

## O 16: Ultrafast Electron Dynamics at Surface and Interfaces II

Time: Monday 15:00–17:30

Location: TRE Phy

O 16.1 Mon 15:00 TRE Phy

**Time Resolved Photoemission Study of the Charge Transfer Dynamics in Rutile TiO<sub>2</sub>(110) for CO Photooxidation to CO<sub>2</sub>** — ●HELENA GLEISSNER<sup>1,2,3</sup>, MICHAEL WAGSTAFFE<sup>2</sup>, LUKAS WENTHAUS<sup>4</sup>, SIMON CHUNG<sup>2</sup>, STEFFEN PALUTKE<sup>4</sup>, SIARHEI DZIARZHYTSKI<sup>4</sup>, DMYTRO KUTNYAKHOV<sup>4</sup>, MICHAEL HEBER<sup>4</sup>, GÜNTER BRENNER<sup>4</sup>, HARALD REDLIN<sup>4</sup>, HESHMAT NOEI<sup>1,2</sup>, and ANDREAS STIERLE<sup>1,2,3</sup> — <sup>1</sup>The Hamburg Centre for Ultrafast Imaging, Hamburg, Germany — <sup>2</sup>Center for X-ray and Nano Science (CXNS), Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany — <sup>3</sup>Fachbereich Physik Universität Hamburg, Hamburg, Germany — <sup>4</sup>Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany

In a pump-probe experiment at the free electron laser in Hamburg (FLASH) we gained insight into the ultrafast charge transfer on rutile TiO<sub>2</sub>(110) during CO oxidation to CO<sub>2</sub>. Pumped with a 770 nm optical laser and probed with 643 eV FEL soft x-rays we monitored the changes in the O 1s and Ti 2p core levels on a picosecond timescale using time-resolved photoemission spectroscopy.

We find that oxygen gets activated and reacts with CO to CO<sub>2</sub> in 0.2 ps up to 1 ps after the laser excitation. A complementary study found that the CO oxidation on anatase TiO<sub>2</sub>(101) takes place between 1.2 and 2.8 ps after irradiation with an ultrashort laser pulse.[1]

[1] Wagstaffe, M. et al. ACS Catal. 10, 13650-13658 (2020).

O 16.2 Mon 15:15 TRE Phy

**Transient Absorption Spectroscopy of NiO** — ●MAHENDRA KABBINAHITHLU<sup>1</sup>, TOBIAS LOJEWSKI<sup>1</sup>, SERGEY KOVALENKO<sup>2</sup>, HEIKO WENDE<sup>1</sup>, UWE BOVENSIEPEN<sup>1</sup>, JULIA STÄHLER<sup>2</sup>, and ANDREA ESCHENLOHR<sup>1</sup> — <sup>1</sup>Universität Duisburg-Essen, Fakultät für Physik und Center for Nanointegration (CENIDE), Lotharstraße 1, 47057 Duisburg, Germany — <sup>2</sup>Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Straße 2, 12489 Berlin, Germany

In nickel oxide (NiO), a correlated transition-metal oxide, the strong electron-electron repulsion splits the d-bands into an occupied lower Hubbard band (LHB) and an unoccupied upper Hubbard band (UHB). The presence of additional oxygen p-bands at the adjacent sites and their interaction with the Hubbard bands leads to complex properties governed by the Hubbard potential ( $U$ ) and the charge transfer ( $p \leftrightarrow$  LHB) gap  $\Delta$ . NiO is a charge-transfer insulator with the p-bands located between the LHB and the UHB ( $\Delta < U$ ). We present excited state dynamics in NiO thin films via time-resolved optical spectroscopy. NiO is pumped above the band gap with 4.8 eV photons and the transient absorption spectrum is probed using a time-delayed supercontinuum. The time-resolved absorption spectrum, shows within the first 500 fs positive pump-induced changes at 2.2 eV and 3.2 eV which are separated from substrate contributions. We also see a strong negative change around 4.3 eV. The positive changes from in-gap states decay on a time scale of 100 fs, while the negative change represents the bleached ground state which recovers within 6 ps, potentially by interaction with phonons.

