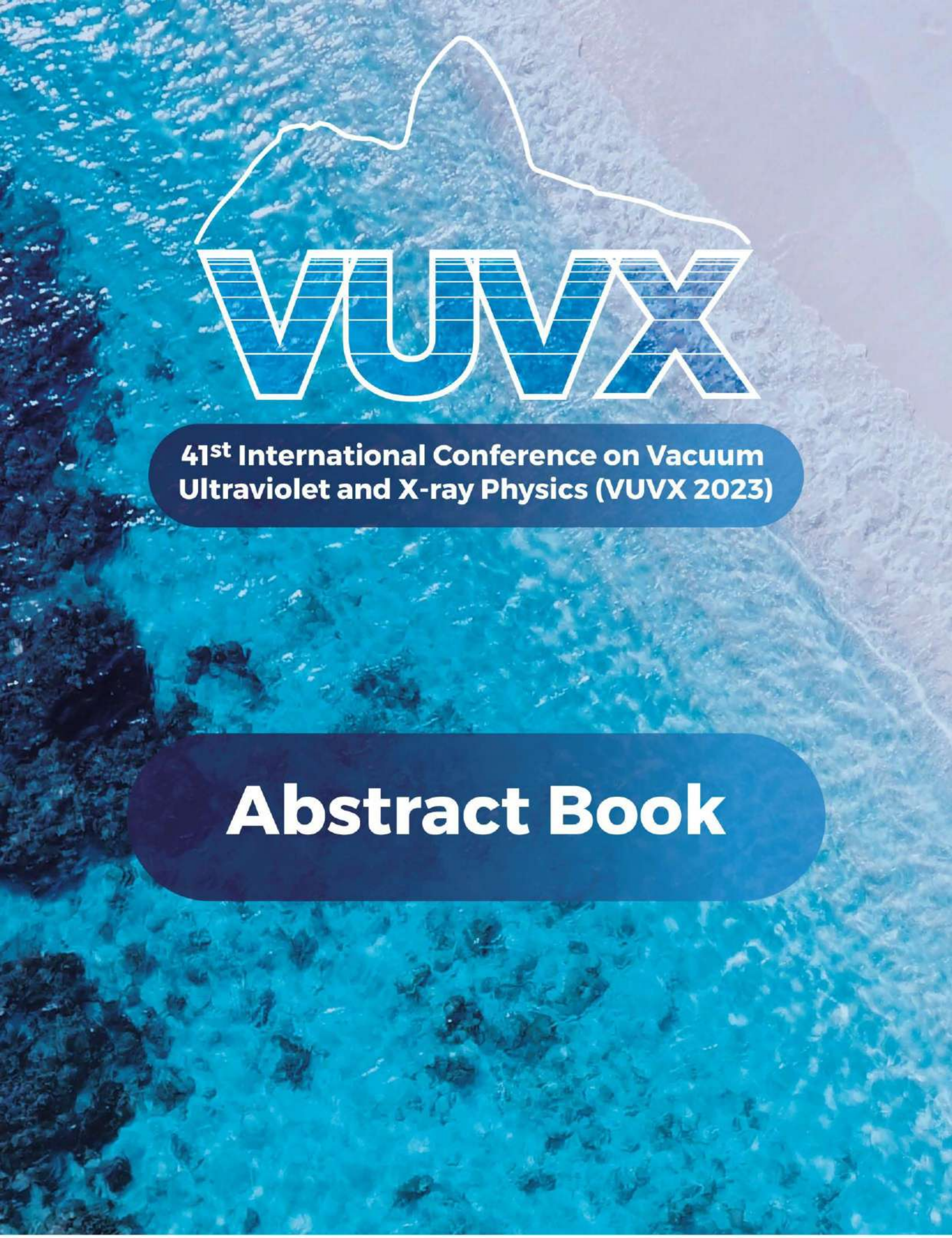

VUVX

41st International Conference on Vacuum Ultraviolet and X-ray Physics (VUVX 2023)

Abstract Book

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LABORATÓRIO NACIONAL DE LUZ SÍNCROTRON (LNLS)

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Summary

PLENARY

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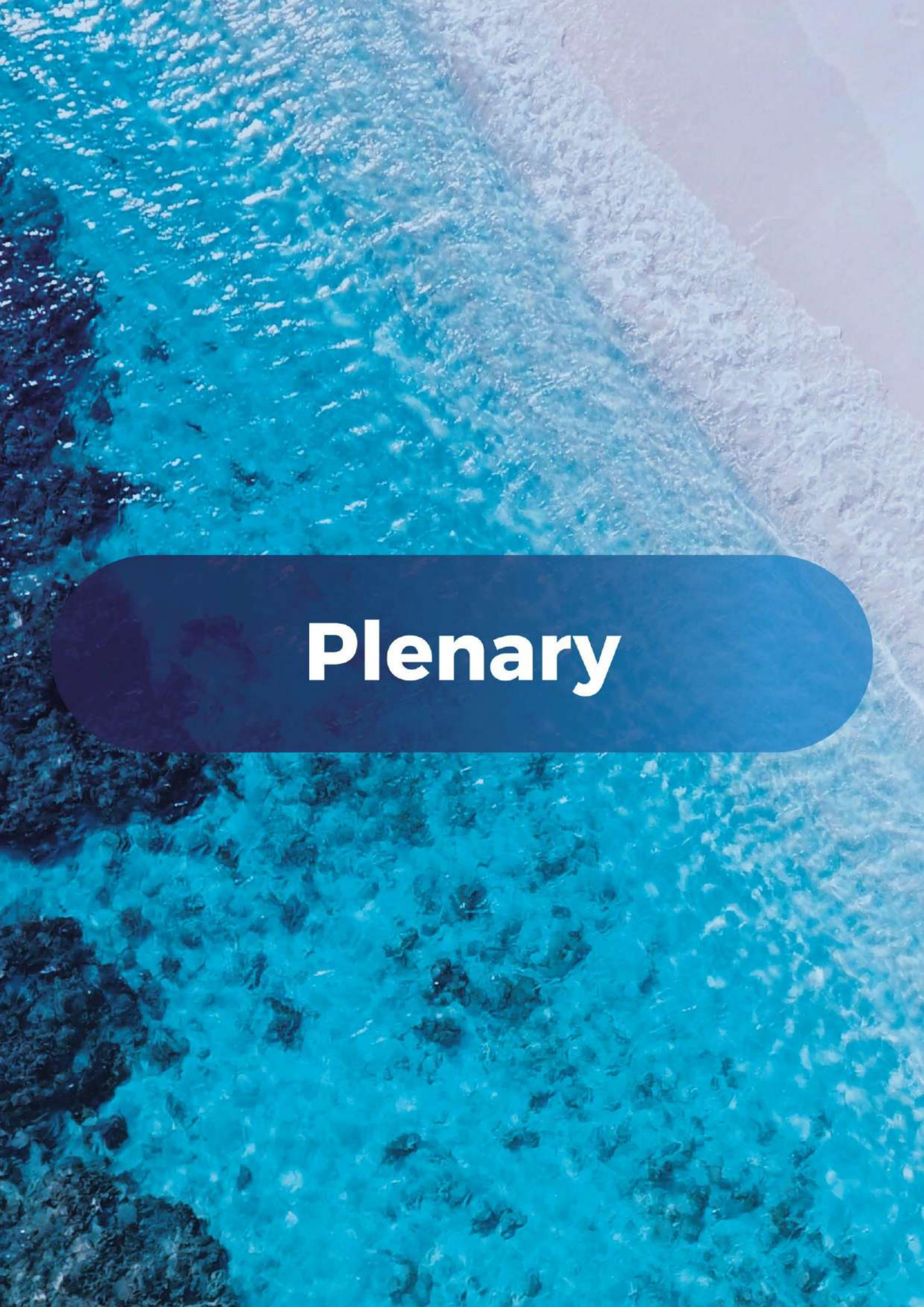
POSTER PRESENTATIONS



Plenary

Brightening the Future of Science with Sirius: Brazil's 4th Generation Synchrotron Light Source

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Sirius, Brazil's newest Synchrotron light source, marks a significant milestone in the field. As one of only three fourth-generation storage ring light sources currently in operation globally, it plays a crucial role in propelling Latin American research forward. This state-of-the-art facility features a 3-GeV storage ring with a 20-cell 5BA magnetic lattice, boasting an emittance of 250 pm.rad. Its innovative storage ring design optimally matched the electron beam's phase space with the X-ray photons' phase space, effectively approaching the diffraction limit for tender X-rays. This fourth-generation storage ring has demonstrated remarkable performance, achieving an rms electron beam stability of approximately 100 nm, reflecting its cutting-edge engineering. Currently, the new Brazilian light source is operating with a current of 100 mA in a transparent top-up mode, with plans to escalate this capacity to 350 mA within the following year. The notable enhancements in source brightness and coherence offered by Sirius, combined with advancements in optics, precision mechatronics, detectors, and computing, open new avenues for research on various spatiotemporal scales. The ambitious first phase of the Sirius project plans for 14 beamlines, with six currently open for regular proposal calls, four in the commissioning stage, and another four under construction. These beamlines offer a range of scattering, imaging, and spectroscopy capabilities, spanning length scales from centimeters to angstroms. Uniquely, this is also the only fourth-generation light source in operation to include IR and UV beamlines. As this new light source evolves, its extensive experimental capabilities and scientific opportunities become increasingly evident. With potential applications across diverse fields, such as biological, hierarchical, and condensed matter systems, Sirius fuels excitement and anticipation within the global scientific community.

