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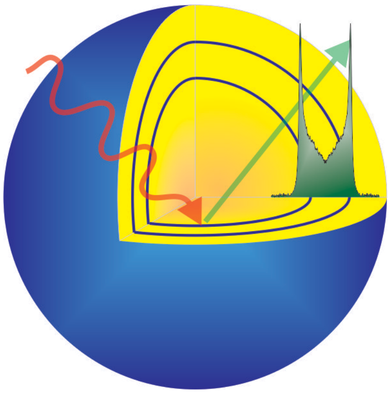

POSTER LIST
AND
ABSTRACTS

POSTER LIST

All abstracts related to the poster sessions are available on the conference website (www.delegia.com/xray) and USB key.
The posters sessions are held at **Norrlands Nation** on **Floor 2**.

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Veritas @ MAX IV

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VERITAS aims at becoming a world leading beamline for Resonant Inelastic X-ray Scattering (RIXS) in the 275-1600 eV range. This goal will be achieved by fully utilizing the high current and extraordinary emittance of the MAX IV 3 GeV storage ring. The beamline will deliver a high flux of highly monochromatic photons of well-defined polarization in a small focal spot at the sample. A large high-resolution soft X-ray spectrometer, rotatable in the horizontal plane will be attached to a custom experimental chamber and manipulator system. The beamline is designed to handle a wide range of samples, from solids to liquids and gases under different environments allowing for fundamental physics research as well as in situ studies of operational applications.

Atomic-level investigation of thin films of CoPi-based catalyst for water splitting reactions; in UHV and at elevated pressure

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Thin films of Cobalt phosphate (CoPi) are electrodeposited and their electrochemical properties and chemical composition are studied. CoPi is used as catalyst in water splitting processes. There are numerous studies on earth-abundant material to be used as electrode for the photocatalytic water splitting, however the self-healing character of CoPi as well as its ability to perform in neutral pH (pH~7) makes it an interesting candidate as a catalyst.

In this work, CoPi films are electrodeposited on FTO substrates as cathode, from an aqueous solution of cobalt and phosphate salt at modest overpotentials. In order to modify the catalytic properties of CoPi, Ni has been added to the solution in different concentrations. The electrochemical properties of these films are measured, which confirm the role of Ni in shifting the potential for the oxygen production. These films are also measured at HIKE beamline at BESSY, which allowed us to measure HAXPES and NEXAFS (Co K-edge) on these samples. Comparison to the reference compounds with known oxidation state allows determination of the metal oxidation state in the prepared films. In Co NEXAFS spectra, the position of edge determines the degree of oxidation, which in this case Co oxidation state is closer to Co^{III}.

In an attempt to move towards in-situ measurements, we have done photoemission measurements at elevated water pressure, using the HiPP-3 instrument at Scienta Omicron. We have succeeded to perform XPS measurements on water-adsorbed CoPi surfaces.

Direct observation of crystal field splitting of 4f levels by Resonant Inelastic soft X-ray Scattering

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Resonant Inelastic soft X-ray scattering (soft-RIXS) is a photon in - photon out spectroscopy sensitive to electronic and collective excitations in 3d and 4f compounds at the $L_{2,3}$ and $M_{4,5}$ edges. The last years' improvement in the energy resolution opened up the possibility of studying new excitations. Among these, electronic excitations within the 4f shell (*ff excitations)* can now bring much more information about the properties of lanthanides' compounds.

In Cerium intermetallic compounds of the "122" family, 4f levels can hybridise with the wave functions of the surrounding atoms influencing the electronic, magnetic and thermal properties of the system [1]. As a result, peculiar behaviors such as superconductivity, heavy fermions and Kondo-lattice may arise [2-4]. The full description of the energy and symmetry of the 4f levels, split by spin-orbit interaction (~300 meV) and by the crystal field effect (~30 meV), is therefore necessary to the understanding of the physics of these compounds.

The new soft-RIXS spectrometer of ID32 at ESRF has an energy resolution at the Ce M_5 edge (880 eV) of 30 meV, comparable to the energy of *ff excitations*. We will present the first observation of ff excitations with soft-RIXS in Cerium intermetallic compounds [Figure 1]. The ability of soft-RIXS to solve the 4f crystal field scheme will be discussed. With the help of simulations, it provides results complementary to INS and in agreement with other indirect techniques.

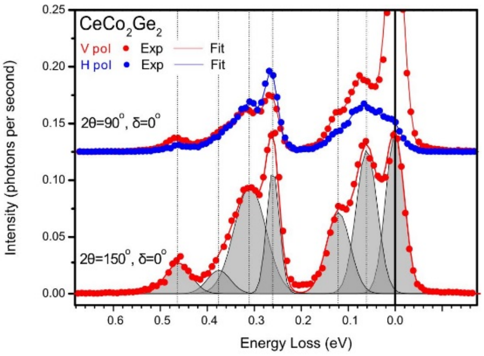

Figure 1: RIXS spectra of CeCo2Ge2. The gaussians used for the fit, representing the 7 4f doublets, are also shown.

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Carbon windows for X-ray-based research on gases, liquids and solutions

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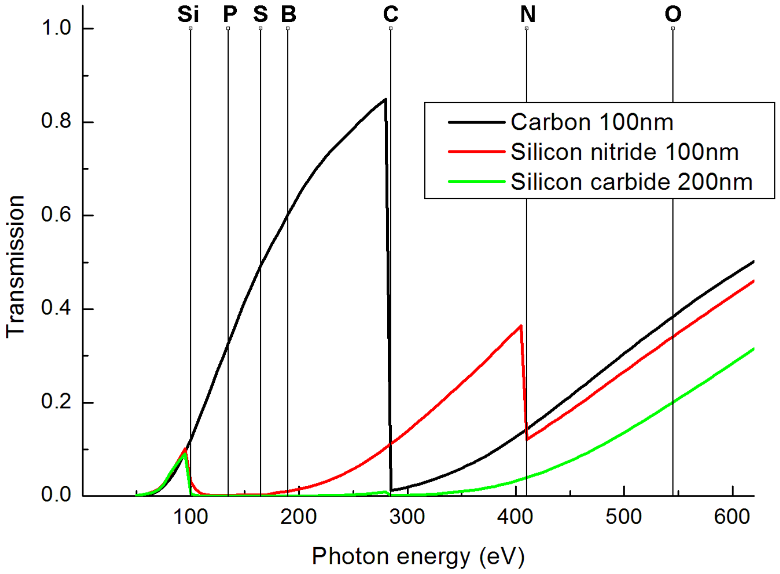
Membranes allow separation of the UHV in the beamline and experimental station from gases and liquids, thus allowing a plethora of novel experiments utilizing synchrotron radiation. Examples are high precision molecular spectroscopy in the gaseous and liquid phases, *in situ* investigations on surface reactions such as corrosion and catalysis as well as *in operando* studies on devices like batteries and solar cells.

Carbon membranes are highly transparent to photons in the energy range 150-280 eV, encompassing the absorption edges of boron, sulfur and phosphorous. The high transmission leads to better signal-to-noise ratio and/or shorter acquisition times which is important when using high cost equipment with limited accessibility like a synchrotron. Additionally they are useful to edges in the range 90-150 eV, for example silicon, and on the nitrogen and oxygen edges, 400 and 535 eV respectively. These membranes are mechanically and chemically stable in most environments and can be coated with thin films for added functions.

Some examples of original research using carbon membranes will be presented, for example high energy-resolution spectroscopy of the oxygen molecule revealing quantum beats [1], characterization of different functional groups in bio-molecules at different pH [2], and *in situ* correlation of water and chloride-induced corrosion of iron to the evolution of soft X-ray spectral features [3].

Although the carbon membranes are surprisingly robust, their longevity is challenged by the recent generation of high-brightness beamlines. Future research aims at understanding and mitigating the mechanisms behind this limitation.



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X-ray Spectroscopy Properties of Ruthenium Complex Catalysts from First-principles Theory

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The Ruthenium complexes has attracted a great deal of attention due to their potential applications as electrocatalyst in solar fuel production involving both water oxidation reaction and reduction of CO_2 to higher energy products. However, the underlying mechanisms of these complex reactions are not yet fully resolved, hindering the rational design of novel photoelectrocatalysts. In this work, we envision the possibility of employing X-ray spectroscopy to shed light on this challenging problem. We have employed first-principles theory to calculate the X-ray photoelectron spectroscopy (XPS) properties and the near edge X-ray absorption fine structure (NEXAFS) of a number of molecular systems with the aim of fingerprinting possible reaction pathways for the CO_2 reduction process catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ complex [1]. First, it was found that both XPS and NEXAFS display specific features that correlate with the complex charge state and the coordination number of Ru atom. Furthermore, we have identified clear fingerprints for the hydride formation, interaction between CO_2 molecule and the metal hydride and Ru-C chemical bonding formation. The solvation effects have also been investigated through a sequential approach combining molecular dynamics simulations (classical and ab initio) and spectroscopy calculations. These results indicate that the understanding of the electrochemical properties of the electrocatalyst as well as the reaction pathways could be significantly advanced through *operando* X-ray spectroscopy experiments based on synchrotron radiation.

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Laboratory von Hámos X-ray Spectroscopy for Routine Sample Characterization

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High energy resolution hard X-ray spectroscopies are powerful element selective probes of the electronic and local structure of matter, with diverse applications in chemistry, physics, biology and materials science. The routine application of these techniques is hindered by the complicated and slow access to synchrotron radiation facilities. Due to the progress in monochromatization, detection technology and sources the development of table-top instruments for X-ray absorption and emission spectroscopy (XAS and XES, respectively) became reality [1-2].

We have developed a new, economic, easily operated laboratory high resolution von Hámos type X-ray spectrometer, which offers rapid transmission experiments for X-ray absorption, and is also capable of recording X-ray emission spectra. The use of a conventional X-ray tube, a cylindrical analyzer crystal and a position sensitive detector enabled us to build a maintenance free, flexible setup with low operational costs, while delivering synchrotron grade signal to noise measurements in reasonable acquisition times (~a few hours). The instrument does not contain any scanning components and can operate in air [3].

The poster demonstrates the proof of principle as well as some case studies for both measurement types. The chemical sensitivity (oxidation state and coordination geometry) of the method is demonstrated on a series of Ni K-edge XANES spectra in solid state (see Figure), and on different Cr compounds in aqueous solution. In addition, the potential of the instrument to measure XES is also presented.

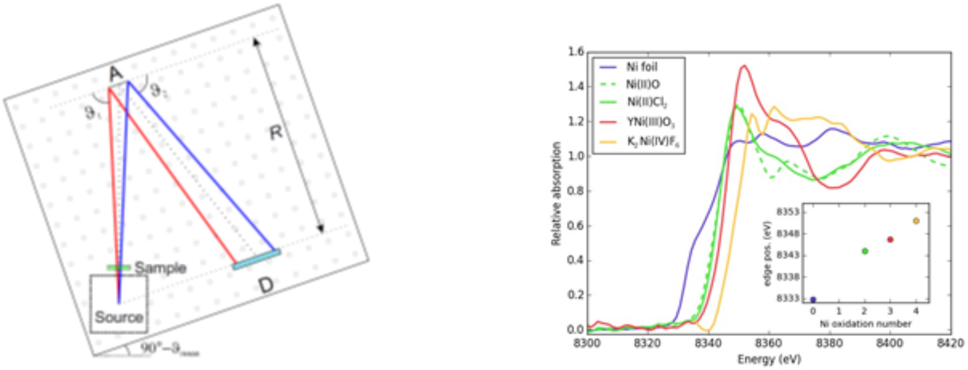

Figure. (Left) Schematic top view of the new X-ray spectrometer with high and low energy X-ray traces (red and blue, respectively). (Right) XANES spectra of selected Ni compounds. Inset: deduced K edge positions vs. oxidation number. Error bars are smaller than the dot size.

