

## O 78: Electronic Structure of Surfaces I: Photoelectron Spectroscopy

Time: Thursday 10:30–13:15

Location: H14

O 78.1 Thu 10:30 H14

**Multidimensional photoemission and the "Inverse LEED State"** — ●BENEDIKT SCHÖNHENSE<sup>1</sup>, KATERINA MEDJANIK<sup>2</sup>, SERGEY BABENKOV<sup>2</sup>, DMITRY VASILYEV<sup>2</sup>, SERGEY CHERNOV<sup>2</sup>, HANS-JOACHIM ELMERS<sup>2</sup>, and GERD SCHÖNHENSE<sup>2</sup> — <sup>1</sup>Imperial College London, Dept. of Bioengineering, UK — <sup>2</sup>Johannes Gutenberg-Universität, Institut für Physik, D-55099 Mainz, Germany

Using a high-energy version of the time-of-flight  $k$ -space microscope we recorded  $I(E_B, k)$  data arrays at many photon energies in the range of 2.6 to 7 keV at the new hard X-ray beamline P22 at PETRA III (DESY, Hamburg), extending our earlier work at lower energies [1]. Full-field  $k$ -imaging of many Brillouin zones (BZs) paves the way to a new type of photoemission experiment, which was impossible with conventional  $k$ -microscopes (imaging typically one BZ). The final state in photoemission is a "time-reversed LEED state" [2], since it contains the contribution of all scattering paths experienced by the outgoing electron wave. At keV energies, the valence-band pattern contains substantial contributions from X-ray photoelectron diffraction XPD, which are superimposed on the band features. The results confirm our new model of XPD on the basis of the Laue-equations [3]. The high count rates pave the way towards spin-resolved HAXPES using an imaging spin filter.

[1] K. Medjanik et al., *Nature Mat.* 16, 615 (2017); [2] S. Hüfner, *Photoelectron Spectroscopy*, Springer Berlin, (2003); [3] G. Schönhense et al., arXiv: 1806.05871 (2018).

O 78.2 Thu 10:45 H14

**Momentum-resolved hard X-ray photoelectron spectroscopy with eliminated diffraction** — ●S. BABENKOV<sup>1</sup>, K. MEDJANIK<sup>1</sup>, D. VASILYEV<sup>1</sup>, S. CHERNOV<sup>1</sup>, O. FEDCHENKO<sup>1</sup>, C. SCHLÜTER<sup>2</sup>, A. GLOSKOVSKI<sup>2</sup>, YU. MATVEYEV<sup>2</sup>, W. DRUBE<sup>2</sup>, B. SCHÖNHENSE<sup>3</sup>, K. ROSSNAGEL<sup>2,4</sup>, H.J. ELMERS<sup>1</sup>, and G. SCHÖNHENSE<sup>1</sup> — <sup>1</sup>JGU, Inst. für Physik, Mainz — <sup>2</sup>DESY, Hamburg — <sup>3</sup>Imp. Col. London, Dept. of Bioengineering — <sup>4</sup>CAU, Inst. für Exp. und Angew. Physik, Kiel

Hard X-ray angular-resolved photoelectron spectroscopy is a powerful tool to study the electronic band dispersions of buried layers and inner interfaces[1]. Up to now, one had to struggle against experimental obstacles such as low cross-section and strong X-ray photoelectron diffraction (XPD) modulating the spectral density of states. Using a combination of a high-energy version of a time-of-flight  $k$ -microscope and the high-brilliance hard X-ray beamline P22 at PETRA III, we are able to acquire full  $I(E_B, k)$  data arrays up to  $h\nu = 7$  keV in short time[2] and thus overcome the previous acquisition time limitations. In order to eliminate the XPD modulation[3] we present a novel method: the normalization of the valence band data by high-resolution core-level XPD patterns, measured at the same kinetic energy and  $k$ -field of view, reveal the non-modulated spectral removal function. We present valence band dispersions of molybdenum, graphite and the prototypical dichalcogenide TiTe<sub>2</sub> single crystals. [1] A. Gray et al., *Nat. Mat.* 10, 759 (2011) and *Nat. Mat.* 11, 957 (2012); [2] K. Medjanik et al., *Nat. Mat.* 16, 615 (2017); [3] G. Schönhense et al., arXiv 1806.05871 (2018).

