

O 6: New Methods: Experiments and Theory

Time: Monday 10:30–13:00

Location: GER 39

O 6.1 Mon 10:30 GER 39

A Newly Developed IRAS System to Investigate Adsorbates on Metal-Oxide Single Crystal Surfaces — ●DAVID RATH, JIRI PAVELEC, ULRIKE DIEBOLD, MICHAEL SCHMID, and GARETH S. PARKINSON — Institute of Applied Physics, TU Wien, Austria

The IRAS system GRISU (GRazing incident Infrared absorption Spectroscopy Unit) was developed to investigate adsorbates on metal oxide single crystals in the research field of single-atom catalysis [1]. It combines the commercially available FTIR spectrometer Bruker Vertex 80v with an UHV chamber [2]. The compact design requires only one CF150 port for the main optical components, features five mirrors for beam guidance placed in HV and UHV environment and optimises the system's performance, flexibility, and usability. The result is a small controllable focal-spot diameter (max. 3 mm) on the sample, motorised optical components, and an aperture limiting the incidence angle range (variable, 49° to 85°) on the sample. Based on ray tracing results and preliminary intensity measurements, the system shows up to 10× higher intensities compared to a commercial system with two parabolic mirrors with a focal length of 250 mm. First IR spectra measured with the recently installed IRAS measurement system will be shown.

[1] G. S. Parkinson, *Catal. Lett.* 149, 1137 (2019)

[2] J. Pavelec, et al., *J. Chem. Phys.* 146, 014701 (2017).

O 6.2 Mon 10:45 GER 39

Insights on the Liquid/vacuum interface of ionic liquids by ARXPS and UHV Pendant Drop — ULRIKE PAAP, ●AFRA GEZMIS, FLORIAN MAIER, and HANS-PETER STEINRÜCK — Friedrich-Alexander Universität, Erlangen, Germany

Ionic liquids (ILs) are characterized by a low melting point and a low vapor pressure. Many ILs exhibit high gas solubility along a high chemical and thermal stability. Such properties are beneficial in many areas such as gas absorbents, refrigerants, lubricants, antistatics and surfactants. The low vapor pressure of ILs opens the possibility to investigate them under ultra-high vacuum (UHV) conditions. In this context, angle-resolved X-ray photoelectron spectroscopy (ARXPS) has already proven to be a particularly powerful tool. We now combine information on the surface composition derived from ARXPS and measurements of the surface tension performed under ultraclean conditions with our new pendant drop setup, which operates in UHV. Our results allow for a deeper understanding of enrichment and molecular orientation processes at the outermost surface of these systems on the microscopic and the macroscopic scale. This work was supported by the Collaborative Research Center (CRC) 1452: Catalysis at Liquid Interfaces.

O 6.3 Mon 11:00 GER 39

Kintetic In Situ Synthesis (KISS) technique of large-area 2D materials exfoliation — ●ANTONIJA GRUBISIC-CABO^{1,2}, MATTEO MICHARDI³, CHARLOTTE E. SANDERS⁴, MARCO BIANCHI⁵, DAVIDE CURCIO⁵, DIBYA PHYUAL², MAGNUS H. BERNTSEN², QINDA GUO², and MACIEJ DENDZIK² — ¹University of Groningen, Netherlands — ²KTH, Sweden — ³University of British Columbia, Canada — ⁴Central Laser Facility, UK — ⁵Aarhus University, Denmark

Two-dimensional (2D) materials provide an extremely rich platform to investigate novel quantum phenomena and to design nanostructures with desired functionalities. Some of the key techniques employed in studies of 2D materials, such as photoemission spectroscopy, have stringent requirements for the quality, sample size and cleanliness of the surface. Fulfilling these conditions using a standard mechanical exfoliation in a glove box is often problematic. Here, we present a novel method for in situ exfoliation of 2D materials performed directly in ultra-high vacuum, which yields large flakes of excellent crystallinity and purity. In our experiments, multiple semiconducting and metallic transition metal dichalcogenides were exfoliated onto Au, Ag and Ge substrates, showing the versatility of the technique, and characterised by angle resolved photoemission spectroscopy. Importantly, the proposed method is straightforward, simple, and does not require any specialised equipment. This technique is ideally suited for the electronic structure research of air-sensitive 2D materials since the sample preparation process happens entirely in ultra-high vacuum.