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Table top time-resolved photoemission for chemical kinetics

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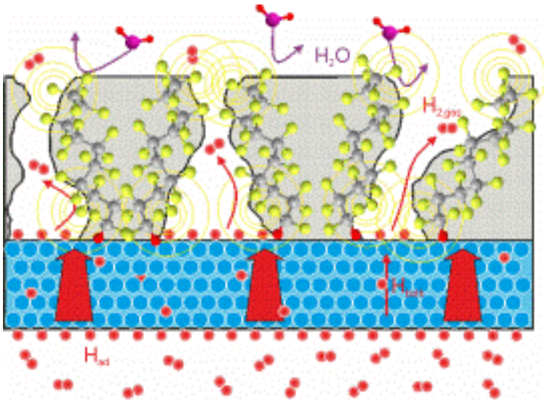
In order to improve materials for technical heterogeneous catalysis, one requires analytical tools capable of giving insights into the surface chemistry of a multiplicity of systems. Time-resolved photoemission at near-ambient pressure (20 mbars), typically performed at synchrotron sources, can provide these insights. Its application is usually reserved to ”flagship” projects, due to the huge effort of the corresponding instrumentation and operation. Here we present a new experimental approach to study materials exposed to high hydrogen “pressures” by means of XPS, which is compatible with a small, laboratory-based installation. Instead of exposing the sample under investigation to gaseous hydrogen, the sample is in contact with a hydrogen permeation membrane, through which hydrogen is transported from the outside to the sample as atomic hydrogen. Thereby, we can reach local hydrogen concentrations at the sample inside a UHV chamber, which correspond to hydrogen pressures up to 1 bar, without affecting the sensitivity or energy resolution of the attached electron spectrometer. A success story of the method is the development of new hydrogen-selective membranes. We have demonstrated that the hydrogen desorption from Pd is significantly improved by a fluorinated polymer layer, which dramatically enhances the overall permeability of the membrane.



The measured time-dependence of the hydrogen flux is interpreted by models of surface reactions, but need to be experimentally confirmed by an equally fast time-resolved probe of the surface chemistry. For this we are developing a table-top pulsed laser-plasma source providing EUV-photons for (ns) time-resolved photoemission. We discuss the concept and show first results.

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First-principles modelling of the L-edge X-Ray Absorption Spectroscopy of Transition Metal Oxides

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We present a novel computational scheme for the calculation of the $L_{2,3}$ edges x-ray absorption spectra (XAS) based on the combination of Density Functional Theory + Dynamical Mean Field theory[1](DFT+DMFT) and Multiplet Ligand Field Theory (MLFT)[2].

The L edge x-ray absorption spectroscopy implies the excitation of core 2p electrons into valence 3d levels. In materials like transition metal oxides and in molecules with transition metal centers, the highly correlated 3d electrons are responsible for the magnetic properties as well as for many-body effects like Kondo resonances and superconductivity. The theoretical treatment of these electronic excitations poses a big challenge for ab initio methods. In addition to the intrinsic difficulty in describing the strong correlation of the d electrons, complex effects like the ligand field generated by the neighboring atoms, the multiplet structure associated with the spin-orbit coupling in 2p and 3d shells as well as the final state with a 2p hole have necessarily to be included. In the developed method, the impurity and bath states of the MLFT are constructed from ab-initio DFT calculations. The XAS Hamiltonian accounts for the 2p to 3d excitations, and is obtained through a multiplet approach, where correlation effects are included according to the Single-Impurity Anderson Model[3]. The transition probabilities are computed within the dipole approximation.

In the present work, this method has been applied to the calculations of L-edge spectra of a series of transition metal oxides, such as MnO, FeO, CoO, NiO, resulting in a very good agreement with the experimental data.

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Theoretical core level XPS and NEXAFS investigations of the C_{60} derivative PCBM: the influence of oxygen adsorption

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Organic photovoltaics (OPVs) have been recently developing as an alternative to silicon solar cells, especially owing to device flexibility, low production cost and low environmental impact [1, 2]. Although efficiencies of above 10% have been achieved by OPVs, one of the main remaining issues with this technology is the stability of organic solar cells. Both the electron donor (organic polymer) and the electron acceptor (fullerene derivative) have been shown to undergo degradation during device functioning [3].

In the case of the main electron acceptor in OPVs (the fullerene derivative $PC_{60}BM$) several deterioration mechanisms have been proposed. These include oxidation, impurity related degradation [4, 5] and dimerization [6].

We have addressed in this study one of the possible degradation mechanisms of $PC_{60}BM$, analyzing by means of density functional theory (DFT) the possible final products of oxygen adsorption on the C_{60} cage. Several configurations of $PC_{60}BM$ with oxygen have been studied from the point of view of the molecular structure, of the O 1s near edge x-ray absorption fine structure (NEXAFS) and of the x-ray photoelectron spectrum (XPS). Our study shows that a joint O1s XPS and NEXAFS experiment can give insight into both the nature of the adsorbate (molecular or atomic oxygen) and the bonding configuration at the adsorption site.

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Time-resolved photoelectron spectroscopy of solar cell materials

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Solar cells have a great potential in replacing fossil fuels in electricity generation, if requirements of low production costs can be met. In the last years, much research has been focused on developing new solar cells made from organic or hybrid materials, which can be fabricated by cheap methods. The success of this development crucially depends on understanding the energetics of the interfaces of different materials in a solar cell as well as the transfer kinetics of excited electrons across these interfaces. X-ray based techniques such as photoelectron spectroscopy are powerful for obtaining such information. This poster will present a new approach for studying the time-dependence of the electronic structure by direct pump-probe measurements of the excited electrons in such materials.

Specifically, we show results from extreme ultraviolet (XUV) based time-resolved photoelectron spectroscopy in the HELIOS laboratory at Uppsala University [1]. In these experiments, the fundamental of a femtosecond Ti:sapphire laser was used to generate XUV pulses in a high harmonic generation process. These pulses with an energy of 39 eV were used to emit photoelectrons from a sample, which were then measured with an angular resolved time-of-flight spectrometer [2]. Another part of the laser was used as the pump pulse to electronically excite the sample. By varying the relative arrival times of the pump and the probe at the sample, the electronic structure could be measured as a function of pump-probe delay time. This poster will present our results of the successful application of this technique to the study of the solar cell polymer PCPDTBT.

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Probing of Hall coefficient sign variation in thin niobium layers buried in silicon by XPS

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Si/Nb/Si trilayers formed by 9.5 and 1.3 nm thick niobium layer buried in amorphous silicon were prepared by magnetron sputtering and studied using XPS depth-profile technique in order to investigate the change of Hall coefficient sign with thickness. The analysis of high-resolution (HR) XPS spectra revealed that the thicker layer sample has sharp top interface and metallic phase of niobium, thus holes dominate the transport. On the contrary, the thinner layer sample, demonstrating semiconducting behaviour of the temperature dependence of the resistivity, indicates on a Si_xNb_{1-x} formation at top interface. Amorphous silicide niobium layer formed at the Nb/Si interface can be responsible for appearance of a second conduction channel which leads to change of Hall coefficient. The depth-profile reconstruction was performed by SESSA software tool confirming that it can be reliably used for quantitative analysis/interpretation of experimental XPS data.

High photon energy spectroscopy of NiO: experiment and theory

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We have revisited the valence band electronic structure of NiO by means of hard x-ray photoemission spectroscopy (HAXPES) together with theoretical calculations using both the GW method and a combination of local density approximation and dynamical mean-field theory (LDA+DMFT). The effective impurity problem in LDA+DMFT is solved through the exact diagonalization (ED) approach. We show that the LDA+DMFT method provides a very good description of the d-derived states of Ni. However, the LDA+DMFT method alone cannot explain all the observed structures in the HAXPES spectra. GW corrections are required for the O bands and Ni-s and -p derived states, to properly position their binding energies. Our results establish that a combination of the GW and DMFT methods is necessary for correctly describing the electronic structure of NiO in a proper ab-initio framework. We also demonstrate that the inclusion of photoionization cross sections is crucial to interpret the HAXPES spectra of NiO.

XAS and RIXS studies of novel Li-ion batteries and Co catalyst systems for water splitting

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The improvement of energy storage systems poses an important scientific challenge, both from an economic perspective as well as to facilitate the feasibility of intermittent type renewable energy sources. A better understanding of the properties of and the processes in these systems on a fundamental level hold the potential to advance these improvements. This poster presents the results of soft X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) studies of two very different systems related to chemical energy storage: $Li_{1.2}[Ni_{0.2}Mn_{0.6}]O_2$ Li-ion battery cathodes and Co-P_i as a catalyst of the oxygen evolution reaction, necessary for the production of hydrogen.

Li-ion battery systems such as $Li_{1.2}[Ni_{0.2}Mn_{0.6}]O_2$ show an intriguing extra capacity, the explanation for which has been controversial so far. In our study [1] we found that the oxygen redox plays a crucial rule. O K RIXS spectra show the reversible formation of localized states upon charging.

Co-based catalysts show great promise for efficient water splitting. We studied the influence of transition metal (TM) dopants (Mn, Fe, Ni) and we present our initial results using X-ray spectroscopy, at the TM L- and O K-edges.

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BEYOND – Batteries for the future and X-ray spectroscopies

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The battery research at Uppsala University is heavily dependent on X-ray spectroscopic techniques. It is at the interfaces between the electrode and the electrolyte that many important reactions take place that influence the health and the life-time of a battery. All kinds of X-ray techniques are used in this research: PES, HAXPES, NEXAFS, soft X-ray spectroscopy, RIXS, EXSAFS, to mention some [1]. This presentation will depict some of the most striking results obtained for lithium-ion and sodium-ion batteries which are the basis for future more powerful battery concepts. These new concepts are described as “beyond” lithium-ion batteries and consist of metallic anodes of lithium, sodium or magnesium. These metals are highly reactive which is seen in battery operation in formation of new unstable electrode/electrolyte interfaces. To combine knowledge of the chemistry and physics taking place at these interfaces with development of new electrolytes are important for future success. A battery is, however, not useful without a high-capacity cathode. The future means to got to 5V cathode materials which are layered oxides containing 3d or 4d metals. Our latest results show that X-ray spectroscopic techniques are vital for understanding underlying mechanisms of changes in material as a battery is operated [2].

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Fe-carbene high efficient light harvester

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For more than a decade, ruthenium-based compounds were the most successful and efficient sensitizers involved in photovoltaics and photocatalysis for solar energy conversion [1,2]. However the fact that Ru is both expensive and environmentally unfriendly while also being unfit for large scale industrialization due to its limited availability (<12 tons/year) [3] has motivated the scientific community to look for alternative materials. Great efforts have been made to replace ruthenium with more abundant analogues like iron, but without much success due to the very short-lived excited states of the resulting classical iron based complexes [4-8]. Recently we have succeeded in designing a novel Fe nitrogen–heterocyclic-carbene (NHC) sensitizer with an excited-state lifetime that is nearly a thousand-fold longer than that of traditional iron polypyridyl complexes allowing its incorporation in photovoltaics applications [9, 10].

