ECDCD-14

14<sup>th</sup> European Conference on Surface Crystallography and Dynamics

Eibsee • Germany • 2020

## Preface

The European Conference on Surface Crystallography and Dynamics (ECSCD) is one of the central conference series in the field of surface science and surface crystallography in Europe. It is successfully bringing together scientists (both theoreticians and experimentalists) working on structural and related electronic properties of (surfaces, interfaces, hybrid systems and – with increasing relevance – two dimensional systems. Particular attention of was paid to an accurate quantitative description of surface structures, to surface reactions and phase transitions, and to their consequences for technologically relevant questions like epitaxial growth, self-assembly of nanostructures or surface catalysis. More recently, so called "novel material" systems moved into the focus of condensed matter research. This started with the large success of graphene and other two-dimensional materials, and nowadays involves spin-selective, topological and superconductive materials. For all of them, surfaces and interfaces play an important, often even a decisive role.

The ECSCD series has been always reflecting the newest trends in the field, and hence was a central venue for scientific intercommunication. Therefore, the ECSCD-14 follows the latest developments in the field and particularly turns its scientific scope toward novel material systems, without excluding the more traditional topics. Other recent developments that will feature prominently are the extension of ultrafast experiments, for example in scanning probe microscopy and photoemission spectroscopy, in order to achieve time-resolved description of surface dynamics, and the exciting possibility to craft artificial atomic and molecular structures (by self-assembly or nanoscale manipulation) that opens the way for the creation of designer materials with tailored properties. This significantly broadens the scope of the conference and positions ECSCD series centrally in the 2D-materials and surfaces/interfaces scientific community.

The scope of the conference includes the following topics:

- Two-dimensional materials
- Topological materials
- Magnetic structures
- Designer materials at surfaces
- Adatoms and molecular adsorbates
- Nanostructures and self-assembly
- Oxide surfaces and oxide-based heterostructures
- Phase transitions at surfaces
- Dynamic processes and catalysis

The previous ECSCD conferences have been held in

Erlangen, Germany (1985) Cambridge, United Kingdom (1988) San Miniato, Italy (1991) Aarhus, Denmark (1993) Banz, Germany (1995) La Grande Motte, France (1998) Leiden, Netherlands (2001) Segovia, Spain (2004) Vienna, Austria (2007) Reading, United Kingdom (2010) Edinburgh, United Kingdom (2012) Trieste, Italy (2015) Donostia-San Sebastian, Spain (2017)

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## **Eibsee Bus line**



#### Garmisch-Partenkirchen station – Untergrainau station – Eibsee route

Garı Partenk	misch- irchen												
S	Station	6:23	8:14	9:14	10:14	11:14	12:14	13:04	14:14	15:14	16:14	17:14	18:14
Unterg S	rainau Station	x	8:30	9:30	10:30	11:30	12:30	13:20	14:30	15:30	16:30	17:30	18:30
I	Eibsee	6.46	8:55	9:55	10:55	11:55	12:55	13:45	14:55	15:55	16:55	17:55	18:55

#### Eibsee – Untergrainau station – Garmisch-Partenkirchen station route

Eibsee	6:48	9:10	10:10	11:10	12:10	13:00	13:50	15:10	16:10	17:10	18:10	19:10
Untergrainau Station	7:07	9:35	10:35	11:35	12:35	13:25	14:15	15:35	16:35	17:35	18:35	19:35
Garmisch-	7:23	9:51	10:51	11:51	12:51	13:41	14:31	15:51	16:51	17:51	18:51	19:51
Partenkirchen Station												

Detailed timetable including intermediate stops is available at www.eibseebus.de

## **Conference outing**



- 11:25 Gathering for excurtion in the hotel lobby
- 11:45 Taking train (Zahnradbahn) from Eibsee station
- 12:28 Arriving to Zugspitzplatt, continue with Glescherbahn
- 12:45 Arriving to Zugspitze
- 13:00 Conference photo
- 13:15 Lunch at "PANORAMA 2962"
- 15:15 or 16:15 Return with the Gletscherbahn to Zugspitzplatt
- 15:30 or 16:30 Train from Zugspitzplatt
- 17:30 Poster session
- 19:00 Diner
- **20:00 Hans Peter Schmid**, *General and regional aspects of climate change*.

**Conference program** 

Monday, 04.05.2020					
15:00 – 17:00 Registration					
Opening session					
17:00 – 17:15 Welcome					
17:15 – 17:50	Katharina Franke				
17:50 – 18:25	Kristian Sommer Thygesen				
19:00	Dinner				

Tuesday, 05.05.2020						
7:00 - 8:40	Breakfast					
	2D materials I					
8:45 – 9:20	Roman Fasel					
9:20 - 9:40	Jens Falta					
9:40 - 10:00	Peiyu Chen					
10:00 - 10:20	Francesco Tumino					
10:20 - 10:50	Coffee break					
	Dynamics I					
10:50 - 11:25	Michael Horn von Hoegen					
11:25 - 11:45	Hannes Böckmann					
11:45 – 12:05	Gary S. Harlow					
12:05 – 12:25	Matthias Muntwiler					
12:30 - 14:00	Lunch					

Electron diffraction and holography						
14:00 - 14:35	Hiroshi Daimon					
14:35 - 14:55	Lutz Hammer					
14:55 - 15:15	Michele Riva					
15:15 - 15:45	Coffee break					
	2D materials II					
15:45 – 16:20	David A. Duncan					
16:20 - 16:40	Benjamin Stadtmüller					
16:40 - 17:00	Soon jung Jung					
17:00 - 17:20	You-Ron Lin					
17:30 - 19:00	Poster session					
19:00	Dinner					

Wednesday, 06.05.2020						
7:00 – 8:40 Breakfast						
	SPM techniques I					
8:45 - 9:20	Ingmar Swart					
9:20 - 9:55	Peter Liljeroth					
9:55 - 10:15	Coffee break					
Catalysis / Theory I						
10:15 - 10:50	Mie Andersen					
11:30 - 17:15	Zugspitze excursion					
17:30 - 19:00	Poster session					
19:00	Dinner					
20:00	Peter Schmid					

Thursday, 07.05.2020						
7:00 - 8:40	Breakfast					
	2D materials III					
8:45 - 9:20	Marie-Laure Bocquet					
9:20 - 9:40	Harold J.W. Zandvliet					
9:40 - 10:00	Aran Garcia-Lekue					
10:00 - 10:20	María Blanco-Rey					
10:20 - 10:50	Coffee break					
	Dynamics II					
10:50 - 11:25	Ralph Ernstorfer					
11:25 - 11:45	Matthias Hengsberger					
11:45 - 12:05	Dietrich Menzel					
12:05 - 12:25	Lisa Grad					
12:30 - 14:00	Lunch					
	Molecules I					
14:00 - 14:35	Michael Ramsey					
14:35 – 14:55	Anja Haags					
14:55 – 15:15	Phil Woodruff					
15:15 – 15:35	Georg Held					
15:35 – 15:55	Adam Matěj					
15:55 – 16:30	Coffee break					
Molecules and oxides						
16:30 - 17:05	Moritz Sokolowski					
17:05 – 17:25	Julian Barnett					
17:25 – 17:45	Jacek Goniakowski					
17:45 - 18:05	Juan de la Figuera					
18:05 - 18:25	M. Alexander Schneider					
19:00	Conference dinner					

Friday, 08.05.2020						
7:00 - 8:40	Breakfast					
	SPM techniques II					
8:45 – 9:20	Yousoo Kim					
9:20 - 9:40	Aleksandr Baklanov					
9:40 - 10:00	Florian Albrecht					
10:00 - 10:20	Lyderic Bocquet					
10:20 - 10:50	Coffee break					
C	Catalysis / Theory II					
10:50 - 11:25	Dino Novko					
11:25 - 11:45	Karsten Reuter					
11:45 – 12:05	Carmen Ocal					
12:05 - 12:20	Closing remarks					
12:30 - 14:00	Lunch and departure					

#### Monday, 04.05.2020

15:00 – 17:00 Registration

#### **Opening session**

#### 17:00 - 17:15 Welcome

#### 17:15 – 17:50 Katharina Franke (keynote)

*Yu-Shiba-Rusinov states of single magnetic atoms and nanostructures probed by scanning tunneling spectroscopy.* 

- **17:50 18:25 Kristian Sommer Thygesen (**invited**)** *High-throughput modeling and discovery of two-dimensional materials.*
- 19:00 Dinner

#### Tuesday, 05.05.2020

7:00 – 8:40 Breakfast

#### 2D materials I

8:45 – 9:20 Roman Fasel (invited)

Nanographenes with intrinsic  $\pi$ -magnetism: From molecules to spin chains.

9:20 – 9:40 Jens Falta

*Massive step pushing: the growth mechanism of micron-sized single-domain molybdenum disulfide islands on Au(111).* 

#### 9:40 – 10:00 Peiyu Chen

*Epitaxial Growth of Monolayer MoS*<sub>2</sub> *on SrTiO*<sub>3</sub> *Single Crystal Substrates.* 

#### 10:00 – 10:20 Francesco Tumino

*In-situ surface investigation of low-dimensional organic/inorganic materials synthesized on metal substrates.* 

10:20 – 10:50 Coffee break

#### **Dynamics I**

#### 10:50 – 11:25 Michael Horn von Hoegen (invited)

*Structural dynamics in atomic wire systems studied by ultrafast-RHEED: Excitation, metastable states and relaxation.* 

#### 11:25 – 11:45 Hannes Böckmann

*Coherent vibrational control of a structural phase transition in a solid-state surface system.* 

#### 11:45 – 12:05 Gary S. Harlow

*Electrode Structure Movies: High-Energy Surface X-ray Diffraction for In Situ Electrochemistry.* 

#### 12:05 – 12:25 Matthias Muntwiler

*Microscopic Details of Switching a Ferroelectric Surface observed by Operando Photoelectron Diffraction.* 

#### 12:30 - 14:00 Lunch

#### Tuesday, 05.05.2020

#### **Electron diffraction and holography**

#### 14:00 – 14:35 Hiroshi Daimon (keynote)

*Three-dimensional atomic-resolution holography and effective twodimensional analyzer for photoelectron holography.* 

#### 14:35 – 14:55 Lutz Hammer

Oxygen on Rh(100) - when surface dynamics fakes symmetry.

#### 14:55 – 15:15 Michele Riva

One step towards popularizing LEED-IV.

15:15 – 15:45 Coffee break

#### 2D materials II

**15:45 – 16:20 David A. Duncan** (invited) Unravelling transition metal chalcogenides one layer at a time.

#### 16:20 – 16:40 Benjamin Stadtmüller

*Chemical decoupling of graphene from the Ni(111) surface by intercalation of the heavy metal Pb.* 

#### 16:40 – 17:00 Soon jung Jung

Strain induced band gap modulation in 2D semiconductor.

#### 17:00 - 17:20 You-Ron Lin

Unveiling the role of Sr atoms in a  $Sr_xBi_2Se_3$  topological superconductor.

- 17:30 19:00 Poster session
- 19:00 Dinner

#### Wednesday, 06.05.2020

7:00 – 8:40 Breakfast

#### **SPM techniques I**

- 8:45 9:20 Ingmar Swart (invited) Electronic quantum materials simulated with artificial model lattices.
- **9:20 9:55 Peter Liljeroth (**invited**)** Designer electronic states in atomic lattices and hybrid 2D system.
- 9:55 10:15 Coffee break

#### Catalysis / Theory I

#### 10:15 - 10:50 Mie Andersen (invited)

Active sites in solid and liquid surface catalysis.

- 11:30 17:15 Conference outing: Zugspitze excursion
- 17:30 19:00 Poster session

#### 19:00 Dinner

20:00 Hans Peter Schmid (designated lecturer)

General and regional aspects of climate change.

#### Thursday, 07.05.2020

7:00 – 8:40 Breakfast

#### 2D materials III

8:45 – 9:20 Marie-Laure Bocquet (invited)

*Two-Dimensional 2D Materials interfacing Liquid Water : the New Frontier from Ab Initio Simulations.* 

9:20 – 9:40 Harold J.W. Zandvliet Probing topologically protected 1D states in 2D Dirac materials.

#### 9:40 – 10:00 Aran Garcia-Lekue

Inducing magnetism in graphene nanoribbons by chemical doping.

#### 10:00 – 10:20 María Blanco-Rey

Magnetic anisotropy switching and chiral spin textures in ultrathin *Pt/Co/Graphene heterostructures*.

#### 10:20 – 10:50 Coffee break

#### **Dynamics II**

#### 10:50 - 11:25 Ralph Ernstorfer (invited)

*Electronic structure of non-equilibrium states: from electron and exciton dynamics to light-induced phase transitions.* 

#### 11:25 – 11:45 Matthias Hengsberger

Interface state dynamics in hexagonal boron nitride monolayers.

#### 11:45 – 12:05 Dietrich Menzel

Ultrafast charge transfer dynamics in, at and under Graphene and BN monolayers.

#### 12:05 - 12:25 Lisa Grad

Hot electron dynamics in the potential photocathode materials  $Cu_2O$  and  $Sb_2Se_3$  by time-resolved two-photon photoemission.

#### 12:30 - 14:00 Lunch

#### **Molecules I**

#### 14:00 - 14:35 Michael Ramsey (invited)

Do charged and uncharged species co-exist in adsorbate monolayers?

#### 14:35 – 14:55 Anja Haags

*Revealing electronic and chemical structure of adsobates with photoemission tomography.* 

#### 14:55 - 15:15 Phil Woodruff

Alkali doping leads to salt formation in a two-dimensional metal-organic framework: K and TCNQ on Ag(111).

#### 15:15 – 15:35 Georg Held

*Combining NEXAFS and DFT to determine Adsorption Structures of mediumsized organic Molecules.* 

#### 15:35 – 15:55 Adam Matěj

Tailoring  $\pi$ -conjugation and vibrational modes to steer on surface synthesis of pentalene-bridged ladder polymers.

#### Thursday, 07.05.2020

#### 15:55 – 16:30 Coffee break

#### Molecules and oxides

#### 16:30 – 17:05 Moritz Sokolowski (invited)

Decoupling of molecules at the metal interface by thin interfacial layers.

#### 17:05 – 17:25 Julian Barnett

Extracting the local electronic properties of the two-dimensional electron gas at the LaAIO<sub>3</sub>/SrTiO<sub>3</sub> interface by phonon-enhanced near-field spectroscopy.

#### 17:25 – 17:45 Jacek Goniakowski

Understanding the structural diversity of freestanding Al<sub>2</sub>O<sub>3</sub> ultrathin films through DFTB-aided global optimization.

#### 17:45 – 18:05 Juan de la Figuera

Oxides of divalent 3d transition metals on Ru(0001) grown by oxygen assisted molecular beam epitaxy: structure and magnetism.

18:05 – 18:25 M. Alexander Schneider Wurtzite Cobalt Oxide Films Grown on Au(111).

#### 19:00 Conference dinner

#### Friday, 08.05.2020

7:00 – 8:40 Breakfast

#### **SPM techniques II**

- 8:45 9:20 Yousoo Kim (keynote) Single-molecule chemistry and spectroscopy using localized surface plasmon at STM junction.
- 9:20 9:40 Aleksandr Baklanov Adsorption of Zn-porphines on h-BN/Cu(111).
- 9:40 10:00 Florian Albrecht Charge state dependence of single molecules' chemical structure observed in real space.

#### 10:00 - 10:20 Lyderic Bocquet

Atomic rheology of gold nanojunctions.

#### 10:20 – 10:50 Coffee break

#### **Catalysis / Theory II**

#### 10:50 - 11:25 Dino Novko (invited)

*Dynamics of adsorbates on metal surfaces under equilibrium and non-equilibrium conditions.* 

#### 11:25 – 11:45 Karsten Reuter

Insight into the Structural Evolution of Working IrO<sub>2</sub> Catalysts in Proton-Exchange Membrane Electrolyzers.

#### 11:45 – 12:05 Carmen Ocal

*Surface-catalyzed dehalogenation of fluorinated fullerenes on coinage metals.* 

12:05 – 12:20 Closing remarks

12:30 – 14:00 Lunch and departure

#### Posters

#### Benito Arnoldi

*Spin-dependent photoelectron diffraction at a molecular overlayer.* 

#### Brian David Baker Cortés

*Coverage-dependent structural transformation & on-surface atom exchange reactions in porphyrin-based metal-organic coordination networks on Au(111).* 

#### **Christian Brand**

Temperature-controlled rotational epitaxy of graphene.

#### **Emmanuel Kentzinger**

Nanoscience crystallography at a high brilliance laboratory X-ray diffractometer: from mesoscopic to interatomic length scales.

#### Florian Kraushofer

*The TensErLEED management package: a new environment for analysis and calculation of LEED I(V) data.* 

#### Fubiao Gu

STM study of the on-surface synthesis stages of a single-layer  $\pi$ -conjugated 2D MOF.

#### Ilya Balash

*Measurement of the dynamics of residual stresses in copper and tungsten during heating.* 

#### Iulia Cojocariu

*Surface trans-effect pinning low valence Ni(I)TPP on copper against irreversible structural changes.* 

#### Jana Martincová

*The air stability of the MoS*<sub>2</sub> *monolayers.* 

#### Jan-Henrik Herrig

Delayed surface phonon excitation in Bi(111) films.

#### Johannes Küchle

*Can one control the interface alloying between 2D-sheets and a supporting silver substrate?* 

#### Katariina Pussi

*Structural properties of PbTe quantum dots revealed by high-energy x-ray diffraction.* 

#### Khadiza Ali

Growth and electronic structure of hexagonal BN on a curved Rh(111) crystal.

#### L. Fernández

Monolayers of rare-earth gold surfaces as template for the growth of magnetic molecules.

#### Maurizio De Santis

*Growth-mode and interface structure of epitaxial ultrathin MgO/Ag(001) films: a surface x-ray diffraction study.* 

#### P. T. P. Ryan

*Quantitative confirmation of the inverted adsorption structure for 2H-tetraphenyl porphyrin on Cu(111).* 

#### Rajan Adhikari

*Formation of highly ordered molecular porous 2D networks from cyano-functionalized porphyrins on Cu(111).* 

#### Sara Fiori

N-doped Graphene: growth and reactivity.

#### Sergey Kazantsev

*Dynamic measurements of the x-ray Laue diffraction on single-crystal tungsten during pulsed heat load and reconstruction of the residual stress distribution in the sample.* 

#### Simeon D. Beinlich

*Electrochemical interfaces getting real - theoretical modeling of transition states at applied electrode potential.* 

#### Simon Moser

A sideways perspective on electronic band structure.

#### Stefan Förster

*Structure determination of a large unit cell quasicrystal approximant in twodimensional SrTiO3 on Pt(111).* 

#### Stefano Albertin

*Red-ox of single crystal Ir(100): an in-situ high energy surface x-ray diffraction study.* 

#### Tilman Kißlinger

Unexpected submonolayer structures of Te on Cu(111) and Ag(111).

#### V. Feyer

*Multi-orbital charge transfer at metalorganic/metal interfaces: electronic structure and catalitical activity.* 

# **Abstracts: Talks**

## Yu-Shiba-Rusinov states of single magnetic atoms and nanostructures probed by scanning tunneling spectroscopy

Eva Liebhaber<sup>(a)</sup>, Michael Ruby<sup>(a)</sup>, Sergio Acero Gonzalez<sup>(a)</sup>, Yang Peng<sup>(a)</sup>, Benjamin Heinrich<sup>(a)</sup>, Gaël Reecht<sup>(a)</sup>, Sebastian Rohlf<sup>(b)</sup>, Kai Rossnagel<sup>(b)</sup>, Felix von Oppen<sup>(a)</sup>, and <u>Katharina Franke<sup>(a)</sup></u>

<sup>(a)</sup> Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany <sup>(b)</sup> Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

The exchange coupling of individual magnetic atoms with the Cooper pairs of a superconducting substrate leads to Yu-Shiba-Rusinov (YSR) bound states inside the superconducting energy gap. Their bound state energy and spatial extent can be probed by scanning tunneling spectroscopy [1]. Chains of magnetic adatoms have attracted particularly strong attention due to the formation of Majorana bound states at their terminations [2].

