

O 28: Organic Molecules at Surfaces 3: Theory

Time: Tuesday 10:30–12:45

Location: S051

O 28.1 Tue 10:30 S051

Switchable interfaces based on bistable molecules: tetrachloropyrazine on Pt(111) — ●LUKAS HÖRMANN, ANDREAS JEINDL, and OLIVER T. HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

Organic/inorganic interfaces govern the properties of many organic electronic devices. To imbue devices with additional functionality, it would be useful to make these interface properties reversibly switchable by means of easily accessible external parameters, such as the temperature.

In this work, we realize such a switchable interface with tetrachloropyrazine (TCP) on Pt(111). TCP can either chemisorb or physisorb on the Pt(111) surface, forming a double-well potential with strongly differing adsorption geometries. These allow forming diverse interface structures with notably different work functions and coherent fractions (obtained by X-ray standing wave measurements).

We model this switchable interface using a machine learning algorithm, based on Gaussian process regression. This facilitates structure search for commensurate as well as higher-order commensurate adlayers. We find three different classes of interface structures with varying work functions and coherent fractions and demonstrate that external stimuli, such as temperature and pressure, allow to reversibly shift between these different classes. Based on our insights, we discuss how systems need to be constructed so that the switch between different states leads to an even larger change in their properties.

O 28.2 Tue 10:45 S051

Substrate enhanced Jahn-Teller effect in single molecule junctions — ●MORITZ FRANKERL¹, LAERTE PATERA^{2,3}, THOMAS FREDERIKSEN⁴, JASCHA REPP³, and ANDREA DONARINI¹ — ¹Institute for Theoretical Physics, University of Regensburg — ²Catalysis Research Center, Technical University of Munich — ³Institute of Experimental and Applied Physics, University of Regensburg — ⁴Donostia International Physics Center (DIPC), Spain

The stabilization of several charge states of single molecules deposited on non-conductive NaCl films [1] allows to map out the electronic transition between different charge states by means of single-electron alternate-charging scanning tunneling microscopy [2]. Copper-phthalocyanine (CuPc) revealed a Jahn-Teller splitting (JTS) of its doubly degenerate LUMOs upon charging and, more surprisingly, the occupation of the same LUMO for both electrons upon double charging. We show by DFT calculations complemented by a group-theoretical analysis how the JTS for CuPc in gas phase is not sufficient to explain this behavior. We propose, instead, a cooperation between molecule and substrate deformation which enhances the strength of the JT coupling. The result is based on a microscopic model of the electron-phonon coupling between the molecule and the underlying thick layer of NaCl. The magnitude of the obtained substrate-induced JTS highlights the impact of the substrate on the electronic configuration of charged molecules, far beyond the mere charge stabilization. [1] Fatayer S. et al., Nature Nanotechnology 13, 376-380(2018) [2] Patera L.L. et al., Nature 566, 245-248(2019)

O 28.3 Tue 11:00 S051

Impact of electron-phonon interaction on metal-organic interface states — ●LUKAS ESCHMANN, JAN NEUENDORF, and MICHAEL ROHLFING — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany

We discuss electron phonon interaction (EPI) in the context of metal-organic adsorbate systems and the occurring nearly-free electron-like interface states (IS) whose energy E is strongly coupled to the vertical binding distance d with a coupling strength of $\lambda = \Delta E/\Delta d$ that is in the order of $1\text{ eV}/\text{Å}$ for several adsorbate systems.

We present an EPI model that is based on ab-initio data and uses the nearly-free electron-like character of the IS to obtain an analytic expression for the temperature induced renormalization of the latter^{1,2}. We find that the energy shift is dominated by the coupling to the out-of-plane phonon modes that change the average binding distance and scales quadratically with the coupling strength, i.e., $\sim \lambda^2$. Applied to the system of a NTCDA layer adsorbed on Ag(111), our model predicts a renormalization of the IS onset energy through quantum mechani-

cal coupling with the adsorbate phonons by -10 meV per 100 K . With this, we are able to explain the discrepancy between a classical lifting-effect and the experiment, thus revealing the important impact of EPI on spectroscopic states at metal-organic internal interfaces.