Catching and steering atoms and electrons in action by light

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The talk will first illustrate status of the titled study with short-wavelength free-electron lasers (FELs), focusing on characteristic properties of different facilities. The advent of hard x-ray FELs, such as SACLA in Japan, opened a route to extract a structure of a single nanoparticle [1] and its change upon the intense laser irradiation that transforms the nanoparticle into a nanoplasma [2]. The first high repetition rate soft X-ray FEL, European XFEL, combined with REMI/COLTRIMS, made a long-standing dream to watch atoms in action, initiated by photoexcitation of a molecule, a tangible reality [3]. Generations of two-colour attosecond pulses at LCLS in the USA opened the door to watch charge in action that occurs in the attosecond timescale [4]. Generating phase-coherent multi-colour pulses at FERMI, on the hand, provided a novel approach to coherently control the electronic wave-packet [5] and to read out the photoionization phase, or attosecond photoionization time delay [6]. The talk will also address the titled study with laboratory attosecond pulse train light sources, complementary to FELs, combined with combined with REMI/COLTRIMS [7,8].

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Acknowledgments

I acknowledge all the collaborators in the authors list of [1-8] for fruitful collaborations.

Dynamics of water molecules exposed to x-rays (over 25 years and 6 light sources)

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The dynamical behaviour of water molecules exposed to an intense x-ray beam is of utmost interest from both a fundamental point of view and the possible implications in a multiplicity of fields, from radiation damage in living tissues to problems in oncology treatments to even interstellar phenomena.

High-energy radiation can induce a variety of processes in water, such as the production of multiply charged species and fragmentation pathways yielding ions or radicals.

Water has been the subject of many of our papers. I will present an overview of dynamical effects, ranging from details on resonant processes at the O K-edge (1-3) to ultrafast dissociation phenomena (4), production of double core holes (5,6), all studied at synchrotron radiation sources, and finally electronic and geometrical structural changes upon nonlinear processes by multiphoton absorption at a free-electron laser source (7).

These results span a period of 25 years and have been obtained at 6 different light sources. This overview will underline some technical progress, some different methods to derive the timescale of dynamical processes (core-hole-clock or time-resolved source), and finally, the depth of information spectroscopic methods can provide concerning a problem of both fundamental and applied interest.

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Momentum Resolved Resonant Inelastic X-Ray Scattering on Quantum Materials

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Resonant Inelastic X-ray Scattering (RIXS) is a powerful probe of excitations from the electronic ground state of quantum materials involving lattice, charge, orbital and spin degrees of freedom. RIXS gives direct information as a function of momentum and energy transfer, on the elementary excitations within these degrees of freedom. For $Bi_2Sr_2CaCu_2O_{8+x}$ we extract the spin dynamical structure factor from Cu L_3 RIXS spectra by disentangling the spin and charge excitations based on the respective scattering tensors in an azimuthal dependent analysis of the cross section [1]. This confirms unambiguously the persistence of the collective spin excitations in large parts of the Brillouin zone [2]. The magnetic excitations of uniaxial-strain detwinned FeSe in Fe L_3 RIXS [3] reveal a prominent anisotropy between H and K directions well above the d_{xz}/d_{yz} orbital splitting and below the tetragonal-to-orthorhombic transition, suggesting that the nematic phase transition is primarily spin-driven. We disentangle by combined O K- and Ni L_3 RIXS the concomitant evolution of phonon and magnon excitations associated with the breathing distortion of the lattice and the antiferromagnetic phase in rare-earth (Re) nickelates $ReNiO_3$, respectively [4]. The results reveal a clear hierarchy of the insulator-metal and magnetic transitions of $ReNiO_3$ where weakening of electron-lattice interactions upon warming first drive their electronic transition and triggers melting of the antiferromagnetic phase.

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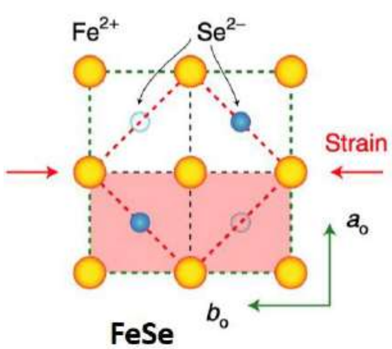
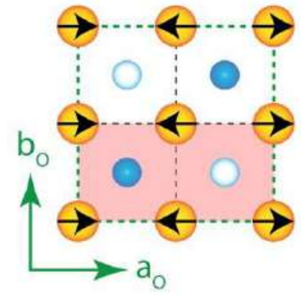
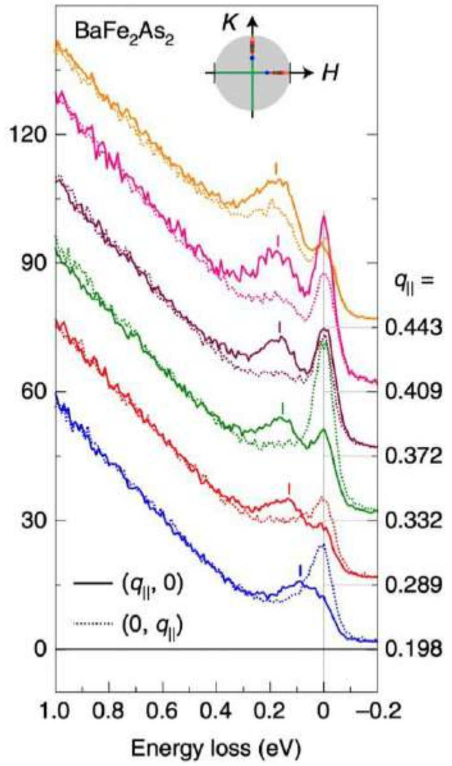
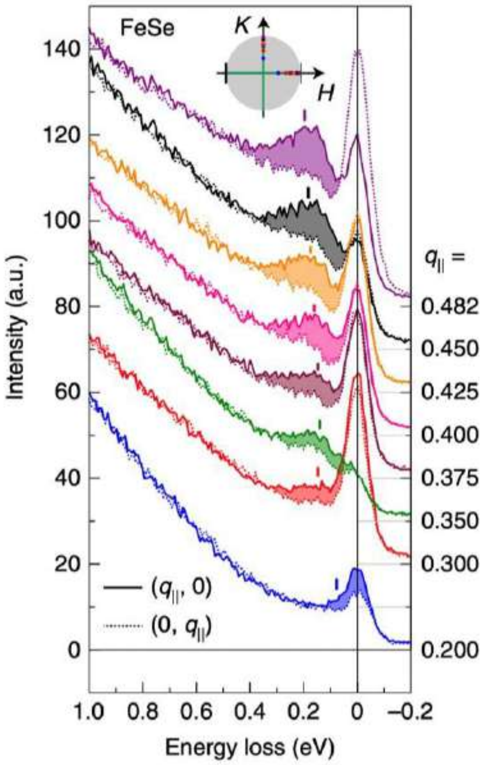


FeSe



BaFe$_2$As$_2$





Highly oxidized transition-metal oxides in high-energy battery cathodes studied by soft X-ray RIXS

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The bottleneck of today's battery performance in energy density lies in the transition-metal (TM) oxide based cathodes. Operating a battery under high-energy, i.e., high-voltage, conditions unfortunately, triggers complex chemical and structural evolutions. This provides the opportunities for soft X-ray RIXS as a powerful characterization technique to reveal the relevant fundamental physics and functional chemistry in battery materials. This presentation first demonstrates RIXS capabilities in studying transition metal-based battery electrodes especially in the high-voltage range. We argue that, regardless of the chemical composition, the high-energy operation spontaneously triggers a highly oxidized oxide state in the battery cathode. Such a highly oxidized transition-metal oxide is a complex system, in which conventional ionic crystal models fail and a significant amount of oxygen activities are involved in the electrochemical operations, the so-called oxygen redox reaction. Soft X-ray resonant inelastic X-ray scattering (RIXS) is a powerful tool for detecting and distinguishing different types of oxygen activities; however, the interpretation of soft X-ray RIXS results on this topic remains a highly debated topic, which calls for collaborations in Physics, Chemistry and Material Science scientists to collaborate on the fundamental understanding and practical optimization of highly oxidized oxide systems towards high energy-density batteries.