Here, we investigate individual magnetic atoms on Pb and NbSe<sub>2</sub> substrates. We observe intriguing patterns of YSR states around the adatoms, which are determined by the adatom's d-levels as well as local symmetries of the adsorption potential [3,4]. When the adatoms are sufficiently close, the YSR states hybridize [5], and eventually give rise to YSR bands in atomic chains.

- [1] A. Yazdani, B. A. Jones, C. P. Lutz, M. F. Crommie, D. Eigler, *Probing the Local Effects of Magnetic Impurities on Superconductivity*, Science **275**, 1767 (1997).
- S. Nadj-Perge, I. K. Drozdov, J. Li, H. Chen, S. Jeon, J. Seo, A.H. MacDonald, B. A. Bernevig, A. Yazdani, *Observation of Majorana fermions in ferromagnetic atomic chains on a superconductor*, Science **346**, 602 (2014).
- [3] M. Ruby, Y. Peng, F. von Oppen, B. W. Heinrich, K. J. Franke, *Orbital Picture of Yu-Shiba-Rusinov Multiplets,* Phys. Rev. Lett. **117**, 186801 (2016).
- [4] E. Liebhaber, S. Acero Gonzalez, R. Baba, G. Reecht, B. W. Heinrich, S. Rohlf, K. Rossnagel, Felix von Oppen, Katharina J. Franke, Yu-Shiba-Rusinov States in the Charge-Density Modulated Superconductor NbSe<sub>2</sub>, Nano Lett. **20**, 339 (2020).
- [5] M. Ruby, B. W. Heinrich, Y. Peng, F. von Oppen, K. J. Franke, *Wave-function hybridization in Yu-Shiba-Rusinov dimers*, Phys. Rev. Lett. **120**, 156803 (2018).

# High-throughput modeling and discovery of two-dimensional materials

#### Kristian Sommer Thygesen

#### Department of Physics, Technical University of Denmark (DTU), Denmark

Atomically thin two-dimensional (2D) materials represent a rapidly moving frontier of condensed matter physics. The reduced phase space and low dielectric screening in these extremely thin materials lead to enhanced many-body effects and unique physics, which can be further tuned by external probes or by stacking the 2D materials into van der Waals heterostructures.

In this talk I will show how the electronic and optical properties of 2D materials and their heterostructures can be accurately predicted by combining classical electrostatic models with many-body quantum mechanics. I will discuss novel types of excitonic states in 2D semiconductor heterostructures and illustrate the concept of dielectric band structure engineering, which exploits the dependence of the exciton- and quasiparticle energy on the screened Coulomb interaction [1]. Finally, I will present our recent efforts to establish a comprehensive computational database of 2D materials using an automatic high-throughput framework [2] and demonstrate how it can be used to identify novel 2D materials with interesting physical properties such as ferromagnetism [3] and non-trivial band structure topologies [4].



Fig. 1: The materials in the C2DB are initially generated by decorating an experimentally known crystal structure prototype with atoms chosen from a (chemically reasonable) subset of the periodic table.

- [1] K. S. Thygesen, *Calculating excitons, plasmons, and quasiparticles in 2D materials and van der Waals heterostructures,* 2D Materials **4**, 022004 (2017).
- [2] S. Haastrup et al., *The Computational 2D Materials Database: High-throughput modeling and discovery of atomically thin crystals*, 2D Materials **5**, 042002 (2018).
- [3] D. Torelli, K. S. Thygesen, and T. Olsen, High throughput computational screening for 2D ferromagnetic materials: the critical role of anisotropy and local correlations, 2D Materials 6, 045018 (2019).
- [4] T. Olsen et al., *Discovering two-dimensional topological insulators from high-throughput computations*, Phys. Rev. Mat. **3**, 024005 (2019).

### Nanographenes with intrinsic $\pi$ -magnetism: from molecules to spin chains

#### Roman Fasel

Empa, Swiss Federal Laboratories for Materials Science and Technology, nanotech@surfaces Laboratory, Überlandstrasse 129, 8600 Dübendorf, Switzerland

Topologies of the edge bonds and  $\pi$ -electron network critically influence the electronic structure of polybenzenoid hydrocarbons ('nanographenes'), and may lead to properties that are otherwise absent in the parent material graphene. Among various properties that arise in hydrocarbon compounds due to the chemical versatility of carbon, intrinsic magnetism remains one of the most desirable but also elusive [1].

In this presentation, I will discuss the on-surface synthesis and scanning tunneling microscopy / spectroscopy-based characterization of nanographenes with peculiar structural topologies entailing intrinsic  $\pi$ -magnetism on metal surfaces. In particular, I will present the first experimental realization of Clar's goblet (Fig. 1), an elusive non-Kekulé compound that has been predicted since decades [2]. Magnetism in Clar's goblet arises due to complete topological frustration of the  $\pi$ -electron network, and the predicted antiferromagnetic ground state is confirmed through inelastic spin excitation spectroscopy. Furthermore, I will discuss recent progress towards synthesis of nanographenes with complete zigzag edge topology [3], which represents a distinct route towards inducing magnetism in carbon-based nanomaterials. Presence of unpaired spins renders these structures susceptible to spin quenching, and the controllable switching of magnetic ground state through atomic manipulation will be discussed. While the first approach is based on the covalent interlinking of magnetic nanographenes [4], a promising alternative builds on topological electronic quantum phases in edge-extended graphene nanoribbons [5].



Fig. 1: Left: 3D-rendered highresolution scanning tunneling micrograph of Clar's goblet. The spin excitation process is schematically illustrated, where the lower spin (initially pointing down) is flipped up (blue arrow: spin up, red arrow: spin down). Right: Experimental inelastic electron tunneling spectrum of Clar's

goblet. The peaks in the spectrum (marked by dashed lines) correspond to the threshold energy of 23 meV required for the schematically illustrated spin excitation.

- [1] O.V. Yazyev, Rep. Prog. Phys. **73**, 056501 (2010).
- [2] S. Mishra *et al.*, Nat. Nanotechnol. **15**, 22 (2020).
- [3] S. Mishra *et al.*, submitted (2020).
- [4] S. Mishra *et al.*, arXiv:2003.00753 (2020).
- [5] O. Gröning *et al.*, Nature **560**, 209 (2018).

# Massive step pushing: the growth mechanism of micron-sized single-domain molybdenum disulfide islands on Au(111)

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Molybdenum disulfide ( $MoS_2$ ) is subject of strong interest due to its transformation from an indirect to a direct semiconductor when reducing its thickness to a single layer of  $MoS_2$ , i.e. one triple layer of S-Mo-S. This raises the need for detailed control of the growth when designing possible applications. The Au(111) surface has been established as model substrate for the growth of  $MoS_2$  on Au(111). Using molecular beam epitaxy, the growth has been reported to proceed by the formation of large  $MoS_2$  areas [1,2].

Here, we present an in-situ low-energy electron microscopy (LEEM) study of the growth of  $MoS_2$  at high temperatures between 700°C and 750°C. These conditions lead to the formation of  $\mu$ m-sized single-layer  $MoS_2$  islands. The growth of the  $MoS_2$  islands leads to a progressive pushing of the Au steps leading to an expansion of the Au terrace on which the island resides. This process is accompanied by a massive rearrangement of the Au surface. The single-domain character of the  $MoS_2$  islands is demonstrated by microdiffraction and dark-field LEEM imaging allowing to quantify the relative coverage of the two mirror domains of  $MoS_2$ . Selected area angle-resolved photoelectron spectroscopy directly confirms the threefold symmetric of the electronic bandstructure of the  $MoS_2$  domains. Additionally, partial bilayer nucleation at higher  $MoS_2$  coverage can be identified by I(V)-LEEM measurements. Factors favoring the growth of one of the two mirror domains are identified by using two distinctly different deposition rates, enabling the growth of single-domain single-layer  $MoS_2$ .



Fig. 1: LEEM images at 16 eV of a growing MoS<sub>2</sub> island at 700°C.

- [1] J.A. Miwa, S. Ulstrup, S. G. Sørensen, M. Dendzik, A. Grubišić Čabo, M. Bianchi, J. V. Lauritsen, and P., *Electronic structure of epitaxial single-layer MoS*<sub>2</sub>, Phys. Rev. Lett. **114**, 046802A (2015).
- H. Bana, E. Travaglia, L. Bignardi, P. Lacovig, C.E. Sanders, M. Dendzik, M. Michiardi, M. Bianchi, D. Lizzit, F. Presel, D. De Angelis, N. Apostol, P.K. Das, J. Fujii, I. Vobornik, R. Larciprete, A. Baraldi, P. Hofmann, and S. Lizzit, *Epitaxial growth of single-orientation high-quality MoS*<sub>2</sub> monolayers, 2D Mater. 5, 35012 (2018).

# Epitaxial growth of monolayer MoS<sub>2</sub> on SrTiO<sub>3</sub> single crystal substrates

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Monolayer molybdenum disulfide (MoS<sub>2</sub>) crystals grown on amorphous substrates such as SiO<sub>2</sub> are randomly oriented [1]. However, when MoS<sub>2</sub> is grown on crystalline substrates, the crystal shapes and orientations are also influenced by their epitaxial interaction with the substrate [2]. In this paper, we present the results from chemical vapor deposition growth of MoS<sub>2</sub> on three different terminations of single crystal strontium titanate (SrTiO<sub>3</sub>) substrates. On SrTiO<sub>3</sub>(111), the monolayer MoS<sub>2</sub> crystals form equilateral triangles with two main orientations, in which they align their  $<2\overline{11}0>$ -type directions (i.e., the sulfur-terminated edge directions) with the  $<1\overline{1}0>$ -type directions on SrTiO<sub>3</sub>. This arrangement allows nearperfect coincidence epitaxy between seven MoS<sub>2</sub> unit cells and four SrTiO<sub>3</sub> unit cells. On SrTiO<sub>3</sub>(110), the MoS<sub>2</sub> crystals tend to align their edges with both the  $<1\overline{1}0>$  and  $<1\overline{1}\overline{2}>$ directions on SrTiO<sub>3</sub> as these both provide favorable coincidence lattice registry. This distorts the crystal shapes and introduces an additional strain detectable by photoluminescence (PL). When triangular MoS<sub>2</sub> crystals are grown on SrTiO<sub>3</sub>(001), they again show a preference to align their edges with the  $<1\overline{1}0>$  directions on SrTiO<sub>3</sub>. Our observations can be explained if the interfacial van der Waals (vdW) bonding between MoS<sub>2</sub> monolayers and SrTiO<sub>3</sub> is greatest when maximum commensuration between the lattices is achieved. Therefore, a key finding of this paper is that the vdW interaction between MoS<sub>2</sub> and SrTiO<sub>3</sub> substrates determines the supported crystal shapes and orientations by epitaxial relations. Controlled crystal orientations make the growth of large sheets of MoS<sub>2</sub> possible when there are multiple nucleation sites. This minimizes the number of grain boundaries and optimizes electronic properties of the material, e.g., charge mobility, which is crucial for the application of monolayer MoS<sub>2</sub> in next-generation nanoelectronic devices.



Fig. 1: SEM image, atomic model, and PL spectrum of MoS<sub>2</sub> monolayers on SrTiO<sub>3</sub>(111).

- [1] S. Wang, Y. Rong et al., Chem. Mater. 26, 6371 (2014).
- [2] Q. Ji, M. Kan et al., Nano Lett. 15, 198 (2015).

### In-situ surface investigation of low-dimensional organic/inorganic materials synthesized on metal substrates

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The synthesis and study of low-dimensional materials represents a flourishing research activity for future nanotechnology applications. Great effort has been devoted to enriching the family of 2D materials beyond graphene, e.g. investigating 2D transition metal dichalcogenides (TMD) like MoS<sub>2</sub> and WS<sub>2</sub>, or theoretically studying novel low-dimensional carbon allotropes based on sp-sp<sup>2</sup> hybridization, like graphyne and graphdiyne. Moreover, combining different low-dimensional materials, both organic and inorganic, to form mixed-dimensional van der Waals heterostructures (vdWH) tremendously increases the possibility to design novel systems with tailored properties [1].

In our work, we adopted a Surface Science approach to synthesize and characterize lowdimensional organic/inorganic materials supported by metal substrates (Au and Ag). We mostly used Scanning Tunneling Microscopy (STM) to investigate in-situ the morphological, structural and electronic properties at the nano- and atomic scale. Our synthesis approach exploited the combination of different deposition techniques in the same ultra-high vacuum system: we used Pulsed Laser Deposition (PLD) to produce single-layer nanocrystals of MoS<sub>2</sub> and WS<sub>2</sub> and to study their growth from sub-monolayer to complete monolayer coverage of the substrate surface [2], while we synthesized atomically thin sp-sp<sup>2</sup> carbon structures on the Au(111) surface by depositing brominated molecular precursors [3]. In-situ STM/STS investigation was complemented by Raman spectroscopy, which is very sensitive to the vibrational properties of the synthesized materials. The exploration of these synthesis methods set the basis for the study of vdWH heterostructures between different materials. By tuning PLD parameters, we could study the growth of MoS<sub>2</sub>/WS<sub>2</sub> heterostructures, while, by combining PLD with organic molecular beam epitaxy, we observed at the molecular scale the formation of a mixed-dimensional vdWH between pentacene and MoS<sub>2</sub>, forming welldefined in-plane heterointerfaces.

This work enriches the surface science of low-dimensional TMD and sp-sp<sup>2</sup> carbon allotropes and set the basis for the nano-scale study of mixed-dimensional vdWH between organic and inorganic nanomaterials.

- [1] D. Jariwala, T.J. Marks, and M.C. Hersam, *Mixed-dimensional van der Waals heterostructures*, Nature Materials **16**, 170 (2017).
- [2] F. Tumino et al., *Pulsed laser deposition of single-layer MoS2 on Au (111): from nanosized crystals to large-area films*, Nanoscale advances **1**, 643 (2019).
- [3] A. Rabia et al., Scanning tunneling microscopy and Raman spectroscopy of polymeric sp–sp2 carbon atomic wires synthesized on the Au(111) surface, Nanoscale **11**, 18191 (2019).

# Structural dynamics in atomic wire systems studied by ultrafast-RHEED: excitation, metastable states and relaxation

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The assembly of single atoms into wires has attracted a lot of attention, because of inherent peculiar properties like anisotropic conductivity, intrinsic electronic and structural instabilities. Such atomic wires can be realized by self-assembly through the adsorption of metal atoms both on vicinal or well-oriented Si surfaces.

Here we present results on the structural dynamics in the prototypical atomic wire system, i.e., the (4×1) reconstructed In atomic wires on a well oriented Si(111) surface which undergoes a Peierls like symmetry breaking at  $T_c = 130$  K. During this first order structural phase transition the system doubles the periodicity along and perpendicular to the wires resulting in a (8×2) reconstructed ground state [1]. The structural dynamics of these wires upon impulsive excitation by fs-IR laser pulses is probed through ultra-fast time resolved electron diffraction at a temporal resolution of 350 fs [2,3]. The optical excitation results in a non-equilibrium population of the electronic surface states which causes transient changes of the atomic wires to the (4×1) excited state is driven in only 700 fs [4,5].

Transient heating of the In atoms from 30 to 60 K occurs delayed at 6 ps [6]. Thus, the phase transition is driven by electronic entropy and not thermally. An energy barrier for the atoms collective motion from the excited (4×1) state to the (8×2) state hinders the immediate recovery of the ground state: the In layer remains for many nanoseconds in a super cooled metastable (4×1) state, which is not accessible under equilibrium conditions. The relaxation into the (8×2) ground state happens through the nucleation of the (8×2) at pre-existing defects like adsorbates [7,8] or step edges [9] which then trigger a recrystallization front. This front propagates 1-dimensionally at a speed of ~100 m/s as determined from a correlation of the step morphology to recovery time constant [9].

- [1] F. Klasing et al., Phys. Rev. B 89, 121107(R) (2014)
- [2] A. Janzen et al., Rev. Sci. Inst. 78, 013906 (2007)
- [3] T. Frigge, B. Hafke, T. Witte, C. Brand, M. Horn-von Hoegen, Rev. Sci. Inst. 90, 045119 (2019))
- [4] T. Frigge et al., Nature 544, 207 (2017)
- [5] C.W. Nicholson et al., Science **362**, 821 (2018)
- [6] T. Frigge, B. Hafke, T. Witte, B. Krenzer, M. Horn-von Hoegen, Struct. Dyn. 5, 025101 (2018)
- [7] S. Wall et al., Phys. Rev. Lett. **109**, 186101 (2012)
- [8] T. Frigge et al., Phys. Rev. Lett. 111, 149602 (2013)
- [9] B. Hafke, T. Witte, T Frigge, D. Janoschka, P. Dreher, M. Horn von Hoegen, Struct. Dyn. 6, 045101 (2019)

# Coherent vibrational control of a structural phase transition in a solid-state surface system

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The use of laser pulses to actively steer a system along the transition pathway from a reactant towards a product state far from equilibrium, is a fundamental scheme in the field of femtochemistry. Transferring this concept to solid-state surface systems requires the ultrafast manipulation of coherent phonons, associated with the reaction coordinate. In this context, metal-insulator transitions are generally an important target for optical manipulation, exhibiting dramatic and ultrafast changes of the electronic and lattice properties. Here, we demonstrate coherent vibrational control over the Peierls metal-to-insulator phase transition of In/Si(111). Tailored pulse sequences are used to drive the system from the insulating to a metastable metallic state, and the corresponding structural changes are monitored by ultrafast low-energy electron diffraction. We observe strong oscillations in the switching efficiency as a function of pulse delay and identify two key structural modes governing the transition. Finally, we demonstrate selective excitation of these modes and explore the potential energy surface spanned by the amplitude modes of the system.



Fig. 1: (a) Experimental scheme of the ultrafast LEED experiment to monitor the microscopic structure of atomic indium wires on the Si(111) surface after optical excitation with multiple pulses. (b) Delaydependent relative switching efficiency with one (blue) and two (green) first weak pulses (red) and corresponding Fourier transform.

## Electrode structure movies: high-energy surface x-ray diffraction for in situ electrochemistry

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The importance of electrode surface structure in electrochemistry is well established. There is a complex interplay of defects, steps-edges, atomic coordination, electronic effects and stress/strain that hinders our complete understanding of electrode reactions. One effective way to study these problems is to use well-defined single crystal model electrodes to isolate how differences in the electrode structure affect the reaction of interest.

In this talk, results showing how recent advances in high-energy surface X-ray diffraction can be used to rapidly probe electrode surface structures in situ are presented. Measurement of the Au(111) surface in 0.1 M perchloric acid are presented, where the lifting and reforming of the herringbone reconstruction can be observed both out-of-plane and in-plane through the computation of LEED-like in-plane maps. Simultaneous CTR profiles are collected, allowing the dynamics of the electrode structure to be observed in exquisite detail. Furthermore, we combine our measurements with 2D surface optical reflectance to show how this relatively inexpensive technique can be used to monitor electrode roughness in the laboratory.



