O 35: Organic-inorganic hybrid systems and organic films IV

Time: Tuesday 14:00–15:45 Location: MA 042

O 35.1 Tue 14:00 MA 042

The role of Anchoring groups on Ruthenium (II) Bipyridine sensitized p-type semiconducor solar cells: A Quantum Chemical Calculation — •Anik Sen[1], Stephan Kupfer[2], Stefanie Grafe[2], and Axel Gross[1] — [1]Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany — [2]Institute for Physical Chemistry and Abbe Center of Photonics, Friedrich Schiller University Jena, D-07743 Jena, Germany

Ru (II) bipyridine complexes connected with p-type inorganic semiconductors (p-SC) such as NiO are promising systems for photocatalytic applications such as in dye sensitized solar cells (DSSC). The working principle is based on hole injection into the valence band of the p-type semiconductor from the photo excited semiconductor. We have performed both density functional theory (DFT) and time Dependent DFT calculations in order to understand the influence of different anchoring groups and spacer molecules attached to a photoactive Ruthenium bipyridine complex. The conversion efficiency of the dye molecules is predicted through our calculation. A model calculation of the anchors with the NiO surface is also calculated with the cluster approach, and implicit solvent model calculations are performed to understand the influence of the liquid environment.

In our discussion, we will try to shed light on the promising anchoring groups for the photocatalytic applications for p-SC.

O 35.2 Tue 14:15 MA 042

Theory of the geometry-dependent excitation transfer across a semiconductor/molecule interface — •Judith Specht[1], Björn Bieniek[2], Patrick Rinke[2,3], Andreas Knorr[1], and Marten Richter[1] — [1]Technische Universität Berlin, Berlin, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — [3]Aalto University, Aalto, Finland

Förster-type non-radiative coupling can transfer electronic excitations from inorganic semiconductor substrates to Frenkel excitons in organic molecular films. We analyze the excitation transfer efficiency as a function of the molecular geometry and other parameters such as charge carrier densities and temperatures.

Using a density-matrix equation technique, we study the case of creating excitons in an optically active layer of ladder-type quarterphenyl (L4P) molecules by strong electrical pumping of the electron-hole continuum in a ZnO quantum well substrate. Ab initio calculations provide the microscopic input parameters for our density-matrix equation technique [1,2]. Our findings reveal that the coupling efficiency strongly depends on multiple, but tunable parameters such as resonance energy detuning, molecular coverage, charge carrier occupation in the semiconductor substrate, distance between the constituents, and spatial orientation of the flat-lying molecules on the substrate. Our parameter study enables us to explore the operating regimes for optimized device performance.

[1] Verdenhalven et al., Phys. Rev. B 89, 235314 (2014).

[2] Specht et al., arXiv:1711.08955.

O 35.3 Tue 14:30 MA 042

Predictive first-principles modeling of complex inorganic/organic interfaces: PTCDA on Au(111) — •Victor G. Ruiz[1,2] and Alexandre Tkatchenko[1] — [1]Fritz-Haber Institut der MPG, Theory Department, Berlin, Germany — [2]Current affiliation: Helmholtz-Zentrum Berlin, Berlin, Germany

Understanding the properties of hybrid inorganic/organic systems has implications in both fundamental science and technology. An ab-initio modeling of these interfaces require efficient electronic-structure methods that capture accurately covalent and non-covalent interactions plus an atomistic model that includes complex adsorption configurations and an accurate surface representation. We present a predictive characterization of the structure and stability of perylenetetracarboxylic dianhydride (PTCDA) adsorbed on Au(111) within density-functional theory. Our calculations include collective many-body effects in the modeling of non-covalent interactions and a quantification of the self-interaction error in the adsorption energy of the system. We address effects due to single molecule/monolayer surface coverage and the role of the experimentally observed $22 \times \sqrt{3}$ surface reconstruction. Our approach yields an adsorption geometry in agreement with experiments within 0.1 Å and explains a difference of approximately 0.5 eV in the adsorption energy of the system which is observed when comparing atomic-force microscope and temperature-programmed desorption experiments. Our work shows that the inclusion of all relevant collective effects yields predictive power in the first-principles simulation of complex interfaces.

O 35.4 Tue 14:45 MA 042

Energy shift of the Ag (111) Shockley state due to adsorption of NTCDA — •Lukas Eschmann, Peter Krüger, and Michael Rohlfing — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität, 48149 Münster, Germany

Molecular adsorption causes interaction between the electronic structure of adsorbate and substrate. One particular case is the energy shift of the Shockley surface state on Ag(111) and other surfaces: upon adsorption of organic molecules the state turns into an interface state and is shifted towards higher energy by as much as $\sim 0.5\,\mathrm{eV}$.