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A new HAXPES-Lab for bulk measurements beyond synchrotrons

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The activities on hard x-ray photoelectron spectroscopy (HAXPES) pioneered in Uppsala with Siegbahn and co-workers using a Cu based source. Later Al Kα became the most common lab source for XPS applications leading to more surface sensitive measurements. Today the use of high energy light for spectroscopy applications is most commonly used at synchrotrons. With HAXPES the field of photoemission opens up the window to the bulk, allowing studies of pure bulk properties of a solid, such as buried interfaces, highly correlated systems, nanophysics, solar cells, etc.

We have developed a 9.25 keV monochromated x-ray source utilizing a Ga metal jet technique, allowing analysis in the full kinetic energy range up to 9.25 keV. This opens up new possibilities for bulk measurements with a mean free path substantially greater than Al Kα (Figure 1) probing > 100 Å into the bulk. Here we present first proof of principle measurements using this system, here illustrated in Figure 2 by an overview spectrum on a gold sample recorded between 1000 and 9000 eV kinetic energy, clearly illustrating the range available using this new system.

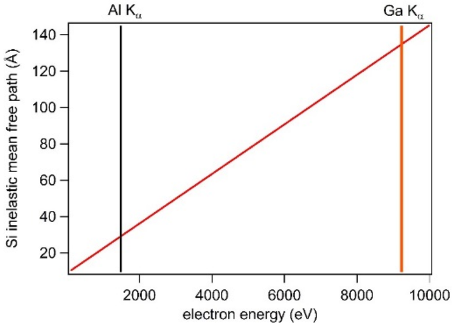

Figure 2. Illustration of the mean free path for different energies.

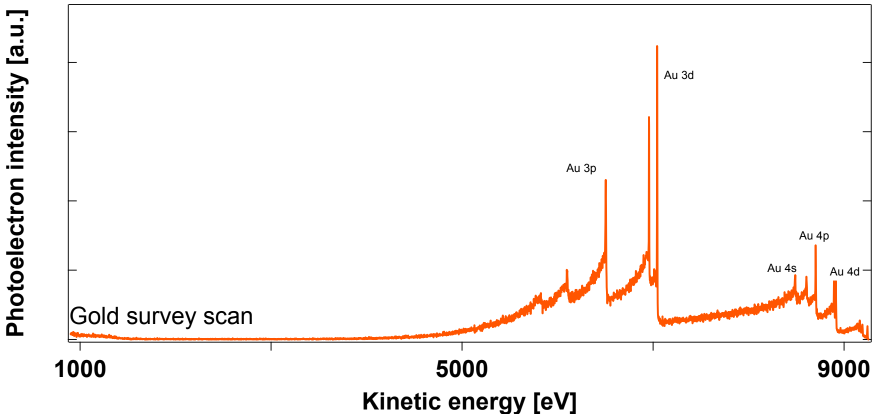

Figure 3. An overview spectrum of gold recorded using a 9.25 keV monochromatic Ga-source.

Current Status of the Liquid-Metal-Jet X-ray Source Technology

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We have previously demonstrated prototype performance of a metal-jet anode x-ray source concept [1,2] with unprecedented brightness in the range of one order of magnitude above current state-of-the art sources. This type of source is suitable for a wide range of x-ray analytic and imaging applications. As many high-end x-ray applications today are limited by the x-ray source brightness, they would greatly benefit from such an increase in brightness, both in terms of resolution and exposure time.

Over the last years, the MetalJet technology has developed from prototypes into fully operational and stable X-ray tubes running in many labs over the world. Key applications include X-ray diffraction and scattering, as well as X-ray imaging so far. However, this X-ray source can be applied in all fields where a small focus with high brilliance would be needed.

This presentation will review the current status of the technology specifically in terms of stability, lifetime, flux and brightness. It will also discuss details of the liquid-metal-jet technology with a focus on the fundamental limitations of the technology.

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X-ray Photoelectron Spectroscopy of ionic liquids–
how to close the pressure gap in electrochemistry research

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Electrochemical reactions occur at the electrode/electrolyte interface. In order to understand the manifold reactions taking place at that interface, the development and application of analytical tools probing this interface *in situ* in an electrochemical cell are of outmost importance. Although, X-ray Photoelectron Spectroscopy (XPS) is widely accepted to be a powerful tool to study electrochemically induced changes of electrode surfaces, it can usually not be applied *in situ* as common electrolytes evaporate into the ultrahigh vacuum (UHV). Therefore, the so-called electrode emersion technique was established, which can be described as a *quasi in situ* analysis of the electrode/electrolyte interface [1]. However, all these measurements require the critical step of electrode preparation and subsequent transfer from ambient pressure into vacuum.

Unlike common electrolytes, ionic liquids (IL) provide the unique opportunity to overcome this issue as these electrolytes are UHV compatible [2]. IL are also known to provide large electrochemical stability windows making them attractive for electrochemical applications such as electrochemical double layer capacitors or lithium ion batteries. In this presentation, quasi *in situ* [3] and *in situ* [4] electrochemical XPS setups will be presented and discussed in terms of opportunities and limits of both approaches with respect to investigations of interfacial behavior, stability windows of IL, and interpretation of XPS data.

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Ambient pressure photoelectron spectroscopy on Li-ion batteries

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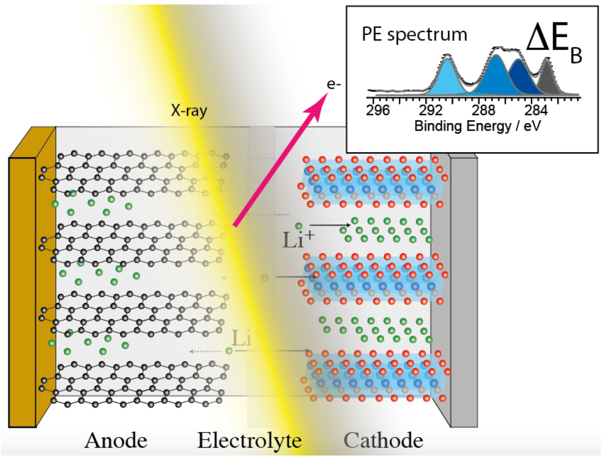
One of the greatest challenges of modern society is to meet the demand for clean energy, and energy storage is a key issue. The Li-ion battery is the battery with the highest volumetric and gravimetric energy density of all know batteries, and is therefore particularly important for portable applications, e.g. mobile phones, laptops, and electric vehicles.

In most Li-ion batteries electrolyte degradation occurs at the negative electrode forming a molecular interphase between the active electrode material and the electrolyte. This molecular interphase is often referred to as the solid electrolyte interface (SEI), and it functions as a barrier that limits further electrolyte degradation. The electrode/electrolyte interfaces in Li-ion batteries are known to contain various organic and inorganic compounds distributed at different depths and the composition of the interface influences e.g. the safety and long-term cycling stability of the battery [1].

The interfaces are suggested to form through the initial formation of highly reactive species, which in turn further react and form the SEI. Today much of our current knowledge about the interphases comes from post mortem analysis, where pre-cycled batteries are opened and dismounted within an Ar filled glovebox and subsequently transferred to the PES instrument. The recent developments in ambient pressure photoelectron spectroscopy opens for direct investigation of the SEI formation, by allowing liquids to be present during the spectroscopic measurements [2]. We will present our latest results and development towards in operandi APPES on Li-ion batteries.



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Element Specific Ultrafast Magnetization Dynamics using a table top High Harmonic X-ray source

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We have used femtosecond X-ray pulses generated by high harmonic generation of an infrared (IR) laser source to probe the element specific ultrafast magnetization dynamics. The elemental specificity enables us to separate competing interactions that conspire to the ultrafast response of a magnetic system, i.e. interatomic exchange interaction, spin-orbit coupling, interlayer exchange etc. Achieving ultrafast time resolution for an element specific probe like XMCD at a synchrotron is very expensive and usually suffers from very low photon flux due to the way the short x-ray pulses are produced at a storage ring. A tabletop setup that combines a very high temporal resolution (few fs) and the element specificity is therefore a very attractive combination for studies of ultrafast processes in magnetic materials. Our instrument relies on studies of the transverse magneto-optical Kerr effect (T-MOKE)[1], and is based on a soft x-ray spectrometer with Rowland Circle geometry[2].

In the T-MOKE geometry the change of reflected intensity with the change of magnetization direction is picked up at the M-edges of the transition metals, which spreads over ~35 to 70 eV. The efficiency of our instrument is superior to the grating-on sample solutions that were used in the first studies of ultrafast demagnetization using element specific T-MOKE[3]. A change in magnetization within few fs could be well resolved with our setup. With the very high time and energy resolution of our instrument and the fact that our setup preserves the integrity of the sample, our new instrument offers very good opportunities for ultrafast studies of magnetization dynamics.

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2D-materials, charge delocalization on the few attosecond scale

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Layered materials, were the 2D-layers are Van der Waals bound, have attracted huge interest in the last decade. Two such materials are black phosphorous (BP) and 2H-MoS_2 which now are widely studied as novel materials for photovoltaics and electronics [1]. We have studied the electron dynamics of these materials using the core-hole clock method [2] and can show charge delocalization times (CDT) of 21.86 as (BP) and 56.42 as (MoS_2). For both systems the 1s to 3p (K-edge) resonant excitation and subsequent resonant auger decay has been used to calculate the CDT with the core-hole clock method. The data were obtained on the HIKE end station on the KMC-1 beamline at Bessy II.

These results imply that layered materials are excellent choices for fundamental studies of truly ultra fast processes.

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Circularly polarized light for probing ultrafast dynamics with HHG sources

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A pump-probe beamline at the high harmonic generation (HHG) source (HELIOS) at Ångström laboratory in Uppsala is equipped with a spectrometer for studying changes in the reflectivity of samples when excited by an ultrafast IR laser pulse. By varying the polarization of the probe light, it is possible to choose if the measured contrast comes from changes in the electronic reflectivity or from an ultrafast response of the magnetization. The magnetic measurements have so far been limited to the T-MOKE geometry, which unlike other geometries produce the necessary changes in the reflectivity. Due to inherent limitations of the HHG process, it has not been possible to efficiently generate circularly polarized high harmonics until recently. The use of circularly polarized light provides the means of doing transmission measurements rather than reflectivity measurements, and also provides a magnetic contrast for out-of-plane magnetized samples rather than the in-plane component measured in the T-MOKE geometry. Furthermore, the XUV reflectivity in the T-MOKE geometry is generally low and the transmission geometry can hence significantly increase the number of photons that will reach the detector. Here I will present results obtained at JILA in Boulder, USA, where we have showed the possibility of using circularly polarized HHG for studying magnetic materials [1][2][3][4].