Fig. 1: LHS – Concept Image of HESXRD from reconstructed Au (111) surface. RHS – Measured diffraction pattern showing the scattering from the single atomic layer surface reconstruction (right streak in inset).

# Microscopic details of switching a ferroelectric surface observed by operando photoelectron diffraction

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The control of the electron spin in functional materials by an external electric field is a key issue for spintronic devices. Because the spin is not directly influenced by a realistic electric field, the coupling has to be indirect and, thus, especially ferroelectric and multiferroic materials bear large promise. Switching the spin polarization using magnetic or electric fields has recently been demonstrated in thin films of multiferroic (Mn,Ge)Te [1-4]. The presence of surface-related bands and resonances in the valence spectrum points out that the surface plays an important role in the switching and the stability of the ferroelectric polarization.

In this contribution, we use synchrotron-based photoelectron diffraction to study the atomic details of the surface structure of rhombohedral  $\alpha$ -GeTe(111) in an operando setup under an applied electric field. Atomic layer positions are determined from angle and energy scans of the Ge and Te core level photoelectron peaks to a depth of six atomic layers below the surface. In bulk GeTe, the electric polarization arises from a substantial sub-lattice shift induced by the directional nature of the covalent bonds. At the surface, however, we find a significant polarization-dependent relaxation the structure of which deviates from the truncated bulk structure. Below the surface, the local structure resembles the one of the non-polar, cubic  $\beta$ -GeTe, which indicates the presence of a domain wall directly below the surface. Upon cycling the external field, we observe the relative displacement of the individual layers.

- J. Krempaský et al., Disentangling bulk and surface Rashba effects in ferroelectric α-GeTe, Phys. Rev. B 94, 205111 (2016).
- [2] J. Krempaský et al., Entanglement and manipulation of the magnetic and spin-orbit order in multiferroic Rashba semiconductors, Nature Comm. **7**, 13071 (2016).
- [3] J. Krempaský et al., Phys. Rev. X, Operando Imaging of All-Electric Spin Texture Manipulation in Ferroelectric and Multiferroic Rashba Semiconductors, **8**, 021067 (2018).
- [4] J. Krempaský et al., Spin-resolved electronic structure of ferroelectric  $\alpha$ -GeTe and multiferroic  $Ge_{1-x}Mn_xTe$ , J. Phys. Chem. Solids **128**, 237 (2019).

# Three-dimensional atomic-resolution holography and effective two-dimensional analyzer for photoelectron holography

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An investigation of 3D atomic structure around local specific atoms with no translational symmetry has been impossible. However recent development of atomic-resolution holography such as photoelectron holography enabled such analysis [1]. Hence we started a new project [2]. One result of analysis for high-concentration As-dopants in Si is shown in Fig. 1 [3]. The highest, middle, and lowest binding-energy chemically-shifted components in XPS spectrum were revealed to be the As at the substitutional site, slightly shifted from the substitutional site due to a vacancy next to this As, and that in the interstitial site, respectively.

In order to obtain photoelectron hologram it is required to measure  $2\pi$  sr angular distribution of core-level photoelectrons from specific atoms at around 700 eV kinetic energy. So far we have used a display-type spherical mirror analyzer called DIANA [4] which can display the angular distribution of  $1\pi$  sr at once. Because the energy resolution of DIANA is not high enough to separate core-level chemical shift, we have developed DELMA (display-type ellipsoidal mesh analyzer) [5] by combining a wide acceptance angle electrostatic lens (WAAEL) [6] and a commercial analyzer (R4000 from VG-Scienta Co.). Although the energyresolution is high enough, the scanning time is long. Hence we are developing a third analyzer Compact-DELMA [7] which is shown in Fig. 2. This system can display the angular distribution of 0.01%.



Fig. 1: (a) As 3d XPS spectrum, (b) Holograms, and (c) Revealed structures of each component [3].

Fig. 2: Compact DELMA [7].

- [1] H. Daimon, Jpn. J. Appl. Phys. **59**, 010504 (2020). https://doi.org/10.7567/1347-4065/ab5f48
- [2] URL: http://www.en.3d-activesite.jp/
- [3] K. Tsutsui et al., Nano Letters, **17**, 7533 (2017).
- [4] H. Daimon, Rev. Sci. Instrum. **59**, 545 (1988).
- [5] H. Matsuda et al., J. Electr. Spectr. Relat. Phenom. 195, 382 (2014).
- [6] H. Matsuda, H. Daimon, M. Kato and M. Kudo, Phys. Rev. E **71**, 066503 (2005).
- [7] H. Matsuda, L. Tóth, and H. Daimon, Rev. Sci. Instrum. 89, 123105 (2018).

### Oxygen on Rh(100) - when surface dynamics fakes symmetry

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Thermal activation of a long-range ordered adsorbate phase must not necessarily lead into a disordered phase, it can also break up into heavily fluctuating ordered domains. Temporal and/or spatial averaging over these fluctuations may pretend both a wrong periodicity and a false local symmetry. This can happen even below liquid-nitrogen temperature, so that the true nature of the phase might remain undetected. We demonstrate this scenario at the catalytically active Rh(100) surface covered by 1/2 monolayer (ML) of oxygen, which is known to induce a clockwise-anticlockwise reconstruction of the Rh top layer [1,2].

By a concerted application of variable-temperature STM and DFT we find theoretically and in experiment (at 6 K) a so far unknown ground state structure with  $c(4\times4)$  periodicity and fourfold rotational axis as the only symmetry element (p4). At 77 K and above, in contrast, STM as well as LEED show the well-known (2×2) pattern with two additional glide planes (p4g) [1]. By a high-precision LEED intensity analysis (Pendry R-factor R = 0.072) we prove that this state still exhibits the  $c(4\times4)$ -40 structure locally and verify in detail the structural model predicted by DFT. On a larger scale, the structure is broken up into a multitude of antiphase and mirror domains (diameter  $\approx 20$  Å), all of them strictly coupled spatially via the rigid substrate reconstruction. Thus, the *coherent* superposition of their scattering contributions leads to both the extinction of quarter-order spots and the pretense of glide symmetry. Atomic hopping rates at domain boundaries in the MHz range (estimated from DFT) lead to fast spatial domain fluctuations below the STM tip so that a time-average is imaged again with wrong symmetry. By that we resolve long-standing and seemingly unbridgeable inconsistencies concerning the true symmetry and local atomic structure of this O/Rh(100) phase [1,2].



Fig. 1: (a) STM image (6 K) with overlaid DFT simulation and (b) ball model of the c(4×4)-4O ground state. (c) STM appearance (77 K) as (2×2)-p4g and (d) LEED pattern (100 K).

- [1] A. Baraldi, J. Cerdá, J. A. Martín-Gago, G. Comelli, S. Lizzit, G. Paolucci, and R. Rosei, Phys. Rev. Lett. **82**, 4874 (1999).
- [2] D. Alfè, S. de Gironcoli, and S. Baroni, Surface Science **437**, 18 (1999).

### One step towards popularizing LEED-IV

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The quantitative modelling of the intensity of LEED spots as a function of the electron energy (LEED IV) is an exceptionally powerful technique to solve the atomic-scale structure of wellordered single-crystalline surfaces. As opposed to the qualitative information offered by comparing experimental STM images with their DFT-simulated counterparts, LEED-IV provides a direct, quantitative measure of the agreement between experimental data and the corresponding structural model. LEED-IV is also particularly attractive as its experimental realization is relatively straightforward, as long as a standard LEED is available. And yet, LEED-IV is rarely used nowadays. One possible reason is that the well-established programs for calculating I(V) curves and fitting structural parameters to achieve the best agreement with experimental data (e.g., TensErLEED [1]) present a high entry barrier for novices.

To make the prowess of LEED-IV accessible to the broad community, we have developed a new software package that allows (i) automated data acquisition and processing; (ii) generation of the input necessary to TensErLEED, based on a few parameters and a structure input compatible with the standard results of DFT calculations; (iii) smart detection of convergence of the fit that can be used to help pursuing the structural optimization.

I will show how the package can be used to solve the structure of a few selected surfaces, including some whose models have been previously established, as well as a few more exotic examples.

#### References

[1] V. Blum, K. Heinz, Computer Physics Communications **134**, 392 (2001).

### Unravelling transition metal chalcogenides one layer at a time

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Monolayers of van der Waals layered materials have become one of the most studied fields of surface science over the last decade. Much of this work has focused around graphene and hexagonal boron nitride. These monolayer films are only a single atomic layer thick, and thus lend themselves well to structure determination by normal incidence X-ray standing waves (NIXSW), and such studies have provided significant insight into the physical interactions of these monolayers with the underlying substrate[1-2]. However, in recent years transition metal chalcogenides, particularly dichalcogenides, have come to the fore. Due to the wide variety of possible combinations of the metal and chalcogenide, these materials can exhibit a wide variety of interesting electronic properties[3-4]. Yet a monolayer of these materials, as shown schematically in Fig. 1, typically consists of three atomic layers - specifically a layer of metal atoms sandwiched between two chalcogenide layers. Thus, while NIXSW can be used to directly probe the adsorption height of the metal layer, it is generally not possible to separate the contributions from the two chalcogenide layers. Energy scanned photoelectron diffraction (PhD), however, is well suited to this task. Due to the strong dependence of PhD on backscattering, and the comparatively large scattering cross-section from both the metal and chalcogenide layers, the intralayer structure can be directly probed. By the combination of these two techniques we can gain insight into both the height of the whole layer above the substrate as well as the internal structure of the monolayer.



Fig. 1: Schematic of the tri-layer structure of a transition metal dichalcogenide monolayer.

- [1] J. Sforzini et al., *Physical Review Letters*, **114**, 106804 (2015).
- [2] M. Schwarz et al., ACS Nano, **11**, 9151 (2017).
- [3] J. Zhou, *Nature*, **556**, 355 (2018).
- [4] S. Tan, Nature Materials, **12**, 634 (2013).

## Chemical decoupling of graphene from the Ni(111) surface by intercalation of the heavy metal Pb

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In the last decade, graphene and other 2D honeycomb materials have emerged as highly promising materials to reduce the size of the functional layers of spintronic assemblies to the nanometer limit. So far, however, graphene was mainly employed as passive element in such assemblies due to its lack of intrinsic spin functionalities.

One way to overcome this limitation is chemical functionalization, for instance, by hybridization of the graphene layer with ferromagnetic surfaces or by intercalation of heavy metal atoms. In this project, we studied the modifications of a graphene sheet on the magnetic Ni surface upon intercalation of the heavy metal Pb using static and time-resolved momentum-resolved photoemission and NIXSW.

We show that the strong hybridization between the graphene layer and the Ni(111) surface is significantly reduced by the intercalation of Pb. In particular, the Dirac cone of the intercalated graphene/Ni interface exhibits all signatures of quasi-freestanding graphene: it exhibits a linear dispersion around the Dirac point, which is located at the Fermi level (see Fig. 1). These signs for a chemical decoupling of graphene from Ni are also reflected in the vertical adsorption geometry. In NIXSW, we find a significant increase of the vertical bonding distance between graphene and the Ni surface upon intercalation of Pb as illustrated in Fig. 1. Similarly, the chemical decoupling of graphene also affects the hot electron dynamics of the graphene/Ni interface upon Pb intercalation.

In this way, our study clearly shows that heavy metal intercalation is a highly promising approach to alter and control the charge and spin carrier functionalities of 2D honeycomb materials on surfaces.



*Fig. 1: Band structure and vertical adsorption geometry of the graphene (gr) Ni interface after the intercalation with Pb atoms.* 

### Strain induced band gap modulation in 2D semiconductor

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A strain-induced band gap modification of 2D materials, which affects directly on their electronic and opto-electronic properties, plays an important role in the development of future quantum devices. However, an atomic-scale understanding of how strain affects the electronic properties remains challenging due to its technical limitations. Here, we investigated strain-induced charge localization and quantum confinement in monolayer MoS<sub>2</sub> on a SiO<sub>2</sub>/Si substrate using a gate-tunable home-built scanning tunneling microscope at ~4.9 K. Monolayer MoS<sub>2</sub> follows surface roughness of the substrate, which exhibits a bending strain with band gap reduction. This band gap reduction at a local regime acts like a potential well leading to charge localization. When the bending strain in MoS<sub>2</sub> is larger than 2 % at a local region of ~4 nm, quantum-confined energy levels are observed near the conduction or valence band edge due to the significant band gap reduction of ~1 eV. We observed a spatial flattening of the conduction (valence) band edge occurs by heavy electron- (hole-) doping. Moreover, we will present a motor-based strain controller, which enabled us to apply uniaxial bending strain in atomic precision.

# Unveiling the role of Sr atoms in a Sr<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub> topological superconductor

<u>You-Ron Lin</u><sup>(a,b,\*)</sup>, François C. Bocquet<sup>(a,b)</sup>, Serguei Soubatch<sup>(a,b)</sup>, Mahasweta Bagchi<sup>(c)</sup>, Jens Brede<sup>(c)</sup>, Yoichi Ando<sup>(c)</sup>, F. Stefan Tautz<sup>(a,b)</sup>, and Christian Kumpf<sup>(a,b)</sup>

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The topology of superconducting states is not only of fundamental interest but also of significant technological importance as the interface of a topological superconductor can sustain Majorana quasiparticles [1]. Majorana modes are suggested as potential building blocks for a quantum computer and are placed therefore in the focus of intense research efforts at present [2].

The topological character of the superconducting state of  $Sr_xBi_2Se_3$  is well established [3, 4]. This material is considered to be an archetypical topological superconductor. Nonetheless, the exact chemical and electronic state of the Sr-atoms incorporated in  $Bi_2Se_3$  matrix remains unclear so far. This makes interpretation of topological properties of this material challenging. Here, we propose a structural model for  $Sr_xBi_2Se_3$ , in particular revealing the vertical position of strontium, based on the normal incidence x-ray standing wave technique.

- M. Sato and Y. Ando, *Topological superconductors: a review*, Rep. Prog. Phys., **80**, 076501 (2017).
- [2] S. Das Sarma *et al., Majorana zero modes and topological quantum computation*, npj Quantum Information, **1**, 15001 (2015).
- [3] Z. Liu et al., Superconductivity with topological surface state in Sr<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub>, JACS 137, 10512 (2015).
- [4] V. K. Shruti *et al., Superconductivity by Sr intercalation in the layered topological insulator Bi*<sub>2</sub>*Se*<sub>3</sub>, Phys. Rev. B, **92**, 020506 (2015).

SPM techniques I, Wednesday, May 6, 8:45, Invited talk

# Electronic quantum materials simulated with artificial model lattices

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In a visionary colloquium nearly sixty years ago, Richard Feynman proposed to study complex and elusive quantum systems using more controllable analogues, an approach known as quantum simulation [later published, 1]. Quantum simulators based on ultra-cold atoms, nanophotonics, trapped ions, and superconducting circuits have been developed and successfully applied to study a host of different phenomena [2]. In contrast, electronic quantum simulators have been lacking behind.

In this talk, I will demonstrate that electron gases on well-defined metal surfaces form an excellent platform for quantum simulation. By patterning the surface with atomic scale precision using a scanning tunneling microscope, the electrons can be corralled into artificial lattices of nearly any geometry. The same microscope can then be used to measure the local density of states at all positions of interest and to probe the spatial extend and shape of the electronic states. I will show several examples of how we exploit the tunability of this platform. Particular emphasis will be given to our recent efforts to create and study topological insulators.

- [1] R. P. Feynman, Simulating physics with computers, Int. J. Theo. Phys. **21**, 467 (1982).
- [2] Nature Physics Insight Quantum Simulation, Nat. Phys. 8, 263 (2012).

### Designer electronic states in atomic lattices and hybrid 2D system

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There has been a surge of interest in designer materials that would realize electronic responses not found in naturally occurring materials. I will discuss this approach using examples based on atomic manipulation by the tip of a scanning tunneling microscope (STM), and direct growth of heterostructures of 2D materials. Using atomic manipulation, it is possible to construct lattices where every atom is in a well-defined, predetermined position. This opens possibilities for creating artificial materials and I will illustrate this concept by showing how chlorine vacancies on Cu(100) [1] can be used to implement various one-dimensional lattices with topological domain wall states and engineered band structures with flat bands [2,3].

In the second part of the talk, I will focus on designer van der Waals (vdW) heterostructures, where the desired physics emerges from the engineered interactions between the different components. Molecular-beam epitaxy growth allows the construction of vertical heterostructures with clean and high-quality interfaces [4]. Combining 2D ferromagnetism with superconductivity allows the realization of topological superconductivity and we characterize the resulting one-dimensional edge modes using low-temperature STM. The use of vdW heterostructures with uniform and high-quality interfaces allows straightforward integration into device structures and potential further control through external stimuli (e.g. electrostatic gating).

- [1] F.E. Kalff, M. P. Rebergen, E. Fahrenfort, J. Girovsky, R. Toskovic, J. L. Lado, J. Fernández-Rossier, A. F. Otte, *A kilobyte rewritable atomic memory*, Nat. Nanotechnol. **11**, 926 (2016).
- [2] R. Drost, T. Ojanen, A. Harju, P. Liljeroth, *Topological states in engineered atomic lattices*, Nat. Phys. **13**, 668 (2017).
- [3] M.N. Huda, S. Kezilebieke, T. Ojanen, R. Drost, P. Liljeroth, *Tuneable topological domain wall states in engineered atomic chains*, arXiv:1806.08614.
- S. Kezilebieke, M. N. Huda, P. Dreher, I. Manninen, Y. Zhou, J. Sainio, R. Mansell, M.M. Ugeda,
   S. van Dijken, H.-P. Komsa, P. Liljeroth, *Electronic and Magnetic Characterization of Epitaxial* VSe<sub>2</sub> Monolayers on Superconducting NbSe<sub>2</sub>, arXiv:1909.10208.
- S. Kezilebieke, M. N. Huda, V. Vaňo, M. Aapro, S.C. Ganguli, O.J. Silveira, S. Głodzik, A.S. Foster,
   T. Ojanen, P. Liljeroth, *Topological superconductivity in a designer ferromagnet-superconductor* van der Waals heterostructure, arXiv:2002.02141.

## Active sites in solid and liquid surface catalysis

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Scaling relations between the adsorption energies of surface intermediates and their transition states allow for a rapid screening of potential catalyst materials and have greatly contributed to our trend understanding of the reactivity of transition metals and their alloys [1]. Typically, only a minimal number of possible active site motifs are considered, since a separate scaling relation needs to be established for every different site (e.g. terrace or step

top, bridge, three- and four-fold sites, see Fig. 1). We used compressed sensing methods to identify new low-cost and accurate descriptors that allow to predict adsorption energies at all potential surface sites simultaneously, and thereby also the most stable geometry [2]. The descriptors are expressed as non-linear functions

of intrinsic properties of the clean catalyst surface, e.g. coordination Fig. 1: Adsorption sites of numbers and *d*-band moments. I will discuss active sites at both the fcc(211) facet. transition metal, oxide, and carbide catalysts as well as applications in the screening for improved methanation catalysts.

Modeling the active site is even more challenging when the catalytic material is present in the liquid state, which is the case for the recently discovered liquid Cu catalyst for highquality graphene synthesis [3]. I will discuss two approaches to tackle this challenge. On the one hand we carried out an *ab initio* thermodynamics study to assess the stability of a wide range of hydrocarbon adsorbates under various reaction conditions (temperature, methane and hydrogen pressures) used in experimental graphene growth protocols at solid and liquid

Cu surfaces [4]. This gives insight into the stable intermediates as well as the role of the hydrogen content during synthesis for the relative stability of hydrogen-passivated versus pure carbon clusters. Subsequently, we performed molecular dynamics (MD) simulations using both ab initio and semiempirical methods to characterize the structural and electronic properties of the liquid Cu / graphene interface (see Fig. 2) [5]. Fig. 2: MD snapshot of The results are used to rationalize the experimentally observed micrometer-range self-alignment of graphene flakes on liquid Cu [2].



graphene flake on liquid Cu.