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Invited Talks

Attosecond charge migration and conical intersection dynamics probed by X-ray absorption spectroscopy

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The development of table-top attosecond soft-X-ray spectroscopy in the gas and liquid phases will be discussed. This technique has been applied to observe the decoherence and revival of attosecond charge migration driven by nuclear motion, as well as the transfer of electronic coherence through a conical intersection in the neutral silane molecule [1]. These results demonstrate a broadly applicable approach to inducing and probing charge migration in molecules, opening the door to controlling molecular dynamics on the electronic time scale. Extending this technique from the silicon L-edge to the carbon K-edge [2] has enabled the observation of the fastest conical-intersection dynamics observed to date, i.e. the sub-7-femtosecond electronic relaxation from the A to the X state in the ethylene cation [3]. Turning from the gas phase to the liquid phase, I will discuss recent results on the observation of femtosecond conical intersection dynamics of photoexcited pyrazine. The direct comparison of dynamics measured in the gas phase and in aqueous solution highlight the impact of solvation on these dynamics. These results demonstrate the potential of attosecond soft-X-ray spectroscopy for studying electronic dynamics of chemically relevant systems in aqueous solutions under ambient conditions.

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Attosecond X-ray free-electron lasers: recent developments and future directions

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Attosecond XFELs are the subject of an intense research effort worldwide that involves large X-ray facilities, advanced particle accelerators and cutting-edge laser technology. Our attosecond science effort at SLAC has evolved from an accelerator R&D project (1) to a new scientific program, producing observations of coherent electronic phenomena with atomic site specificity and unprecedented temporal resolution (2).

I will then present our results on attosecond pulse generation and its application to attosecond pump/probe experiments at the Linac Coherent Light Source. I will then discuss our research on attosecond pulse shaping, and its applications to the temporal shaping of electronic wavepackets in molecular systems.
Finally, I will discuss our ongoing research efforts towards plasma-based attosecond sources, capable of combining the peak power of XFELs with the fractional bandwidth of state of the art few-cycle lasers (3).

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Status of the Shenzhen Innovation Light Source Facility

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The Shenzhen Innovation Light Source Facility (SILF) is a fourth generation of medium energy synchrotron radiation light source, which include beamline system and accelerator system. The accelerator complex is composed of the 200 MeV linac, the 0.2-3.0GeV booster and the 3.0GeV storage ring. The circumference of the storage ring is 696.0m, which include 28 hybrid-7BA Lattice periodic unit to achieve the emittance below 100pm.rad. The SILF focuses to support the development of the domestic core industries, basic science frontier research and major strategic requirement, such as integrated circuits, biomedicine, advanced materials and advanced manufacturing. With the Shenzhen Municipal Government’s approval of the SILF project proposal on Sep10 2020, the feasibility study and the conceptual design report of the SILF was completed in 2022. The preliminary design of the SILF are in progress.

the Shenzhen Innovation Light Source

Synchrotron SOLEIL and applications in Quantum Materials

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Here I would like to give an update of SOLEIL synchrotron facility and capabilities.

I will in particular present recent findings using imaging and spectroscopy techniques at synchrotron SOLEIL concerning quantum materials, including topological insulators, two-dimensional materials, superconductors, materials for spin and charge conversion, magnetic skyrmions,...

Important progress in using these materials could open new perspectives for future electronics and spintronics devices and technology.

The benefit expected from new brilliant and coherent sources and the Upgrade of SOLEIL in particular will be emphasized.

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X-ray Free-Electron Lasers are Driving a Revolution in X-ray Science: Recent Highlights, Future Opportunities & Development Plans at LCLS

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X-ray free-electron lasers (XFELs) have opened a new era in X-ray science with important applications in materials science, chemistry, physics, and biology. Coherent ultrafast X-ray pulses (fs and sub-fs) from XFELs, with unprecedented peak and average brightness, provide powerful new insight to electronic and atomic structural dynamics and correlations that underpin complex matter. They further offer promising new approaches to understand fluctuations, heterogeneity, and rare events that often determine the functionality of materials. This talk will provide a brief overview of the rapidly evolving field of XFEL science, with a particular focus on the world's first XFEL in the hard X-ray range – the Linac Coherent Light Source (LCLS). Recent science highlights in the areas of quantum materials, catalysts, materials in extreme environments, and other complex materials will be discussed, along with important results in other science areas.

A major upgrade of LCLS (LCLS-II) is now nearing completion. LCLS-II is being developed as a high repetition rate ultrafast X-ray laser with two simultaneously operating, independently tunable FELs producing uniformly spaced (or programmable) ultrafast X-ray laser pulses at a repetition rate up to ~1 MHz spanning the energy range from 0.25 to 5 keV. A further upgrade (LCLS-II-HE) will extend high-repetition-rate operation to energies above 12 keV. Exciting new science opportunities, enabled by these upgrades, will be discussed.

Acknowledgments
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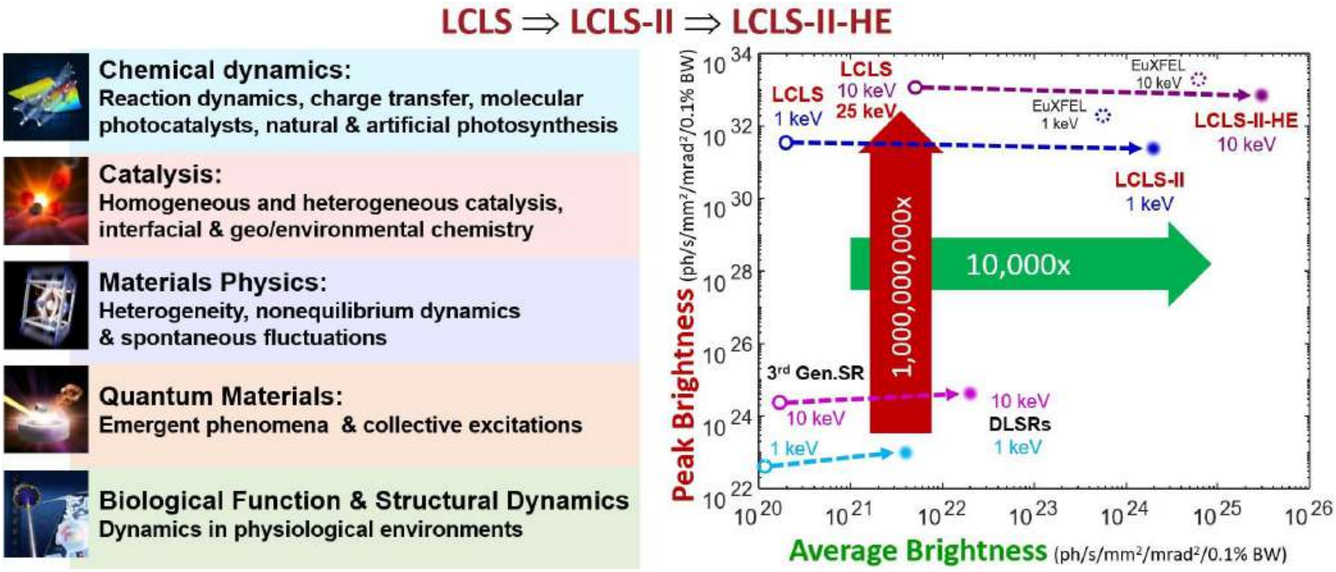

