

O 12: Ultrafast Electron and spin dynamics at interfaces II

Time: Monday 15:00–18:15

Location: MA 005

O 12.1 Mon 15:00 MA 005

Excited states mapping of a transition metal dichalcogenide semiconductor — •MICHELE PUPPIN^{1,2}, CHRIS NICHOLSON¹, ADRIEL DOMÍNGUEZ GARCÍA³, HANNES HUEBENER³, ANGEL RUBIO³, LAURENZ RETTIG¹, MARTIN WOLF¹, and ERNSTORFER RALPH¹ — ¹Fritz-Haber Institut, Berlin Germany — ²École polytechnique fédérale de Lausanne, Lausanne Switzerland — ³Max Planck Institut for the dynamics of matter, Hamburg, Germany

Time-resolved photoemission combined with scanning of the emission angle can extend established band-structure mapping to excited states which are only occupied out-of-equilibrium. The full potential of time- and angle-resolved photoemission spectroscopy (trARPES) is reached by performing the experiment at high repetition rates of hundreds of kHz, limiting space charge effects and data acquisition time. Extreme ultraviolet (XUV) photon energies grant access to the whole Brillouin zone: by performing high-harmonic generation at 0.5 MHz with a novel laser light source, we demonstrate trARPES with a photon energy of 21 eV, ≈ 100 meV resolution and sub-50 fs time resolution. A 3.1 eV pump pulse populates the conduction band of the layered transition metal dichalcogenide WSe₂ followed by relaxation toward the band minimum within 1 picosecond. About 100 fs after excitation, most of the normally unoccupied conduction band states are populated due to scattering of the photo-excited carriers, allowing excited state band mapping throughout the whole Brillouin zone.

O 12.2 Mon 15:15 MA 005

Ultrafast dynamics in bilayer MoS₂ — •KLARA VOLCKAERT¹, SØREN ULSTRUP¹, CHARLOTTE E. SANDERS¹, JILL A. MIWA¹, DEEPNARAYAN BISWAS², CEPHISE CACHO³, PAULINA MAJCHRAK³, IGOR MARKOVIĆ², FEDERICO ANDREATTA¹, ADAM WYATT³, MARCO BIANCHI¹, SANJOY K. MAHATHA¹, LUCA BIGNARDI⁴, DANIEL LIZZIT⁴, PAOLO LACOVIG⁴, SILVANO LIZZIT⁴, PHIL D. C. KING², and PHILIP HOFMANN¹ — ¹Aarhus University, Aarhus, Denmark — ²University of St Andrews, St Andrews, UK — ³Central Laser Facility, Didcot, UK — ⁴Elettra Sincrotrone Trieste, Trieste, Italy

The recent development of ultrafast time-resolved photoemission experiments has led to novel findings concerning non-equilibrium electron dynamics. Of particular interest are the 2D semiconducting transition metal dichalcogenides (TMDCs) that can be seen as graphene analogues with strong spin-orbit interactions. Here, the ultrafast dynamics of bilayer MoS₂ on Ag(111) are investigated using time and angle resolved photoemission spectroscopy (TR-ARPES) following an optical excitation with tunable polarisation. Curiously, we find that the nature of the light polarisation dependence for excitation between the valence and conduction bands is different from what would be naively expected on the basis of valley-selection rules. Our results could provide new insight into the interlayer coupling and inter-valley dynamics at play in bilayer TMDCs.

O 12.3 Mon 15:30 MA 005

Ultrafast charge transfer in epitaxial WS₂/graphene van der Waals heterostructures — •ISABELLA GIERZ¹, SVEN AESCHLIMANN¹, MARIANA CHAVEZ-CERVANTES¹, RAZVAN KRAUSE¹, ANTONIO ROSSI², and CAMILLA COLETTI² — ¹Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany — ²Center for Nanotechnology @ NEST, Istituto Italiano di Tecnologia, Pisa, Italy

Reduced screening together with confinement results in strong electron-electron interactions in two dimensional solids. Since the discovery of graphene, a semi-metal with linear band structure, many other layered materials have been reduced to monolayer thickness. One example are monolayer group VI transition metal dichalcogenides, direct band gap semiconductors with broken inversion symmetry that, in the presence of strong spin-orbit coupling, produces a sizable spin splitting of the band structure up to several hundreds of meV. Stacking different two-dimensional materials to form van der Waals heterostructures offers the possibility to tune their electronic properties and to produce new functionalities. We use femtosecond laser pulses to photo-dope epitaxial WS₂/graphene heterostructures [1,2] and investigate the resulting carrier dynamics with time- and angle-resolved photoemission spectroscopy (tr-ARPES). We find evidence for ultrafast charge transfer between the layers that rapidly fills the photo-induced

holes in the valence band of WS₂.