O 16.3 Mon 15:30 TRE Phy

**Photoinduced dynamics of flat bands in the kagome metal CoSn by TR-ARPES** — ●DENNY PUNTEL<sup>1</sup>, WIBKE BRONSCH<sup>2</sup>, MANUEL TUNIZ<sup>1</sup>, MINGU KANG<sup>3</sup>, PAUL NEVES<sup>3</sup>, SHIANG FANG<sup>3</sup>, EFTHIMIOS KAXIRAS<sup>4,5</sup>, JOSEPH G. CHECKELSKY<sup>3</sup>, RICCARDO COMIN<sup>3</sup>, FULVIO PARMIGIANI<sup>1,2</sup>, and FEDERICO CILENTO<sup>2</sup> — <sup>1</sup>Dipartimento di Fisica, Università degli Studi di Trieste, Trieste (Italy) — <sup>2</sup>Elettra - Sincrotrone Trieste S.C.p.A., Trieste (Italy) — <sup>3</sup>Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, USA — <sup>4</sup>Department of Physics, Harvard University, Cambridge, MA, USA — <sup>5</sup>John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA

In kagome systems, the geometry of the lattice localises the electrons in real space, enhancing the correlations and giving rise to flat bands. In CoSn two flat bands with nontrivial topological character lie below the Fermi level [1]. In order to study the response of the localisation mechanism to impulsive excitation, we performed the first time- and angle-resolved photoelectron spectroscopy study on CoSn. At temporal overlap we observe an increase in the electronic temperature, along with a shift and broadening of the flat bands by few meV. A smaller broadening of the flat band persists for the whole duration of the in-

vestigated time delay range (about 6 ps). A possible explanation for this broadening is the partial disruption of the real-space electron localisation, because of the increased mobility of the carriers due to the energy injected by the infrared pump pulse.

[1] M. Kang et al., Nat. Commun. 11, 4004 (2020)

Topical Talk

O 16.4 Mon 15:45 TRE Phy

**Microscopic insight into non-equilibrium dynamics through time-resolved x-ray absorption spectroscopy** — ●ANDREA ESCHENLOHR — Faculty of Physics and CENIDE, University Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany

Time-resolved x-ray absorption spectroscopy provides access to element- and chemically sensitive information on the femto- to picosecond timescales of the elementary microscopic processes involving charge, spin and lattice dynamics in solids via optical pump, x-ray probe experiments. Recently implemented specialized x-ray optics at the SCS instrument of European XFEL allow for a simultaneous acquisition of the ground state and optically excited x-ray spectra as well as a reference signal for normalization of the data to the incident x-ray intensity, and thus provide excellent data quality in combination with kHz repetition rates [1]. We employ this scheme to analyze the temporal evolution of the electronic structure of ferromagnetic Ni after optical excitation and distinguish transient broadening and energy shifts in the absorption spectra, which we show to be caused by electron repopulation and correlation-induced modifications of the electronic structure, respectively. Crucially, an ab initio theoretical description requires taking the local Coulomb interaction into account, revealing the temporal interplay between electron correlations and ultrafast spin-dependent charge dynamics [2].

[1] L. Le Guyader et al., arxiv.org/abs/2211.04265

[2] T. Lojewski et al., arxiv.org/abs/2210.13162

O 16.5 Mon 16:15 TRE Phy

**Direct observation of light-induced ultrafast currents in black phosphorus** — ●MACIEJ DENDZIK<sup>1,2</sup>, ANDREA MARINI<sup>3</sup>, SAMUEL BEAULIEU<sup>2</sup>, SHUO DONG<sup>2</sup>, TOMMASO PINCELLI<sup>2</sup>, JULIAN MAKLAR<sup>2</sup>, R. PATRICK XIAN<sup>2</sup>, ENRICO PERFETTO<sup>3,4</sup>, MARTIN WOLF<sup>2</sup>, GIANLUCA STEFANUCCI<sup>4,5</sup>, RALPH ERNSTORFER<sup>2</sup>, and LAURENZ RETTIG<sup>2</sup> — <sup>1</sup>KTH Royal Institute of Technology, Stockholm, Sweden — <sup>2</sup>Fritz Haber Institute of the Max Planck Society, Berlin, Germany — <sup>3</sup>CNR-ISM, Rome, Italy — <sup>4</sup>Tor Vergata University of Rome, Rome, Italy — <sup>5</sup>INFN, Rome, Italy