LCLS ⇒ LCLS-II ⇒ LCLS-II-HE

Chemical dynamics:
Reaction dynamics, charge transfer, molecular photocatalysts, natural & artificial photosynthesis

Catalysis:
Homogeneous and heterogeneous catalysis, interfacial & geo/environmental chemistry

Materials Physics:
Heterogeneity, nonequilibrium dynamics & spontaneous fluctuations

Quantum Materials:
Emergent phenomena & collective excitations

Biological Function & Structural Dynamics
Dynamics in physiological environments

Absolute electronic energetics and quantitative work functions of aqueous solutions from photoelectron spectroscopy

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This presentation will report about low-energy constraints on photoelectron spectra measured from liquid water and aqueous solutions, accurate vertical ionization energy and work function determinations of liquid water and aqueous solutions, quantitative electronic structure and work-function changes of liquid water induced by solute, as well as how to measure work functions from aqueous solutions. The recent application of concepts from condensed-matter physics to photoelectron spectroscopy of volatile, liquid-phase systems has enabled the measurement of electronic energetics of liquids on an absolute scale. Particularly, vertical ionization energies of liquid water and aqueous solutions, both in the bulk and at associated interfaces, can now be accurately, precisely, and routinely determined. These ionization energies are referenced to the local vacuum level, which is the appropriate quantity for condensed matter with associated surfaces, including liquids. We connect this newly accessible energy level to another important surface property, namely, the solution work function. We lay out the prerequisites for and unique challenges of determining the work function of aqueous solutions and liquids in general. We demonstrate that concentration-dependent work functions can be accurately measured under controlled conditions. These studies mark the beginning of a new era in the characterization of the interfacial electronic structure of aqueous solutions and liquids in general.

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Cuts through the manifold of molecular H2O potential energy surfaces in liquid water at ambient conditions

Annette Pietzsch[1], Johannes Niskanen[2], Vinícius Vaz da Cruz[3], Sebastian Eckert[4], Lars Birger Mattis Fondell[3], Alexander Foehlisch[5,1]

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Liquid water at ambient conditions is ubiquitous in chemistry and biology as well as in technology, energy, and atmospheric processes. Since parts of the phase diagram of water are unsettled, repercussions thereof on our molecular-level understanding for even the common ambient conditions remain. Breathtaking advances in X-ray–based approaches over the last decade give us now the tools to derive molecular potential energy surfaces as a quantitative view on the molecular manifold within the fluctuating hydrogen bonding network. With selective cuts along the local asymmetric OH bond coordinate and the symmetric normal mode excitations an experimental foundation to benchmark competing molecular-level models of water has been achieved. The fluctuating hydrogen bridge network of liquid water at ambient conditions entails a varied ensemble of the underlying constituting H2O molecular moieties. This is mirrored in a manifold of the H2O molecular potentials. Subnatural line width resonant inelastic X-ray scattering allowed us to quantify the manifold of molecular potential energy surfaces along the H2O symmetric normal mode and the local asymmetric O–H bond coordinate up to 1 and 1.5 A, respectively. We find in liquid water at ambient conditions H2O molecular potentials ranging from the weak interaction limit to strongly distorted potentials which are put into perspective to established parameters, i.e., intermolecular O–H, H–H, and O–O correlation lengths from neutron scattering.

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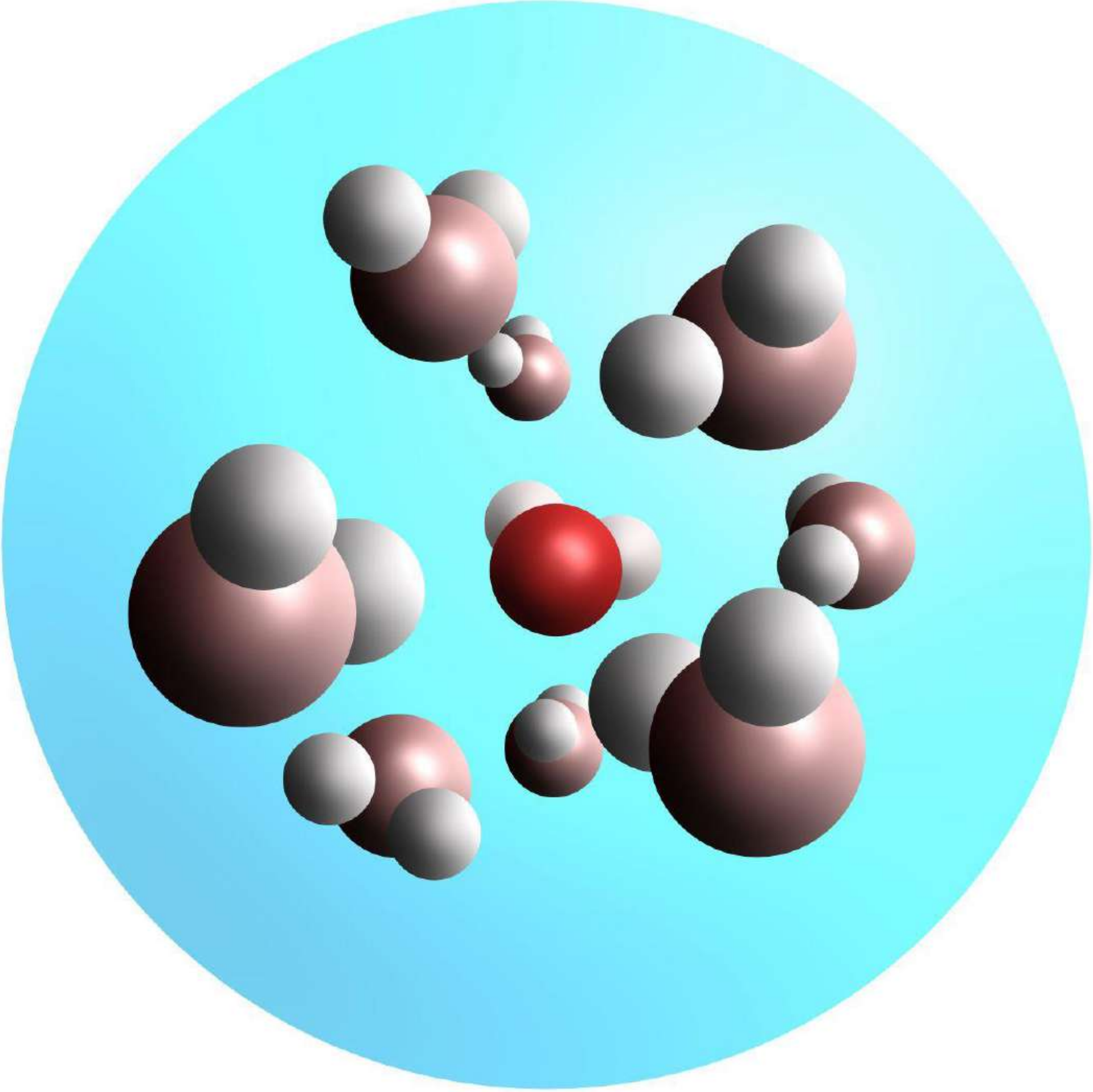

Double Core Hole dynamics studied with Synchrotron and XFEL radiations.

Marc Simon[1,2]

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Double Core Hole (DCH) electronic states of molecules and atoms are interesting, mainly because of their high chemical sensitivity to their chemical environment and because their potential energy surfaces are strongly dissociative [1]. In more than 99% of the case, the DCH states decay through successive Auger decay and the first Auger decay, called hypersatellite Auger decay, measurements using Synchrotron radiation and XFEL have been recently reported [1-2].

The spectral purity of Synchrotron radiation measurements combined with good signal/noise ratio allows to obtain high resolution spectra of the DCH states. The high brightness and intensity of XFEL allows to efficiently produce these states through a successive photon absorption within the pulse duration.

Thanks to the use of the complementarity of these two photon sources, recent results obtained on neon atom, H_2O and CH_3F molecules with theoretical simulations have been obtained and will constitute the heart of this talk. These results are showing new pathways to produce Double Core Hole states [3], ultrafast nuclear dynamics occurring within their very short lifetime [4] as well as the possibility to measure Two-Site Double Core Hole states through the hypersatellite Auger decay.