O 6.4 Mon 11:15 GER 39

Two new methods for the analysis of TPD data — ●MICHAEL SCHMID, GARETH S. PARKINSON, and ULRIKE DIEBOLD — Institute of Applied Physics, TU Wien, Austria

Temperature programmed desorption (TPD) is the most common experimental technique for obtaining the binding energies of adsorbates. TPD data are usually analyzed using the Polanyi–Wigner equation; this is far from straightforward. We present two new methods, based on equilibrium thermodynamics, bypassing the use of the Polanyi–Wigner equation or transition state theory: In the case of all adsorption sites being equivalent, the adsorption energy can be directly calculated from the desorption temperature, the width of the TPD peak, the sticking probability (at the desorption temperature), and thermodynamic data [1]. This “magic formula” is remarkably robust; in many cases even wrong assumptions about the desorption order or the presence of a distribution of adsorption energies lead to negligible errors. In more complex cases, with a distribution of adsorption energies, we show that TPD spectra are approximately given by a convolution integral. We present a method (and computer program) for TPD inversion, i.e. the determination of the energy distribution from a single TPD spectrum at saturation coverage [1]. Although this method is derived for the case of non-interacting adsorbates, we argue that it is a good approximation in cases of short-range repulsion and it can also reveal (though not quantitatively analyze) the presence of attractive interactions between adsorbates.

[1] M. Schmid et al., doi:10.1021/acsphyschemau.2c00031 (2022)

O 6.5 Mon 11:30 GER 39

Surface-Sensitive Spectroscopy from First Principles — ●YAIR LITMAN^{1,2}, JINGGANG LAN³, KUO-YANG CHIANG², VENKAT KAPIL¹, YUKI NAGATA², and DAVID WILKINS⁴ — ¹University of Cambridge, Cambridge, United Kingdom — ²MPI for Polymer Research, Mainz, Germany — ³Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland — ⁴Queen's University Belfast, Belfast, United Kingdom

Our current understanding of the structure and dynamics of aqueous interfaces at the molecular level has grown substantially in the last decades due to an increasing synergy between experimental measurements and atomistic simulations. However, the latter are either based on empirical force field models, which are neither suitable to describe bond breaking and formation nor systems with complex electronic structure, or on *ab initio* calculations which due to their computational cost cannot be statistically converged. In this work, we overcome all these limitations by combining high-dimensional neural network potentials with symmetry-adapted Gaussian process regression [1] to simulate the sum-frequency generation (SFG)[2] spectra of the water-air interface with *ab initio* accuracy. We obtain a good agreement with last-generation experiments and show how these models can in principle be improved systematically towards exact results. Overall, the machinery presented in this work paves the way for the modelling of surface-sensitive spectroscopy of complex interfaces. [1] V. Deringer, *et al.*, *Chem. Rev.* 16, 121 (2021) [2] A. Morita, J. Hynes, *J. Phys. Chem. B* 106, 673 (2002).

O 6.6 Mon 11:45 GER 39

Artificial Neural Network based Interatomic Potentials to Describe Laser-Excited Materials — ●BERND BAUERHENNE, PASCAL PLETTENBERG, and MARTIN E. GARCIA — Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

Femtosecond laser pulses create a transient state with hot electrons at temperature T_e and cold ions, in which ultrafast nonthermal effects occur. Later, the decay of this state due to electron-phonon interactions gives rise to ultrafast effects of more thermal character. Quantum mechanical methods like T_e -dependent density functional theory (DFT) allow a precise description of the non-thermal state with hot electrons. However, simulations of laser material interactions at surfaces on experimentally relevant sizes require to take a huge amount of atoms into account, which is only possible by the usage of interatomic potentials. Most known interatomic potentials are determined assuming that electrons are in their ground state and cannot describe nonthermal effects initiated by bond-softening or hardening. In order to take ultrafast thermal and non-thermal effects on the same theoretical level, T_e -dependent interatomic potentials are needed. Here, we present an T_e -dependent interatomic potential based, for the first time, on an ar-

tificial neural network. We studied silicon and show that the phonon band structure, the cohesive energy curves for several crystal structures, the electronic specific heat, atomic forces and cohesive energies are described in excellent agreement with DFT calculations for a wide range of Te. In addition, we simulated the laser-induced annealing of surface defects on a thin silicon film.

O 6.7 Mon 12:00 GER 39

Real-time TD-DFTB full periodic implementation for solids and low-dimensional materials — ●CARLOS R. LIEN-MEDRANO¹, FRANCO P. BONAFÉ², CRISTIÁN G. SÁNCHEZ³, and THOMAS FRAEUNHEIM¹ — ¹University of Bremen, Bremen, Germany — ²MPSD, Hamburg, Germany — ³University of Cuyo, Mendoza, Argentina

The current implementation of the real-time TD-DFTB dynamics for molecules and finite systems in the DFTB+ package[1] is based on the length gauge of the electric field. Here we show a proof-of-concept implementation of the vector potential in the velocity gauge of the electric field that in principle would allow us to extend the real-time dynamics to any periodic direction, making the new implementation suitable for the study of photo-induced dynamics processes in bulk, low-dimensional materials and surfaces. Instead of the dipole moment, the observable of choice is the frequency dependent conductivity which can be obtained from the Fourier transform of the autocorrelation function of the electric current density averaged over a unit cell. The conductivity provides access to the dielectric constant of the system allowing the calculation of optical properties.