- J. K. Nørskov, F. Abild-Pedersen, F. Studt, and T. Bligaard, Density functional theory in surface [1] chemistry and catalysis, Proc. Natl. Acad. Sci. U.S.A. 108, 937 (2011).
- [2] M. Andersen, S. Levchenko, M. Scheffler, K. Reuter, Beyond scaling relations for the description of catalytic materials, ACS Catal. 9, 2752 (2019).
- D. Geng et al., Uniform hexagonal graphene flakes and films grown on liquid copper surface, [3] Proc. Natl. Acad. Sci. U.S.A. 109, 7992 (2012).
- M. Andersen, J.S. Cingolani, K. Reuter, Ab initio thermodynamics of hydrocarbons relevant to [4] graphene growth at solid and liquid Cu surfaces, J. Phys. Chem. C 123, 22299 (2019).
- [5] J.S. Cingolani, M. Andersen, K. Reuter (in preparation).
# Two-dimensional 2D materials interfacing liquid water: the new frontier from ab initio simulations

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To date basal planes of 2D materials like graphene (G) and hexagonal boron nitride (BN) are considered inert in aqueous conditions. However recent ionic transport experiments have unveiled a considerable electrification of the water-BN surfaces [1], with a contrasting response for its water-G homologue [2]. This surface charging increasing with pH was conjectured to originate in the differential hydroxide adsorption at the surface of these twin materials, but the considerable challenge of simulating the hydroxide ion in liquid water has precluded a proper explanation up to now.

In this talk I will first show by means of Ab Initio Molecular Dynamics (AIMD) that *pristine* 2D materials do strongly interact with the hydroxide ion in liquid water. We highlight a strong (covalent) chemisorption of the OH<sup>-</sup> anion on BN, while the OH<sup>-</sup> ion is only physisorbed on the G layer [3]. Seconds, I will extend the scope of water reactivity to *activated* 2D materials, like graphene oxide GO surfaces. We indeed explore with AIMD the properties of various GO models in neutral water. This unveils a number of key results: clustering of oxygen functions are more stable; GO is not chemically inert but its reactivity with water results in a negative surface charging – fully consistent with experimental results – , as well as several reactive processes (acid/base reactions, ring-opening of epoxides, dehydration, ...); unexpectedly fast water dynamics in the GO slits, in spite of the hindering hydrophilic groups [4].

In spite of their difficulty, quantum dynamics insights open unprecedented avenues for the use of 2D materials for nanofluidics [5].

This work has been performed in local collaboration with B. Grosjean, F. Mouhat, R. Vuilleumier and also with F.X. Coudert from Chimie Paris Tech, Paris.

- [1] A. Siria et al., *Giant osmotic energy conversion measured in a single transmembrane boron nitride nanotube*, Nature **494**, 455 (2013).
- [2] E. Secchi et al., Scaling Behavior for Ionic Transport and its Fluctuations in Individual Carbon Nanotubes, Phys. Rev. Lett. **116**, 154501 (2016).
- [3] B. Grosjean, M.-L. Bocquet, R. Vuilleumier, Versatile electrification of two-dimensional nanomaterials in water, Nat. Comm. **10**, 1656 (2019).
- [4] F. Mouhat, F.X. Coudert, M.-L. Bocquet, Structure and Chemistry of Graphene Oxide in Liquid Water from First Principles, arXiv preprint arXiv:1911.04987, in revision (2020).
- [5] A. Siria, M.-L. Bocquet, L. Bocquet, New avenues for the large-scale harvesting of blue energy, Nat. Rev. Chem. **1**, 0091 (2017).

### Probing topologically protected 1D states in 2D Dirac materials

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The quantum state of matter of a two-dimensional Dirac material with a buckled honeycomb lattice can be tuned by an electric field. In the absence of an external electric field the material is a topological insulator owing to the spin-orbit coupling, which opens a band gap at the K and K' points of the Brillouin zone. The size of this band gap decreases with increasing electric field until eventually the band gap completely closes at a critical electric field  $E_c$  and the material becomes a semi-metal. For electric fields exceeding  $E_c$  the band gaps reopens again and the material undergoes a topological phase transition from a semi-metal to a normal band insulator. Here we show how scanning tunneling microscopy can be employed to simultaneously apply an electric field and study the electronic structure of the material. The electric field applied by the scanning tunneling microscope offers the possibility to locally alter the quantum state of matter of two-dimensional topological insulator normal band insulator. This results in the development of one-dimensional topologically protected spin polarized edge states *within* the material. Here I present a spectroscopic method to probe these one-dimensional topologically protected states.

### Inducing magnetism in graphene nanoribbons by chemical doping

#### Aran Garcia-Lekue

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Graphene nanoribbons (GNRs) constitute a novel platform for carbon-based electronics. Moreover, the atomically precise bottom-up shaping of GNRs is now possible by on-surface synthesis methods, which unite the sturdiness of covalently bonded networks with the easy tunability of molecular materials.[1] This unprecedented level of control of the overall lattice and chemical structure has given rise to the exploration of novel features in GNRs, such as magnetic properties and topological phases.[2,3]

Using density functional theory (DFT), and in close collaboration with our experimental colleagues, we have investigated the emergence of magnetism in GNRs substitutionally doped with boron atoms.[4] In first place, we explore the spin texture induced by several boron dimers in a 7-armchair GNR. Our calculations reveal that, for a single boron dimer, a parallel spin configuration between doping sites is clearly favored. When a second dimer is placed nearby, an antiferromagnetic effective interaction between neighboring sites emerges, altering the net spin-polarization of the ribbon. Subsequently, we expand our study to width-modulated GNRs, focusing on the influence of the dopant concentration and location.



Fig. 1: DFT simulation of the magnetization of a 7-armchair GNR with two boron dimers.

- [1] M. Corso et al., *Bottom-up fabrication of atomically precise graphene nanoribbons* in "Onsurface synthesis II". Springer 2018.
- [2] D. J. Rizzo et al., *Topological band engineering of graphene nanoribbons*. Nature **560**, 2094 (2018).
- [3] O. Gröning et al., *Engineering of robust topological quantum phases in graphene nanoribbons*. Nature **560**, 209 (2018).
- [4] N. Friedrich et al., (submitted).

# Magnetic anisotropy switching and chiral spin textures in ultrathin Pt/Co/graphene heterostructures

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The Dzyaloshinskii-Moriya interaction (DMI) has its origin in the spin-orbit correction of the Heisenberg exchange interactions. It is an antisymmetric exchange interaction, characterized by the so-called D vector, that favours canting of neighbouring spins. It governs long-range non-collinear spin textures that exhibit chirality, promoting skyrmion formation [1] and magnetic domain wall propagation [2].

Since the DMI is forbidden for spin pair sites related by inversion symmetry, it localizes at surfaces and interfaces. Therefore, in multilayer heterostructures the interactions present at each interface are combined additively [3]. For example, recent data [4] of domain wall propagation velocities suggest that the strong DMI at a Pt/Co interface may be reduced at Pt/Co/Graphene heterostructures grown by Co intercalation between Pt and Graphene with fcc stacking [4]. Furthermore, the intercalation helps to stabilize the perpendicular anisotropy from 7 ML of Co up to about 15 ML.

For Pt/Co/Graphene, I will present DFT calculations featuring spin-orbit interactions and spin spirals [5] that describe the non-trivial dependence of the DMI and the magnetocrystalline anisotropy energy (MAE) on the Co film thickness. We find that the in-plane component of the D vector has a non-trivial oscillatory behaviour up to 3ML of Co, which would modulate the Néel-type domain wall velocity. Interestingly, we find a significant out-of-plane component of D, compatible with a more complex chiral spin structure. In summary, the additivity of interfacial DMI breaks down in ultrathin films.

As it regards the magnetic anisotropy, we find that the proposed system shows strongly oscillating MAE values in the ultrathin limit and that the shape anisotropy contribution sets the switching to plane anisotropy well below the experimental thickness of 15 ML. We have explored the role of the stacking geometry and mixing at the Co/Pt interface as factors that can explain the anisotropy behaviour.

- [1] A. Fert, V. Cros, J. Sampaio, Nat. Nanotech. 8, 152 (2013).
- [2] Z. Luo et al., Science **363**, 1435 (2019).
- [3] C. Moreau-Luchaire et al, Nat. Nanotech. 11, 444 (2016).
- [4] F. Ajejas et al., *Nano Lett.* **18**, 5364 (2018); arXiv:1911.07549
- [5] M. Heide, G. Bihlmayer, and S. Bluegel, *Physica B*, **404**, 2678 (2009).

# Electronic structure of non-equilibrium states: from electron and exciton dynamics to light-induced phase transitions

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The dynamics of quasi-particles in non-equilibrium states of matter reveal the underlying microscopic coupling between electronic, spin and vibrational degrees of freedom. We aim for a quantum-state-resolved picture of coupling on the level of quasi-particle self-energies, which goes beyond established ensemble-average descriptions, and which requires ultrafast momentum-resolving techniques. The dynamics of electrons and excitons is measured in momentum space with four-dimensional time- and angle-resolved photoelectron spectroscopy (trARPES), featuring a high-repetition rate XUV laser source [1] and momentum microscope detector. I will exemplify this experimental approach by discussing electron and exciton dynamics in the semiconducting transition metal dichalcogenide WSe<sub>2</sub> [2] and discuss its extension to nanoscale heterostructures. In addition, the laser-induced structural phase transition of indium nanowires on a silicon surface is investigated. TrARPES reveals the full transient electronic structure driving the structural transition along the reaction coordinate and enables a combined momentum- and real-space description of the dynamics of bands and bonds [3].

- [1] M. Puppin et al., *Time- and angle-resolved photoemission spectroscopy of solids in the extreme ultraviolet at 500 kHz repetition rate*, Rev. Sci. Inst. **90**, 23104 (2019).
- [2] R. Bertoni et al., *Generation and Evolution of Spin-, Valley-, and Layer-Polarized Excited Carriers in Inversion-Symmetric WSe*<sub>2</sub>, Phys Rev. Lett. **117**, 277201 (2016).
- [3] C.W. Nicholson et al., Beyond the molecular movie: Dynamics of bands and bonds during a photoinduced phase transition, Science **362**, 821 (2018)
- [4] C.W. Nicholson et al., *Excited-state band mapping and momentum-resolved ultrafast population dynamics in In/Si(111) nanowires investigated with XUV-based time- and angle-resolved photoemission spectroscopy*, Phys. Rev. B **99**, 155107 (2019).

### Interface state dynamics in hexagonal boron nitride monolayers

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Hexagonal boron nitride (*h*-BN) is one of the prime candidate materials for electronic 2D heterostructures. It can conveniently be grown as single layers by chemical vapor deposition on solid surfaces [1]. Here we will review the electronic structure of *h*-BN on Ni(111). Due to a small lattice mismatch, *h*-BN grows epitaxially on Ni(111), and the electronic structure of the *h*-BN layer resembles the one of a free-standing single sheet [2]. While in bulk *h*-BN, the optical properties are supposed to be dominated by an indirect gap of about 6 eV between  $\pi$  and  $\pi^*$  bands, additional states appear at  $\Gamma$  with free-electron-like dispersion [3]. Due to their delocalized charge density within the layers, they are likely to be important for interfaces in layered heterostructures [4]. Indeed, such states were predicted for *h*-BN /Ni(111) [2] and found in two-photon-photoemission experiments [5] and inverse photoemission [6].

We will present these and recent experiments, and analyze the unoccupied electronic states of h-BN/Ni(111): Beside the interface state described above, an image-potential state is found close to the vacuum level. Both states show exchange splitting induced from the ferromagnetic substrate [4]. An optical resonance between the interface state and the image-potential state leads to enhanced photoemission in two-color pump-probe experiments [5], which cannot be explained by large optical matrix elements alone but by inferring interference effects between different excitation channels. Eventually, in all two-photon photoemission data, the interface state is found at lower energy than expected from inverse photoemission [6] and density-functional calculations [2]. Moreover, the lifetime of 100 fs of this state is found to be surprisingly large. We will show that the findings can be explained by exciton formation at  $\Gamma$  with exciton binding energies of about 200 meV [4].

- [1] W. Auwärter, *Hexagonal boron nitride monolayers on metal supports: Versatile templates for atoms, molecules and nanostructures*, Surf. Sci. Rep. **74**, 1 (2019).
- G.B. Grad et al., Density functional theory investigation of the geometric and spintronic structure of h-BN/Ni(111) in view of photoemission and STM experiments, Phys. Rev. B 68, 085404 (2003).
- [3] A. Catellani et al., *Electronic interlayer states in hexagonal boron nitride*, Phys. Rev. B **32**, 6997 (1985).
- [4] M. Hengsberger et al., *Dynamics of excited interface states in hexagonal boron nitride monolayers*, J. Phys. D: Appl. Phys., accepted (2020).
- [5] M. Muntwiler et al., Energetics and dynamics of unoccupied electronic states at the h-BN/Ni(111) interface, Phys. Rev. B 75, 075407 (2007); D. Leuenberger et al., Disentanglement of electron dynamics and space-charge effects in time-resolved photoemission from h-BN/Ni(111), Phys. Rev. B 84, 125107 (2011).
- [6] K. Zumbrägel, K. Wulff, C. Eibl, M. Donath, and M. Hengsberger, *Exchange-split interface state at h-BN/Ni(111)*, Phys. Rev. B **78**, 085422 (2008).

# Ultrafast charge transfer dynamics in, at and under graphene and BN monolayers

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In the past decade we have extensively used the so-called core hole clock (CHC) method [1, 2) to study the processes given in the title. Parts of this work have been presented at previous ECSCD conferences [3, 4] and have been published [5, 6]. This contribution will give an overview of our results, emphasize some new results, and aim at some conclusions about the positive and negative aspects of our method and about what we can learn from the amassed data.

The CHC method [1,2] is based upon the use as time mark of the core hole lifetime to extract the life time of a core exciton resonantly excited by narrow band soft x-rays. The delocalisation time of the excited electron is determined by comparing the intensities of decay spectra with and without charge transfer. We have extensively used the 2p<sub>3/2</sub>>4s excitation of Ar atoms adsorbed on or deposited below Gr or BN monolayers to determine the CT times to and through these monolayers [3-5]. Variation of the substrates has allowed extracting the influence of the substrate coupling, i.e. the chemical interaction of the ML with the substrates; but effects of the final state band structure and of other properties have also become obvious. For the investigation of CT within the Gr and BN monolayers, we used C 1s for Gr, and B 1s or N 1s core excitations. It has turned out that the excited electrons in C 1s (Gr) and N 1s (BN) core excitons are delocalized extremely fast, while B 1s excitons clearly live longer. This is attributed to the energetic position of the respective excited electrons relative to the ML bands. As to intercalated and compressed Ar [6], we have reported in the last ECSCD [4] and another conference [7] that our method can be used to distinguish Ar states within Gr and BN blisters with strongly differing properties. If time allows I will add some new insights we gained recently about these systems.

These results have been obtained by an international collaboration with minimal funding. I thank all contributors (see author lists of refs.) for their excellent work and pleasant collaboration, in particular Silvano Lizzit (Trieste), Rosanna Larciprete (Rome), and Peter Feulner (München). We are very grateful to Elettra (Trieste) for the allotment of beamtime despite our lack of funds.

- [1] See, e.g., P.A. Brühwiler, O. Karis and N. Martensson, Rev. Mod. Phys. 74, 703 (2002).
- [2] D. Menzel, Chem. Soc. Rev. 37, 37 (2008).
- [3] S. Lizzit et al., ECSCD-2015 Trieste Lizzit, S. et al., New J.Phys. 11, 053005 (2009).
- [4] R. Larciprete et al., ECSCD-2017 San Sebastian.
- [5] S. Lizzit et al., ACS Nanolett. 7, 4359 (2013).
- [6] R. Larciprete et al., ACS Nanolett. 16, 1808 (2016).
- [7] Menzel., D. et al., abstract EWEG-2D 2018, and to be submitted.

# Hot electron dynamics in the potential photocathode materials Cu<sub>2</sub>O and Sb<sub>2</sub>Se<sub>3</sub> by time-resolved two-photon photoemission

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Photocatalytic water splitting represents a sustainable way to store solar light in the form of chemical bonds. For high conversion efficiencies transport of photoexcited electrons to the interface without major energy loss is required.

Two of the most promising abundant and non-toxic photocathode materials are cuprous oxide ( $Cu_2O$ ) [1] and antimony selenide ( $Sb_2Se_3$ ) [2]. The electronic structure and the charge carrier dynamics of these materials are compared based on time-resolved two-photon photoemission experiments. On the (111) surface of  $Cu_2O$  two conduction bands could be resolved and phonon-assisted relaxation into the conduction band minimum (CBM) was identified. The direct band gap was determined as 2.1eV. Ultrafast, elastic transport of electrons within the conduction band towards the surface was identified as main source to populate the surface CBM and a decay constant of 10ps was determined. Contrary, on the (100) surface of  $Sb_2Se_3$  ultrafast scattering from various conduction bands into the CBM was observed, where the electrons exhibit a lifetime of 30ps. An indirect band gap of 1.1eV could be found. Unexpectedly, no difference in the charge carrier dynamics along or perpendicular to the one-dimensional ribbon structure [3] could be found.



Fig. 1: Unit cell and time-dependent energy distribution of photoexcited electrons of (a)  $Cu_2O(111)$ and (b)  $Sb_2Se_3(100)$  near the  $\overline{\Gamma}$ -point. The measurement was conducted with a 3eV pump and a 6eV probe pulse at a repetition rate of 100 kHz.

- [1] A. Paracchino, V. Laporte, K. Sivula, M. Grätzel and E. Thimsen, *Highly active oxide photocathode for photoelectrochemical water reduction*, Nature Materials **10**, 456-461 (2011).
- [2] Y. Zhou, M. Leng, Z. Xia, J. Zhong, H. Song, X. Liu, B. Yang, J. Zhang, J. Chen, K. Zhou, J. Han, Y. Cheng and J. Tang, *Solution-Processed Antimony Selenide Heterojunction Solar Cells*, Adv. Energy Mater. 4, 1301846 (2014).
- [3] R. Totani, F. O. von Rohr, J. Zhao, Z. Novotny, W.-D. Zabka, A. Soluyanov and J. Osterwalder, *Sb*<sub>2</sub>*Se*<sub>3</sub>(*100*): *A strongly anisotropic surface*, Phys. Rev. Materials **3**, 125404 (2019).

# Do charged and uncharged species co-exist in adsorbate monolayers?

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The generally accepted wisdom is that for a homogeneous ad-layer all adsorbates interact similarly and are, apart from perhaps subtle differences in adsorption site, electronically similar. I will suggest here that this is not always the case and that even on metal surfaces charged and neutral species may co-exist.

I will start with comprehensive analysis of the phenomenon of charge transfer to adsorbates on thin, defect free dielectric interlayers. Our experimental approach allows the control of either the thickness of the dielectric interlayer or its work function. We show that the charge transfer process is governed by charged and uncharged molecular species, with distinct energy levels, co-existing in the first monolayer. I will then turn to the evidence for similar behaviour for adsorption on clean metal substrates and suggest that it may be quite common but easily overlooked.



Fig. 1: STM of charged(I) and uncharged(II) pentacene on MgO(100) [2]. Photoemission tomography of charge and neutral tetracene on Ag(110)[3].