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Heavy-atom-containing imidazoles as potential radiosensitizers

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Radiosensitizers increase the effectiveness of radiotherapy, in which common problem is hypoxia, where tumors have low oxygen concentration. Since oxygen in combination with x-rays is quite effective in destroying malignant cells, hypoxic cells are more resistant to the treatment. There is an active search for compounds that can release cell-destroying radicals and overcome the effects of hypoxia. Imidazoles form a are class of radiosensitizers in which the release of NO radicals is thought to be the primary mechanism of action[1]. However, as containing only light elements, imidazoles have low cross-section for the absorption of medical x-rays. Heavy-element substitution is one way of enhancing its absorption cross-section [2,3]. For example, bromodized nitroimidazoles could combine these two enhancement mechanisms. An in-depth knowledge of the molecular dynamics following x-ray absorption is needed in order to understand, if the various enhancement mechanisms would indeed combine in a way increasing the effectiveness of radiotherapy.

We present an overview of our recent studies of various imidazole-based compounds, addressing the x-ray induced molecular dynamics at a single-molecule level [1,3,4]. They were carried out as a series of electron-energy-resolved electron-multiion coincidence (PEPIPICO) measurements at the gas-phase endstation of the FinEstBEAMS beamline of MAX IV synchrotron.

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High-resolution photoelectron spectroscopy of molecules, nanoparticles and liquids with Synchrotron Radiation

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The PLEIADES beamline at Synchrotron SOLEIL provides an intense beam of VUV through soft x-ray wavelengths for 10 – 1000 eV for experiments with dilute matter and liquid micro-jets. Two inline undulator sources in the 2.75 GeV SOLEIL storage ring provide the source of radiation, one an electromagnetic undulator with a 256mm period and the other and APPLE-II type permanent magnet undulator with an 80 mm period. A plane grating monochromator uses gratings with variable line spacing and variable groove depths to optimize its performance in terms of flux and resolution. Four end-stations are permanently installed at the end of the beamline with two open ports available for user-provided experimental set-ups.

Recent results from photoelectron experiments a molecular target [1], a nanoparticle sample [2] and a protein in solution [3] will be presented and discussed. In all three cases, the Scienta photoelectron spectrometer permanently mounted on the beamline was used to measure the spectra. Three different sample environments were used to introduce the samples into the photon beam within the spectrometer and will also be discussed.

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Imaging Soft X-ray Spectroscopy at the Small Quantum Systems Instrument of the European XFEL

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We present the first measurements with the 1D imaging soft X-ray spectrometer [1], recently installed at the at the Small Quantum Systems (SQS) instrument [2] of the European XFEL. The imaging capability allows for separation of emission spectra excited along the path of the X-ray incident beam, intended to facilitate investigation of non-linear X-ray-matter interactions in dense gaseous media, and time-resolved pump-probe measurements.

The soft X-ray fluorescence spectra of Ne and Xe show a rich phenomenology with a multitude of emission lines, critically depending on photon energy, fluence, and target density. The dependence on the incident photon energy shows a complex resonant behavior that enables a detailed characterization of the population mechanisms for core excited states in multiply ionized species [3], for Ne including all charge states. Core excited states with lifetimes in the ps-ns range are studied with time resolution, and as a function of target density, thereby enabling us to address interactions with the surrounding plasma. Pulse propagation effects become manifest in non-trivial spectral variations over the imaged path of the incident photons.

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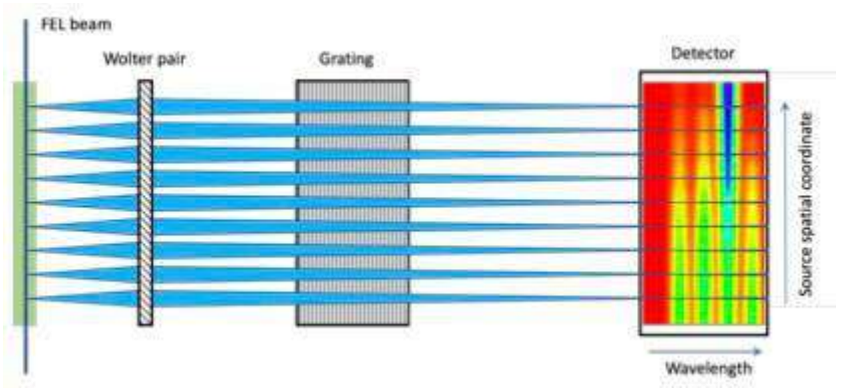
We acknowledge European XFEL in Schenefeld, Germany for provision of the x-ray free-electron laser beam time at the SQS instrument and would like to thank the staff for their assistance. Support from the Swedish Science Council is gratefully acknowledged.



Photoelectron-photoion experiments and their application to molecules of biological and astrochemistry interest

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The interaction of VUV and/or soft X-ray radiation with a molecule in the gas phase results in a single or multiple ionization event. The experiments to characterize this event therefore must involve the detection of electrons and ions. Photoelectron-photoion coincidence, PEPICO, experiments which combine photoelectron spectroscopy with mass analysis thanks to their selectivity provide valuable and unique information on dissociation dynamics following photoionization. Thus PEPICO experiments with synchrotron radiation have become one of the most powerful tools to investigate dissociative photoionization. In this presentation some applications of PEPICO experiments to the study of molecular species of biological and astrochemistry interest in the gas phase will be presented. Among them the use of PEPICO data from valence photoionization to extract information on the energy distribution in collision experiments relevant to radiotherapy[1], the study of potential radiosensitizer[2] and possible role of dipeptide in the origin of life[3] will be discussed.

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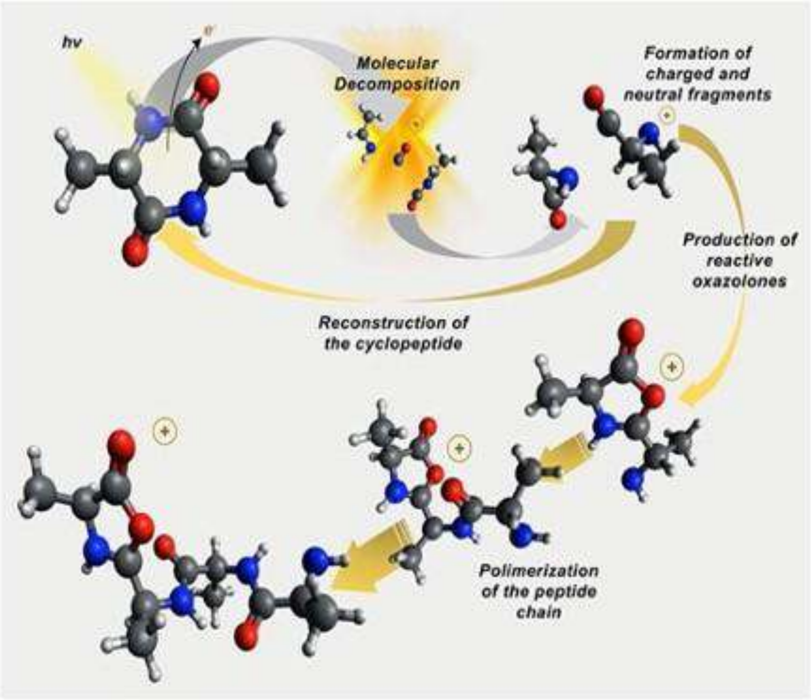

Figure 1: VUV radiolysis of cyclo-dipeptides results in a molecular decomposition with fragments that might lead to polymerization in peptide chains.

Molecular Resonant Inelastic Soft X-Ray Scattering Spectra as Function of Scattering Angle

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The inversion-symmetric oxygen molecule has been the showcase for demonstration of phenomena revealed by advances in the Resonant Inelastic X-ray Scattering (RIXS) technique [1], including mapping of the coupling dynamics at avoided potential-curve crossings [2], observation of spatial quantum beats [3], and interference between resonant and non-resonant scattering channels [4]. The early RIXS investigation [1] provided evidence that inversion symmetry remains unbroken in the core-excited states, as only transitions in compliance with the parity selection rules were observed. It has often been assumed that the observed parity selectivity constitutes a general rule in the sub-keV region.

In contrast, we observe violation of the parity selection rules in the RIXS spectra of the oxygen molecule excited on the p* resonance. We exploit the capabilities of the new Veritas beamline at MAX IV to measure high-quality molecular RIXS spectra, while simultaneously varying the scattering angle. The intensity ratio between parity forbidden and allowed final states is measured accurately as a function of scattering angle, and the results are well described with a theory that emphasizes the analogue to Young’s Double Slit Experiment [5,6], where the crucial parameter is the phase difference in the scattering at the two atomic centers of the molecule.