**Invited Talk**

O 78.3 Thu 11:00 H14

**Photoemission of correlated electron pairs from metals excited by megahertz high-order harmonics** — ●CHENG-TIEN CHIANG<sup>1,2</sup>, ANDREAS TRÜTZSCHLER<sup>1,2</sup>, MICHAEL HUTH<sup>2</sup>, ROBIN KAMRLA<sup>1,2</sup>, FRANK O. SCHUMANN<sup>2</sup>, and WOLF WIDDRA<sup>1,2</sup> — <sup>1</sup>Institute of Physics, Martin-Luther-Universität Halle-Wittenberg — <sup>2</sup>Max-Planck-Institut für Mikrostrukturphysik

Electron correlation has been an important topic of solid state physics, which underlies phenomena ranging from magnetism, superconductivity, to metal-insulator transitions. However, direct spectroscopy of correlated electron pairs in solids is a challenging task. By our recent development of laser-based high-order harmonic generation at megahertz repetition rates [1-3] in combination with a pair of time-of-flight spectrometers [4,5], we resolve interacting electron pairs in metals and oxides, and identify their associated valence band character [6]. Our results indicate a band-dependent electron-electron interaction, and the experiments will pave the way towards time- and angle-resolved photoelectron spectroscopy of electron pairs in solids.

[1] C.-T. Chiang, "Angle-resolved photoelectron spectroscopy at sur-

faces with high-order harmonic generation", Reference module in chemistry, molecular sciences and chemical engineering, edited by K. Wandelt, Elsevier (2018). [2] C.-T. Chiang *et al.*, *New J. Phys.* 17, 013035 (2015). [3] C.-T. Chiang *et al.*, *J. Electron Spectroscop. Relat. Phenomena*, 200, 15 (2015). [4] M. Huth *et al.*, *J. Appl. Phys.* 124, 164504 (2018). [5] M. Huth *et al.*, *App. Phys. Lett.* 104, 061602 (2014). [6] A. Trüttschler *et al.*, *Phys. Rev. Lett.* 118, 136401 (2017).

O 78.4 Thu 11:30 H14

**Breakthrough in HAXPES Performance Combining Full-Field  $k$ -Imaging with Time-of-Flight Recording** — ●K. MEDJANIK<sup>1</sup>, S. BABENKOV<sup>1</sup>, D. VASILYEV<sup>1</sup>, S. CHERNOV<sup>1</sup>, O. FEDCHENKO<sup>1</sup>, B. SCHÖNHENSE<sup>2</sup>, C. SCHLÜTER<sup>3</sup>, A. GLOSKOVSKI<sup>3</sup>, YU. MATVEYEV<sup>3</sup>, W. DRUBE<sup>3</sup>, H.J. ELMERS<sup>1</sup>, and G. SCHÖNHENSE<sup>1</sup> — <sup>1</sup>JGU, Inst. für Physik, Mainz — <sup>2</sup>Imperial College, London — <sup>3</sup>DESY, Hamburg

In order to overcome the intensity/resolution problem of hard X-ray angular-resolved photoelectron spectroscopy (HARPES), we have developed a  $k$ -microscope with a modified lens system optimized for high kinetic energies ( $>7$  keV) and very large field of view in  $k$ -space (up to 20 Å<sup>-1</sup> diameter) [1]. First results with this instrument have been taken at the new beamline P22 at PETRA III (Hamburg) [2]. The high X-ray brilliance (1.1x10<sup>13</sup> hv/s in a spot of  $< 20 \times 15 \mu\text{m}^2$ ) allows mapping of the 3D bulk Brillouin zone in a few hours. We found that the concept of tomographic  $k$ -space mapping previously demonstrated in the soft X-ray regime [3] works equally well in the hard X-ray range. Sharp valence band  $k$ -patterns of Re collected at an excitation energy of 6 keV correspond to direct transitions to the 28<sup>th</sup> repeated Brillouin zone. X-ray photoelectron diffraction (XPD) patterns with  $< 0.1^\circ$  resolution are recorded within minutes. The high count rates pave the way towards spin-resolved HAXPES using an imaging spin filter.

[1] K. Medjanik et al., arXiv:1810.11366 (2018); [2] C. Schlueter et al., *Synchr. Radiation News* 31, 29 (2018); [3] K. Medjanik et al., *Nature Materials* 16, 615 (2017).