¹Eschmann, et al., Phys.Rev.B 104, L241102 (2021).

²Eschmann, et al., Phys.Rev.B 104, 245403 (2021).

O 28.4 Tue 11:15 S051

X-ray spectroscopic fingerprints of chemical bonding at molecule-metal interfaces revealed by first-principles core-level simulation — ●SAMUEL J. HALL¹, BENEDIKT P. KLEIN^{1,2}, and REINHARD J. MAURER¹ — ¹Department of Chemistry, University of Warwick, Coventry, UK — ²Diamond Light Source, Harwell Science and Innovation Campus, Didcot, UK

Characterisation of the chemical environment and electronic structure of organic materials and metal-organic interfaces can be carried out with x-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. The adsorption of molecules onto surfaces has been shown to change various spectral features which have previously been connected to changes in chemical bonding and charge distribution. However, these can be difficult to interpret due to overlapping features of multiple species and widely broadened spectra. Through the use of density functional theory (DFT) calculations we study two molecular isomers, azulene and naphthalene, adsorbed onto three metal (111) surfaces of silver, copper, and platinum. Categorised into three regimes of molecule-metal chemical bonding, we connect the changes seen in the spectra to the chemical bonding behaviour and decompose the signatures into initial core-state and final valence-state contributions. We analyse the effect of charge transfer, electronic hybridisation and dispersion effects, and aim to provide guidance for experimental spectral analysis.

O 28.5 Tue 11:30 S051

The sensitivity of NMR chemical shifts to organic/inorganic interfaces — ●VIVIANA PICCINNI¹, EMMANOUIL VEROUTIS², KARSTEN REUTER¹, JOSEF GRANWEHR², and CHRISTOPH SCHEURER¹ — ¹Fritz Haber Institute of the Max Planck Society, Berlin — ²Forschungszentrum Jülich, IEK-9, Jülich

Composite polymer/ceramic solid electrolytes are promising materials for Li-ion batteries due to their high stability and safety. Yet, their organic/inorganic interface is believed to hinder the ionic conduction. NMR experiments on a poly(ethylene oxide)/Li_{1.5}Al_{0.5}Ti_{1.5}(PO₄)₃ electrolyte have shown that Li ions cross the interface on a timescale of seconds. To remedy the problem, mechanistic insights are required, but even the polymer/ceramic interface structure is unknown.

We therefore investigate representative potential binding situations between the two materials by computing the NMR shielding tensors, in order to verify whether there is a significant change in the chemical shifts depending on the interface structure. Due to the high computational cost, a simplified model exhibiting the same local chemical interactions is constructed, composed by an AlPO₄ slab and ethane-1,2-diol. NMR measurements on an AlPO₄/methanol system have also been carried out.

While the computed NMR properties are sensitive to changes in the interface structure, experiments reveal no chemical shifts variations in the ¹H NMR methanol/AlPO₄ spectra relative to neat methanol. This can be ascribed to the presence of surface water in AlPO₄, which would leave no available binding sites for methanol/AlPO₄ interactions.

O 28.6 Tue 11:45 S051

Classifying Chiral Structure by a Convolutional Neural Network — ●PEER KASTEN¹, MANDY STRITZKE², JOHANNES TIM SEIFERT¹, BJÖRN MÖLLER³, TIMO DE WOLFF², TIM FINGSCHIEDT³, and UTA SCHLICKUM¹ — ¹Institut für Angewandte Physik, Technische Universität Braunschweig — ²Institut für Analysis und Algebra, Technische Universität Braunschweig — ³Institut für Nachrichtentechnik, Technische Universität Braunschweig

Scanning tunneling microscopy (STM) is an important tool to image surfaces at atomic scale. To examine structures of molecules in STM images can be a difficult and time-consuming task. We present a method to recognize chirality within experimentally observed self-assembled molecular structures using the convolutional neural network

(CNN) based object detection framework Faster R-CNN. Thereby we can classify unit cells in the image towards one of both chiral structures.