Here we address the interface state between the Ag(111) surface and adsorbed NTCDA within density-functional theory (DFT). To identify the interface state we have developed a projection technique which maps the states of the adsorbate system onto the original Shockley state. The projection also handles the loss of the surface periodicity due to the adsorbate, thus recovering the parabolic dispersion of the interface state in its original periodicity. We find that the energy shift of the Shockley state, as well as changes of its effective mass, are proportional to the adsorption coverage.

O 35.5 Tue 15:00 MA 042

Orbital Imaging of Non-Planar Molecules Beyond the Free Electron Finalstate Approximation — •Christian Metzger, Manuel Grimm, Martin Graus, Achim Schöll, and Friedrich Reinert — Julius-Maximilians-Universität Würzburg, Experimentelle Physik VII, 97074 Würzburg, Germany

It has been shown that the imaging of molecular orbitals is possible by angle-resolved photoelectron spectroscopy (ARPES). For planar aromatic molecules the approximation of the photoemission final state by a simple plane wave allows for a particularly straightforward interpretation of the experimental data. Here we present a combined experimental and theoretical study on the angular intensity distribution of photoelectrons from non-planar molecules. The ARPES data of a single layer of C60 on Ag(110) was acquired by a momentum microscope which enables the efficient detection of photoelectrons emitted into the entire hemisphere above the sample. The symmetry of the recorded photoelectron momentum maps (PMM) immediately demonstrates that the molecules adsorb with a single specific alignment and do not rotate even at room temperature. On the theoretical side, a simple plane-wave approximation of the finalstate is bound to fail due to the 3D geometry of C60. A more suitable description can be realized within the framework of independent atomic centers (IAC), where the finalstate can be assembled by the composite contributions of the individual atoms inside the molecule. We demonstrate that this IAC approach provides a very good simulation of the experimental PMM and thus allows the assignment of different initialstate orbitals.

O 35.6 Tue 15:15 MA 042

Influence of Molecule Size on Surface Polymorph Formation — •Andreas Jeindl, Michael Scherbela, Lukas Hörmann, and Oliver T. Hofmann — Institute of Solid State Physics, Graz University of Technology, Austria

Many properties of thin films, such as solubility or conductivity, are determined by the polymorph they assume upon adsorption on the (metal) substrate. In order to engineer functional interfaces, it is therefore imperative to understand and predict which polymorphs form for a given material combination. Yet, there are surprisingly few systematic studies that allow to deduct authoritative relationships between the molecular structure and the interface polymorph that will form. Computational studies are hindered by the intractably vast number of possible polymorphs, also known as 'configurational explosion'.

In this talk, we systematically investigate the influence of molecule size on the formation of surface polymorphs on the example of acenequinones on Ag(111). We present the SAMPLE approach that combines a physically motivated coarse-graining of the potential energy surface with machine learning as a method to overcome the configurational explosion. Precomputing the electrostatic and van-der-Waals interaction between adsorbate molecules allows us to extend the applicability of the method from model systems to technologically relevant molecules, such as acenequinones. For this example, we discuss the impact of the molecule size on the relative energies of selected polymorphs and the propensity to form low-energy defects.

O 35.7 Tue 15:30 MA 042

Rectification in molecular charge transfer systems — •Simon Liebing, Torsten Hahn, and Jens Kortus — TU Bergakademie Freiberg, Institute for Theoretical Physics, Germany

Charge transfer enabling rectification in molecular junctions was suggested by Ratner in 1974.[1] In the early 2000's strongly coupled system were excluded, because the strong coupling leads to symmetric transport behavior.[2] That left only weakly coupled charge transfer systems as candidates.[3] The authors studied different weakly coupling charge transfer dimers combining polycylic hydrocarbons and TNCQ-derivatives between gold leads. The observed rectifications are comparable to molecular systems using an asymmetric coupling to metallic leads. This shows that charge transfer is not alone suffient to achieve rectification in molecular electronics systems.

[1] Aviram, A. & Ratner, M. Chem. Phys. Lett. 29, 277 (1974)
[2] Mujica, V., Ratner, M. & Nitzan A. Chem. Phys. 281, 147 (2002)
[3] Hahn T., Liebing S., & Kortus J. Nanoscale 6, 14508 (2014)