Understanding intricate details of light-matter interaction on the femtosecond timescale is at the heart of modern photonics and optoelectronics. However, fundamental coupling between charge carriers response and corresponding induced electromagnetic fields upon an ultrafast optical excitation remain largely unexplored in many quantum materials. Here, we present an experimental time- and momentum-resolved photoemission study of black phosphorus (BP) combined with state-of-the-art simulations of ultrafast carrier dynamics and induced fields. We find dramatically different electron dynamics following excitation by light polarized along the zigzag and armchair directions which we associate with a difference in initial population momentum distributions. Remarkably, we observe a sub-picosecond population imbalance of excited carriers with opposite momenta, which correspond to the generation of transient in-plane currents. The results provide a comprehensive picture of the ultrafast carrier dynamics in BP and pave the way for novel applications in optoelectronics or quantum computing.

O 16.6 Mon 16:30 TRE Phy

**Band-resolved relaxation of laser-excited gold.** — ●TOBIAS HELD<sup>1</sup>, PASCAL D. NDIONE<sup>1</sup>, SEBASTIAN T. WEBER<sup>1</sup>, DIRK O. GERICKE<sup>2</sup>, and BAERBEL RETHFELD<sup>1</sup> — <sup>1</sup>RPTU, Kaiserslautern, Germany — <sup>2</sup>CFSA, University of Warwick, Coventry, UK

Irradiation of gold with visible light may excite d-band electrons into the free sp-electron states. This process increases the energy content of the electron system and induces an occupational nonequilibrium. Since the particle exchange is significantly slower than the energy transfer between the electron subsystems, the nonequilibrium band occupation persists long after a temperature can be well defined. Subsequently, density equilibration and the electron-phonon relaxation need to be considered consistently. In Ref. [1], we have simulated the non-

equilibrium band occupation with electron density-resolved rate equations and coupled them with a two-temperature model to include the energy transfer from the electrons to the lattice. The results are sensitive to the electron-phonon coupling parameter applied.

Here, we investigate the electron-phonon coupling strength in more detail. We describe the interaction of the d- and sp-electrons with the lattice by complete Boltzmann collision integrals and show that the extracted electron-phonon coupling parameters strongly depend on the band occupation. Consequently, we incorporate this aspect into the simulation by assigning different temperatures to these bands and couple them separately to the phonons.

[1] Ndione, Weber, Gericke, and Rethfeld. *Sci Rep*, 12(1), 2022

O 16.7 Mon 16:45 TRE Phy

**Multi-directional energy transfer across hybrid plasmonic-excitonic interface** — ●TOMMASO PINCELLI<sup>1</sup>, THOMAS VASILEIADIS<sup>1</sup>, SHUO DONG<sup>1</sup>, SAMUEL BEAULIEU<sup>1</sup>, MACIEJ DENDZIK<sup>1</sup>, DANIELA ZAHN<sup>1</sup>, SANG-EUN LEE<sup>1</sup>, HÉLÈNE SEILER<sup>1</sup>, YINPENG QI<sup>1</sup>, RUI PATRICK XIAN<sup>1</sup>, JULIAN MAKLAR<sup>1</sup>, EMERSON COY<sup>2</sup>, NICLAS S. MUELLER<sup>3</sup>, YU OKAMURA<sup>3</sup>, STEPHANIE REICH<sup>3</sup>, MARTIN WOLF<sup>1</sup>, LAURENZ RETTIG<sup>1</sup>, and RALPH ERNSTORFER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG, Berlin, Germany — <sup>2</sup>NanoBioMedical Centre, Adam Mickiewicz University, Poznan, Poland — <sup>3</sup>Freie Universität Berlin, Berlin, Germany

