Beijing, China

An internal donor-acceptor system is formed by thiophene polymers coupled with pyrrole chains. Different alkyl side chains can improve the interchain packing and affect the backbone conformation, further they can directly influence the charge transporting behavior. Although OFETs and organic photovoltaic cells have been already successfully utilized, the exact internal dynamics of the system are still under investigation. In this presentation we show the results of a time-dependent photoemission study on the thiophene polymers PDPP4T and DTT on a Si(100) substrate. Occupied electronic levels were analyzed with UPS. The fundamental and third harmonics of a Ti:Sapphire laser system with a time-of-flight spectrometer are utilized for static 2PPE to determine the energetic positions of high lying occupied and intermediate unoccupied states. Dynamic 2PPE is then used to study the electron dynamics of the intermediate states directly in the time domain and shows three distinct electronic lifetimes. Depending on the electron kinetic energy lifetimes of a few hundred femtoseconds, up to 3 ps and a slow channel around 15 ps are observed. After annealing at 180°C an unoccupied state at an exitation energy of 0.40 eV loses its long-lived component.

O 60.4 Wed 15:45 H24

Single photon plasmonic emission from STM-induced quantum dots — •Christopher C. Leon[1], Dimas G. de Oteyza[2,3,4], Anna Rosławska[1], Pablo Merino[1,5], Abhishek Grewal[1], Klaus Kuhnke[1], and Klaus Kern[1,6] — [1]Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany. — [2]Donostia International Physics Center, San Sebastian, Spain. — [3]Centro de Fisica de Materiales, CSIC-UPV/EHU, San Sebastian, Spain. — [4]Ikerbasque, Basque Foundation for Science, Bilbao, Spain. — [5]present address: Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid, Spain. — [6]Institut de Physique, École Polytechnique Fédérale de Lausanne, Switzerland.

A hallmark of quantum control is the ability to make photons at the nanoscale whose temporal features are distinct from classical light sources. Through scanning tunneling microscopy induced luminescence (STML) we are able to generate plasmonic light originating from inelastic tunneling processes that occur in few-nanometer thick molecular films of C_{60} deposited on Ag(111). This light is antibunched with a $1/e$ recovery time of less than one nanosecond, as shown through Hanbury Brown and Twiss photon intensity interferometry. These phenomena are attributed to a Coulomb blockade that occurs when tunneling electrons are forced to hop through a discrete quantum state that is created from the strong electric field of the tip and its confinement effects. The spatial extent of this state can be varied by adjusting the degree of band bending through the sample.

O 60.5 Wed 16:00 H24

Adsorption, Orientation and Reactivity of Phenylphosphonic Acid on Rutile TiO_2(110) — •Julia Köbl, Daniel Wechsler, Elmar Kataev, Hans-Peter Steinrück, and Ole Lytken — Lehrstuhl für Physikalische Chemie 2, Universität Erlangen Nürnberg, Egerlandstraße 3, D-91058

To fully understand organic electronic devices, such as dye-sensitized solar cells, it is necessary to understand the interactions of organic molecules with oxide substrates at the atomic level. To facilitate this understanding, we have studied the adsorption and reactivity of phenylphosphonic acid on TiO_2(110) - 1 × 1. Using Synchrotron Radiation Photoelectron Spectroscopy (SRPES) and Near-Edge X-ray Absorption Fine-Structure Spectroscopy (NEXAFS) we have studied the thermal stability and bonding mechanism of phenylphosphonic acid at temperatures up to 900 K. High-resolution O 1s spectra exhibit three distinct oxygen species on the surface, and NEXAFS C K-edge measurements reveal a mostly upright standing adsorption geometry at all temperatures. Supported by the DFG through FOR 1878 (funCOS).

O 60.6 Wed 16:15 H24

Adsorption of phosphonate functionalized porphyrin molecules on TiO2(110) surfaces — Cynthia Fernandez[1], Daniel Weschler[2], Hans-Peter Steinrück[2], Ole Lytken[2], and •Federico Williams[1,2] — [1]Departamento de Química Inorgánica, Analítica y Química Física, Universidad de Buenos Aires, Argentina — [2]Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Erlangen, Germany

Solar energy technologies including dye-sensitized solar cells and water-splitting photoelectrochemical cells are constructed linking chromophores to semiconductor surfaces. Promising systems are based on porphyrins bonded to TiO2 surfaces. One of the critical factors affecting device performance is the molecular adsorption geometry. Therefore, fundamental research studying the interaction of porphyrins with TiO2 surfaces is important. Here, we studied the bonding and adsorption geometry of tetraphenyl porphyrin molecules containing one or four phosphonate groups. The investigation was carried out by means of synchrotron radiation X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) measurements. Our results show that the number of linker groups have a great influence on the adsorption geometry. Molecules with one phosphonate group adsorb with the macrocycle tilted away from the surface whereas molecules with four phosphonate groups adsorb with the macrocycle close to the surface. This is an important finding for the design of dye-sensitized solar and photoelectrochemical cells. This project is supported by the DFG through FOR 1878 (funCOS).

O 60.7 Wed 16:30 H24

X-Ray Small Angle In-Situ Study of Porphyrin Adsorption on Stabilized Rutil Surfaces — •Klaus Götz, Annemarie Pfnür, and Tobias Unruh — Institute for Crystallography and Structural Physics, Erlangen, Germany

Dye sensitized solar cells (DSSCs) based on TiO2 have been studied as an easy to produce, low-cost alternative to classical semiconductor solar cells with recent efficiencies of up to 13% for a long time [1][2]. We synthesized tunable titania nanoparticles with a diameter of 2-3 nm that are stabilized by oleic acid. Special emphasis of our work is focused on the exchange process of the oleic acid with porphyrins designed for a particular application.