- M. Hollerer, D. Lüftner, P. Hurdax, T. Ules, S. Soubatch, F. S. Tautz, G. Koller, P. Puschnig, M. Sterrer, M. Ramsey, *Charge Transfer and Orbital Level Alignment at Inorganic/Organic Interfaces: The Role of Dielectric Interlayers*, ACS Nano 17, 6252 (2017).
- [2] P. Hurdax, M. Hollerer, P. Puschnig, D. Lüftner, L. Egger, M. Ramsey, M. Sterrer, *Controlling the charge transfer across dielectric interlayers*, submitted 2020.
- [3] X. Yang, L. Egger, J. Fuchsberger, M. Unzog, D. Lüftner, F. Hajek, P. Hurdax, M. Jugovac, G. Zamborlini, V. Feyer, G. Koller, P. Puschnig, F. S. Tautz, M. G. Ramsey, S. Soubatch, *Coexisting Charge States in a Unary Organic Monolayer Film on a Metal*, J. Phys. Chem. Lett. **10**, 6438 (2019).

# Revealing electronic and chemical structure of adsobates with photoemission tomography

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The important aspect in a study of organic adsorbates on surfaces is to identify their precise electronic and chemical structure. The latter is particularly crucial, because the catalytic nature of the substrate can trigger a reaction leading to chemical transformations of adsorbed species. Although a significant progress in chemical identification of molecules and reaction paths has been recently achieved using high-resolution atomic force microscopy [1], it is more applicable to the molecular backbone structure compared to its molecular periphery. The alternative approach based on the-momentum space resolved photoemission spectroscopy provides an immediate access to the "orbital" structure of organic adsorbates [2]. This reveals the energy level alignment at the molecule/substrate interface and is very sensitive to the chemical states of molecules [3].

Here we demonstrate how the precise character of frontier molecular orbitals is accessible by the photoemission tomography technique. Comparing the angular distributions of the photoelectrons, both experimental and simulated, allows to determine the electronic and chemical states of adsorbates. For instance, we identify the products of surface chemical reactions – bisanthene [3] and kekulene formed on copper surfaces and describe the effects caused by their interaction with the metal surface.

- [1] L. Gross, F. Mohn, et al., *The chemical structure of a molecule resolved by atomic force microscopy*, Science **325**, 1110 (2009).
- [2] P. Puschnig, et al., Reconstruction of molecular orbital densities from photoemission data, Science 326, 702 (2009); S. Weiß, et al., Exploring three-dimensional orbital imaging with energy- dependent photoemission tomography, Nat. Commun. 6, 8287 (2015).
- [3] X. Yang, L. Egger, et al., *Identifying surface reaction intermediates with photoemission tomography*, Nat. Comm. **10**, 3189 (2019).

# Alkali doping leads to salt formation in a two-dimensional metal-organic framework: K and TCNQ on Ag(111)

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Using a combination of STM, LEED, SXPS, NIXSW and dispersion-corrected DFT calculations we have identified the ordered structural phases of coadsorbed TCNQ and K on Ag(111) and determined the key structural parameters of a commensurate  $\begin{bmatrix} 3 & 0 \\ 1 & 5 \end{bmatrix}$  phase with the stoichiometry of K<sub>2</sub>TCNQ. Heights of the atomic components of this structure above the

Ag(111) surface provided important benchmark values to refine the DFT calculations; in particular, it proved to be important to take account of the ionic character of the adsorbed K, both for a K overlayer alone and when coadsorbed with TCNQ. We find the interaction of the strong electron acceptor molecule, TCNQ, and the electron donating K, leads to the formation of a charge-transfer salt in which the bonding within the layer is strong but the interaction with the substrate is weak, as shown by a detailed breakdown of the different bonding components. This contrasts with the situation of the commensurate phase of pure TCNQ on Ag(111) [1] which also forms a 2D metal organic framework involving Ag adatoms and TCNQ molecules, but in this case the molecule-substrate interaction remains strong whereas the bonding within the 2D MOF is much weaker.



Fig. 1: Top and side views of the commensurate K<sub>2</sub>TCNQ phase on Ag(111).

#### References

[1] P.J. Blowey, S. Velari, L.A. Rochford, D.A. Duncan, D.A. Warr, T.-L. Lee, A. De Vita, G. Costantini, and D.P. Woodruff, '*Re-evaluating how charge transfer modifies the conformation of adsorbed molecules*', Nanoscale **10**, 14984 (2018).

# Combining NEXAFS and DFT to determine adsorption structures of medium-sized organic molecules

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Hydrogenation reactions of chiral bio-molecules can be catalyzed by simple metal surfaces in an enantioselective way when they are modified by chiral molecules, such as amino acids (e.g. aspartic acid) or tartaric acid [1]. The enantioselective hydrogenation of methyl acetoacetate (MAA) is a key model reaction this context, as it represents the only example of this class of reactions catalysed by base metals. Yet, there is very little molecular-level information available about the adsorption complex formed by the reactants and modifiers. Here, we report a series of combined experimental and theoretical studies of the reactant MAA and a modifier, aspartic acid (Asp), adsorbed on the Ni{100} and {111} surfaces. X-ray photoelectron spectroscopy (XPS) shows that, both MAA and Asp, form single chemisorbed layers around room temperature, which decompose at higher temperatures. DFT modelling predicts enolate species with bidentate coordination for MAA and five-fold surface coordination for Asp (see Figure 1) as the most stable chemisorbed species. Comparison of XPS and NEXAFS data with simulations using the adsorption models proposed by DFT show good qualitative and quantitative agreement. These adsorption geometries break the symmetry of the underlying metal surfaces and thus provide important hints for the reaction mechanism of the enantio-selective hydrogenation.



Fig. 1: Proposed adsorption structure of aspartic acid on Ni{111}.

- C. J. Baddeley and G. Held, Chiral molecules on surfaces, in Comprehensive Nanoscience and Technology Vol. 3 Chapter 3.04, 105 (Springer 2010)
- [2] Ontaneda et al., Adsorption of methyl acetoacetate at Ni{111}: experiment and theory, J. Phys. Chem. C **120**, 2749 (2016).
- [3] Tsaousis et al., A combined experimental and theoretical study of methyl acetoacetate adsorption on Ni{100}, J. Phys. Chem. C **122**, 6186 (2018).

# Tailoring $\pi$ -conjugation and vibrational modes to steer on-surface synthesis of pentalene-bridged ladder polymers

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The rational design of increasingly complex electronic materials for molecular electronics and quantum technologies has been an active field of research in organic electronics. Particularly appealing are  $\pi$ -conjugated polymers [1] due to their relevant optical and electronic properties stemming from the delocalization of  $\pi$ -electrons, which are the key for the incoming revolution of transparent and plastic electronics. However, despite great advances in the field from the synthetic point of view, we still lack one-dimensional (1D)  $\pi$ -conjugated polymers that feature intrinsic ultra-narrow or even zero bandgaps, accomplishing the dream of engineering intrinsic metallic organic polymers [2].

Recent development of on-surface synthesis opened a novel strategy to synthesize a new class of intrinsically quasi-metallic 1D  $\pi$ -conjugated polymers featuring topologically non-trivial quantum states [3,4]. Thus, it bridges the two distinct worlds of topological band theory (condensed matter physics) and  $\pi$ -conjugation polymer science (chemistry), which may stimulate new routes towards a design of organic polymers with unprecedented material properties (very low bandgap and magnetic properties).

In this work, we employ quantum-mechanical calculations for the description of structural and electronic properties of  $\pi$ -conjugated ethynylene bridged polymers [3,4]. Additionally, we introduce novel synthetic strategy forming  $\pi$ -conjugated ladder polymers with non-benzenoid pentalene bridges by exploiting the relation between  $\pi$ -conjugation, topological phase and vibrational modes of the polymer. Selected vibrational mode of bisanthene polymer is shown to be the key feature allowing the cyclization of ethynylene into pentalene linker, which is not observed in topologically trivial anthracene polymer. Finally, we present reaction mechanism highlights differentiating anthracene and bisanthene polymers, leading to successful cyclization in bisanthene but prevent the reaction on anthracene polymer completely, which is in direct agreement with experiments.

This work provides insight into experimentally observed properties in these novel systems and offers the possibility to qualitatively predict molecules suitable for on-surface tailored molecular chains.

- [1] A.J. Heeger, Angew. Chem. Int. Ed. 40, 2591-2611 (2001).
- [2] J. Roncali, J. Chem. Rev. 97, 173-206 (1997).
- [3] A. Sánchez-Grande et al., Angew. Chem. Int. Ed. 58, 6559 (2019).
- [4] B. Cirera *et al.*, arXiv:1911.05514 (2019).

## Decoupling of molecules at the metal interface by thin interfacial layers

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Over the last years, many examples of large organic molecules were studied concerning their bonding and electronic interaction to metal surfaces. In particular, the role of functional groups in relation to the  $\pi$  system was considered, and the impact of the interfacial bonding on the structure of the adsorption complex was measured with high precision [1].

However, in order to preserve functional properties of molecules, e.g. fluorescence yields, an effective "decoupling" of the molecular states from metallic states is required. This is generally achieved by spatial separation which is obtained by molecular spacer groups or interfacial thin films of wide band gap materials. Here we report on experiments using either thin alkaline halide films or monolayers of hexagonal boron nitride (hBN) as interfacial layers on Ag(100) and Cu(111) surfaces, respectively.

A direct comparison with the situation on the bare metal surfaces is interesting. For a monolayer of hBN/Cu(111) we deduce the impact of the interfacial layer on the structure of the adsorption complex, the binding energy, the lateral ordering and finally, the obtained interfacial decoupling which is deduced from the ratio of radiative versus non-radiative decay rates of an optical excitation. For PTCDA/hBN/Cu(111) we find a considerable structural and electronic decoupling [1]. However, concerning the fluorescence we see a significant remaining impact of the underlying metal interface. This related to the large time constant of the decay process. Direct comparison of the hBN layer with a molecular layer identifies the former as more efficient. Hence, fluorescence spectra can serve as a sensitive tool for the electronic interactions at the organic/substrate interface.



Fig. 1: Side view of a PTCDA molecule along the long and short molecular axes on one monolayer hexagonal boron nitride on Cu(111). Vertical distances within the molecule are enlarged by a factor of 4. Van der Waals spheres are indicated.

[1] C. Brülke et al., Quantitative analysis of the electronic decoupling of an organic semiconductor molecule at a metal interface by a monolayer of hexagonal boron nitride, Phys. Rev. B **99**, 121404(R) (2019).

# Extracting the local electronic properties of the two-dimensional electron gas at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interface by phonon-enhanced near-field spectroscopy

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In the family of functional oxide materials one interesting system is the interface between  $SrTiO_3$  and  $LaAIO_3$  (LAO/STO), which are large-bandgap insulators in their bulk state but give rise to a confined two-dimensional electron gas (2DEG) when combined [1]. This 2DEG exhibits remarkable properties such as superconductivity and gate tunability, and displays the possibility for future transistor applications. Until recently, its investigation was limited to destructive or non-local (i.e. averaging over larger areas) methods.

Scanning near-field optical microscopy (SNOM) was shown to overcome this limitation by measuring the properties of buried 2DEGs using highly confined optical near-fields, opening the possibility for quantitative analysis by comparison to theoretical predictions using the simple point dipole model [2].

As the quantitative analysis of local electronic properties can be enhanced by exploiting plasmon-phonon coupling [3], our SNOM measurements were done in a nano-FTIR setup in conjunction with synchrotron radiation to obtain nanoscale IR spectra of LAO/STO interfaces in the range of their near-field phonon resonances.

In addition to the enhanced spectroscopic approach, an improved theoretical model [4] was incorporated. In combination we were able to predict the spectral response of different LAO/STO samples to a much better degree when systematically comparing to synchrotron nano-FTIR measurements. As a result, local electronic properties of the interfacial 2DEG could be extracted quantitatively, enabling the possibility of its nanoscale lateral mapping in the future.

- [1] A. Ohtomo and H.Y. Hwang, A high-mobility electron gas at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> heterointerface, Nature **427**, 423 (2004).
- [2] W. Luo, M. Boselli, J.-M. Poumirol, I. Ardizzone, J. Teyssier, D. v. d. Marel, S. Gariglio, J.-M. Triscone, and A. B. Kuzmenko, *High sensitivity variable-temperature infrared nanoscopy of conducting oxide interfaces*, Nature Communications **10**, 2774 (2019).
- [3] M. Lewin, C. Baeumer, F. Gunkel, A. Schwedt, F. Gaussmann, J. Wueppen, P. Meuffels, B. Jungbluth, J. Mayer, R. Dittmann, R. Waser, and T. Taubner, *Nanospectroscopy of Infrared Phonon Resonance Enables Local Quantification of Electronic Properties in Doped SrTiO<sub>3</sub> Ceramics*, Adv. Funct. Mater. **28**, 1802834 (2018).
- [4] B. Hauer, A.P. Engelhardt, and T. Taubner, *Quasi-analytical model for scattering infrared near-field microscopy on layered systems*, Optics Express **20**, 13173 (2012).

# Understanding the structural diversity of freestanding Al<sub>2</sub>O<sub>3</sub> ultrathin films through DFTB-aided global optimization

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(Sub)nanometer-thin alumina films are frequently encountered due to the self-limited oxidation of Al and its alloys, and seem to display an even larger structural variety than bulk alumina itself. While the nature of the underlying substrate and the oxidation kinetics are known to modulate the structure of supported films, understanding the intrinsic stability of freestanding films constitutes an important first step in itself, especially when the interaction with the substrate is rather weak. Using a combined tight-binding/DFT global optimization approach, we identify particularly stable  $\theta(100)$ -type films along with a host of novel stable thin film structures. Several of these correspond to cuts from relatively high energy bulk structures, e.g. dehydrated boehmite, pseudo-CaIrO<sub>3</sub>, defective rocksalt and LuMnO<sub>3</sub>, which are not commonly associated with alumina. DFT calculations allow to rationalize this stability reversal with respect to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in terms of low surface energies compared to  $\alpha(0001)$  and to identify the underlying mechanisms: breaking a low density of relatively weak Al-O bonds, filling of Al surface vacancies, and polarity-induced relaxation of the whole film. These observations provide interesting insights into existing supported ultrathin films.

# Oxides of divalent 3d transition metals on Ru(0001) grown by oxygen assisted molecular beam epitaxy: structure and magnetism

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Antiferromagnetism has been traditionally seldom used in spintronic devices. However, there is currently a concerted effort to take advantage of the fast dynamics and lack of stray fields in antiferromagnets [1]. The family of antiferromagnetic 3d transition metal oxides comprises FeO, CoO, NiO as well as Cr and Mn oxides. Here we focus on the former, which share the same halite structure. We demonstrate a route for preparing high quality ultrathin oxide antiferromagnetic nanostructures on a metallic substrate: the oxides have been grown on Ru(0001) by high temperature oxygen-assisted molecular beam epitaxy. The nucleation and growth process are observed in real time by either Low Energy Electron Microscopy (LEEM)[2], enabling to optimize the growth parameters (LEEM). A comprehensive characterization is performed combining LEEM and LEED for structural characterization and PEEM with synchrotron radiation for chemical and magnetic analysis via x-ray Absorption Spectroscopy and x-ray Magnetic Dichroism. Using the later we observe the spatial distribution of the antiferromagnetic domains and determine their spin direction in selected cases, and we show how in mixed nickel-cobalt oxides the Néel temperature can be modified by changing the Ni/Co ratio [3].



Fig. 1: Islands of FeCoO, CoO and NiCoO respectively.

- T. Jungwirth, X. Marti, P. Wadley, and J. Wunderlich, *Antiferromagnetic spintronics*, Nat Nano 11, 231 (2016).
- [2] L. Martín-García, A. Quesada, L. Pérez, M. Foerster, L. Aballe, and J. de la Figuera, *Initial Stages* of the Growth of Mixed Iron-cobalt Oxides on Ru(0001), Phys. Proc. **85**, 12 (2016).
- [3] A. Mandziak et al., Tuning the Néel temperature in an antiferromagnet: the case of Ni<sub>x</sub>Co<sub>1-x</sub>O microstructures, Sci. Rep. 9, 13584 (2019).

### Wurtzite cobalt oxide films grown on Au(111)

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Wurtzite (w)-CoO, identified unambiguously as nanocrystalline powder [1], has attracted much attention due to its special catalytic [2], semiconducting [3], and antiferromagnetic [4] properties different from the standard rock salt CoO. While several publications mention recipes for reactive growth of w-CoO on metal surfaces [3,5-7], none of them demonstrate the growth of a well-oriented and closed film beyond the double-bilayer (DBL) limit.

In this work we present the growth and analysis of several nanometer thick w-CoO films on Au(111) that may be regarded prototypical for non-existing bulk w-CoO. We characterize the films experimentally by quantitative low energy electron diffraction (LEED), scanning tunneling microscopy (STM) and spectroscopy (STS) as well as theoretically by density functional theory (DFT) calculations based on hybrid functional or LDA+U schemes.



Fig. 1: (a) Ball model of a w-CoO (0001) film on Au(111) made up of CoO bilayers (BL) and double bilayer (DBL). (b) LEED pattern of a 15 BL thick film. (c) IV-spectrum of the (11)-beam and its bestfit (R = 0.100). (d) STM image of a nearly closed DBL film. (e) STS measurements show the opening of the bandgap with increasing film thickness.

- [1] A. S. Risbud et al., Chem. Mater. **17**, 834 (2005).
- [2] J. Fester et al., Nat. Commun. 8, 14169 (2017).
- [3] Y. Wang et al., Chem. Commun. 54, 13949 (2018).
- [4] A. G. Roca et al., Small 14, 1703963 (2018).
- [5] A. S. Walton et al., ACS Nano **9**, 2445 (2015).
- [6] J. Fester et al., Top. Catal. **60**, 503 (2017).
- [7] M. De Santis et al., Phys. Rev. B **84**, 125430 (2011).

# Single-molecule chemistry and spectroscopy using localized surface plasmon at STM junction

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Excitation of molecules triggers various important energy conversion processes, such as luminescence, photochemical reactions, and photovoltaics. Detailed understanding of the molecular excited states is crucial to develop organic energy conversion devices based on opto-electronic/opto-chemical processes. We developed a scanning tunneling microscope (STM) combined with optical systems both for photon detection and for optical illumination to investigate energy transfer, conversion and dissipation processes at the single molecule level. The localized surface plasmon (LSP) generated near the STM tip either by applying bias voltage or by optical illumination has recently been attracting great attention mainly as a novel light source to overcome diffraction limit of optical wavelength. In recent years, we have applied the LSP towards exploring novel chemical reaction and spectroscopy based on the interaction between the LSP and electronic/vibrational quantum states of a single molecule at the STM junction. In this talk, I will discuss recent issues focusing on single-molecule chemistry and spectroscopy based on the molecular excitation by localized surface plasmon at the STM junction.

We have developed single-molecule absorption spectroscopy [1] by use of the interaction

between the STL and a molecule, in which the STL is participated in the exciton formation in a target molecule [2]. Further, in combination with the already developed single-molecule emission spectroscopy, we visualized energy transfers between two molecules [3]. We have also explored detailed mechanism of single-molecule chemical dynamics induced by the LSP generated by laser illumination [4]. Recently, we applied the LSP to measure resonance Raman spectra of a molecule at the plasmonic nanogap under the STM tip [5].