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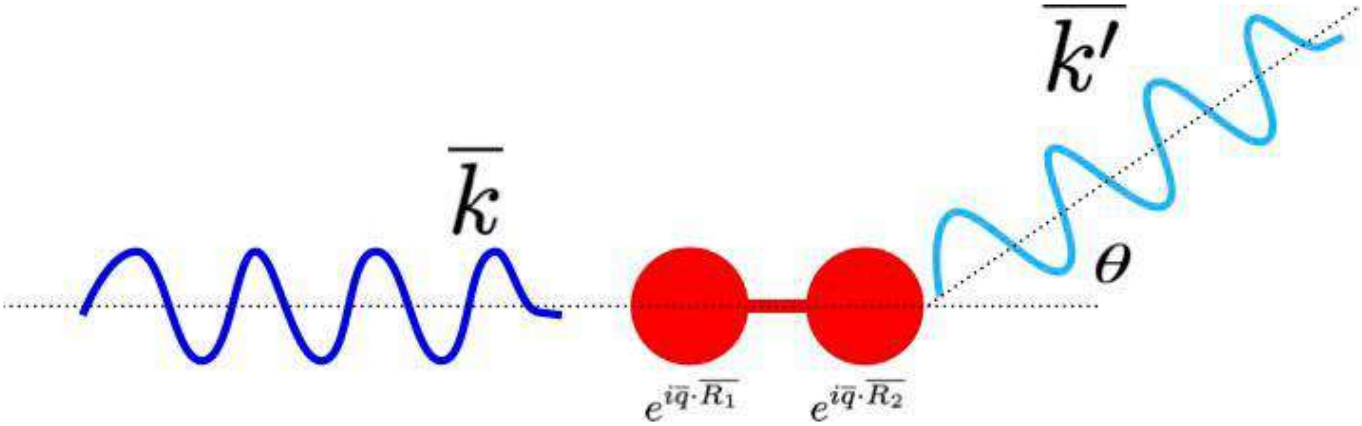

Observable inner-shell absorption for doubly and triply excited states of diatomic molecules

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Shake-up satellites following the single ionization of core and valence electrons of localized character have been widely investigated as typical examples of final-state configuration interaction (FSCI), intensity borrowing and core hole screening/relaxation. For example, diatomic molecules and conjugated molecules show strong π-π* shake-up satellites, and divalent copper compounds $[2p^6][L^2 3d^9]$ show strong shake-up (or shake-down) bands of ligand(L)-to-metal charge transfer $[2p^5][L^1 3d^{10}]$ following singly Cu 2p ionized states $[2p^5][L^2 3d^9]$. On the other hand, shake-up like satellites following the single core excitation have been discussed for some specific molecules and divalent copper compounds. For example, in the case of N_2 with the singlet ground state $[(1s)^4][(\pi)^4(\pi^*)^0]$ denoted hereafter by [4][4,0], singly (1s-π*) and doubly (1sπ-π*π*) excited states, [3][4,1] and [3][3,2], can be regarded as π* bound state resonance converging to the singly ionized state [3][4,0] and strong shake-up satellite states with [3][3,1]; therefore, we can expect rather strong doubly excited states in the 1s region of N_2.

Here, we choose N_2 with singlet [4][4,0], NO with doublet [4][4,1], and O_2 with triplet [4][4,2] and their cations, and investigate energy levels, spin couplings (multiplets), and bond-length dependence for singly and shake-up like doubly excited states, [3][4,1] and [3][3,2], [3][4,2] and [3][3,3], and [3][4,3] and [3][3,4], respectively, and also for triply excited states.

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Optimization of high-order harmonic generation in gases

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High-order harmonic generation (HHG)[1,2] provides broadband, spatially and temporally coherent extreme ultraviolet (XUV) radiation with photon energies up to hundreds of eV, making it interesting for e.g. coherent imaging. HHG has also opened up the field of attosecond science and the study of electron dynamics on unprecedented timescales[3].

In applications of HHG, a high number of photons is often desired. However, the conversion efficiency (CE) is usually below 10^{-5}. Strong efforts are being made to increase either the average photon number using compact, high-repetition rate sources, or the number of photons per pulse, typically with long beam lines and loose focusing.

The successful application of such vastly different driving lasers to the same fundamental process can be attributed to scaling laws of HHG[4], describing how the driving pulse focusing, and the characteristics of the generation medium, should be scaled to reach a similar CE when the input pulse energy is scaled. However, how to choose the medium length and gas density to optimize the CE remains an open question.

We propose an analytic model[5], which predicts, independently of the focusing, that efficient HHG is possible for a range of densities and medium lengths if these follow a hyperbolic relation. The model is verified through simulations and experiments, and is remarkably universal, i.e. to a large extent independent of intensity, pulse duration, generating gas and harmonic order.

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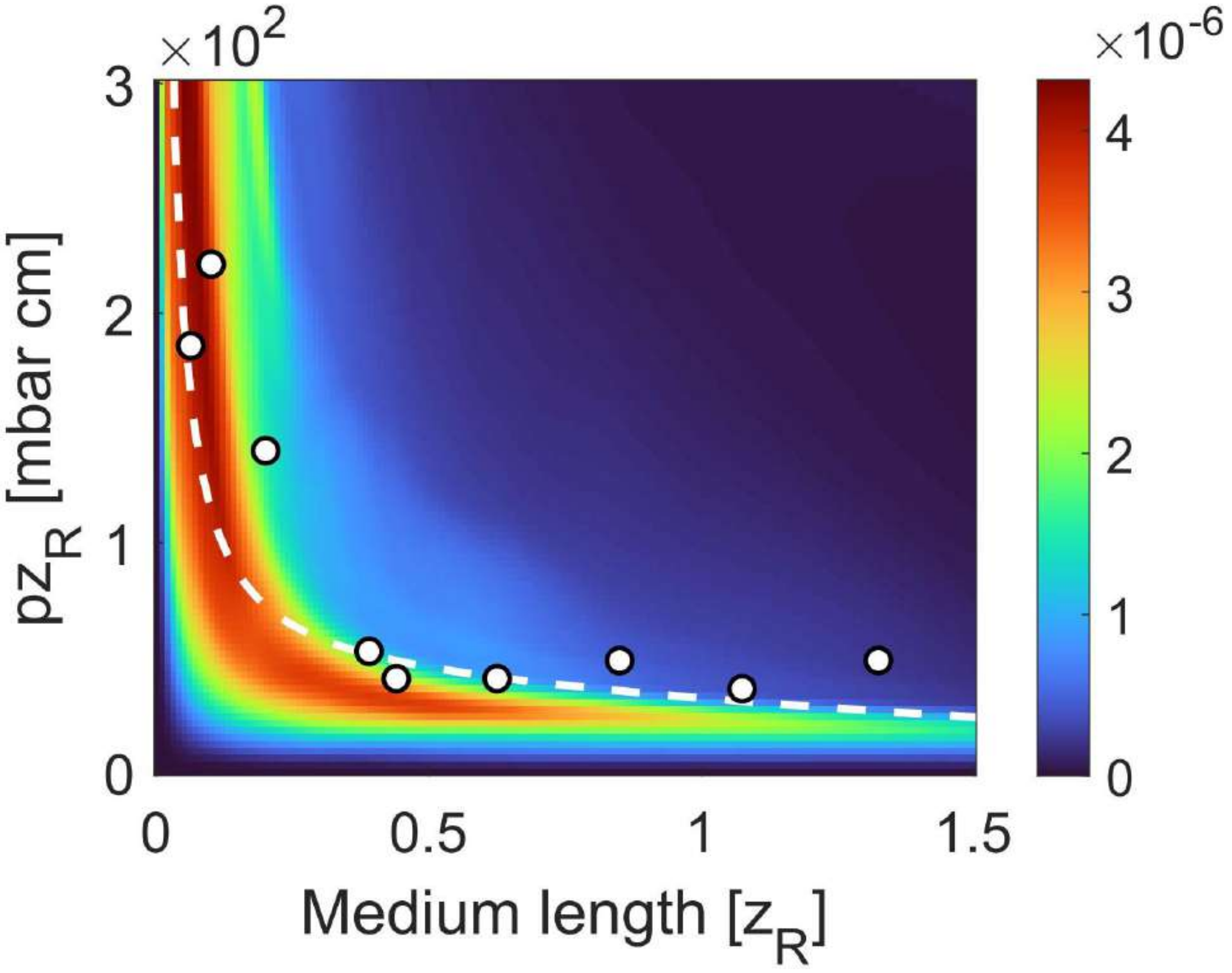
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Photoelectron Circular Dichroism (PECD) on chiral amino-acids based systems: from free molecules to nanoparticles

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Dilute matter in the gas phase offers unique opportunity to template intrinsic structural and dynamical properties of small neutral biomolecules, elementary bricks of life.