[1] Rossi et al., 2D Mater. 3, 031013 (2016)

[2] Forti et al., Nanoscale 9, 16412 (2017)

O 12.4 Mon 15:45 MA 005

Ultrafast electron transfer across a ZnO-organic interface — •LUKAS GIERSTER¹, SESA VEMPATI¹, JAN-CHRISTOPH DEINERT^{1,2}, ANTON ZYKOV³, STEFAN KOWARIK³, YVES GARMSHAUSEN⁴, STEFAN HECHT⁴, and JULIA STÄHLER¹ — ¹Fritz-Haber-Institut Berlin, Dpt. Phys. Chem. — ²Helmholtz-Zentrum Dresden-Rossendorf — ³Humboldt-Universität zu Berlin, Dpt. of Physics — ⁴Humboldt-Universität zu Berlin, Dpt. of Chemistry

Combining organic molecules with inorganic semiconductors is a promising route towards novel optoelectronic devices, such as organic LEDs or photovoltaics [1]. The electron transfer across the hybrid interface is a crucial factor for the efficiency of such devices. We investigate this fundamental process at the ZnO/p-quinquephenyl pyridine (5P-Py) surface using time-resolved two-photon photoelectron spectroscopy. Upon adsorption of 5P-Py (mass equivalent of 2 ML) on ZnO (10-10) we find an occupied interfacial hybrid state close to the Fermi level. It can be used as an initial state to populate the molecular LUMO without direct excitation of the molecules. The LUMO population decays within 90 fs by electron transfer to ZnO. Furthermore, a bulk 5P-Py film (16 nm) was investigated, which was characterized by AFM and XRD showing a grainy and crystalline structure. Here, excitons were created by HOMO-LUMO excitation, which decay on a picosecond timescale due to exciton diffusion followed by charge separation at the interface as well as recombination. [1] N. Koch, ChemPhysChem 8, 1438-1455 (2007)

O 12.5 Mon 16:00 MA 005

The Unoccupied Electronic Structure of CuPc/PTCDA/Ag(111) Probed with Two-Photon Photoemission — •KLAUS STALLBERG, JONAS ZIMMERMANN, ALEXANDER LERCH, ANDREAS NAGALIES, and ULRICH HÖFER — Fachbereich Physik, Philipps-Universität, D-35032 Marburg

Stacked layers of copper-phthalocyanine (CuPc) and PTCDA on Ag(111) represent a structurally well-defined model for an organic donor-acceptor interface above a metal substrate. The unoccupied electronic structure of this model system is investigated by means of time-resolved two-photon photoemission (2PPE). The 2PPE spectra comprise several photoemission bands which originate from both occupied and unoccupied electronic states. More specifically, we observe direct 2PPE from the CuPc HOMO as well as photoemission involving the n=1 and n=2 image potential states (IPS), a Shockley-derived interface state (IS) at the PTCDA/Ag(111) interface, and excitonic states in the organic heterolayer as intermediate states. Photoemission from the IS is measured for pump photon energies ranging from 1.6 eV to 2.5 eV and is found to follow the optical absorption of CuPc. This indicates efficient transfer of photoexcited electrons from the CuPc layer to the IS at the PTCDA/silver interface which takes place on a timescale of 40 fs. Moreover, we discuss the origin of excitonic bands in the 2PPE spectra and investigate the relaxation dynamics of excitonic states in the CuPc/PTCDA donor-acceptor type heterosystem.