- H. Imada, K. Miwa, M. Imai-Imada, S. Kawahara, K. Kimura, and Y. Kim, Phys. Rev. Lett. 119, 013901 (2017).
- [2] K. Kimura, K. Miwa, H. Imada, M. Imai-Imada, S. Kawahara, J. Takeya, M. Kawai, M. Galperin and Y. Kim, Nature 570, 210 (2019).
- [3] H. Imada, K. Miwa, M. Imai-Imada, S. Kawahara, K. Kimura, and Y. Kim, Nature 538 (2016) 364.
- [4] E. Kazuma, J. Jung, H. Ueba, M. Trenary, and Y. Kim, Science **360**, 521 (2018).
- [5] R.B. Jaculbia, H. Imada., K. Miwa1, T. Iwasa, M. Takenaka, B. Yang, E. Kazuma, N. Hayazawa, T. Taketsugu, and Y. Kim, Nat. Nanotech. (2020), in press.

### Adsorption of Zn-porphines on *h*-BN/Cu(111)

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Two-dimensional hexagonal boron nitride (h-BN) is an insulating layer that can be used to decouple adsorbed organic molecules from the underlying metal single crystal support, thus preventing the strong influence of the latter on the molecular geometric and electronic configurations [1]. Investigating the assembly and conformation of adsorbed molecules by means of X-ray standing waves (XSW), X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy/spectroscopy (STM/STS) measurements yields insight into the physical properties of the system [2]. Here, we present a comparison of zinc-porphine (Zn-P) adsorbed on h-BN/Cu(111) and Cu(111), demonstrating the effect of the h-BN decoupling layer. The experiments reveal a temperature dependence of the adsorption height and the molecular conformation. At low temperature and low Zn-P coverage, the molecules are trapped in the pore areas of the corrugated *h*-BN. Increasing the temperature leads to a larger average adsorption height and a reduced coherent fraction. A higher mobility of Zn-P and a transient occupation of the wire areas can contribute to this effect. In contrast to Zn-P on Cu(111), molecules adsorbed on h-BN/Cu(111) can readily bind water molecules, resulting in a change of the Zn-P adsorption height and conformation. Finally, the temperature-induced intercalation of Zn-P yields a h-BN/Zn-P/Cu(111) heterostructure and thus opens a pathway to modify the *h*-BN - support interaction and to study molecules in a confining environment [3].

- [1] W. Auwärter, *Hexagonal boron nitride monolayers on metal supports: Versatile templates for atoms, molecules and nanostructures*, Surf. Sci. Rep. **74**, 1 (2019).
- [2] M. Schwarz, D. A. Duncan, M. Garnica, J. Ducke, P. S. Deimel, P. K. Thakur, T-L. Lee, F. Allegretti and W. Auwärter, *Quantitative determination of a model organic/insulator/metal interface structure*, Nanoscale **10**, 21971 (2018).
- [3] J. Ducke, A. Riss, A. Pérez Paz, K. Seufert, M. Schwarz, M. Garnica, A. Rubio and W. Auwärter, Layered Insulator/Molecule/Metal heterostructures with molecular functionality through porphyrin intercalation, ACS Nano **12**, 2677 (2018).

# Charge state dependence of single molecules' chemical structure observed in real space

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Functionalizing the tip of an atomic force microscope (AFM) – operated in ultra-high vacuum at low temperatures – allows for highest spatial resolution down to the chemical structure determination of individual molecules [1, 2]. In addition, AFM has been shown to be capable of detecting, manipulating and controlling the charge state of individual adsorbates [3]. Suppressing charge leakage to the metallic substrate by means of multilayer insulating films allows for more charge states of individual adsorbates to be stable. Thereby, real space investigation of charge transfer between adjacent adsorbates [4] as well as the energetics and the directional dependence of charge state transitions became experimentally accessible [5, 6].

Here, we combine CO-functionalization of the AFM tip to achieve highest spatial resolution with the deliberate charge state control of single molecules on multilayer insulating films. We investigate different molecules to determine the effect of charge state on molecular conformation as well as on adsorption geometry. For certain molecules, our experiments allow for the observation of minute intramolecular changes related to aromaticity [7].

- [1] L. Gross et al., Science **324**, 5933 (2009).
- [2] L. Gross et al., Nature Chemistry 2, 821 (2010).
- [3] L. Gross et al., Science **325**, 5944 (2009).
- [4] W. Steurer et al., Nature Communications 6, 8353 (2015).
- [5] S. Fatayer et al., Nature Nanotechnology **13**, 376 (2018).
- [6] L. Patera et al., Nature **566**, 245 (2019).
- [7] S. Fatayer et al., Science **365**, 142 (2019)

### Atomic rheology of gold nanojunctions

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Despite extensive investigations of dissipation and deformation processes in micro- and nano-sized metallic samples, the mechanisms at play during the deformation of systems with ultimate (molecular) size remain unknown. Although metallic nanojunctions, which are obtained by stretching metallic wires down to the atomic level, are typically used to explore atomic-scale contacts, it has not been possible until now to determine the full equilibrium and non-equilibrium rheological flow properties of matter at such scales. Here, by using an atomic-force microscope equipped with a quartz tuning fork, we combine electrical and rheological measurements on angström-size gold junctions to study the non-linear rheology of this model atomic system. By subjecting the junction to increasing subnanometric deformations we observe a transition from a purely elastic regime to a plastic one, and eventually to a viscous-like fluidized regime, similar to the rheology of soft yielding materials, although orders of magnitude different in length scale. The fluidized state furthermore exhibits capillary attraction, as expected for liquid capillary bridges. This shear fluidization cannot be captured by classical models of friction between atomic planes and points to an unexpected dissipative behaviour of defect-free metallic junctions at ultimate scales. Atomic rheology is therefore a powerful tool that can be used to probe the structural reorganization of atomic contacts [1].



Fig. 1: Schematic of the experimental setup using a tuning-fork to probe the nanoscale mechanical response of gold nanojunction with sizes down to molecular diameters.

#### References

[1] J. Comtet, A. Lainé, A. Niguès, L. Bocquet, A. Siria, *Atomic Rheology of gold nanojunctions*, Nature **569**, 393-397 (2019).

### Dynamics of adsorbates on metal surfaces under equilibrium and non-equilibrium conditions

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Understanding the fundamental processes that bring about the specific time scales of surface reactions is a long-standing aim in surface science. The resonant infrared absorption and ultrafast time-resolved vibrational spectroscopies constitute an invaluable tool for exploring the equilibrium and non-equilibrium surface dynamics, respectively. Here we bring forth consistent nonadiabatic *ab initio* theories that clarify the microscopic intricacies behind thermal and nonthermal vibrational relaxations of CO on metal surfaces, bringing us a step closer to the above-mentioned goal.

First, the result for the vibrational lifetime of the CO internal stretch (IS) mode on Cu(100) in equilibrium condition will be shown. Recent first-principles studies showed how the standard Fermi's golden rule formula for nonadiabatic coupling is unable to explain the experimental lifetimes of the CO IS. Here we present the theory of electron-mediated vibrational intermode coupling that is able to resolve this issue [1]. Namely, the results demonstrate a strong electron-mediated coupling between the internal stretch and low-energy CO modes, but also a significant role of surface motion.

Further, we introduce the first robust theoretical framework [2] that successfully explains the observed nonthermal frequency and linewidth changes of the CO IS mode on Cu(100) induced by subpicosecond laser pulses [3]. Our results show how the nonadiabatic coupling underlies the nonthermal frequency shifts, while electron-mediated vibrational mode coupling gives rise to linewidth changes. In fact, under highly nonequilibrium condition hot electrons promote an intramode coupling between coherent and incoherent internal stretch modes, while after the first picosecond coupling with low-energy modes prevail. Furthermore, surface modes are also decisive and stay active until equilibration.

At the end, we show our results for the vibrational relaxation of physisorbed CO on Au(111)[4]. It is shown that the nonadiabatic theory reproduces the long CO lifetime measured in Au(111)[5] provided the molecule–surface interaction is properly described.

- [1] D. Novko, M. Alducin, and J. I. Juaristi, Phys. Rev. Lett. **120**, 156804 (2018).
- [2] D. Novko, J. C. Tremblay, M. Alducin, and J. I. Juaristi, Phys. Rev. Lett. **122**, 016806 (2019).
- [3] K.-i. Inoue et al., Phys. Rev. Lett. **117**, 186101 (2018).
- [4] I. Lončarić, M. Alducin, J. I. Juaristi, and D. Novko, J. Phys. Chem. Lett. 10, 1043 (2019).
- [5] S. Kumar et al., Phys. Rev. Lett. **123**, 156101 (2019).

# Insight into the structural evolution of working IrO<sub>2</sub> catalysts in proton-exchange membrane electrolyzers

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Iridium dioxide is currently the preferred material for highly active, yet chemically stable nanoparticle catalysts enabling the electrochemical oxygen evolution reaction (OER) in proton exchange membrane electrolyzers (PEM). Notwithstanding, at high cell voltages required to reach technically viable current densities, even this material seems to undergo a hitherto only incompletely characterized transformation from its rutile crystalline to some amorphous hydrous state with Ir in higher oxidation states. The nature of the active sites in this new state is thereby presently largely unclear. In-depth characterization work has hitherto almost exclusively focused on the rutile  $IrO_2(110)$  facet – in the understanding that this facet is the lowest-energy facet of rutile crystals at open circuit potential and that this facet was indeed repeatedly found as dominant in *ex situ* characterization of synthesized  $IrO_2$  particles.

In this work [1], we therefore conduct *ab initio* thermodynamic calculations to specifically address the high potential range. Constructing the surface phase (Pourbaix) diagrams for all low-index surfaces of rutile  $IrO_2$ , we find the stabilization of highly oxidized superoxo species at the surface to induce a general thermodynamic instability of the rutile structure already at potentials not much above the OER onset. While this concurs with the experimentally observed transformation to the amorphous state, we find this instability to be preceded by a general shape change already at much lower potentials. Combining the first-principles surface free energy data into a Wulff construction, this equilibrium shape exclusively exhibits hitherto not considered  $IrO_2(111)$  facets already at OER onset potentials. These first insights into the structural evolution of working  $IrO_2$  catalysts highlight the urgent need to extend systematic characterization and mechanistic endeavors to higher potentials to identify the true active sites governing the OER at technologically relevant current densities.

Explicitly addressing the structural evolution of the  $IrO_2$  nanoparticle into the suspected hydrous amorphous state would require full *ab initio* molecular dynamics (MD) simulations of the reactive processes at the electrified nanoparticle surface. As this is computationally not tractable for a foreseeable time, MDs based on machine-learned interatomic potentials are an appealing alternative. We are currently undertaking first steps in this direction using a Gaussian Approximation Potential (GAP) for  $IrO_2$  combining two-body and smooth overlap of atomic positions (SOAP) descriptors to capture the atomic environment. The potential is trained with density-functional theory (DFT) data comprising  $IrO_2$  bulk, various surface slabs, Wulff shape nanoparticles, as well as semi-amorphous structures iteratively obtained from short MD trajectories based on the developing GAP. Extensive simulated annealing simulations based on a thus optimized GAP immediately reveal hitherto unknown surface reconstructions of  $IrO_2$  that are now fully confirmed by explicit DFT calculations.

#### References

[1] D. Opalka, C. Scheurer, and K. Reuter, ACS Catal. 9, 4944 (2019).

### Surface-catalyzed dehalogenation of fluorinated fullerenes on coinage metals

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In a multidisciplinary frame that crosses chemistry and physics frontiers, reactions involving organic molecules on metal surfaces can be exploited to achieve surface-catalyzed nanostructures. Hence the importance of understanding the role that the organic-metal interactions have on the chemical stability of the molecules. In this work, we demonstrate that the integrity of  $C_{60}F_{48}$  depends on the particular metal surface it approaches. Whereas on Au(111) the molecule preserves its chemical structure, on other surfaces such as Cu(111) and Ni(111) it rapidly loses the fluorine atoms and eventually transforms into  $C_{60}$  at room temperature. By molecular dynamics simulations with reactive force fields, the mechanisms of this surface-induced catalytic de-fluorination have been elucidated. The formation of specific fullerene 2D structures observed in STM, accompanied by the corresponding electronic changes in the XPS core levels and in the density of states of the UPS near Fermiedge valence band, confirms the whole picture.



Fig. 1: Schematic model of the deposition of chemically stable  $C_{60}F_{48}$  on Au(111) and its defluorination on Cu(111).

# **Abstracts: Posters**

#### Spin-dependent photoelectron diffraction at a molecular overlayer

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The angle resolved photoemission (ARPES) yield of noble metals recorded with low photon energies is dominated by direct optical transitions between free electron like sp-bands of the bulk band structure, the so called Mahan cones [1]. They typically reveal a characteristic spin-polarization, which depends on the strength of the spin-orbit coupling of the material.

Here, we investigate the contributions of the spin-polarized electrons of Mahan cone transitions to the photoemission yield of low dimensional adsorbates on noble metal surfaces. In particular, we focus on long range ordered molecular layers of the molecular adsorbates CuPc and H2Pc on the Au(111) surface. For these systems, photoelectron diffraction and band folding effects can redistribute the electrons of the central Mahan cone transition and hence can mask the intrinsic spin-polarization of adsorbate states.

We employ spin and angle resolved photoemission with linear polarized light and 6eV photons to analyze the spin-polarization of the central and the back-folded Mahan cones after the adsorption of the molecular layers. For both molecular adsorbates, we observe a clear spin-polarization for the main Mahan cone, but not for the back-folded cones. These findings suggest a spin-flip scattering mechanism in the molecular layer leading to a complete loss of spin-polarization of the photoelectrons. Finally, we compare our results to findings obtained for atomic adsorbates on Au(111). This will allow us to gain insight into spin-dependent scattering of substrate electrons at adsorbate films.



Fig. 1: Scattering of photoemitted eletrons at an overlayer structure (left), Mahan cone back-folding scheme for an fcc 3D Brillouin zone (middle) and photoemission spectra taken for the  $H_2Pc/Au(111)$  interface at  $E-E_F = -0.25$  eV (right).

#### References

[1] A. Winkelmann et al., *Direct k-space imaging of Mahan cones at clean and Bi-covered Cu(111) surfaces*, New J. Phys. **14**, 083027 (2012).

# Coverage-dependent structural transformation and on-surface atom exchange reactions in porphyrin-based metal-organic coordination networks on Au(111)

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Porphyrin derivatives have been frequently used as building blocks for the formation of metal-organic coordination networks (MOCNs) on metal surfaces under ultra-high vacuum (UHV). The porphyrin backbone can be tailored with different functional endgroups – that can coordinate to metal atoms - in order to fabricate structurally different MOCNs. In addition, the porphyrin core can host a variety of 3d transition metals which are usually incorporated in solution. Despite the extensive literature available for MOCNs, the influence of molecular coverage on the 2D structure, along with the replacement of a preexisting metal atom in the porphyrin core by a different metallic species has been rarely reported under UHV. Herein, the self-assembly process of a cobalt-porphyrin (Co-TCNPP) on Au(111) was studied under UHV with scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) [1]. Deposition of Co-TCNPP onto Au(111) gave rise to a close-packed network, which was independent of coverage as revealed by STM and LEED. However, a coverage dependent behavior emerged upon metal-coordination with either Co-atoms or Fe-atoms (Figure 1a). The MOCNs coordinated by Co or Fe-atoms were identical in structure. At monolayer coverage, a four-fold coordinated MOCN was formed. By reducing the molecular coverage, a structural transformation took place. The four-fold coordinated MOCN coexisted with a second MOCN, i.e., a three-fold coordinated chevron structure. In addition, an atom exchange reaction at the porphyrin core was observed for the MOCNs prepared with Fe-atoms, that gave rise to a second (brighter) molecular species as evidenced by STM, i.e., an iron-porphyrin (Fe-TCNPP) (Figure 1b). We attribute the coverage-dependent structural transformation to the in-plane compression pressure exerted by the molecules deposited on the surface.



Fig. 1: (a) STM images of the Co-coordinated MOCNs of Co-TCNPP on Au(111) upon increasing molecular coverage. (b) Schematic of the atom exchange reaction between a Fe-atom and Co-atom at the porphyrin core on Au(111) (inset: STM image of Co-TCNPP and Fe-TCNPP).

#### References

[1] Baker Cortés, B. D.; Schmidt, N.; Enache, M.; Stöhr, M. *Coverage-Dependent Structural Transformation of Cyano-Functionalized Porphyrin Networks on Au(111) via Addition of Cobalt Atoms*, J. Phys. Chem. C **123**, 19681–19687 (2019).

### Temperature-controlled rotational epitaxy of graphene

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When graphene is placed on a crystalline surface, the periodic structures within the layers superimpose and moiré superlattices form. Small lattice rotations between the two materials in contact strongly modify the moiré superlattice, upon which many electronic, vibrational, and chemical properties depend. Here we report on the structural manipulation of epitaxial graphene grown on metallic Ir(111) and semiconducting SiC(0001) surfaces.

The spontaneous reorientation in the degree- and sub-degree-range of graphene on Ir(111) depends on the substrate temperature during growth [1]. This effect is described by a 2D coincidence network favored by strain reduction together with the dissimilar thermal expansion of the substrate and graphene. The resulting effective compressive biaxial pressure is more easily accommodated in graphene by small rotations rather than by compression.

For graphene on SiC(0001) only the R30°-oriented phase is found due to the higher bonding strength to the substrate. Upon H and Sn intercalation this interaction can be reduced such that the graphene layer is lifted from the substrate.

Finally, we present a detailed analysis of an unusually broad diffraction background [2] found for graphene and hex-BN on both substrates.



*Fig. 1: SPA-LEED pattern of graphene on Ir(111) and corresponding linescans for different growth temperaures.* 

- K.M. Omambac, H. Hattab, C. Brand, G. Jnawali, A.T. N'Diaye, J. Coraux, R. van Gastel, B. Poelsema, T. Michely, F.-J. Meyer zu Heringdorf, and M. Horn-von Hoegen, *Temperature-Controlled Rotational Epitaxy of* Graphene, Nano Lett. **19**, 4594-4560 (2019).
- [2] S. Chen, M. Horn-von Hoegen, P.A. Thiel, and M. Tringides, *Diffraction paradox: An unusually broad diffraction background marks high quality graphene*, Phys. Rev. B **100**, 155307 (2019).

# Nanoscience crystallography at a high brilliance laboratory x-ray diffractometer: from mesoscopic to interatomic length scales

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The high brilliance laboratory small angle X-ray scattering instrument GALAXI [1] is used to investigate, on mesoscopic length scales, structural correlations in bulk materials or between objects deposited on a surface. The instrument is capable to perform SAXS experiments in reflection at grazing incidence as well as in transmission geometry. The X-ray flux on sample is comparable or higher than the one obtained at a comparable beamline at a second-generation synchrotron radiation source.

Some results of studies on energy and soft materials as well as materials for information technology will be given.

The device properties of thin film heterostructures crucially depend on the structure of the surface and interfaces, not only at the mesoscopic length scale but also at the interatomic length scale. We therefore aim at extending the instrument's capabilities towards wide-angle scattering. In this contribution, we will emphasize on the science case of such a development. Also, the possible realisation of this project will be discussed, taking into account the wavelength distribution of the photons emitted by the source

#### Reference

[1] Jülich Centre for Neutron Science. (2016). GALAXI: Gallium anode low-angle x-ray instrument. Journal of large-scale research facilities, **2**, A61. http://dx.doi.org/10.17815/jlsrf-2-109.