A new observable in angle-resolved photoelectron spectroscopy, encapsulating Photoelectron Circular Dichroism (PECD), has been introduced in the case of randomly-oriented chiral species, leading to very intense forward/backward asymmetries with respect to the photon axis in the angular distribution of photoelectrons produced by circularly-polarized light ionization of pure enantiomers. PECD happens to be an orbital-specific, photon energy dependent chiroptical effect, as well as a subtle probe of the molecular potential, very sensitive to static molecular structures (conformers, clustering), and to vibrational motion, much more so than other observables such as the cross section or the β parameter (see [1]). PECD has also been suggested as a possible process involved in the origin of life’s homochirality, the fact that only L-amino-acids and D-sugars are found in the biosphere [2].

Recent results of valence-shell one-photon PECD obtained via double imaging electron/ion coincidence will be presented, on various systems based upon amino-acids, the chiral building blocks of proteins:

- Alanine, the simplest chiral proteic amino-acids, with astrochemical implications [3,4]
- Proline, on which a direct a conformer-specific PECD was observed [5]
- The effect of condensation on Serine homochiral nanoparticles [6]

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Photoexcitation of gas-phase biomolecules to probe functional structure

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It is important to understand the structure-function relationship in biomolecules and how this is precisely influenced by physical properties and responses to stressors. An advanced complementary technique for investigating the structure and dynamics of biological systems is action spectroscopy using state-of-the-art mass spectrometry and soft X-ray techniques.

Electrospray ionisation mass spectrometry provides a high degree of sensitivity and selectivity, while action spectroscopy allows the observation of the interactions of X-rays with proteins, nucleic acids and other biological components. Based on resonant inner-shell excitation and fragment-resolved yield spectra, this technique can be used to gain insight into the (electronic) structure, conformational changes of biomolecules as well as their interactions with small molecules.

In this talk I will present recent results from soft X-ray action spectroscopy studies on peptides [1-3] and related molecules [4]. Not only spatial and electronic structures, but also damage processes, protonation sites, site-selective dissociation and orbital-dependent deexcitation pathways will be discussed as well as future perspectives.

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Photoionization and photofragmentation studies on small molecular compounds using synchrotron radiation and coincidence techniques

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Unimolecular photofragmentation mechanisms of small molecules after photoionization with synchrotron radiation were investigated using coincidence techniques. The energies of valence, shallow- and core-shell electrons were determined by VUV and X-ray absorption, as well as by the detection of ions and electrons. Transitions of these electrons to unoccupied molecular orbitals were also observed in the spectra, allowing an experimental determination of their energy differences. Valence electron ionization energies were also determined by means of photoelectron spectroscopy. The experimental findings were interpreted aided by ab initio and DFT theoretical calculations and Natural Bond Orbital analysis. The photofragmentation mechanisms after single ionization were studied by Photoelectron-Photoion-Coincidence (PEPICO) technique as a function of the excitation energy. Unimolecular photofragmentation mechanisms of double ionized molecules were inferred from the analysis of the shape and slope of the coincidence island between two charged fragments in the bi-dimensional Photoelectron-Photoion-Photoion-Coincidence (PEPIPICO) spectra. Several examples of these studies on different families of compounds containing groups such as -C(O)S-, -NCO, -NCS, -SO_2-, -OH and halogen atoms, will be discussed.

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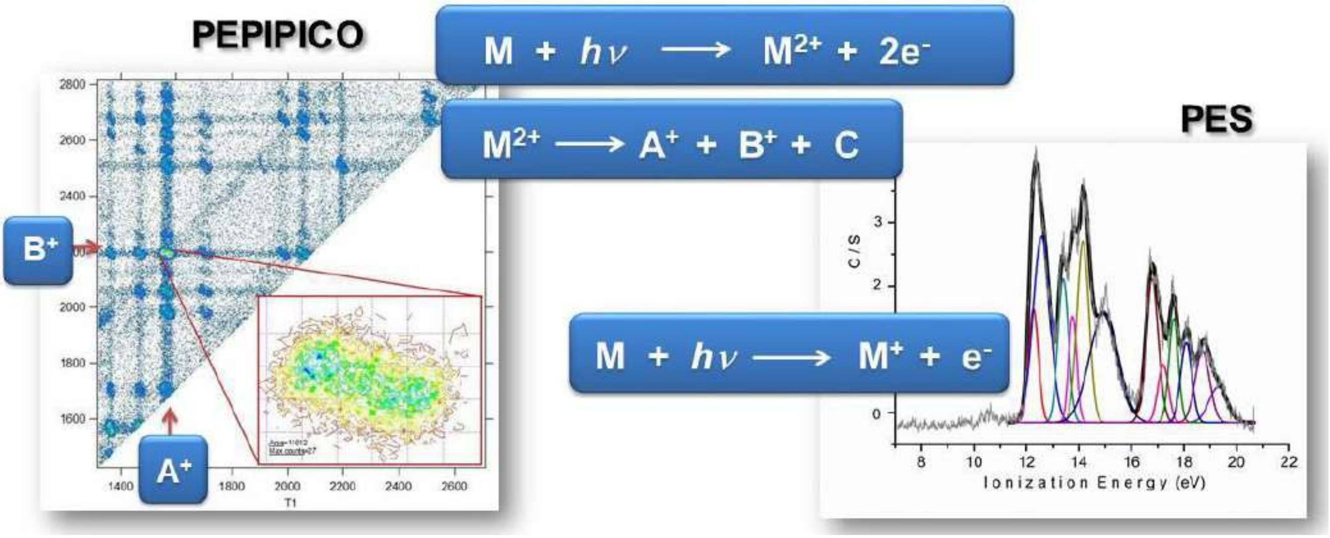

$M + h\nu \longrightarrow M^{2+} + 2e^-$

$M^{2+} \longrightarrow A^+ + B^+ + C$

$M + h\nu \longrightarrow M^+ + e^-$

Separating the electronic spectral response of individual tautomers in aqueous equilibrium via resonant inelastic X-ray scattering

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Tautomerism constitutes one of the most fundamental and important forms of isomerism. Such systems exist as a mixture of two or more tautomers, which interconvert via proton transfer. This seemingly small difference imparts large changes in properties and functionality, caused by the modification of the valence electronic structure of the molecule upon tautomerization. Separating the spectroscopic signal of individual tautomers is a long standing challenge in chemistry, as tautomers are often inseparable. In this contribution, we propose a solution to this problem by turning to core-level spectroscopy, more precisely to resonant inelastic X-ray scattering (RIXS), as reported by Vaz da Cruz et. al[1]. Thereby, we tune the X-ray photon energy to the edge of the elemental site of the proton transfer connecting the tautomers, therefore exploiting the large protonation shift between different tautomers. Using RIXS, we are able to disentangle the overlapping excited states of each species in the mixture, obtaining tautomer-specific spectra experimentally. The data is analysed by means of QM/MM molecular dynamics and RSA-TD-DFT spectral simulations[2]. A detailed description of the electronic structures is presented, based on the detected RIXS transitions, which shed light on both intrinsic and hydrogen-bond induced orbital polarisation and hybridization within the sigma and pi occupied orbital manifolds at the proton transfer site.