O 12.6 Mon 16:15 MA 005

The role of small polarons in ultrafast electron localization near a model electrolyte/metal interface — •SARAH KING, KATHARINA BROCH, and JULIA STÄHLER — Department of Physical Chemistry, Fritz-Haber Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

In the current study, we investigate the formation dynamics of small polarons in thin films of dimethyl sulfoxide (DMSO) near a Cu(111) metal interface using time- and angle-resolved two-photon photoemission spectroscopy. A delocalized electronic state within the second DMSO monolayer is initially formed upon photoexcitation and dynamically becomes a small polaron in DMSO on a 200 fs timescale, consistent with localization due to vibrational dynamics of the DMSO film. The polaron is subsequently further stabilized through longer-range screening on a 600 fs timescale. As the small polaron formation dynamics are the same for both 6 ML and 2 ML of DMSO, the mechanism observed in our experiments is relevant to bulk DMSO near metal

surfaces. Furthermore, the small polaron acts as a precursor state for a surface-bound electronic state with a lifetime thirteen orders of magnitude longer. This highlights the way in which electronic states near metal surfaces with femtosecond lifetimes are important precursors for long-lived states of solvents and electrolytes.

15 min. break

Invited Talk

O 12.7 Mon 16:45 MA 005

Nonlinear Surface Phonon Polariton Spectroscopy — NIKOLAI C. PASSLER¹, ILYA RAZDOLSKI¹, CHRISTOPHER J. WINTA¹, SANDY GEWINNER¹, WIELAND SCHÖLLKOPF¹, STEFAN A. MAIER², JOSHUA D. CALDWELL³, MARTIN WOLF¹, and •ALEXANDER PAARMANN¹ — ¹Fritz-Haber-Institut, Berlin, Germany — ²Imperial College London, UK — ³Vanderbilt University, Nashville, USA

There has been much increasing interest recently in the mid-infrared to terahertz spectral response of polar dielectric crystals due to a novel branch of nanophotonics based on surface phonon polaritons (SPhPs) [1], which arise at the surface of these materials due to optical phonon resonances in their dielectric response. Using our in-house free-electron laser [2] as intense and tunable infrared light source, we have developed new approaches of nonlinear solid state spectroscopy, focusing on phonon resonances in polar dielectrics.

Specifically, mid-infrared second harmonic generation (SHG) spectroscopy [3] is used to probe the optical field enhancement associated with resonantly excited SPhPs in sub-diffractive nanostructures [4], as well as prism-coupled propagating SPhPs using the Otto geometry [5]. The latter approach enables mapping of the full SPhP dispersion which can, for instance, reveal the SPhP hybridization in heterostructures.

[1] Caldwell, et al. *Nanophotonics* 4, 1 (2015) [2] Schöllkopf et al., *Proc. SPIE* 9512, 95121L (2015) [3] Paarmann, et al. *Appl. Phys. Lett.* 107, 081101 (2015) [4] Razdolski, et al., *Nano Letters* 16, 6954 (2016) [5] Passler, et al., *ACS Photonics* 4, 1048 (2017)

O 12.8 Mon 17:15 MA 005

Ultrafast hot electron dynamics of quantum-well states in momentum space — •FLORIAN HAAG¹, LISA GRAD¹, JOHANNES SEIDEL¹, NORMAN HAAG¹, MIRKO CINCHETTI², MARTIN AESCHLIMANN¹, and BENJAMIN STADTMÜLLER¹ — ¹Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schrodinger-Strasse 46, 67663 Kaiserslautern, Germany — ²Experimentelle Physik VI, Technische Universität Dortmund, 44221 Dortmund, Germany

Excited electrons play a crucial role for many fundamental chemical and physical phenomena occurring at surfaces, (hybrid) interfaces, or in bulk materials. Here, we use time-resolved 2 photon momentum microscopy to follow the hot electron dynamics in momentum space and to determine the momentum dependent scattering processes of excited electrons.

As model system, we examined the electron dynamics of the quantum-well system Pb on Ag(111) for different laser polarizations and laser fluencies. The momentum dependent hot electron lifetime can be directly correlated to the band dispersion of the QWS. After adsorption of the organic molecule PTCD, we find an orbital selective hybridization between molecular levels and QWS as well as a significant increase of the momentum dependent electron lifetime throughout the entire momentum space.