# The TensErLEED management package: A new environment for analysis and calculation of LEED I(V) data

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Low-Energy Electron Diffraction (LEED) is a structure-sensitive technique commonly available in most surface science laboratories. Beyond the usual application as a tool to determine periodicity and degree of order of a surface phase, the method also gives access to the surface's crystallographic structure via a quantitative analysis of the modulation of beam intensities as a function of electron energy/voltage (LEED I(V)). This, however, requires complex full-dynamical intensity calculations as well as a time-consuming optimization of structural parameters minimizing the deviation between experimental and calculated I(V)curves. The Erlangen program package TensErLEED [1] readily performs this task, but its required user input is almost prohibitively complex. This not only presents a significant hurdle for potential new users seeking to adopt the technique, but also carries a potential for human error even if the user has extended experience with the program.

We show that for most cases, the necessary TensErLEED input can be generated automatically by combining a handful of user parameters, a set of default values, and a structure file in a standard format. Based on this, we introduce a new package that greatly simplifies the use of TensErLEED and substantially reduces the amount of work and potential for errors, even for experienced users. Furthermore, functionality is enhanced by features like automatic detection of the surface symmetry, which can then be enforced during parameter optimization. To improve compatibility with modern data analysis software, output files from TensErLEED are automatically processed to supply *I(V)* curves and optimized atom positions in standard file formats. Utilities for file conversion are supplied to ensure backwards compatibility with older data processed by TensErLEED.

The package is completed by a versatile utility for extracting experimental *I(V)* spectra from a LEED video or a stack of LEED images. This combination of a powerful data acquisition tool and simplified data analysis will allow LEED I(V) to become a more easy-to-implement, mainstream technique in the future.

#### References

[1] V. Blum, K. Heinz, *Fast LEED intensity calculations for surface crystallography using Tensor LEED*, Comput. Phys. Commun. **134**, 392 (2001).

# STM study of the on-surface synthesis stages of a single-layer $\pi$ -conjugated 2D MOF

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 $\pi$ -conjugated honeycomb networks made with square planarly coordinated metal centres and trinucleating bidentate organic ligands can have high electrical conductivity that can be utilised in devices like chemiresistive sensors. However, such metal-organic frameworks (MOFs) synthesised via wet chemistry tend to have shortcomings constraining their performance, such as contact issues and stacking [1], retained water during crystallisation [2], and local thickness variations due to film folding [3].

A monolayer of such a 2D MOF can be created through on-surface synthesis in a vacuum environment, although these materials have to date been limited in size and coverage [4]. Here we show the vacuum phase self-assembly of a monolayer of the ligand molecule HHTP on Au(111) surfaces and the interactions between the H-bonded network and Ni. Apart from the reported zip and honeycomb phases [5,6], we have also observed two further phases as shown in Fig. 1. The STM image in Fig. 1(a) shows a high density H-bonded HHTP network on Au(111). By evaporating a low dose of Ni atoms onto the surface, the self-assembly monolayer evolves into close-packed domains of Ni<sub>3</sub>(HHTP)<sub>4</sub>, as shown in Fig. 1(b). The successful growth of the monolayer over a large area will enable the interaction of certain analytes like NH<sub>3</sub> and CO, which are relevant to chemiresistive sensing, to be studied at a single-molecule level by STM.

### Measurement of the dynamics of residual stresses in copper and tungsten during heating

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In a fusion reactor plasma impacts the divertor as periodic heat pulses. These heat pulses cause residual plastic deformations and mechanical stresses in the divertor which leads to the divertor material destruction [1]. Residual deformations and stresses can be relieved due to high temperature of the divertor which is caused by the constant flow of plasma. The relaxation of deformations and stresses may bring the material back to its initial state during the time interval between two subsequent heat pulses, so that after the second plasma pulse stresses would not exceed ultimate tensile strength and the material would not be destroyed. The temporal dependence of residual stresses is needed to be examined in order to test the possibility. The relaxation of stresses in copper samples were measured using Xray diffractometry in development of the technique. A similar measurement was later conducted with tungsten samples. In order to create residual stresses one sample was irradiated by an electron beam on the BETA facility while another one was left in its initial state for the comparison. Experimental station "Anomalous scattering" was used to film diffractograms that were used to obtain scattering angle - tilt angle dependencies. By expressing the variation of crystal lattice interplanar distance and using it in Bragg's law, a formula of scattering angle – tilt angle dependency was derived. The dependencies were used for calculation of deformation and stress tensors components. In case of tungsten samples, the measurement was also made with spatial resolution along the surface of the sample. For the dynamic measurement of the residual stresses samples were examined at a constant tilt angle and changing temperature at scattering station "Diffraction movie". The samples were heated for the relaxation of stresses. Time dependencies of temperature and diffraction maximums were measured and the diffraction maximum angle - temperature dependencies were acquired. The relaxation of the samples in the condition of changing temperature was studied by comparing of the irradiated sample's graph to the nonirradiated sample's graph with the latter having no relaxation effect. During the study of the experimental results of the copper samples an anomalous alteration of the diffraction peak was discovered. This alteration made precise calculation of the peak's center impossible. The data obtained from the tungsten samples is yet to be analyzed.

- [1] Yu. Trunev, A. Arakcheev, et al, *Heating of tungsten target by intense pulse electron beam*, AIP Conference Proceedings, **1771**, 060016 (2016).
- [2] O. Evdokov, V. Titov, et al, *In situ time-resolved diffractometry at SSTRC*, Nuclear Instruments and Methods in Physics Research A., **603**, 1-2 (2009).

### Surface trans-effect pinning low valence Ni(I)TPP on copper against irreversible structural changes

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In powders, porphyrin molecules are usually robust to thermal treatments. However, when deposited on an electrode surface, the molecule-substrate interaction influences dramatically the stability of the molecular film. It has been previously<sup>1,2</sup> reported that the on-surface annealing on coinage substrates, *e.g.*, silver, copper, and gold, promotes the partial dehydrogenation of polycyclic aromatic hydrocarbons that may lead to the formation of organometallic oligomers or the cyclo-dehydrogenation of peripheral ethyl groups. Furthermore, also intramolecular structural changes can occur at the macrocycle moiety within the porphyrin core. These changes affect irreversibly the electronic structure of the molecule and its magnetic properties<sup>3</sup>.

In contrast to silver and gold substrates, no dehydrogenation followed by a ring-closing reaction takes place for NiTPP single layer deposited on copper upon heated treatment. Using a multi-technique approach the thermal stability of a catalytically active Ni(I)TPP monolayer on copper is demonstrated up to the thermal limit of decomposition (620 K). Molecules undergo a structural transition at 420 K, which is associated with a downward bending by 10° of the phenyl terminations and a corresponding increase of charge transfer from the substrate to the phenyls without further chemical modifications. The surface transeffect (charge transfer) that drives the reduction of the Ni oxidation state, from gas-phase Ni(II) to Ni(I), also anchors the Ni metallic center to the surface. This mechanism prevents any molecular displacement within the molecular lattice across the phenyl reorientation, and preserves the stability of the Ni(I) ion, thus allowing the molecule to experience only minor conformational changes. The demonstrated high thermal stability is fundamental for any application where thermal cycles are used for regenerating the pristine properties of the reactive Ni(I) ion.

- [1] Williams, C. G. et al. *Dehydrocyclization of peripheral alkyl groups in porphyrins at Cu(100) and Ag(111) surfaces*, Surf. Sci. **653**, 130 (2016).
- [2] Ruggieri, C. et al. *Zinc(II) Tetraphenylporphyrin on Ag(100) and Ag(111): Multilayer Desorption and Dehydrogenation, J. Phys. Chem. C* **120**, 7575 (2016).
- [3] Arruda, L. M. et al. *Modifying the Magnetic Anisotropy of an Iron Porphyrin Molecule by an on-Surface Ring-Closure Reaction*, J. Phys. Chem. C **123**, 14547 (2019).

### The Air Stability of the MoS<sub>2</sub> monolayers

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Molybdenum disulphide ( $MoS_2$ ) is a prototypical member of the transition metal dichalcogenide (TMD) compounds. The MoS<sub>2</sub> naturally occurs in a hexagonal (2H) form, which has been extensively studied because of its potential applications in catalysis, electronic and optoelectronic devices, and composite nanostructures. Additionally, a synthesized metallic trigonal (1T) polytype of MoS<sub>2</sub> exists and has shown excellent catalytic activity in hydrogen evolution reaction (HER) [1]. Nevertheless, sparse experimental evidence indicates that both forms (1T as well as 2H) degrade rapidly in air via an unknown oxidation mechanism [2]. We studied the oxidation of MoS<sub>2</sub> monolayers using theoretical calculations based on the density functional theory (DFT). Our results suggest that monolayers of both polytypes (1T and 2H) oxidize almost instantaneously because there are negligible energetic barriers to the dissociation of dioxygen molecules at the edge sites. However, after an oxygen molecule dissociates, the further reaction steps are different for the 1T and 2H polytype. In case of 2H, the oxidation can proceed by the replacement of sulphur edge atoms by oxygen and ultimately causes formation of a one-dimensional chain-like structure resembling of the bulk MoO<sub>3</sub> [3]. Conversely, in 1T-MoS<sub>2</sub> the oxygen dissociates and directly adsorbs at the edge molybdenum atoms. By that, the intermediate S-O-Mo structure is formed at the edge which slows the further oxidation. Based on that, we suppose an edge degradation of single-layer 1T and 2H-MoS<sub>2</sub> is very likely in air and has to be considered and controlled in experiments and applications.

- D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V.B. Shenoy, G. Eda and M. Chhowalla, *Conducting MoS<sub>2</sub> Nanosheets as Catalysts for Hydrogen Evolution Reaction*, Nano Lett. 13, 6222–6227 (2013).
- [2] J. Gao, B. Li, J. Tan, P. Chow, T.M. Lu and N. Koratkar, *Aging of Transition Metal Dichalcogenide Monolayers*, ACS Nano **10**, 2628–2635 (2016).
- J. Martincová, M. Otyepka and P. Lazar, *Is Single Layer MoS<sub>2</sub> Stable in the Air?*, Chem. A Eur.
   J. 23, 13233–13239 (2017).

### Delayed surface phonon excitation in Bi(111) films

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We used ultra-fast reflection high energy electron diffraction [1,2] to follow the excitation of surface phonons on an epitaxial Bi(111) film on Si(111) upon impulsive excitation with a femtosecond laserpulse. The thermally induced vibrational motion  $D\mathbf{u}$  of the atoms is determined from the transient intensity drop described through the Debye-Waller effect [3].

While it is well known that the Bi bulk is heated on timescales of 2 to 3 ps we observe that the excitation of vibrational motion of the surface atoms occurs much slower at a time constant of 12 ps [4]. From the absence of a fast component in the transient diffraction intensity we conclude that bulk phonon modes are strongly suppressed at the surface [5]. For strained Bi(111) films grown on Si(001) we observe a bi-exponential behavior with a fast (< 6 ps) and slow (12 to 60 ps) component for the vibrational excitation of the surface.

We attribute the different response to the presence of an electronic surface state for relaxed 4.5 nm thick Bi films on Si(111) while this state is absent on the strained 4.5 nm thick Bi films grown on Si(001). In the first case the excited carriers populate the surface state without heating the bulk and weak electron phonon coupling excite surface phonons on a timescale of 12 ps. On Si(001) the excited carriers remain in the bulk of the film, couple to phonons on a fast time scale  $\tau < 6$  ps, and surface phonons are excited only by anharmonic coupling between bulk and surface phonon modes. Direct coupling is hampered by the missing overlap between the phonons bulk and surface dispersion. The temperature dependence of the time constant of the slow component of  $\tau_{ph-ph} \sim 60$  ps at 30 K and  $\tau_{ph-ph} = 12$  ps at 200 K reflects the increased anharmonic coupling at higher temperatures. In contrast, for Bi films on Si(111) no such pronounced temperature dependence is observed supporting the excitation of phonons is mediated by electron phonon coupling in the surface state.

- [1] A. Janzen et al., Rev. Sci. Inst. **78**, 013906 (2007).
- [2] T. Frigge, B. Hafke, T. Witte, C. Brand, M. Horn-von Hoegen, Rev. Sci. Inst. 90, 045119 (2019).
- [3] V. Tinnemann, C. Streubühr, B. Hafke, A. Kalus, A. Hanisch-Blicharski, M. Ligges, P. Zhou, D. von der Linde, U. Bovensiepen, M. Horn-von Hoegen, Struc. Dyn. **6**, 035101 (2019).
- [4] C. Streubühr, A. Kalus, P. Zhou, M. Ligges, A. Hanisch-Blicharski, M. Kammler, U. Bovensiepen,
   M. Horn-von Hoegen, D. von der Linde, Appl. Phys. Lett. **104**, 161611 (2014).
- [5] V. Tinnemann, C. Streubühr, B. Hafke, T. Witte, A. Kalus, A. Hanisch-Blicharski, M. Ligges, P. Zhou,
   D. von der Linde, U. Bovensiepen, and M. Horn-von Hoegen, Struc. Dyn. 6, 065101 (2019).
## Can one control the interface alloying between 2D-sheets and a supporting silver substrate?

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Two-dimensional (2D) materials possess unique structural and electronic properties and thus hold promise for a variety of applications. Specifically silicene, the 2D allotrope of silicon, and germanene, the 2D allotrope of germanium, were in the focus of intense research in the past decade [1]. When investigating silicene and germanene, we observed the presence of a surface alloy, which cannot be avoided during the respective growth, as seen for Si nanoribbons [2]. The resulting interfacial interactions might modify the functional properties of the resulting layer, but surprisingly, their role is often underestimated. Here, we present our recent soft X-ray photoelectron spectroscopy (SXPS) experiments at various Ge and Si coverages, indicating that during the growth of the most commonly studied  $(4 \times 4)$ superstructure of silicene on Ag(111) a Si-Ag surface alloy is consistently formed. Our scanning tunneling microscopy (STM) study of this system resolves a yet unreported phase between a bare Ag area and the  $(4 \times 4)$  structure, which we assign to the Si-Ag alloy (Fig. 1d). Notably, we show that the alloy related component in SXPS can be largely suppressed by growing silicene on a GeAg<sub>2</sub> surface alloy on Ag(111) (Fig. 1a-c), resulting in distinct structures observed by low-energy electron diffraction, which differ significantly from all previously reported superstructures. Additionally, we discuss similar observations for the reversed system Ge/Si on Ag(111) and Cu(111) substrates.



Fig. 1: Si 2p SXPS spectra of (a) low coverage Si/Ag(111); (b) silicene (4×4) superstructure on Ag(111);
(c) Si on GeAg<sub>2</sub>-terminated Ag(111). d) High-resolution STM image of Si on Ag(111).

- [1] A. Molle *et al., Silicene, silicene derivatives, and their device applications,* Chem. Soc. Rev. **47**, 6370 (2018).
- [2] G. Prévot *et al., Formation of silicene on silver: Strong interaction between Ag and Si,* Phys. Status Solidi B **253**, 206 (2016).

## Structural properties of PbTe quantum dots revealed by high-energy x-ray diffraction

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High-energy x-ray diffraction combined with atomic-pair-distribution functions analysis is particularly effective in probing reduced dimensional systems such as Lead telluride nanoparticles. PbTe crystallizes in rocksalt structure in normal temperature and pressure with lattice constant 6.462 Å [1]. Each atom is octahedrally coordinated by six nearest neighbors of the other type at distance 3.23 Å. At the scale of 10 nm and below the local crystal geometry may vary substantially with the particle size. Our results for amorphous PbTe nanoparticles illustrate how diffraction data can be used to gain insight into the structural properties of nanoparticle systems. Our experimental data can be interpreted using an orthorhombic Pnma phase of PbTe, which is an orthorhombic distortion of the rocksalt phase. The nanoparticle structure can be described in terms of distorted polyhedra shown in Fig. 1.



Fig. 1: Distorted polyhedral building block for amorphous PbTe nanoparticle. Yellow atoms are Te and cray atom in the middle of the polyhedra outlined by Te-Te bonds is Pb. Different Te-Te and Pb-Te bonds are labelled in (a) and (b) respectively.

## References

[1] Y. Noda, S. Ohba, S. Sato, Y. Saito, *Charge distribution and atomic thermal vibration in lead chalcogenide crystals*, Acta Cryst. B **39**, 312 (1983).

## Growth and electronic structure of hexagonal BN on a curved Rh(111) crystal

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Understanding the growth of a hexagonal boron nitride (h-BN) monolayer has gained interest in the scientific community owing to its many-sided impact in the field of twodimensional materials. We have investigated the growth and electronic structure of h-BN on vicinal rhodium surfaces in a systematic manner, using a crystal curved around the (111) face. While at the flat Rh(111) h-BN forms the "nanomesh" structure due to the lattice mismatch and strong chemical interaction to the substrate [1], h-BN on Rh vicinal surfaces leads to substrate faceting with well-ordered step arrays, that is, in a slightly different way as on vicinal Ni [2]. As an example, figure 1 shows a Scanning Tunnelling Microscopy image of h-BN/Rh(557) where one can observe nanoribbons with hole and wire regions at the (111) facets that are separated by multiple steps. The electronic structure was investigated by X-ray absorption (XAS), core-level and angle-resolved photoemission (ARPES) as a function of the vicinal angle  $\alpha$ . These spectroscopies reveal that the interaction of h-BN and the substrate gets stronger for densely stepped Rh substrates, contrary to nickel. For large vicinal angles  $\alpha > 10^\circ$ , the (111) facets are too short for establishing the nanomesh and a stable side facet emerges tilted by approx.  $\alpha$ =23° with respect to the Rh(111). ARPES measurements finds characteristic h-BN bands for this stable nanofacet.



Fig. 1: STM image of hBN on Rh(557).

- [1] M. Corso, W. Auwärter, M. Muntwiler, A. Tamai et al., Science. 303 (2004) 217.
- [2] L. Fernandez, A.A. Makarova, F. Schiller et al., 2D Materials 6, 2025013 (2019); A. A. Makarova, L. Fernandez, K. A. Bokai, F. Schiller et al., J. Phys. Chem. C 123, 593 (2019).

## Monolayers of rare-earth gold surfaces as template for the growth of magnetic molecules

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Fundamental knowledge of magnetic and electronic interaction phenomena that takes place at the hybrid metalorganic interface is decisive to explore the possibility to create highly spin-polarized spinterfaces to enhance the performance of organic spintronic devices [1]. To this end, tailoring magnetic properties on structurally robust substrates is crucial. Rareearth/noble metal monolayer alloys, grown on gold surfaces, possess a big potential as nanostructured magnetic templates with structural stability. Different elements of the lanthanide series have been observed to form surface-confined alloys in Au(111) [2], characterized by a high crystal quality and nanoscale periodic corrugation. Given the variety of REs and their exotic magnetism, the observations made on GdAu<sub>2</sub> encouraged a thorough search combining different RE elements and noble metals. Here we will present experimental evidence based on photoemission and X-ray magnetic dichroism experiments that magnetic properties of the substrate and the magnetic molecules are influenced by each other depending on the strength of the magnetic moment of each contributor. Moreover, the molecular adsorption on different REAu<sub>2</sub> surfaces has been studied by STM and LEED (Fig.1), finding a commensurate growth of the molecules on these substrates.



Fig. 1: LEED and STM images of 1ML of CuPc grown on 1ML of YbAu<sub>2</sub>.

- [1] S. M. Urdampilleta , S.Klyatskaya, J.-P. Cleuziou, M. Ruben, W. Wernsdorfer . *Supramolecular spin valves*. Nat. Mater. **10**, 502 (2011).
- [2] M. Corso, L. Fernández, F. Schiller and J. E. Ortega. Au(111)-Based Nanotemplates by Gd Alloying. ACS Nano 4, 1603 (2010); M. Ormaza, L. Fernández, S. Lafuente, et al. LaAu<sub>2</sub> and CeAu<sub>2</sub> surface intermetallic compounds grown by high-temperature deposition on Au(111). Phys. Rev. B 88, 125405 (2013).