To train the neural network, a sufficient amount of correctly labeled images is necessary. To obtain such data and labels, we utilize a method to create realistic-looking, synthetic STM images in varying zoom-sizes containing lifelike properties such as noise and step edges along with corresponding labels.

Using this synthetic data, we trained a model capable of classifying synthetic images at sizes ranging from 8 nm to 100 nm with high performance. Evaluations of the CNN's predictions for real images show that this network trained on synthetic data can generalize towards inference on real images.

O 28.7 Tue 12:00 S051

Energy landscaping with external electric fields: Selective stabilization of interface polymorphs — JOHANNES CARTUS, ANDREAS JEINDL, ANNA WERKOVITS, and OLIVER HOFMANN — Graz University of Technology, Graz, Austria

The polymorphs that inorganic/organic interfaces assume can have drastic consequences for the interface properties (such as, e.g., the work function). It is, therefore, of great relevance for applications in organic electronics to achieve precise control of the interface polymorphism. The stability of the respective polymorphs is determined by deposition conditions (e.g., temperature and pressure). In this contribution we investigate electric fields as an additional handle for better control over the polymorphism, thus selectively stabilizing polymorphs at conditions where they were previously inaccessible.

Using density functional theory calculations augmented by a smart-data machine learning approach (SAMPLE) we demonstrate how electric fields can be used to foster desired or even previously unseen polymorphs. Tetracyanoethylene (TCNE) on Cu(111) is an ideal test system because its work function can change by more than 3 eV for different polymorphs.

O 28.8 Tue 12:15 S051

Interlayer orbital overlap governing thin-film geometry: the role of interfacial charge transfer — FABIO CALCINELLI, ANDREAS JEINDL, LUKAS HÖRMANN, and OLIVER HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

Organic thin films exhibit a large structural variability, and the sub-

strate on which they grow has a relevant influence on their polymorphism. Predicting which structure a thin film will assume on a substrate is impossible through traditional first-principle modeling alone, because of the combinatorial explosion in the number of possible polymorphs. However, recent developments in machine-learning assisted structure search have made structure-to-property investigations accessible. Employing smart-data machine learning, we demonstrate the impact that different substrates can have on the geometry of the first two layers of a thin film. We identify the energetically most favourable geometries for benzoquinone on silver and on graphene, and compare their electronic properties. While the polymorphs formed in the first layer of benzoquinone are very similar, for the second layer we find two significantly different structures. We explain this difference as an effect of the interplay between different charge transfer on the two substrates, and different interlayer orbital overlap for the two structures. Furthermore, we investigate the systematic impact of interlayer orbital overlap in defining the most stable polymorphs for different charge transfers.

O 28.9 Tue 12:30 S051

Polymorph trapping by optimized deposition conditions: A first-principles prediction for TCNE/Cu(111) — ANNA WERKOVITS, ANDREAS JEINDL, LUKAS HÖRMANN, JOHANNES J. CARTUS, and OLIVER T. HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

Physical properties of small-molecule organic semiconductors are strongly determined by their polymorphs. Depending on the orientation in which molecules adsorb on the substrate, properties can significantly vary, as is the case, e.g. for tetracyanoethylene (TCNE) on Cu(111).

We propose conditions under which TCNE remains in the energetically less favorable lying position also for higher coverages. This requires fulfilling two prerequisites: To enable ordered growth, the temperature must be high enough to allow for sufficient diffusion of lying molecules, whereas the temperature must be low enough to inhibit the reorientation to the upright-standing position.

In this work, we utilize the nudged elastic band method and density functional theory to compute energy barriers. By means of the harmonic transition state theory temperature-dependent diffusion and reorientation rates are obtained for predicting a temperature range where the kinetic stabilization is attained.