O 78.5 Thu 11:45 H14

**The XPS limit within the one-step model of photoemission: temperature and photon energy effects** — ●LAURENT NICOLAÏ<sup>1</sup>, VLADIMIR STROCOV<sup>2</sup>, JURAJ KREMPASKÝ<sup>2</sup>, FEDERICO BISTI<sup>2</sup>, CHARLES FADLEY<sup>3</sup>, AJITH KADUWELA<sup>4</sup>, and JÁN MINÁR<sup>1</sup> — <sup>1</sup>University of West Bohemia, Plzeň, Czech Rep. — <sup>2</sup>Paul Scherrer Institut, Villigen, Suisse — <sup>3</sup>Berkeley, California, USA — <sup>4</sup>University of California, USA

Angle-Resolved Photoemission Spectroscopy (ARPES) is the method of choice for characterising the electronic structure of a given material. A complete understanding of the experimental spectra requires theoretical analyses as well. However, the development of theoretical tools in order to reproduce experimental conditions remains, to this day, a challenge. Using the one-step model of photoemission[1] as implemented in the SPRKKR package[2], our calculations incorporate temperature- and phonon energy-dependent effects via inclusion of both bulk[3] and surface phonons. We also investigate the photon energy range over which the Angle-Integrated PhotoEmission (AIPES) spectra can be compared to the corresponding Weighed Density of States (WDOS).

[1] Braun, *Rep. Prog. Phys.* 59, 1267-1338 (1996), [2] H. Ebert, D. Ködderitzsch and J. Minár, *Rep. on Prog. in Phys.* 74, 096501 (2011), [3] L. Nicolaï and J. Minár, *AIP Conf. Proc.* 1996, 020033 (2018)

O 78.6 Thu 12:00 H14

**Impact of collective electrostatic effects on the calculation of core-level excitations within the final state approach** — ●THOMAS C. TAUCHER, OLIVER T. HOFMANN, and EGBERT ZOJER — Institute of Solid State Physics, Graz University of Technology, NAWI Graz, Petersgasse 16, 8010 Graz, Austria

In this contribution we discuss complications arising when applying slab-type density functional theory-based band structure calculations to model core-level excitations at metal-organic interfaces:

When performing calculations using the final state approach, a possible complication is that by exciting an electron in every unit cell, an artificial dipole layer is created. Such dipole layers shift the core-level energies.[1] When adsorbing polar molecules, the shift due to the

induced dipole layer is consistent with the actual experimental situation, while in the above mentioned final state calculations, the resulting shifts are artificial.

As a strategy to tackle this issue, we suggest to use larger supercells for the calculations. In this case, the surface coverage stays the same, but only a tiny fraction of the molecules is excited. This approach resembles the actual X-ray photoelectron spectroscopy experiments in a much better way, and is pushing the limitations of today's computational resources.

[1] T. C. Taucher et al., *J. Phys. Chem. C*, 2016, 120, 3428.

O 78.7 Thu 12:15 H14

**The one-step model of 2PPE applied to Co(001)** — •JÜRGEN BRAUN<sup>1</sup> and HUBERT EBERT<sup>2</sup> — <sup>1</sup>Dept. Chemie, LMU München, Germany — <sup>2</sup>Dept. Chemie, LMU München, Germany

Our 2PPE one-step model approach aims at a quantitative description of the time-dependent spectroscopic properties of specific solid systems under consideration, allowing for the inclusion of static correlation effects via the LSDA+DMFT electronic structure approach. To this end we follow Pendry's one-step theory as close as possible and make extensive use of concepts of relativistic multiple-scattering theory within the LKKR method in order to guarantee for angular resolution in the spectroscopic calculations [1]. The fully relativistic formalism has been applied to fcc Co(001). We discuss our results in context with corresponding experimental data [2].

[1] J. Braun, and H. Ebert, *Relativistic theory of 2PPE from ferromagnetic materials*, *Phys. Rev. B* (2018), (submitted)

[2] A. B. Schmidt, M. Pickel, T. Allmers, M. Budke, J. Braun, M. Weinelt, and M. Donath, *Spin-dependent surface electronic structure of fcc Co films*, *J. Phys. D: Appl. Phys.* **41**, 164003 (2008)

O 78.8 Thu 12:30 H14

**Electronic properties of Cobalt-Porphyrin on Cu<sub>2</sub>O(111) - A model electrode for photocatalytic water splitting** — •LISA GRAD, ADRIAN SCHULER, MATTHIAS HENGESBERGER, and JÜRGEN OSTERWALDER — University of Zurich, Physics Institute, Winterthurerstrasse 190, 8057 Zurich, Switzerland

Photocatalytic water splitting represents a sustainable way to store solar energy in the form of chemical bonds. For large-scale use, the combination of molecular catalysts supported on light absorbing substrates is a viable approach.