This process is studied using a variation of different x-ray small angle scattering techniques. One method is the combination of small angle x-ray and neutron scattering (SAXS and SANS) experiments. These are well suited to study core/shell systems because of the different scattering lengths for x-rays and neutrons. On the other hand x-ray reflectivity measurements can be used to study layered systems on flat substrates. This offers the possibility to study the exchange of oleic acid with porphyrins on TiO2 Wafers as a test system. In the talk an overview over the different techniques will be given. Furthermore their usage in the characterization of the morphology of the produced particles and the ligand exchange from oleic acid to porphyrins will be presented.

[1] O'Regan & Grätzel; Nature 353, 737-740 (1991)

[2] Matthew S. et al.; Nat. Chem. 6; 242-247 (2014)

O 60.8 Wed 16:45 H24

Molecular dynamics simulation of transport and nucleation of conjugated organic molecules on inorganic surfaces — •Mila Miletic[1,3], Karol Palczynski[1], Matheus R. Jacobs[3], Ana M. Valencia[3], Caterina Cocchi[3], and Joachim Dzubiella[1,2] — [1]Helmholtz-Zentrum Berlin, Berlin, Germany — [2]Physikalisches Institut, Albert-Ludwigs-Universität, Freiburg, Germany — [3]Physics Department, Humboldt-Universität zu Berlin, Berlin, Germany

We analyze the influence of polarity on the surface transport of single conjugated organic molecules on the inorganic $(10\bar{1}0)$ zinc oxide surface by all-atom molecular dynamics simulations at room temperature and above. In particular, we study the effects of partial fluorination of the *para*-sexiphenyl *p*-6P molecule with chemical modifications of one head group *p*-6PF2 or both head and tail *p*-6PF4. We show that quantum and classical simulations both find consistent and highly distinct dipole moments for the three studied molecules. The diffusion of both p-6P and its fluorinated derivatives is Arrhenius-like, governed by thermally activated energy barrier crossings. Also, *p*-6P has a lower diffusion energy barrier compared to its fluorinated derivatives in the nonpolar direction of the anisotropic surface, while the barrier in the polar direction is about 20 kJ/mol higher. This rather unexpected behaviour is governed by a subtle balance of electrostatic attractive and repulsive molecule-substrate interactions as well as substantial entropic contributions coming from orientational and internal molecular degrees of freedom. Our findings can help to control the kinetics of nucleation and growth in the future design of hybrid organic-inorganic interfaces.

O 60.9 Wed 17:00 H24

Tuning the adsorption geometry of cyano-substituted porphyrins on bulk insulators — •Min-Ken Li, Mirunalini Devarajulu, Jia Liu, Maximilian Ammon, and Sabine Maier — Department of Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

The realization of molecular-based devices requires the adsorption of molecular building blocks on insulating substrates to preserve their original functionality. Therefore, organic molecules on insulating surfaces have been attracting more attention recently. Porphyrins are of particular interest because they are robust, and their adsorption and electronic properties can be changed by chelation of a metal ion or substitution of anchor groups on the macrocycle; both tune the interplay between intermolecular and molecule-surface interactions.[1] Here, we report on the adsorption geometry and self-assembly of cyano-substituted porphyrin derivatives on bulk KBr(001), MgO(001), and Au(111) surfaces using non-contact atomic force microscopy and scanning tunneling microscopy featuring sub-molecular resolution at low temperature. We demonstrate that the adsorption geometry of mono-cyano-substituted porphyrin derivatives can be tuned by functional side groups from nearly up-right standing to flat lying.[2] Moreover, we will discuss the influence of the central metal ion, the number of cyano-groups as well as the substrate on the adsorption geometry and the structure formation of self-assemblies.

[1] J.M.Gottfried, Surf. Sci. Rep., 2015, 70, 3, 259-379

[2] S. Maier, et al. Small, 2008, 4, 1115-1118

O 60.10 Wed 17:15 H24

Metalation and Polymerization of 5,5'-Dibromosalophene on Co-intercalated Graphene — •Julia Goedecke[1], Micha Elsebach[1], Michael Rohde[1], Emil Sierda[1,2], Maciej Bazarnik[1,2], and Roland Wiesendanger[1] — [1]Dept. Physics, University of Hamburg, D-20355 Hamburg, Germany — [2]Institute of Physics, Poznan University of Technology, Piotrowo 3, 60-965 Poznan, Poland

Salophene complexes are suitable for molecular spintronic applications due to their chemical structure and electronic and magnetic properties. In previous work of Bazarnik et al. a concept for an all-spin molecular device with Co-salophenes on Au(111) has already been presented[1]. Using STM and STS we will show that such an approach can also be realized on Co-intercaleted graphene on Ir(111), a much more inert surface that limits the hybridization with the complexes and does not show a Kondo-effect, as is the case with Co-Salophenes on Au(111)[2]. For this purpose 5,5'-Dibromosalophenes were metallized *in situ* via surface reaction in UHV with different transition metals, namely with Co, Cr and Fe. Furthermore, we will show that these *in situ* produced Salophene complexes can be polymerized on the graphene surface via Ullmann like reaction[3] and therefore are suitable for a molecular spintronic device.

[1] M. Bazarnik et al., Nano Lett. 16, 577 (2016)

[2] A. DiLullo et al., Nano Lett. 12, 3174 (2012)

[3] F. Ullmann et al., Chemische Berichte, 34 (2): 2174 (1901)