Hybrid plasmonic devices involve a nanostructured metal supporting localized surface plasmons to amplify light-matter interaction, and a non-plasmonic material to functionalize charge excitations. We combine the use of time and angle-resolved photoemission spectroscopy and femtosecond electron diffraction to investigate charge carrier and phonon dynamics in such a system: epitaxial Au nanoislands on bulk WSe<sub>2</sub>. The Au nanostructures show delayed electronic temperature increase and cause a shortening of the  $\Sigma$ -exciton lifetime. Lattice heating is accelerated in WSe<sub>2</sub> and delayed in Au. Our results resolve a multi-directional energy exchange on timescales shorter than the electronic thermalization of the nanometal, driven by a non-linear plasmon-exciton interaction. Non-radiative exciton recombination, electron-phonon coupling, and diffusive charge-transfer determine the subsequent energy backflow.

O 16.8 Mon 17:00 TRE Phy

**Electronic hybridization and ultrafast dynamics in Terrylene/WS<sub>2</sub> heterostructure.** — ●SAMUEL PALATO<sup>1</sup>, BOUBACAR TANDA BONKANO<sup>1</sup>, SERGEY KOVALENKO<sup>1</sup>, MICHELE GUERRINI<sup>2</sup>, CATERINA COCCI<sup>2</sup>, and JULIA STÄHLER<sup>1</sup> — <sup>1</sup>Humboldt Universität zu Berlin, DE — <sup>2</sup>Carl von Ossietzky Universität Oldenburg, DE

Hybrid organic-inorganic heterostructures offer the possibility of optoelectronic materials with tailored properties. We report on electronic coupling and charge carrier injection in heterostructures formed of terrylene (T) and monolayer WS<sub>2</sub> investigated using steady-state and femtosecond optical spectroscopy.

Terrylene molecules in solution show a typical Frank-Condon transition to a singlet state with a lifetime of 3.7 ns. TD-DFT calculations indicate a transition dipole moment along the long axis of the molecule. In contrast, the spectrum of the T film is complex and implies strong H-aggregation. We assign the dynamics to thermal reorganization of the molecules in the film, giving rise to changes in the magnitude and sign of charge-transfer coupling.

The response of the T/WS<sub>2</sub> hybrid indicates direct hybridization of higher-lying exciton states. Upon excitation of T/WS<sub>2</sub>, the transient response is similar to that of WS<sub>2</sub>; it suggests direct injection of charge carriers from the organic to the inorganic layer.

The presence of hybrid states and the evidence of direct injection underlines the potential of hybrid organic-inorganic materials with tailored optoelectronic properties.

O 16.9 Mon 17:15 TRE Phy

**Ultrafast electron dynamics at D<sub>2</sub>O/Na<sup>+</sup>/Cu(111) interfaces** — ●FLORIAN KÜHNE<sup>1</sup>, JAYITA PATWARI<sup>1,2</sup>, PING ZHOU<sup>1</sup>, KARINA MORGENSTERN<sup>2</sup>, and UWE BOVENSEPEN<sup>1</sup> — <sup>1</sup>Faculty of Physics and Center for Nanointegration (CENIDE), University of Duisburg-Essen — <sup>2</sup>Department of Chemistry and Biochemistry, Ruhr-University Bochum

Ion-solvent interactions and electron transfer across the ion-metal hybrid interfaces are of fundamental interest because of their widespread application in energy storage and energy conversion. We aim to understand the effect of solvation on the elementary processes involved in electrochemical applications by developing a microscopic insight into the hybrid interfaces in presence of a solvent. Electron transfer across such interfaces and the consequent relaxation dynamics are the key microscopic steps behind all these applications which occur on femtosecond time scales. Thus, to experimentally analyze the underlying elementary dynamics, we use femtosecond time-resolved two-photon photoelectron spectroscopy (*tr*-2PPE). We discuss the influence of the solvent at the D<sub>2</sub>O/Na<sup>+</sup>/Cu(111) interface. We conclude on the local structure - dynamics relation as a function of D<sub>2</sub>O coverage from the measured energy transfer rate determined by the transient energy shift of the Na 3s resonance on Cu(111). We analyze furthermore the screening of the excited electron in this resonance by the solvent based on the relaxation time variation with D<sub>2</sub>O coverage.

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