With photoemission experiments we investigate the electronic properties of one model cathode consisting of the metalorganic molecule Cobalt-Porphyrin (CoPyr) adsorbed on the Cu<sub>2</sub>O(111) surface. Due to its small band gap Cu<sub>2</sub>O(111) is an efficient photoabsorber for solar light. Further it is a p-type semiconductor with downward band bending towards the surface. With angle-resolved X-ray photoelectron spectroscopy the band bending close to the surface could be determined before and after the adsorption of CoPyr molecules.

The related electric field leads to charge separation of photo-generated electron-hole pairs. By means of time-resolved two-photon photoemission we could determine the relaxation dynamics and the lifetime of photo-excited electrons in the conduction band of pristine Cu<sub>2</sub>O(111).

Our current work is focused on the investigation of the energy level alignment, the charge injection into and the lifetime of electrons in the molecular states of CoPyr adsorbed on Cu<sub>2</sub>O(111).

O 78.9 Thu 12:45 H14

**Investigating the surface composition of perfluoro-functionalized ionic liquid mixtures by angle-resolved X-ray photoelectron spectroscopy** — •BETTINA HELLER<sup>1</sup>, MATTHIAS LEXOW<sup>1</sup>, GABRIEL PARTL<sup>2</sup>, HANS-PETER STEINRÜCK<sup>1</sup>, and FLORIAN MAIER<sup>1</sup> — <sup>1</sup>Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany — <sup>2</sup>Institut für Allgemeine, Anorganische und Theoretische Chemie, Leopold-Franzens-Universität Innsbruck, Innsbruck, Austria

Due to their extremely low vapor pressure, ionic liquids (ILs) -salts with a melting point below 100 °C per definition- can be investigated under ultra-high vacuum (UHV) conditions with angle-resolved X-ray photoelectron spectroscopy (ARXPS). Using a unique "Dual Analyzer System for Surface Analysis" (DASSA)<sup>[1]</sup>, simultaneous ARXP spectra taken in 0° (bulk sensitive) and 80° (surface sensitive) emission relative to the surface normal provide detailed information about composition and molecular orientation at the sample surface.<sup>[2]</sup>

In this work, temperature-dependent XPS measurements of IL mixtures consisting of 1-alkyl-3-methylimidazolium hexafluorophosphate [C<sub>n</sub>C<sub>1</sub>Im][PF<sub>6</sub>] and a perfluoro-functionalized IL will be presented, showing a more pronounced surface enrichment of the perfluoro-chain at lower temperature.

[1] I. Niedermaier, C. Kolbeck, H.-P. Steinrück, F. Maier, *Rev. Sci. Instrum.* **2016**, 87, 045105.

[2] H.-P. Steinrück, *Phys. Chem. Chem. Phys.* **2012**, 14, 5010.

O 78.10 Thu 13:00 H14

**Dirac nodal lines and flat-band surface state in the functional oxide RuO<sub>2</sub>** — VEDRAN JOVIC<sup>1,2</sup>, ROLAND J. KOCH<sup>1</sup>, SWARUP K. PANDA<sup>3</sup>, HELMUTH BERGER<sup>4</sup>, PHILIPPE BUGNON<sup>4</sup>, ARNAUD MAGREZ<sup>4</sup>, KEVIN E. SMITH<sup>2,5</sup>, SILKE BIERMANN<sup>3,6</sup>, CHRIS JOZWIAK<sup>1</sup>, AARON BOSTWICK<sup>1</sup>, ELI ROTENBERG<sup>1</sup>, and •SIMON MOSER<sup>1,7</sup> — <sup>1</sup>Advanced Light Source — <sup>2</sup>Auckland University — <sup>3</sup>Ecole Polytechnique — <sup>4</sup>EPFL — <sup>5</sup>Boston University — <sup>6</sup>College de France — <sup>7</sup>Würzburg University

The efficiency and stability of RuO<sub>2</sub> in electro-catalysis has made this material a subject of intense fundamental and industrial interest. The surface functionality is rooted in its electronic and magnetic properties - determined by a complex interplay of lattice-, spin-rotational, and time-reversal symmetries, as well as the competition between Coulomb- and kinetic energies. This interplay was predicted to produce a network of Dirac nodal lines (DNL), where the valence- and conduction bands touch along continuous lines in momentum space. Here we uncover direct evidence for three DNLs in RuO<sub>2</sub> by angle resolved photoemission spectroscopy (ARPES). These DNLs give rise to a flat-band surface state (FBSS) that is readily tuned by the electrostatic environment, and that presents an intriguing platform for exotic correlation phenomena. Our findings support high spin- Hall conductivities and bulk magnetism in RuO<sub>2</sub>, and are likely related to its catalytic properties.