[1] Hourahine, B., et al. (2020). DFTB+, a software package for efficient approximate density functional theory based atomistic simulations. The Journal of Chemical Physics, 152(12), 124101.

O 6.8 Mon 12:15 GER 39

Structure discovery in AFM imaging of ice — ●FABIO PRIANTE¹, YE TIAN², DONG GUAN², CHEN XU¹, SHUNING CAI¹, NIKO OINONEN¹, PETER LILJEROTH¹, YING JIANG², and ADAM FOSTER^{1,3} — ¹Department of Applied Physics, Aalto University, Helsinki FI-00076, Finland — ²International Center for Quantum Materials, Peking University, Beijing, 100871, China — ³WPI Nano Life Science Institute (WPI-Nano LSI), Kanazawa University

The interaction of water with surfaces is crucially important in a wide range of natural and technological settings. Using high-resolution AFM and STM, several studies have demonstrated the presence of water pentamers, hexamers, heptamers (and of their combinations) on a variety of metallic surfaces. However, in all these situations, the observed structures were completely flat, providing a relatively straightforward path to interpretation. To address more complex cases, while simultaneously alleviating the interpretation effort, we develop an automated workflow centered around a convolutional neural network (to extract atomic positions) and a neural network potential (to rapidly sort candidate structures with high accuracy). We test our workflow on several high-resolution AFM measurements of water clusters on Cu(111), whose understanding is challenging due to both their highly 3D configuration and to their large size. For each of them, we propose

an underlying atomic structure, finally comparing the experimental images with simulated AFM from Density Functional Theory. These results provide new insights into the early phases of ice formation, which is a ubiquitous phenomenon ranging from biology to astrophysics.

O 6.9 Mon 12:30 GER 39

Designing Covalent Organic Frameworks Through Active Machine Learning — ●YUXUAN YAO^{1,2}, CHRISTIAN KUNKEL³, KARSTEN REUTER³, and HARALD OBERHOFER² — ¹Chair for Theoretical Chemistry, Technische Universität München — ²Chair for Theoretical Physics VII, University of Bayreuth — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft

Covalent organic frameworks (COFs) are a class of materials, that are formed by molecular building blocks (BBs) connected with covalent bonds. They have found application in many fields such as catalysis, or optoelectronics. It is well known that their design space is far too large to sample one by one because numerous available BBs. We modify an earlier active machine learning (AML) approach that explores the massive available BBs space through the use of surrogate models for charge injection and transport descriptors. In this method, the Gaussian Process Regression (GPR) and AML are combined to train the molecular space. This way we ensure that only promising molecules that are very different from already explored ones have their descriptors evaluated by Density Functional based Tight Binding (DFTB) calculations. Specifically, we modify molecular generation rules in order to produce three-fold rotationally symmetric candidates molecules for use in hexagonal COFs. In the future this approach can be generalized for any other symmetries, to potentially even allow for 3-dimensional network generation. We gauge the performance of our AML by evaluating the success ratio, which is the ratio of promising candidates to all generated molecules.

O 6.10 Mon 12:45 GER 39

Machine-learning-backed evolutionary search for SrTiO₃(110) surface reconstructions — ●RALF WANZENBÖCK, FLORIAN BUCHNER, JESÚS CARRETE, and GEORG K. H. MADSEN — Institute of Materials Chemistry, TU Wien, Vienna, Austria

To determine the atomic structure of surface reconstructions, structural models derived from domain knowledge and intuition have historically been essential. Evolutionary algorithms combined with density functional theory have proven to be powerful tools for such structure searches if one accepts the prohibitive cost that comes with a thorough exploration of a potential energy surface. We train a neural-network force field (NNFF) as a surrogate model to drive the exploration of the rich phase diagram of TiO_x overlayers on SrTiO₃(110) utilizing the covariance matrix adaptation evolution strategy (CMA-ES). We verify the transferability of the NNFF by performing CMA-ES runs on SrTiO₃(110) 3×1, 4×1 and 5×1 with a model trained solely on 4×1 data. With the speedup afforded by the surrogate model we were able to perform exhaustive sets of exploratory runs to identify known and new low-energy reconstructions and match different symmetries found in experimental data. [R. Wanzenböck et al., Digital Discovery, 2022, 1, 703-710.]