O 12.9 Mon 17:30 MA 005

Ultrafast band structure dynamics of thin C_{60} films on Ag(111) — •SEBASTIAN EMMERICH¹, BENJAMIN STADTMÜLLER¹, DOMINIK JUNGKERN¹, NORMAN HAAG¹, CHRISTINA SCHOTT¹, SEBASTIAN HEDWIG¹, STEFFEN EICH¹, MARKUS ROLLINGER¹, MAHALINGAM MANIRAJ¹, MARTIN AESCHLIMANN¹, MIRKO CINCHETTI², and STEFAN MATHIAS³ — ¹University of Kaiserslautern, Erwin-Schrodinger-Str. 46, 67663 Kaiserslautern, Germany — ²Physikalisches Institut I, Universität Göttingen, 37077 Göttingen, Germany — ³Experimentelle Physik VI, Technische Universität Dortmund, 44221 Dortmund, Ger-

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The performance of organic based electronic devices is determined by the energy level alignment as well as by the excitation dynamics of electrons in these materials. Although both aspects are intrinsically linked by the polarizability of organic materials, they have mainly been discussed separately so far. In this work, we present new insight into the ultrafast band structure dynamics of thin C_{60} films on Ag(111). The combination of time- and angle resolved photoemission with a fs-XUV light source allows us to follow the transient evolution of the unoccupied as well as of occupied band structure after the fs-optical excitation with visible light. The unoccupied part of the C_{60} band structure reveals the well-known quasi-particle dynamics of the exciton formation and its decay in C_{60} . Most interestingly, we observe a transient inhomogeneous broadening of all occupied molecular orbitals upon optical excitation. This effect is attributed to the transient polarization of the molecular film caused by the exciton formation at distinct C_{60} sites.

O 12.10 Mon 17:45 MA 005

Breakdown of the atto-clock concept in attosecond-time-resolved photoemission from solids — •ANDREAS GEBAUER^{1,2}, SERGEJ NEB¹, WALTER ENNS¹, ULRICH HEINZMANN¹, ANDREY K. KAZANSKY^{3,4,5}, and WALTER PFEIFFER¹ — ¹Molecular and Surface Physics, University of Bielefeld, Germany — ²Ultrafast Phenomena At Surfaces, TU Kaiserslautern, Germany — ³University of the Basque Country, 20080, San Sebastián, Spain — ⁴Donostia International Physics Center (DIPC), 20018 San Sebastián, Spain — ⁵IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain

The availability of single attosecond EUV pulses paved the way to observe electrons at solid surfaces on their natural time scale [1]. In streaking spectroscopy the interaction of a photoelectron with an intense NIR streaking field reveals relative delays of different emission channels with up to 10 as resolution [2].

Here, the impact of an inhomogeneous and penetrating IR field distribution on as-time-resolved photoemission from solid surfaces is simulated based on solving the one-dimensional TDSE [2].

It is shown that the penetration of the IR fields has a substantial impact on the relative delays. Therefore, the phenomenological concept of a classical atto-clock, that can be envisioned as a common finish line for different photoemission channels, needs to be discussed.

[1] A.L. Cavalieri, et al., *Nature* **449**, 1029 (2007).

[2] F. Siek, et al., *Science* **357**, 1274 (2017)

O 12.11 Mon 18:00 MA 005

Spin polarization and attosecond time delay in photoemission from condensed matter — •MAURO FANCIULLI^{1,2}, HENRIETA VOLFOVÁ³, STEFAN MUFF^{1,2}, ANDREW WEBER^{1,2}, JAN MINÁR⁴, ULRICH HEINZMANN⁵, and HUGO DIL^{1,2} — ¹École Polytechnique Fédérale de Lausanne (CH) — ²Swiss Light Source, PSI, Villigen (CH) — ³Ludwig Maximilians Universität München (DE) — ⁴University of West Bohemia, Pilsen (CZ) — ⁵Universität Bielefeld (DE)

Interfering channels in the photoemission matrix elements are at the origin of spin polarization of the photoelectron beam even when the probed initial state is not spin-polarized [1]. Thus the measurement of spin polarization by means of spin- and angle-resolved photoemission spectroscopy allows to have information on the interference process, and in particular on the phase-shift ϕ_s between the channels. An extension of the Eisenbud-Wigner-Smith (EWS) model of particle scattering allows to relate the attosecond time delay in photoemission to the phase term ϕ of the matrix elements [2].

It will be shown that ϕ is closely related to ϕ_s , and that it is possible to make an indirect estimate of EWS time delays from a (non-time-resolved) spin-resolved experiment [3]. After the description of the model, experimental studies performed at the Swiss Light Source on several condensed matter systems of interest will be presented [3,4].

[1] E. Tamura et al., *PRL* 59, 08934 (1987) [2] R. Pazourek et al., *Rev. of Mod. Phys.* 87, 03765 (2015) [3] M. Fanciulli et al., *PRL* 118, 067402 (2017) [4] M. Fanciulli et al., *PRB* 95, 245125 (2017)