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Surface characterization of silicon spheres by combined XRF and XPS analysis for determination of the Avogadro constant

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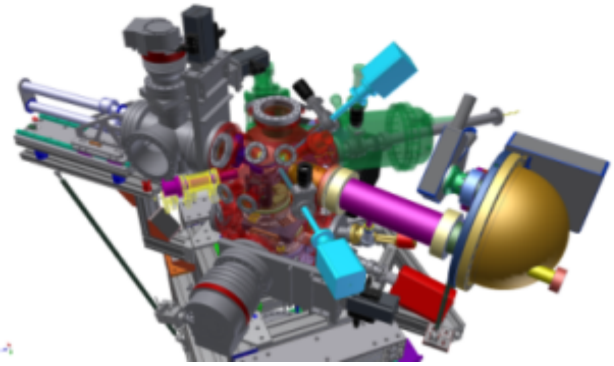
To get independent from a material artifact definition of the mass unit kg, national metrology institutes and the Bureau International des Poids et Mesures (BIPM) aim to find a definition based on fundamental constants. One possible new definition of the mass unit kg is based on the Avogadro constant. The realization of the mass unit can be done by a monocrystalline silicon sphere [1]. To be able to fully characterize the surface of this sphere, complementary methods will be involved.

The instrumentation presented here allows the complementary measurement of fluorescence photons as well as photoelectrons emitted by the sample surface. The excitation channel contains monochromatized characteristic radiation of an Al-anode X-ray tube.



To support the optimal instrument design synchrotron radiation based XRF experiments using calibrated detectors were conducted [2]. Deconvoluting the spectra with detector response functions employing all fluorescence lines as well as background contributions allows the determination of fluorescence intensities for the lines of interest. From these and the knowledge from reference samples the surface can be characterized not only qualitatively (elemental composition) but also quantitatively applying the fundamental parameter approach[3,4].

We present a new instrumentation for the surface characterization of a monocrystalline silicon sphere, which allows a realization of the SI-base unit of the mass based on a fundamental constant. Hereby the exact definition of the Avogadro constant is achieved by "counting" the silicon atoms in a one kilogram silicon sphere. Applying complementary X-ray methods for quantitative surface characterization allows minimizing the influence of the surface on the total uncertainty budget.

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Recent determinations of X-ray fundamental parameters

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The further development of more complex materials with distinct properties needs an analysis independent from any reference material such as X-ray fluorescence analysis (XRF). For a reliable quantitative XRF the exact knowledge of the atomic fundamental parameters involved is inevitable.

In this work, recent experimental determinations of fundamental parameters including mass absorption and photo ionization coefficients, fluorescence yields, Coster-Kronig transition probabilities for several chemical elements using the calibrated instrumentation of the Physikalisch-Technische Bundesanstalt (PTB) are presented [1-6]. The presentation will also summarize novel methodologies employed in recent x-ray fundamental parameter determinations.

The experiments were carried out at both the laboratory of the PTB at the electron storage ring BESSY II, where monochromatized synchrotron radiation of high spectral purity up to 10 keV is available, and at a wavelength shifter beamline (BAMline) at BESSY II, where higher photon energies are available. The determination of atomic fundamental parameters with low experimental uncertainties leads to significant improvements in quantitative reference based as well reference-free XRF analysis and is thus of relevance to the X-ray spectrometry community [7].

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Spin-sensitive spectroscopy studies of chiral molecules adsorbed at surfaces

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Organic chiral molecules have been adsorbed under ultra-high vacuum on metallic surfaces and studied by means of electron spectroscopies. Spin-polarized, angle-resolved valence band photoemission from layers of 1,2-diphenyl-1,2-ethanediol (DPED) on Co/Cu(100) shows that the photoelectrons emitted through the adsorbed layers of both enantiomers of DPED display a clear spin polarization at room temperature, independent of their binding energy. Furthermore, the spins of the photoemitted electrons point along different directions in space: in-plane for (R,R)-(+)-DPED and out-of-plane for (S,S)-(–)-DPED. [1]

Adsorbed layers of DPED on clean Cu(100) have also been studied by X-ray absorption spectroscopy (XAS) at the carbon K-edge and dichroism using circularly polarized radiation. The different features present in the absorption spectra have been identified and assigned to specific electronic transitions. Several clearly dichroic features have been observed and assigned to C–C and C–H π* orbitals. The dichroic asymmetry shows opposite signs for the two enantiomers studied. Measurements using the non-chiral *meso*-DPED form, constitute a cross check and confirm the direct relationship between the circular dichroism and the molecular handedness. The magnitude of the dichroic effects is high, suggesting that the charge transfer between the adsorbed molecules and the substrate might be spin- and enantio-sensitive. The adsorption of the DPED molecules on an epitaxial ferromagnetic Co film, deposited on the Cu substrate, results in enantio-sensitive changes in the magnetic moment of the Co atoms. This finding supports a spin- and enantio-selective bonding between the magnetic substrate and the chiral molecules.

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Time-resolved studies on transition metal dichalcogenides with an ARTOF spectrometer

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Transition metal dichalcogenides (TMDs) f.e. TaS2 are under investigation for many decades, since they show a complex coupling between electronic, lattice and orbital degrees of freedom due to their quasi two dimensional structure.

Ultrafast pump-probe techniques with sub-ps temporal resolution are a powerful tool for tracking the temporal evolution of the sub systems and for getting insight into the nature of the different phases.[1]

Here we present first results of ultrafast electron spectroscopy at the BESSY II femto slicing beamline. The combination of ultrashort (100fs), but low intensity Soft X-Ray pulses with a new high transmission, high resolution and high acceptance angle time of flight electron spectrometer (ARTOF) [2],[3] opens up new ways for ultra fast electron spectroscopy avoiding the problem of space charge broadening were free electron lasers often suffer from.

A second approach for dynamical investigations of TMDs is the cole-hole-clock method[4]. Charge-transfer times of core excited atoms are typically in the sub fs-time domain and therefore not reachable for time resolved pump-probe techniques. By resonant photoemission experiments one can instead use the core-hole lifetime as an intrinsic clock and compare the intensity ratios of competing decay channels which give a signature if the excited electron is still localized at the atom or has moved into the environment.

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HAXPES Studies of Silicon Anodes for Li-ion Batteries

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Silicon is a promising new anode material for Li-ion batteries since it offers high Li-storing capacities and can increase the energy density of the battery. However, the implementation of the Si-based anode is challenged due to large volume variations of the material during charge/discharge. In addition, the low working potentials of this material results in continuous electrolyte decomposition (forming the so-called solid electrolyte interphase (SEI-layer)) that aggravates the electrode performance.

HAXPES is one of few techniques that can probe the amorphous Si-phases formed underneath the SEI-layer during electrochemical cycling. In addition, by using different excitation energies, HAXPES is able to give a depth resolved picture of the SEI-layer build-up and its chemical composition. Thus, HAXPES presents a unique tool to map the degradation mechanisms of the electrolyte and the active Si-material.

In our work, we show that electrolyte additives results in a better cycling performance and that this is linked to a SEI-layer rich in inorganic and polymeric compounds [1]. However, these additives cannot protect the native surface oxide that is affected by the most commonly used electrolyte salt. We show that with the use of a novel electrolyte salt, the native oxide is not affected [2] and that a surface reconstruction is taking place that increases the relative amounts of oxide signal [3]. Additionally, we address binding energy calibration in these samples which is complex due to (i) the composite electrode that consists of many different components with varying electronic properties and (ii) changes in the materials during cycling.

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Spectroscopic, magnetic and cohesive properties of the Rare Earths within the Hubbard I approximation

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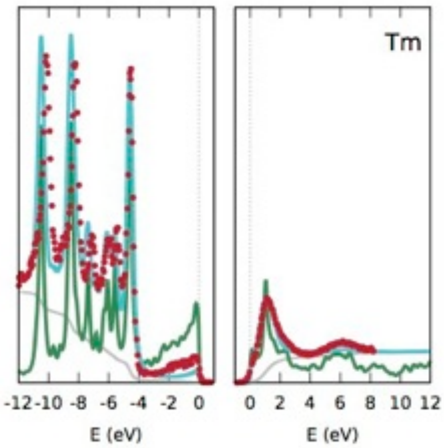

The rare earths show many interesting features, such as large magnetic moments, a large anisotropy energy and valence band spectra with a true many body multiplet structure. Due to their correlated nature, it is difficult to find a good theoretical description for these elements. We apply density functional theory + dynamical mean field theory (DFT+DMFT) within the Hubbard I approximation (HIA) to describe a wide range of properties of the rare earths. Previously also other methods have been proposed [1-4], but none of them is able to describe all properties with good accuracy. We calculated the electronic structure of the rare-earth elements, using DFT+DMFT(HIA). We show that the theory can reproduce a wide range of measured quantities, among which all features in both the occupied and unoccupied states of the (inverse) photoemission spectra (See figure where the valence band spectra for Tm are presented.). We also accurately describe the equilibrium volume, the bulk modulus, the ground state magnetic moments, Heisenberg exchange parameters, critical temperatures and magnon spectra. We conclude that the HIA provides a practical theoretical framework to describe the rare earths and rare earth containing materials.

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Self-doping processes between planes and chains in the metal-to-superconductor transition of $YBa_2Cu_3O_{6.9}$

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ABSTRACT

The interaction between the CuO-chains and the CuO2 planes of YBa2Cu3O61x (YBCO) has been controversial. The CuO-chains are known to be important as charge reservoirs that enable superconductivity for a range of oxygen doping levels in YBCO, but the understanding of the dynamics of its temperature-driven metal-superconductor transition (MST) has remained a challenge. A combined study using x-ray absorption spectroscopy and resonant inelastic x-ray scattering (RIXS) reveals how a reconstruction of the apical O(4)-derived interplanar orbitals during the MST of optimally doped YBCO leads to substantial hole-transfer from the chains into the planes, i.e. self-doping [Scientific Reports 4, 7017 (2014)]. Ionic model calculations show that localized divalent charge-transfer configurations are expected to be abundant in the chains of YBCO. While these indeed appear in the RIXS spectra from YBCO in the normal, metallic, state, they are largely suppressed in the superconducting state and, instead, signatures of Cu trivalent charge-transfer configurations in the planes become enhanced. For understanding the fundamental mechanism for high-Tc-superconductivity (HTSC) in perovskite cuprate materials, the observation of interplanar self-doping process in YBCO opens a unique novel channel for studying the dynamics of HTSC.

Investigating Li-ion Battery Electrodes Using X-ray Spectroscopies: Progress and Challenges

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The performance, safety and lifetime of Li-ion batteries are largely dependent on surface and interface layers. These include both the electrode/electrolyte interface where electrode surface compounds react with the electrolyte forming the solid electrolyte interphase (SEI) and the interface between the SEI and the bulk electrode material. To study the complex chemistry of these crucial layers in Li-based battery systems, we apply Soft X-ray Photoelectron Spectroscopy (SOXPES), Hard X-ray Photoelectron Spectroscopy (HAXPES), X-ray absorption spectroscopy (XANES) and combinations thereof as these techniques offer the unique capabilities in probing chemical surface and interface properties as well as different binding configurations for a given element. Thus, for example redox reactions during lithiation and delithiation can be followed.

We will exemplify the progress on understanding battery interfacial chemistry with two case studies: (i) the detailed investigation of the influence of film forming additives on the SEI formation in silicon electrodes [1] and (ii) a combination approach of HAXPES and XANES to elucidate transition metal crossover in lithium manganese (LMO) / lithium titanate (LTO) batteries [2].