# Growth-mode and interface structure of epitaxial ultrathin MgO/Ag(001) films: a surface x-ray diffraction study

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MgO ultrathin films are of great technological importance as electron tunneling barriers in electronics and spintronics. They are also well suited for on-surface-synthesis of molecular networks for 2D electronics, the wide-band gap of MgO allowing for a decoupling from the substrate. Their crystallographic quality, interface structure, and surface morphology play a crucial role in applications. On Ag(100), MgO films form islands whose morphology is function of the growing temperature [1] and of aftergrowth treatments [2]. Using SXRD, we studied the growth-mode and the structure of MgO/Ag(001) ultrathin films elaborated by reactive molecular beam epitaxy as function of the substrate temperature. At 620 K, MgO is (001) oriented and forms, in a first stage, sharp bilayer islands in coherent epitaxy with the substrate. Oxygen at the interface is on top of silver atoms, as predicted by DFT calculations [3], at an interlayer distance of about 270 pm. The experiment was performed using the new INS2 set-up on the French CRG-IF beamline at ESRF.



Fig. 1: Experimental CTRs of a MgO/Ag(001) film grown by deposition of 0.8 Mg ML in  $10^{-6}$  mbar of  $O_2$  at Ts=620 K (black circles); best fit bilayer model with O on top of Ag (continuous black line,  $\chi^2$ =2.3), monolayer model (red dashed line,  $\chi^2$ =22), and O in hollow sites model (blue dotted line,  $\chi^2$ =7.2).

- [1] A. Ouvrard, J. Niebauer, A. Ghalgaoui, C. Barth, C. R. Henry, and B. Bourguignon, J. Phys. Chem. C **115**, 8034 (2011).
- [2] J. Pal, M. Smerieri, E. Celasco, L. Savio, L. Vattuone, and M. Rocca, PRL 112, 126102 (2014).
- [3] M. Sgroi, C. Pisani, and M. Busso, Thin Solid Films 400, 64 (2001).

## Quantitative confirmation of the inverted adsorption structure for 2H-tetraphenyl porphyrin on Cu(111)

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Particular interest in recent years has been given to determining the adsorption structure of tetraphenyl porphyrin (2H-TPP) on Cu(111). Lepper et. al.[1] and Moreno-López et al.[2] have proposed the so called "inverted model" where two of the pyrrole rings of the 2H-TPP molecule are rotated almost perpendicular to the Cu(111) surface, placing the two iminic N atoms in bridge sites on the surface. Lepper et. al.[1] came to this conclusion through comparison of density functional theory (DFT) calculations with previously publish normal incidence X-ray standing wave (NIXSW) measurements[3]. Yet this NIXSW study exhibited notable radiation damage, and only probed the adsorption height, not the lateral position.

Here, we will present a NIXSW study of H2-TPP on Cu(111) probing both the height and lateral position of the N atoms in the molecule by utilizing multiple Bragg reflections. We find that the iminic N atoms sit in bridge sites,  $1.1 \pm 0.2$  Å off atop in excellent agreement with the DFT calculated position of 1.18 Å [1].



Fig. 1: Refinement maps showing the weighted mean square error for all the lateral positions for the a) iminic and b) amininc N atoms of the H2-TPP molecule on the Cu(111) surface.

- [1] M. Lepper et. al., Chem. Comm. 53, 8207 (2017).
- [2] J. C. Moreno-López et. al., Chem. Mater. **31**, 3009 (2019).
- [3] C. Bürker et. al., J. Phys. Chem. C 118, 13659 (2014).

# Formation of highly ordered molecular porous 2D networks from cyano-functionalized porphyrins on Cu(111)

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We investigated the adsorption of three related cyano-functionalized tetraphenyl porphyrin derivatives on Cu(111) by scanning tunneling microscopy (STM) in ultrahigh vacuum (UHV) with the goal to identify the role of the cyano group and the central Cu atom for the intramolecular and supramolecular arrangement. The porphyrin derivatives studied were Cu-TCNPP, Cu-cisDCNPP, and 2H-cisDCNPP, that Cu-5,10,15,20-tetrakis-(p-cyano)-phenyl-porphyrin, is, Cu-meso-cis-di(p-cyano)phenyl-porphyrin and 2H-meso-cis-di(p-cyano)-phenyl-porphyrin, respectively. Starting from different structures obtained after deposition at room temperature, all three molecules form the same long-range ordered hexagonal honeycomb-type structure with triangular pores, and three molecules per unit cell. For the metal-free 2H-cisDCNPP, this goes along with self-metalation. The structure-forming elements are pores with a distance of 3.1 nm, formed by triangles of porphyrins fused together by cyano-Cu-cyano interactions, with Cu adatoms. This finding leads us to suggest that the twofold cyano-functionalized at "cis" conformation is the minimum prerequisite to form a highly ordered 2D porous molecular pattern.

## N-doped Graphene: growth and reactivity

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Graphene (Gr) has been extensively investigated in the last decade for its peculiar properties in several research fields and, more recently, substantial effort has been focused on its possible use as key material for gas reactors, gas storage and gas sensors. In this context, the functionalization of Gr via the introduction of defects and/or doping is reported to be a promising route to tune its reactivity.

Theoretical calculations and experimental results report Nitrogen (N) as a good candidate to make Gr sensitive to gases like CO [1]. Furthermore, Gr grown on a Ni substrate was demonstrated to be a promising system for the so called "catalysis under cover [2]", thus pointing to a possible key performance of N-doped Gr on Ni as nanoreactors.

To this purpose, a high-quality N-doped Gr layer is mandatory. We developed a new method for the production of homogeneous and flat N-doped Gr on Ni(111) by chemical vapor deposition in ultra high vacuum conditions, combining a commonly used precursor (ethylene, C<sub>2</sub>H<sub>4</sub>) and the N segregation process from the Ni bulk. We characterized its structure by Scanning Tunneling Microscopy and X-ray Photoemission Spectroscopy (see Fig.1). Experimental results have been corroborated by Density Functional Theory calculations and STM simulated images, which confirm the presence of graphitic and pyridinic N defects trapped in the Gr layer.

Exposure of N-doped Gr to near ambient pressure of CO at room temperature results in intercalation at the Gr-metal interface, forming ordered CO ad-layers.

Comparison with previous experiments on the pristine Gr clearly demonstrates an enhanced reactivity, confirming what already reported in literature [3] and opening the way to a potentially scalable production of high-performance devices in the field of catalysis, gas sensing and storage.



Fig. 1: (a) Low-temperature STM image 15x15 nm2 of N-Gr on Ni(111), 77K. N defects are visible as dark and bright triangles. (b) XPS spectrum of N1s core level.

- [1] Ma, C., Shao, X. & Cao, D., Sci. China Chem. 57, 911 (2014).
- [2] M. Wei at al, J. Phys. Chem. C **119**, 13590-13597 (2015).
- [3] G. Carraro et al., Applied Surface Science 428, 775–780 (2018).

## Dynamic measurements of the x-ray Laue diffraction on single-crystal tungsten during pulsed heat load and reconstruction of the residual stress distribution in the sample

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The most promising regime of a fusion plasma confinement at facilities based on a tokamak geometry of the magnetic field involves periodical transient heat loads to divertor plates. The divertor plates of ITER are seem to be covered by tungsten armour. The tungsten tends to crack in case of the pulsed heating. The reasons of the crack formation are deformations and mechanical stresses caused by the sharp rise in temperature of thin surface layer. The diagnostic of the dynamic of the deformations and stresses in tungsten under pulsed heat load is under development at the VEPP-4M beamline 8 (scattering station "Plasma"). The previous experiments are described in the article [1]. The idea of the diagnostic is based on the measurements of the dynamics of diffraction of polychromatic synchrotron radiation (SR) on single-crystals. The deformations in the material caused by pulsed heat load lead to change in scattering angle and consequently in shape and position of the diffraction peak. These changes allow to reconstruct the behavior of deformation and stress distributions in the sample. The two significant modifications of the experiment were done: the two order increasing of the initial SR intensity allowed the using of thicker samples (~500 µm) and the new detector of SR with a silicon sensor was constructed [2]. The increasing of the thickness of samples from 200  $\mu$ m to 500  $\mu$ m significantly changed the behavior of deformations and stresses in the heated samples because the thickness became more then the distance of the temperature propagation during the same duration of pulsed heating (140µs). The fact is confirmed by the measured diffraction during the pulsed heating with the crack formation and the behavior of the residual deformations in the material after several consecutive pulsed heating. The using of new detector of SR with the silicon sensor solved two main problems of the previous detector with the gas sensor: the nonlinear sensitivity and the large width of the instrument function of the measurements at the relatively high energy of photons (~69keV). The last point is especially significant because the width of instrument function became less than the typical size of the changes in the shape of diffraction peak. It increased the accuracy of the calculation of the residual stress distribution.

- [1] A. Arakcheev, V. Aulchenko, et al., *Dynamic observation of X-ray Laue diffraction on single-crystal tungsten during pulsed heat load*, J. Synchrotron Rad. **26**, 1644-1649 (2019).
- [2] A. Arakcheev, V. Aulchenko, et al., *Development of a silicon microstrip detector with single photon sensitivity for fast dynamic diffraction experiments at a synchrotron radiation beam*, Journal of Instrumentation, **12**, C06002 (2017).

# Electrochemical interfaces getting real: theoretical modeling of transition states at applied electrode potential

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Based on recent improvements in the field of computational modeling of electrochemical interfaces, we present a method that explicitly incorporates the influence of an applied electrode potential on reaction transition states.

Commonly, transition state calculations at electrified solid-liquid interfaces are performed at zero-net-charge conditions without including electric field and double-layer effects. Under reaction conditions, however, the energetics is influenced by charge-exchange with the electrode which acts as a thermodynamic bath for the electronic degrees of freedom. Using an implicit solvation scheme in combination with a grand canonical description of the system [1], we provide an approach that is able to accurately model processes at electrochemical interfaces with the electrode potential included explicitly in the simulations.

By comparing the energy profiles of the  $N_2$  dissociation step on a high index Ruthenium surface at constant charge and constant potential conditions to the commonly considered case at zero-net-charge, we discuss the importance of including electric field and double-layer effects in electrochemical simulations.



Fig. 1: Simulation cell showing implicit solvent, planar counter-charge and induced polarization density on a stepped Ruthenium slab (left). Energy profile along the N<sub>2</sub> dissociation reaction pathway at constant charge conditions (right).

## References

[1] N.G. Hörmann, O. Andreussi, and N. Marzari, *Grand canonical simulations of electrochemical interfaces in implicit solvation models*, J. Chem. Phys. **150**, 041730 (2019).

## A sideways perspective on electronic band structure

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Nano-focused angle-resolved photoemission spectroscopy (nano-ARPES) employs a Fresnel zone plate to image momentum resolved electronic band structure on a sub micrometer scale. This opens access to samples of much smaller dimension as covered by conventional ARPES instruments [1]. Among the various nano-ARPES facilities worldwide, the nano-ARPES at the MAESTRO beamline of the Advanced Light Source achieves a cutting-edge spatial resolution of <120 nm. For the first time, this allowed us to measure the lateral band structure across multiple interfaces of an MBE grown CdTe/PbTe multilayer. Our approach thus pioneers pathways to map electronic states across buried layers and interfaces that are inaccessible by conventional techniques.

### References

 Ch. Kastl et al., Effects of Defects on Band Structure and Excitons in WS<sub>2</sub> Revealed by Nanoscale Photoemission Spectroscopy, ACS Nano 13, 2, 1284-1291 (2019).

# Structure determination of a large unit cell quasicrystal approximant in two-dimensional SrTiO<sub>3</sub> on Pt(111)

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The recent discovery of two-dimensional dodecagonal oxide quasicrystals (OQC) based on  $BaTiO_3$  and  $SrTiO_3$  draws attention to aperiodic structure formation from perovskite materials on Pt(111) [1,2]. On the atomic level, the OQC generates an aperiodic self-similar tiling consisting of triangles, squares, and rhombs of equal edge lengths. Periodically repeated patches of a quasicrystal are known as approximants.

Here, we present a structure determination of the largest unit cell approximant known so far by combining low-temperature scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and surface x-ray diffraction (SXRD). This approximant is derived from  $SrTiO_3$  on a Pt(111) surface. Its unit cell is commensurate to Pt(111) with a

 $\begin{pmatrix} 16 & 0 \\ 9 & 18 \end{pmatrix}$ , of superstructure matrix which corresponds to a rectangular cell of 44.3 Å  $\times$  43.2 Å. Figure 1 shows the charge density distribution in the unit cell determined by SXRD. Sharp and intense maxima arise at the position of the Sr and Ti atoms. The assignment of the charge density maxima to either of the two atomic species has been done by the help of STM, which is sensitive to the Ti tiling only [2]. The key feature of this two-dimensional structure is the formation of rings of twelve Ti and Sr atoms surrounding one Ti atom. The characteristic Ti-Sr distance is ~2.5 Å. The residual charge density around the central atom is assigned to oxygen atoms. Assuming a Sr:Ti:O stoichiometry of 1:1:2.5 as determined for a related small unit cell approximant [3], 120 oxygen atoms are present in this unit cell which adds up to 216 atoms in total.



Fig. 1: Charge density distribution within the unit cell of the approximant as derived from SXRD. The system has p2gg symmetry. The shaded area denotes the asymmetric unit.

- [1] S. Förster, K. Meinel, R. Hammer, M. Trautmann, and W. Widdra, *Quasicrystalline structure formation in a classical crystalline thin-film system*, Nature **502**, 215 (2013).
- [2] S. Förster et al., *Quasicrystals and their Approximants in 2D Ternary Oxides*, Phys. Status Solidi B, 1900624 (2019).
- [3] S. Förster et al., Observation and Structure Determination of an Oxide Quasicrystal Approximant, Phys. Rev. Lett. **117**, 095501 (2016).

## Red-ox of single crystal Ir(100): an in-situ high energy surface x-ray diffraction study

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Methane (CH4) conversion has been studied for many years [1]. The rate limiting step in this reaction is methane dissociation, due to the exceptional chemical stability of the C–H bonds.

 $IrO_2(110)$  surface grown on Ir(100) has shown facile dissociation of  $CH_4$  [2], as well as oxidizing  $H_2$  to -OH [3]: all important steps for the development of a new direct methane catalysts.

In this contribution we will present recent results from in-situ Surface X-ray Diffraction (SXRD) recorded at beamline P07 at DESY, Hamburg, from the oxidation/reduction cycle of the Ir(100) surface.

We have observed the oxidation of Ir(100) under different O<sub>2</sub> conditions at a temperature of 775K, similarly to the conditions presented in [2]. A predominance of rutile IrO2(110) has been observed at higher O<sub>2</sub> partial pressure, with a coexistence of multiple IrO<sub>2</sub> sub-oxides such as IrO<sub>2</sub>(110)/(101)/(100) at lower pressures, as was also reported for Ir(111)[4]. Moreover, during reduction cycles, formation of multiple Ir facets was also observed.

Further details will be discussed in this contribution.

- [1] D. M. Bibby, C.D. Chang, R.F. Howe and S. Yurchak, Eds. Methane Conversion, Vol. 36 of Studies in Surface Science and Catalysis (Elsevier, Amsterdam, 1988).
- [2] Z. Liang, T. Li, M. Kim, A. Asthagiri, and J. F. Weaver, Science **356**, 299 (2017).
- [3] T. Li, M. Kim, Z. Liang et al., Top Catal. **61**, 397 (2018).
- [4] Y.B. He, A. Stierle, W.X. Li, A. Farkas, N. Kasper, and H. Over, J. Phys. Chem. C 112, 11946 (2008).

## Unexpected submonolayer structures of Te on Cu(111) and Ag(111)

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Tellurium (Te) based alloys play an important role in metallurgy, thermoelectricity and photovoltaics [1]. Thus, an accurate knowledge of the crystallographic surface structure and elemental composition of such systems is the first step to any understanding of their diverse physical properties. We investigated the growth of submonolayer amounts of Te on Cu(111) and Ag(111) with quantitative low-energy-electron diffraction (LEED), scanning tunnelling microscopy (STM) and density-functional theory (DFT).

Upon deposition (T=100-600°C) we find for both substrates the onset of ordering at about  $\Theta$  = 0.1 ML being most pronounced for  $\Theta$  = 0.33 ML.

On Ag(111) this leads to a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase with a binary AgTe honeycomb structure (Fig. 1 (a) and (b)). Our LEED analysis (R = 0.15) finds the overlayer being located in hcp sites of the substrate and a 0.07 Å outward buckling of Te [2].

For Cu(111) we observe a  $(2\sqrt{3}\times\sqrt{3})R30^\circ$  –2Te phase, in contrast to earlier work [3]. STM shows a perfectly ordered stripe-like structure that is solved by LEED (R = 0.10) to consists of Te<sub>2</sub>Cu<sub>2</sub> chains in hcp positions with a glide plane in the centre (Fig. 1 (c) and (d)).

Both structures are confirmed by DFT calculations to be ground states of the systems, whereby the geometry as determined by LEED is reproduced. STM simulations agree well with the experimentally observed contrasts (insets in Fig. 1(b) and (d)).



Fig.1: Results for the 0.33 ML Te phases grown on Ag(111) (left) and Cu(111) (right).
(a) and (c): LEED image with substrate unit vectors (yellow) and superstructure cell (green).
(b) and (d): STM images of the closed films and insets with DFT simulations.

- [1] J. Ibers, Nat. Chem. 1, 508 (2009)
- [2] M. Ünzelmann et al., Phys. Rev. Lett., submitted
- [3] S. Andersson et al., Surf. Sci. 12, 269 (1968); M.O. King et al., Surf. Sci. 606, 1353 (2012);
   M. Lahti et al., Surf. Sci. 622, 35 (2014).

# Multi-orbital charge transfer at metalorganic/metal interfaces: electronic structure and catalitical activity

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The adsorption behavior of nickel tetraphenyl porphyrin (NiTPP) on Cu(100) has been investigated by applying a comprehensive multi-technique approach based on photoemission electron microscopy (PEEM), X-ray absorption spectroscopy (XAS), photoemission tomography (PT), STM, and complementary DFT calculations.

The adsorbed NiTPP molecules arrange in two different geometrical configurations with different orientation with respect to the [100] crystal direction (Fig. 1a,b). Here we exploited the capability of our PEEM to directly image a wide reciprocal space in one single shoot. The measured momentum maps were then compared to DFT calculations, within the PT framework. The comparison between experiment and theory shows that even the former gas-phase LUMO+3 becomes occupied upon adsorption of NiTPP on the metal surface (see Fig1 c) [1]. This charge rearrangement at the organic/metal interface leads to a reduction of the formerly Ni(II) ion to Ni(I), as indicated by the change of the X-ray absorption spectra and results in enhancing the reactivity of the metal porphyrin film. The Ni(I)TPP moiety is a catalytic core of the F430 cofactor, therefore, low-valence metal porphyrin array on copper substrate can be considered as a biomimetic catalyst for applications [2].



*Fig. 1: (a) STM image, (b) proposed absorption model and (c) projected density of state, momentum maps and DFT calculations for NiTPP/Cu(100).* 

- [1] G. Zamborlini et al., *Multi-orbital charge transfer at highly oriented organic/metal interfaces*, Nat. Comm. **8**, 335 (2017).
- [2] G. Zamborlini et al., On-surface nickel porphyrin mimics the reactive center of an enzyme cofactor, Chem. Comm. 54, 1342 (2018).