However, as cycled battery electrodes are highly complex systems, we have also come to notice that new challenges arise when studying these electrodes. Our PES data indicates that the buried interface between a surface layer (such as the SEI) and the bulk electrode material incorporates an interfacial potential gradient. This gradient influences relative binding energy positions for bulk and surface components and thus creates the need for careful data calibration to achieve consistent spectra interpretation [3].

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Novel systems for research in molecular and x-ray spectroscopies

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Romo Scientific is a company specializing in promoting top-of-the-line scientific instrument manufacturers to the research community. In the presentation a laboratory based HP-PES system will be presented. The focus is on the usability of the system for various types of studies relevant for high level research for photo-catalytic reachtions, light harvesting and solar cell development. Examples will be given from a complete system delivered by Prevac to NCL, Pune India where examples will be given in the following areas: Cu-oxidation via HeI-excited VB studies[1] and studies of the solar water splitting (SWS) activity. Further examples of a novel cell based laboratory ambient pressure system developed by Prevac will be presented.
A short presentation of a new type of RIXS spectrometer to be installed at BESSY, HZB, Berlin will also be given.

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Probing components of advanced 2D crystals spintronic devices using X-ray and ultrafast demagnetization techniques

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Two dimensional (2D) crystal based nanoelectronic and spintronic devices carry incredible potential for next generation low power electronics, sensing and energy harvesting applications. How charge or spin currents can be used to manipulate the properties of materials and vice-versa constitutes the fundamental aspect of nanodevice physics. These devices consist of components of materials such as graphene, molybdenum disulfide/diselenide and other 2D crystals with novel properties, and nanomagnets of magnetic materials. A basic requirement for enhancing the device performance is to have the knowledge of the electronic structure of the constituent materials, ultrafast demagnetization properties of nanomagnets. Various X-ray spectroscopy tools, e.g. XPS, ARPES and the recent development in Angle Resolved Time of Flight (ARTOF) technique in the division of molecule and condensed matter physics are useful for probing the electronic structure and the dynamics. Element specific magnetic pump probe technique developed in the division is a powerful tool for studying magnetic components such as nanowires, nanomagnets. We will present an overview of these devices, our present efforts and future possibilities in understanding their component materials at a very fundamental level.

Perspectives and limitations of time-resolved hard X-ray photoelectron spectroscopy at X-ray free-electron lasers

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Time-resolved hard X-ray photoelectron spectroscopy (trHAXPES) has recently been established as a novel ultrafast spectroscopy technique using the X-ray free-electron laser (XFEL) SACLA (Japan) [1-3]. The technique extends time-resolved photoemission into the hard X-ray regime and, as a core-level spectroscopy, combines atomic site and chemical state specifity with femtosecond time resolution. It can thus open novel opportunities for probing ultrafast electron dynamics, e.g., in strongly excited materials, at buried interfaces, and in electronic devices under *in operando* conditions.

The viability of trHAXPES using microfocused 8 keV XFEL radiation is demonstrated by a systematic investigation of probe and pump pulse-induced vacuum space-charge effects, as a function of pulse energy and photon incidence angle. The measured time and excitation energy dependencies of the spectral shifts and broadenings are compared to the results of numerical *N*-body simulations and simple analytical (mean-field) models. By this, we can deconvolve pump laser-induced space-charge effects from intrinsic charge carrier recombination dynamics in the high excitation density regime.

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In Situ Cell Design for Solid/Vapor Interfaces and First Results in Environmental TiO_2 Photocatalysis

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Near ambient pressure X-ray photoelectron spectroscopy (NAPP) is a powerful tool to investigate elemental composition and chemical specificity of surfaces that offers tremendous opportunities in environmental science. I will first provide a brief outlook on the new analysis chamber that fits the NAPP endstation at the Swiss Light Source. This chamber has been designed for in situ XPS and NEXAFS at solid/vapor interfaces under environmentally relevant conditions of temperature and pressure (up to 20 mbar and 100% relative humidity) [1]. We have used this novel chamber to investigate water adsorption and photocatalysis on titanium dioxide (TiO_2), which is a component of atmospheric dust that represents an important reactive aerosol in the atmosphere. Understanding the bonding structure of water at interfaces is a fundamental step for the interpretation of many environmental processes, but it is also important in the context of ice nucleation in the atmosphere. Earlier NAPP studies have provided important insight into the adsorption mechanism of water on rutile $TiO_2(110)$ [2]. In a previous study from our group the effect of humidity on ozone-induced band bending [3] and on photochemistry of nitrate [4] on rutile $TiO_2(110)$ were quantified. I will discuss our most recent XPS and NEXAFS investigations about the influence of UV light and humidity on the adsorption of water on TiO_2 nanoparticles (Degussa P25). Our results show different coordination of adsorbed water layers for different vapor pressure and temperature combinations, indicating changes in the hydrogen bonding structure.

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Transmission based electron spin detector

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In 1922 Otto Stern and Walter Gerlach proved the existence of the fundamental property of spin by letting a beam of silver ions pass through an inhomogeneous magnetic field [1, 2, 3]. For electrons this mode of spin detection isn't possible due to Lorentz forces acting on the moving electron [4]. Since then many different ways of detecting the electron spin have been realized. The figure of merit is the most important value for any type of spin detector and is calculated using the electron intensity ratio and the Sherman function (which describes the probability of successfully filtering an electron according to polarization) [4] by $\eta = S^2 \frac{I}{I_0}$.

Here we present a transmission based detector consisting of free-standing, ultrathin ($< 10\,nm$) ferromagnetic membranes. These membranes can readily be used in electron spectroscopy, microscopy and diffraction as both detectors and sources. The fabrication utilizes silicon processing techniques such as inductively coupled plasma reactive ion etching (ICP-RIE) and contact lithography. The membranes start out as a silicon-on-insulator (SOI) wafer and ends up as an ultrathin free-standing stack of Au/Co/Au, each about $80\,\mu m$ across. Thanks to extremely well-controlled silicon processing, chips are fabricated containing close to 15000 membranes each. We also present early spin and angle resolved photo emission spectroscopy (SARPES) data taken at the I3 beamline of MAX III at MAXLab and transmission data taken at Scienta.

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Chemical and Electronic Structure Characterization of organic-inorganic perovskite materials by PES

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The use of organic/inorganic perovskite as solar cells material constitutes one of the main breakthrough of this last five years in solar energy research. The so-called perovskite structure adopts the general formula ABX_3 where A and B are two cations and X an anion. CH3NH3PbI3 belongs to this family ($A = CH_3NH_3^+$, $B = Pb^{2+}$, and $X= I^-$) and was the material that initiates this breakthrough. This material was relatively quickly out-performing the common dye-sensitized solar cells (DSSCs) technology reaching in 2012 the symbolic efficiency line of 10%. A lot attention has since been devoted to the development and improvement of these organic/inorganic perovskite materials. Alternative chemistry have been proposed i.e. different nature of the halide (X), the metal (B), or the cation group (A), combination with hole conductors as well as the development and optimization of novel fabrication/deposition techniques that all together brought certified efficiency up to 22.1% in 2016.

While these materials are usually characterized through their structure (XRD) and performance within solar cell communities, not so much attention is devoted to their surface chemical composition and, specifically, the surface composition. Photoelectron spectroscopy (PES) can easily fulfill this task, and, in addition to chemical information, PES provides an overall picture of the electronic structure of the perovskite and its relation to the scaffold layer used (e.g. TiO2, Al_2O_3). when studied with hard X-rays.
Through various recent examples, we will present how PES can be used to investigate perovskite solar cells materials based on different metals (Pb^{2+}, Bi^{3+}), anions (I^-, Br^-, Cl^-) or cations (Cs^+, MA^+, FA^+). [1][2][3]

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Electronic Structure of Cesium Bismuth Iodide Studied by Hard X-Ray Spectroscopy

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Complex bismuth halides are an interesting family of solution-processable compounds, whose potential as an alternative to toxic lead halides is far from fully explored. A key question in the development of ternary bismuth halides is the understanding of the electronic structure. X-ray based techniques such as hard X-ray photoelectron spectroscopy (HAXPES), X-ray absorption spectroscopy (XAS), and resonant X-ray emission spectroscopy (RIXS) are powerful tools for obtaining such information at an atomic level due to the possibility for element specificity. We have previously used such tools to study the electronic structure of perovskites [1,2].

In this study, we use these methods to study the complete electronic structure of $Cs_2Bi_3I_9$ thin films. Photoelectron spectroscopy was used to follow the composition of the materials, as well as relative band position using spectroscopic methods to aid in the design of device interfaces. Element selective mappings of the valence and conduction bands were performed to experimentally verify partial density of states of bismuth and iodine. The valence electrons are also probed directly by monitoring the X-ray fluorescence emitted from the transition of the valence electron to core holes. The valence-to-core (VtC) region, which is largely localized to ligand rather than metal, provides a ‘map’ of ligand electronic structure [3] for these perovskites.

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X-Ray FMR study of asymmetric exchange coupled magnetic trilayers

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In this work we perform layer resolved FMR studies of coupled magnetization dynamics in interlayer exchange coupled asymmetric magnetic trilayer structures by means of time-resolved x-ray magnetic circular dichroism (TR-XMCD) [1,2].

The sample structures of [100 Å Permalloy ($Fe_{19}Ni_{81}$) / t_{Ru} Å Ru / 100 Å Permendur ($Fe_{49}Co_{49}V_2$)] with varying t_{Ru} are deposited on Si_3N_4 membrane to enable measurements in transmission mode. The magnetization precession in magnetic layers is excited by a coplanar waveguide generated microwave field in the GHz range, synchronized with the photon bunches of the synchrotron source. In-situ FMR is carried out in order to determine the resonance conditions. The element specific magnetization precession is then probed at L3 edges of Co and Ni at fields across the resonance curve.

Shown in the Figure is an example of layer resolved studies for two samples with Ru thickness of t_{Ru} = 5 Å and 14 Å, exhibiting correspondingly antiferromagnetic (AFM) and ferromagnetic (FM) coupling. In AFM coupled sample magnetic layers precess almost fully in anti-phase, while for the FM-coupled structure TR-XMCD reveals a significant phase-lag between the layers. The transition between AFM and FM coupling occurs around t_{Ru} = 8 Å. Corresponding trilayer structure is behaving very similar to un-coupled structure with t_{Ru} = 200 Å showing independent dynamics of each magnetic layer.

A very unusual behavior was found in one of the samples. While in-situ FMR for this sample reveals two resonance modes as expected for the system with two different magnetic layers, TR-XMCD study detected no precessional motion of magnetization at one of the FMR modes.

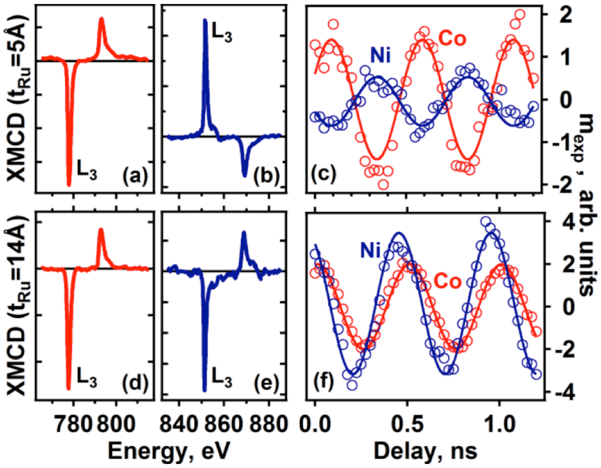

Fig.1. a,b) XMCD and c) TR-XMCD for AFM coupled sample (t_{Ru} = 5 Å); d,e) XMCD and f) TR-XMCD for FM coupled sample (t_{Ru} = 14 Å); Red color is for Co and blue - for Ni. In (c,f) circles are experimental data points, solid curves - sine fit.

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Gas phase vs adsorbate studies for the understanding of the electronic structure of transition metal Phthalocyanines

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A well-established collaboration between Swedish and Italian research groups (Uppsala University, Dept. of Physics and Astronomy), and CNR (Gas Phase beamline, Elettra Laboratory, Trieste) including experiment and theory has resulted, during the last years, in comprehensive studies about the characterization of semiconductor materials starting from the molecular building blocks to deposited films of different thickness.

Our studies have revealed at the fundamental level the electronic structure of macrocycle molecules (phthalocyanines) of high relevance for applications in molecular electronics and spintronics.

The experimental investigations included the characterization of both gas phase and molecular adsorbate[1]. The theoretical input has served as crucial complement to identify and explain the experimental results in details, and in some cases the very DFT predictions have been the inspiration of new challenging experiments[2].

We will review our most recent results, showing comparisons between molecular and surface studies addressing some key issues about the valence character of transition metal phthalocyanines. Results on MnPc[3] and CoPc and FePc[2,4] will be shown.

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Role of local structure around Sn in martensitic transition in transition metal-doped Shape Memory Alloys

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Ni-Mn based Shape Memory Alloys have been an area of continued research interest due to the observance of magneto-structural transitions which lead to interesting properties and hence a wide variety of applications. They are actively employed in magnetic actuators, optical frames, orthodontic wires, prosthetics, robots, bio-medical implants, etc. Stoichiometric Ni_2MnSn has cubic $L2_1$ type structure in its austenite (room temperature) phase, with Ni, Mn and Sn occupying positions X (0.25,0.25,0.25), Y (0,0,0) and Z (0.5,0.5,0.5), respectively, shown in Fig.1. This is a ferromagnetic material with Curie Temperature $T_c \sim 346K$ [1]. Interestingly, non-stoichiometry is a pre-requisite for exhibiting shape-memory effect, and the transformation is believed to be brought about by the additional inter-atomic interactions resulting from this non-stoichiometry [2].

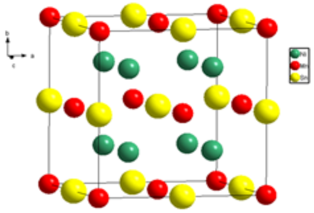

Fig. 1: Ni_2MnSn has $L2_1$ type structure.

Doping at different sites is a popular mode of chemically inducing disorder in these alloys, bringing about significant changes in the martensitic and magnetic transition temperatures [2-4]. We have investigated the effects of Cu doping at Ni site and Si doping at Sn site and in $Ni_{49}Mn_{38}Sn_{13}$ and $Ni_{48}Mn_{39}Sn_{13}$ alloys, wherein a proportional increase in both the martensitic and magnetic transition temperatures was observed with doping [5-6]. Our aim was to understand the structural changes leading to these transitions and also the correlation between them. Employing temperature-dependent XAFS at Sn K edge (29.2 keV), we have deduced the thermal evolution of nearest-neighbor bond distances and the Debye Waller Factor in the martensitic and austenite phases as a function of doping. Our results not only shed light on the relation between the structural and magnetic degrees of freedom in these alloys, but also underline the importance of the local structure around Sn atom in these transitions.

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Methane Dry Reforming studied on Invers Pt/ZrO_2 Model Catalyst

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Being a carbon source, the utilization of carbon dioxide (CO_2) became attractive from both an environmental and economical perspective. However, CO_2 is a very stable molecule, thus to induce a reaction the activation of CO_2 by catalysts is required [1]. One way of activating CO_2 is dry reforming of methane (DRM), when CH_4 is reformed by CO_2 on Ni or Pt particles supported by zirconia (ZrO_2), $CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$. During DRM, CO_2 is reduced to carbon monoxide (CO) via reaction precursors or intermediates, which can further oxidize the carbon formed via CH_4 dissociation. Such activation can occur on the ZrO_2 or on the interfacial sites [2]. As a support, technical ZrO_2 powder material can activate CO_2 by forming carbonate with basic anionic sites, or by forming formate with hydroxyl groups [2]. However, due to the possible different reaction pathways, microscopic mechanisms of the functions of ZrO_2 need to be further understood via a surface science approach.

We therefore conducted a systematic study of the interaction between CO_2/CH_4 and ZrO_2 inverse model systems with ZrO_2 particles supported on Pt single crystals and with the Pt support itself. Prior to actual DRM experiments, the surface was respectively exposed to CH_4 and CO_2. The carbon deposited on the surface during CH_4 exposure could be removed in pure CO_2 starting at 400°C (Figure 1). Accordingly, during DRM the surface stays free of carbon contaminations above that temperature. Only below 150°C carbonate species could be observed.

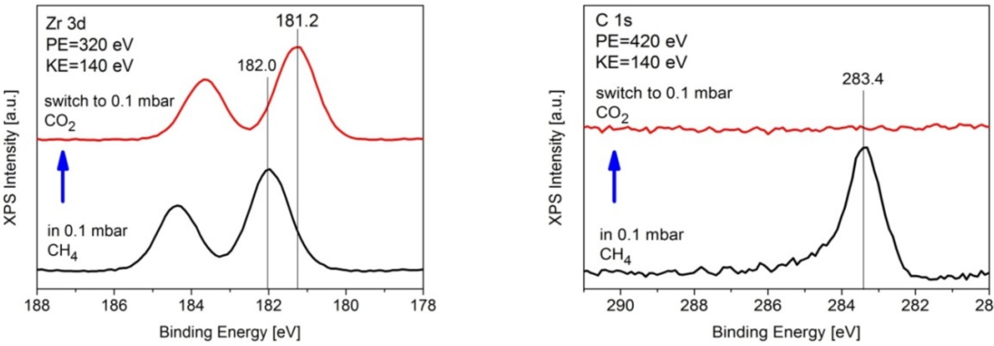

Figure 1: Zr 3d (left) and C 1s (right) in-situ XPS of ZrO2/Pt in different reaction gases: switching from 0.1 mbar CH4 (black) to 0.1 mbar CO2 (red), spectra measured at 400°C in 0.1 mbar gas atmosphere.

Acknowledgement

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Orientation Dependence of the Electronic Structure of RuO_2 from X-ray Photoelectron Spectroscopy

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RuO_2 is a remarkable oxide which combines high electrical conductivity with extraordinary stability in technologically relevant environments. Its outstanding physical properties have led to its implementation in a range of processes from large scale industry to specialized applications, from catalysis to battery materials. RuO_2 belongs to a group of transition-metal oxides, which adopt a rutile structure and exhibit a variety of physical properties, including IrO_2 [1] and OsO_2. Its free $4d^4$ electrons lead to it behaving as a metal-like conductor (see Figure 1a for a schematic description of the electronic structure of RuO_2). The specific crystal orientation of RuO_2 may have a significant influence on its behavior, from efficiency and selectivity of catalytic reactions to high-efficiency and low overpotentials, when used in batteries.

X-ray photoelectron spectroscopy (XPS) can be used to probe the electronic structure of a material with the valence region directly corresponding to the density of states (DOS) of a material. Traditional XPS is a surface sensitive technique and therefore limited to the investigation of the surface electronic structure of a material. Hard X-ray photoelectron spectroscopy (HAXPES) on the other hand provides the bulk electronic information. This work presents both XPS/HAXPES data of epitaxial RuO_2 thin films in four different orientations (see Figure 1b,c for (111) and (100)), which is compared to partial DOS from density functional theory calculations, which were corrected for the specific orbital arrangement in the different thin film orientations. Contributions to the valence band are analyzed in detail and a clear orientation-dependence of the XPS/HAXPES valence band spectra is observed.

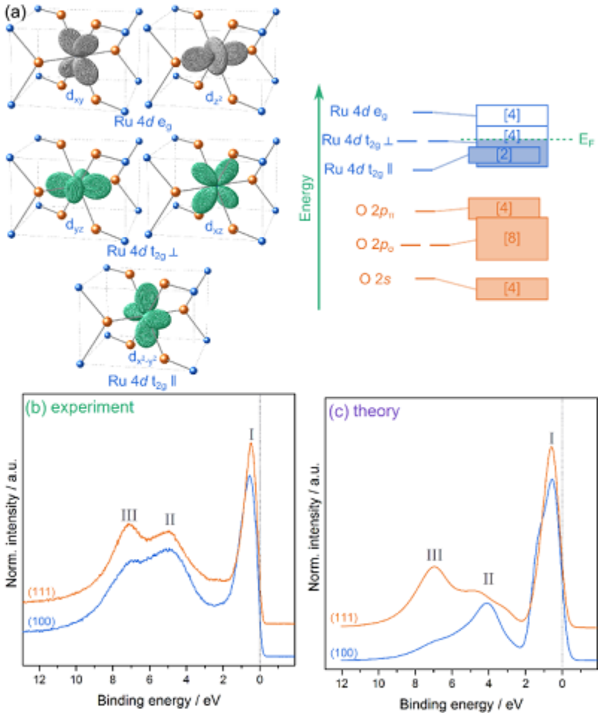

Figure 1: (a) Schematic description of orbital arrangements and electronic structure of RuO_2. (b) HAXPES valence band spectra and (c) DOS of RuO_2 (100) and (111) thin films.

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The Influence of Oxygen on the Catalytic Interaction between CO_2 and Copper studied by High Pressure X-ray Photoelectron Spectroscopy

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CO_2 is a source for the production of carbon based fuels, such as methanol, and presents an attractive alternative to fossil fuels. Copper is an ideal catalyst for the reduction of CO_2, as it is able to direct reactions through stable intermediates, e.g. CO. An important question concerns the influence of oxygen on the catalytic activity and whether oxides are formed on the surface. As this system is an excellent material for the reduction of CO_2 a detailed understanding of the basis of its catalytic activity is essential and absolutely necessary for any further development.

X-ray photoelectron spectroscopy (XPS) is used widely in the solid-state sciences but due to its nature as an ultra high vacuum technique (pressure 10^{-9} mbar) it is not possible to study gas-solid interfaces. Lab-based high-pressure XPS (HPXPS) is an advanced method which allows the measurement of solid samples at elevated pressures of between 1 and 30 mbar. This work presents results on the interaction of CO_2 and CO_2/O_2 with the surface of polycrystalline Cu followed by HPXPS. Cu 2*p* core levels, as well as the Cu $L_3M_{4,5}M_{4,5}$ Auger line are used to investigate the state of the Cu surface. The C1*s* and O1*s* core levels are used to track the interaction between CO_2/O_2 and Cu and are compared to CO_2/O_2 gas phase measurements.

Ultimately, the presented results provide a starting point for the detailed understanding of these catalysts and lead to the identification of possible ways to further improve and develop their properties.

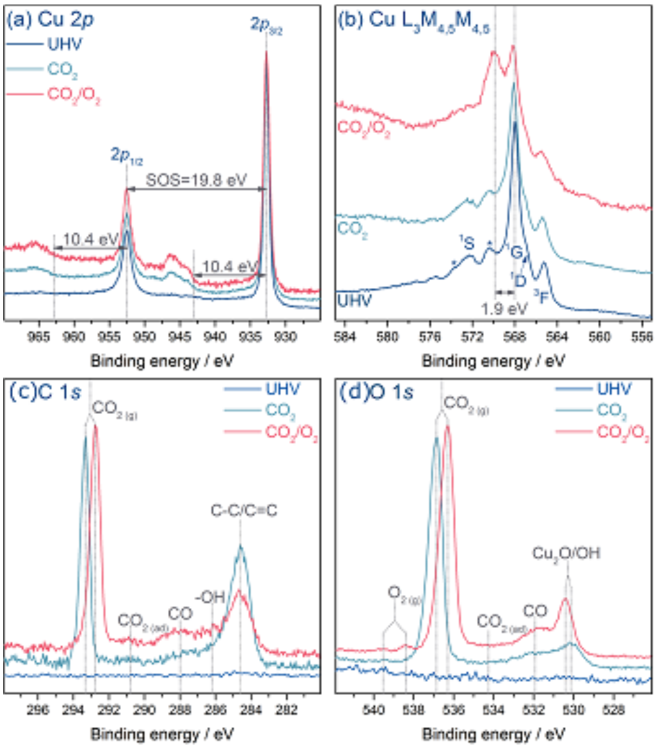

Figure 1: X-ray photoelectron spectra collected in UHV and under CO_2 and CO_2/O_2 atmospheres: (a) Cu 2*p*, (b) Cu $L_3M_{4,5}M_{4,5}$, (c) C 1*s* and (d) O 1*s* spectra.

Properties of Halide Anions in Proximity to the Air/Water Interface - an Energetic Perspective

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The water interface represents a ubiquitous break of bulk symmetry, which creates a wealth of properties that are not observed in the bulk. The underlying mechanisms that drive these effects are, however, still largely unknown. They are most likely a combination of many effects of both entropic and enthalpic nature [1] [2]. In this work we focus on the study of solute properties close to the interface and the subsequent disentanglement of the driving forces behind the observed behaviour. In particular ion surface propensity and ion-ion interaction mechanisms are investigated, which are most likely the result of a delicate interplay between solvent-solute and solvent-solvent interactions. In order to understand both contributors to this balance we study halide salts at the surface, as a function of both concentration and temperature.

Halides are a simple, yet interesting model system, which displays a wide variety of effects such as different surface propensities (iodide is postulated to adsorb to the surface, whereas fluoride avoids it [1]) or the formation of charge layers or ion pairs close to the interface, which are assumed to stabilise the surface. The small molecular size of these systems also allows for a comparison with both *ab initio* and Molecular Dynamics simulations [1], which allows for a direct comparison to theoretical enthalpies and entropies and thereby puts the presented results on a much firmer footing.

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Direct Observation of Changes in Hematite Band Energy Profile During Photoelectrochemical Water Splitting

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Electrochemical properties of a solid-liquid interface between doped/undoped Hematite and electrolyte have been investigated during photoelectrochemical water splitting reaction under various potential and light conditions by means of Ambient Pressure XPS and using “tender” X-rays. In particular we successfully utilized this method as non-contact probe of a local electrical potentials to get better understanding to the band alignment of a semiconductor during different stages of oxygen evolution reaction (i.e. below, at, and above OER overpotential) as well as the effect of solar radiation. We have demonstrated that both doped and undoped hematite follow ideal semiconductor behavior, and contrary to what has been widely accepted in the literature, do not exhibit Fermi level pinning. The last is a strong indication of absence of in-gap (surface) states between 0.4 eV – 1.4 eV below conduction band of Fe_2O_3. This let us conclude that the role of Ti dopants to a large extend can be explained by an increase of semiconductor’s conductivity and carrier diffusion length, whereas interactions with defects should play a smaller role. We have also determined kinetically limiting processes for each combination of potential and light, with the kinetics of OER being dominant at low currents, diffusion of ions to/from anode dominant at high currents for doped semiconductor, and bulk diffusion/recombination for undoped semiconductor.

Development of HELIOS – a facility dedicated for time-resolved XUV-based spectroscopy with few tens of femtoseconds time-resolution

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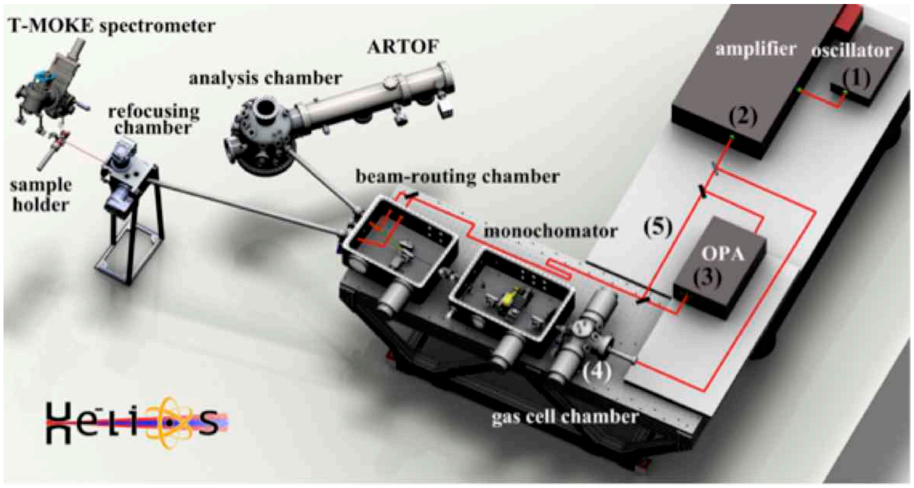
We present the development and characteristics of an HHG laboratory (HELIOS – High Energy Laser Induced Laboratory, see figure below) [1], [2] at Uppsala University. HELIOS is dedicated for time-resolved XUV-based spectroscopy and features an overall temporal resolution of a few tens of femtoseconds combined with an energy resolution of ~100 meV at ~40 eV.

Pump-wavelengths in the span 240 – 20 000 nm are available through a commercial OPerA Solo Optical Parametric Amplifier, while pump-wavelengths in the range ~15 – 72 eV are generated in a gas, typically Argon or Helium. The drive laser is a commercial Coherent 800 nm Ti:Sapphire amplified laser operating at 5 or 10 kHz delivering >2.5 mJ respectively >1.0 mJ with pulselengths <35 fs.

In addition to the overall design and initial performance tests the first results from studies of ultrafast demagnetization using tr-T-MOKE on permalloy [3], time- and angle-resoled photoelectron spectroscopy (tr-ARPES) on graphene [4] as well as time-resolved photoelectron spectroscopy (tr-PES) on a conducting polymer [5].



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HELIOS, an XUV Pump Probe source for Application in Time Resolved Photoelectron Spectroscopy and Demagnetization Dynamics.

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The **H**igh **E**nergy **L**aser **I**nduced **O**vertone **S**ource (**HELIOS**) is a laser based pump probe system, which utilizes **H**igh **H**armonic **G**eneration (**HHG**) to produce monochromatised ultra-short XUV pulses for applications in photoelectron spectroscopy and in demagnetization dynamics[1]. The pump beam is the fundamental 800 nm laser pulse used to drive the harmonics however this wavelength can be modified using either a commercial **O**ptical **P**arametric **A**mplifier (**OPA**) or a recently installed frequency trippler system which utilizes sum frequency generation of the fundamental and its second harmonic to produce an ultra-short 266 nm pump beam useful for gas phase and high energy band gap applications.

In this poster we will present the latest output characteristics of HELIOS including the power of the monochromitised XUV source and the pulse characteristics of the pump beam.

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The competition of intramolecular and intermolecular de-excitation processes after core-ionization in aqueous ammonia and hydrogen peroxide solution

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We expose our bodies to ionizing radiation in our everyday lives e.g. cosmic X-rays on intercontinental flights and during medical X-ray treatment. Upon interaction with matter, this radiation produces electrons, which play an important role in damaging living tissue [1]. Despite the importance of these processes, we still lack a molecular-level understanding of the underlying processes. Auger electron spectroscopy of liquid samples combined with molecular dynamics simulation is a unique tool to study some of the relevant processes [2]. Here, we focus on ultrafast intermolecular charge transfer mechanisms involving proton transfer and their competition with intramolecular relaxation on a femtosecond timescale. After core-ionization of the N1s or O1s levels in ammonia or hydrogen peroxide, respectively, the exited molecules relax either via the Auger decay or via autoionization mechanisms involving neighboring molecules of the originally excited species. Processes involving the environment of the excited species separate the positive charges arising from the autoionization among two molecules. One particular process among these is the proton transfer mediated charge separation (PTM-CS) the efficiency of which is dependent on the proton mass. We compare autoionization spectra from the normal solution and its deuterated equivalent to identify PTM-CS in H_2O_2(aq) and NH_3(aq) [3,4]. In comparison to similar results from neat water, the PTM-CS signal intensity is lower than expected [5]. We argue that the competition between intramolecular relaxation coupled with Auger decay and PTM-CS is responsible for the lower than expected PTM-CS signal.

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The First SPIN and ANGLE-resolved Photoemission Setup at Elettra at APE Low Energy End-station within NFFA Demonstrator

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APE is a facility for spectroscopic investigation of solid surfaces and nanostructured matter for which the sample preparation and survey represent crucial and integral part of the experiment [1]. The APE concept is based on a state-of-the-art surface science laboratory as a support facility for advanced spectroscopies at two distinct beamlines using polarized Elettra synchrotron radiation in the ultraviolet and soft X-ray range. From 2013 APE became an integral part of the NFFA demonstrator [2] that allowed for an important upgrade of the ARPES station: new VG-Scienta DA30 analyzer with deflection mode that allows for the band mapping over the extended angular range at fixed sample geometry, replaced the outdated SES2002. The new analyzer is further equipped with two VLEED detectors for three-dimensional spin analysis that have recently been constructed, installed and commissioned at APE. With this upgrade the users gain access to a state of the art Spin-Resolved ARPES spectrometer with variable polarization undulator radiation, connected directly with the NFFA suite of in situ growth and characterization facilities (including PLD and MBE) as well as the APE-High Energy spectrometer for XAS/XMCD/XMLD/XPS. The new spin-resolved setup is available for users from July 2015. The increase in the APE oversubscription ratio by factor 2 demonstrates the high demand by the users' community, in particular those interested in topological materials, Weyl semimetals or similar, where the spin texture provides crucial information in classifying the material properties. The performance of the system will be demonstrated by a few representative results [3].

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Nanoscale investigation of organic semiconductor materials using X-ray spectromicroscopy

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Organic semiconductors show great promise as an alternative to conventional electronics due to their solution-based processability. However, the convenience of solution-based processing comes at the expense of maintaining a well-defined structure. Since the electronic properties of organic semiconductor devices are strongly dependent on both the chemical composition and local microstructure it is important to employ experimental techniques that provide information on both of these characteristics. Currently, such techniques are lacking and hence there is a need for more complete characterization tools. Here, we present a novel instrument "NanoXAS" which combines two powerful techniques, scanning probe microscopy (SPM) and scanning transmission X-ray microscopy (STXM), in order to fully characterize organic semiconducting materials and devices. While SPM can measure physical properties such as sample topography, elasticity, friction, electrostatic, and magnetic properties with nanometer resolution the X-ray spectromicroscopy provides access to the local chemical composition, electronic structure, molecular orientation, order, and optical density [1-4]. Coaxial alignment of the two microscopes allows several detection modes to be utilized simultaneously. We present measurements on (i) organic field effect transistor (OFET) devices (see Figure 1) and (ii) organic semiconductor blends used in solar cells.

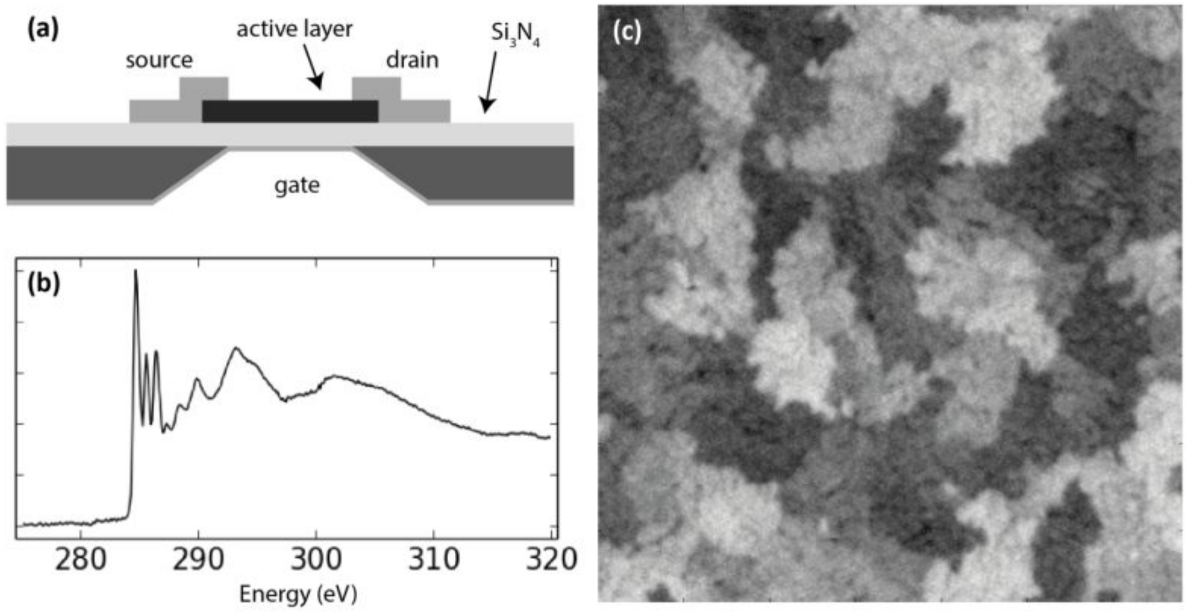

Figure 1. (a) Schematic of an OFET device with lateral source and drain. The active layer is a DHDAP thin film deposited onto a semi-transparent Si3N4 membrane. (b) Carbon K-edge NEXAFS of the DHDAP film. (c) STXM image (10 um x 10 um) of the DHDAP film measured at 284.7 eV.

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Surface Enhancement of Organic Acids by Inorganic Salts with Implications for Atmospheric Nanoparticles

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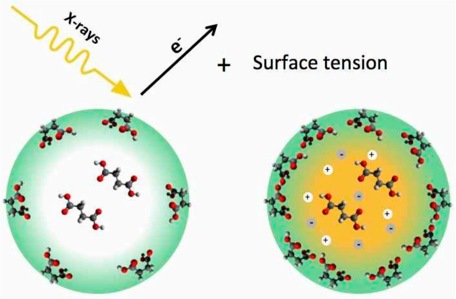
Atmospheric particles are one of the main factors governing the Earth's radiative budget, but their exact effects on the global climate are still uncertain [1]. Knowledge on the molecular-scale surface phenomena as well as interactions between atmospheric organic and inorganic compounds is necessary for understanding the role of airborne nanoparticles in the Earth system [2, 3]. We studied aqueous solutions containing succinic acid only and in mixtures with inorganic salts that are commonly found in the atmosphere using X-ray photoelectron spectroscopy (XPS) on a liquid micro-jet. Through a novel combination of results from XPS studies, surface tension measurements and thermodynamic modeling, the surface composition of the aqueous systems could be determined. We found that succinic acid molecules accumulate in the aqueous surface, yielding a tenfold surface concentration as compared with the bulk of a saturated solution [4]. Co-dissolved inorganic salts enhance this enrichment even further, which can be explained by competition for hydration in the bulk solution. The enhanced surface to bulk partitioning implies a possible increased organic acid content in small atmospheric nanoparticles. The results may be used to explain observations of size-dependent phase-state of atmospheric nanoparticles, suggesting that these particles can display drastically different behavior than predicted by bulk thermodynamics.



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Solid electrolyte interphase in Na-ion batteries studied by Hard X-ray photoelectron spectroscopy (HAXPES)

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In the most common negative electrodes (e.g. graphite and silicon anodes in Li-ion batteries and hard carbon and phosphorous anodes in Na-ion batteries), discharge/charge electrochemical potentials lie outside the electrochemical potential window of common battery electrolytes (e.g. carbonates). This results in decomposition of the electrolyte, and possibly formation of a passivation layer called solid-electrolyte-interphase (SEI) on the negative electrode. The SEI acts as a barrier for electron transfer between the anode and the electrolyte, which is vital to make the battery kinetically stable.[1]

The commercialization of Na-ion batteries has been hampered due to some challenges including the poor properties of the SEI on the negative electrode. For example, the higher solubility of SEI components in Na-ion batteries, compared to that in Li-ion batteries, results in poor performance of the SEI in Na-ion batteries.[2] Therefore, analysis of the SEI on anode materials is a crucial step in order to improve performance of Na-ion batteries.

The analysis of the SEI composition requires employment of advanced analytical techniques because the SEI is a very thin (few nanometer) layer composed of amorphous and crystalline compounds made of inorganic and organic species.[3] In this respect, synchrotron-based photoelectron spectroscopy (PES) is a useful technique to obtain a depth profile of the SEI in order to reveal its composition at different depth.

We have analyzed the surface composition of different types of cycled anode materials, including hard carbon and phosphorous based anodes in Na-ion batteries, using hard X-ray photoelectron spectroscopy (HAXPES) technique at Helmholtz-Zentrum Berlin, BESSY (Germany). In this presentation, we will describe our recent HAXPES results and discuss how HAXPES provides a better understanding of the SEI composition in Na-ion batteries.

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Reactivity of Silicene toward hydrogenation and molecules

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Silicene and germanene, which have attracted enormous interest since publication in 2012 of the epitaxial synthesis of the archetype 3 × 3 reconstructed monolayer silicene phase coinciding with a 4 × 4 supercell on a silver (111) substrate [1], are emergent novel artificial two-dimensional (2D) materials that might rival graphene for logic applications in electronics [2]. Single layer germanene, predicted to be a robust 2D topological insulator at nearly room temperature, has been later grown on a gold substrate [3], next on an aluminum one with just one phase [4]. Strikingly, the first monolayer silicene Field Effect Transistors with ambipolar characteristics have been already fabricated [5]. Multilayer silicene, which is self-protected in ambient air, has been further synthesized on a silver template. Synchrotron radiation photoelectron spectroscopy results acquired at the SOLEIL facility demonstrate that it hosts Dirac fermions with a Fermi velocity about one-third of that of free standing graphene [6].
Ordered hydrogenation of monolayer silicene has been achieved recently in Beijing [7], next at the PIIM Lab in Marseille, with complimentary High Resolution Electron Energy Loss spectroscopy results [8]. Instead, hydrogenation of multilayer silicene leads to an etching process [9].
The poster will summarize these advances [10], and further address the interaction of silicene with organic molecules.

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Selective Bond Breaking On Excited-State Potential Energy Surfaces of 2-Mercaptopyridine

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Influence and control over active sites and bond formation remains an important step for design and understanding of functional materials and biological molecules. In particular, excited state proton transfer (ESPT) is a common process which can affect e.g. the folding and functionality of proteins.

We study the model system of aqueous 2-Mercaptopyridine (2-MP) with time-resolved Resonant-Inelastic X-ray Scattering (RIXS) and high-level quantum chemistry calculations, and demonstrate that bonds can be selectively weakened or broken with optical light and X-ray pulses.

The sensitivity of RIXS with respect to chemical environment and dynamics in excited states is employed to investigate the photo-induced deprotonation of 2-MP. We also show how the short time-resolution of X-ray spectroscopy is essential for studies of ultra-fast dynamics.

Ground state potential energy surfaces around selected atoms from resonant inelastic x-ray scattering

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Thermally driven chemistry as well as materials' functionality are determined by the potential energy surface of a systems electronic ground state. This makes the potential energy surface a central and powerful concept in physics, chemistry and materials science. However, direct experimental access to the potential energy surface locally around atomic centers and to its long-range structure are lacking. Here we demonstrate how sub-natural linewidth resonant inelastic soft x-ray scattering at vibrational resolution is utilized to determine ground state potential energy surfaces locally and detect long-range changes of the potentials that are driven by local modifications. We show how the general concept is applicable not only to small isolated molecules such as O2 but also to strongly interacting systems such as the hydrogen bond network in liquid water. The weak perturbation to the potential energy surface through hydrogen bonding is observed as a trend towards softening of the ground state potential around the coordinating atom [1]. The instrumental developments in high resolution resonant inelastic soft x-ray scattering are currently accelerating and will enable broad application of the presented approach. With this multidimensional potential energy surfaces that characterize collective phenomena such as (bio)molecular function or high-temperature superconductivity will become accessible in near future.

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Is $CH_3NH_3PbI_3$ Polar?

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Organic- inorganic hybrid perovskites have emerged as highly efficient[1] (reaching 20%) photovoltaic materials on par with p-n junction solar cells. Methylammonium lead iodide in particular has been in limelight for its suitably placed band gap of 1.55 eV, low-cost solution based synthesis[2] and strong absorption. Experiments have revealed high open-circuit voltage[1], long electron-hole diffusion lengths[3] exceeding 100 nm and slow recombination rates, which are believed to contribute to the high photovoltaic efficiency. Many believe that the high efficiency is due to ferroelectric nature of the material, since ferroelectricity is believed to give rise to properties like high open circuit voltage and effective separation of charge carriers. With the $CH_3NH_3^+$ ion positioned in the Pb-I octahedral cage of the perovskite and having a sizable dipole moment, there is an exciting possibility of $CH_3NH_3PbI_3$ being ferroelectric. While some report that it is ferroelectric based on XRD, polarization measurements[4], observation of ferroelectric domains and ab-initio calculations; some others report a centrosymmetric structure[5]. In view of the continued controversy on such a fundamental aspect as the polar/non-polar structure of $CH_3NH_3PbI_3$, we have performed time-resolved pump-probe measurement of the second harmonic generation efficiency as well as its more traditional form as a sensitive probe of the absence/presence of the centre of inversion in the system both in its excited and ground states, respectively. Our results show that there is no second harmonic generation(SHG) and the SHG efficiency, if non-zero, is below the limit of detection, indicating a non-polar structure both in the ground state and excited state. These results are supported by P-E loop measurements and also temperature-dependent single crystal X-Ray diffraction data which refine to centrosymmetric space groups in all three phases, thus confirming the non-polar structure of $CH_3NH_3PbI_3$ in all three phases.

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