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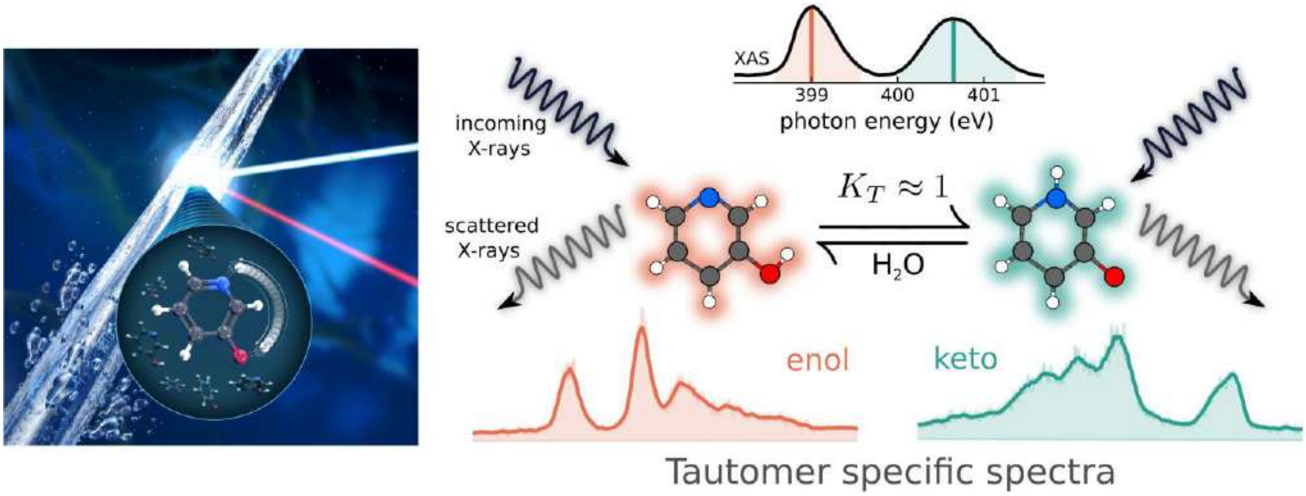
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H_2O
enol
keto
Tautomer specific spectra

The First-Principles Simulation of Ultrafast X-ray Spectroscopy

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In this presentation I will discuss developments by our group in multi-reference electronic structure methods for molecular excited states based on the combined Density Functional Theory / Multi-reference Configuration Interaction approach. These techniques are designed to fill a niche in the description of molecular excited states: possessing the computational efficiency of density functional based methods, but combined with the generality and quantitative accuracy of multi-reference CI. Furthermore, the "black-box" nature of these methodologies lend themselves to widespread use in a variety of application areas. In particular, they are well-suited to the simulation of time-resolved X-ray spectroscopies including TR-XAS and TR-XPS. First-principles simulations of these experiments will be presented and, in particular, the ability of these techniques to resolve specific electronic and nuclear structures associated with ultrafast electron migration and charge transfer that result from nonadiabatic dynamics will be evaluated.

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Towards Molecular Movies made with Synchrotrons and X-Ray Free Electron Lasers

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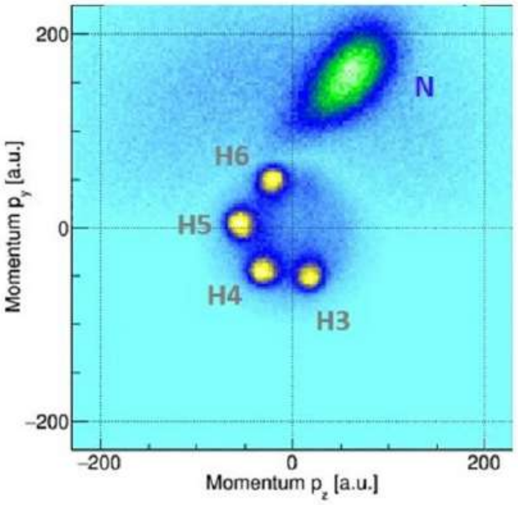
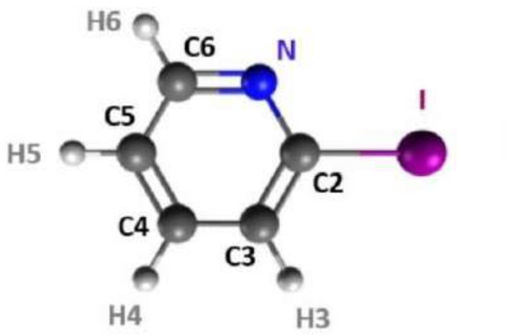
Recording real-time movies of dynamical processes inside molecules and, for example, chemical reactions has been a driving force for many disciplines in fundamental sciences during the last decades. Comparably new are experimental techniques, that involve single particle coincidence detection for imaging single molecules in the gas phase. So-called *Coulomb explosion imaging* uses ultrashort light pulses to fragment molecules allowing to infer the initial molecular geometry from the breakup pattern and *photoelectron diffraction imaging* employs the interference pattern of electrons emitted from molecules to gather such information.

The talk will introduce to the aforementioned experimental techniques and depict several examples of recent measurements performed at the European X-ray free-electron laser. Synchrotrons light sources provide light pulses that are in principle too long to be compatible with the requirements of shooting molecular movies. Yet, there are ways to circumvent this flaw by using the information obtained from the coincidence measurement. The talk will show corresponding examples of such molecular movies recorded using synchrotron light, as well.





Ultrafast Electron Dynamics Probed with Attosecond XFELs

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The ultrafast motion of electrons is a key component of every photochemical process. Given the electron volt-scale energy differences of electronic excited state in small molecular systems, the natural timescale for electronic motion is typically in the few- to sub-femtosecond regime. In my talk, I will highlight our recent developments using x-ray free electron lasers to probe electron motion in small molecular systems.

We exploit the interaction between strong-laser fields and x-ray ionized electrons to study the temporal profile of the electron emission pattern using the angular streaking technique [1]. We have observed the creation and subsequent Auger-Meitner decay of a coherent superposition of core-excited states in nitric oxide [2]. We have performed subsequent experiments exploring the time-domain behavior of an entanglement photo- electron/photo-ion pair.

We have made use of the high peak power pulses from an FEL to develop x-ray nonlinear spectroscopies such as stimulated X-ray Raman scattering (SXRS) [3] and pump/probe spectroscopy. I will also show our first results on attosecond pump/probe experiments of ultrafast charge dynamics following x-ray ionization. These dynamics are probed using x-ray absorption spectroscopy by a time-delayed attosecond x-ray pulse.

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Acknowledgments

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Ultrafast molecular dynamics experiments at the XUV free-electron laser in Hamburg FLASH

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FLASH is an XUV and soft X-ray FEL offering femtosecond light pulses with high repetition rates. It is equipped with XUV split-and-delay units, synchronized pump probe lasers and a synchronized HHG source and thus offers great opportunities of time resolved experiments. I will give an overview of the facility and present recent results from the AMO endstations at FLASH including experiments on X-ray photoelectron spectroscopy, transient absorption spectroscopy and coincidence experiments in atoms and molecules.

Ultrafast x-ray probing of electronic excitation in matter

Professor Jonathan Phillip Marangos[1], Douglas Garratt[1], Mary Matthews[1], Marco Ruberti[1]

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Time-resolved x-ray spectroscopy provides sensitivity to both the localized electronic excitation and electron-nuclear couplings in matter. We have used ultrafast x-ray pulses from both HHG sources and XFELs to study these dynamics in molecular cations and organic semiconductors. This provides not only an incisive probe of electron dynamics on the timescale of electron coherences (<10 fs) but also the unfolding electron-nuclear coupling to vibrational modes over longer timescales. Using a HHG source to generate water window sub-femtosecond pulses [1] we have probed the exciton dynamics in the organic semiconductor polythiophene (P3HT). We observe the signature of atomically resolved electron density changes following exciton formation, and also a transient pre-edge feature attributed to the initial delocalization of the exciton across neighboring polythiophene chains [2]. Electronic dynamics in inner valence states of molecular cations of isopropanol and glycine are probed using an x-ray pump-probe methodology at LCLS and FLASH using few-fs pulses. In isopropanol we capture breathing mode charge migration dynamics of the excitation formed in a superposition of single hole and 2 hole- 1 particle states [3] which is a signature of frustrated Auger-Meitner decay. In glycine we observe oscillatory signatures of charge migration at early times (to 20 fs) that apparently couple to vibrational motion over longer timescales [4]. We report the use of XLEAP (attosecond) pulses at LCLS to excite electronic impulsive x-ray Raman in liquid water with the Raman signature observed in the transmitted x-ray spectrum.

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Unsupported nanoparticles under X-ray analysis

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Gas phase clusters and nanoaerosols are ubiquitous in nature due to natural and anthropogenic activity but also offer tailored platforms for fundamental studies of matter at nanoscale. In this talk, I present some of our recent work about spectroscopic characterization of unsupported clusters and nanoparticles. Fragmentation of argon-water heteroclusters $Ar_M[H_2O]_N$ was studied with electron-ion coincidence technique [1]. Previous studies have shown that they have adjacent domains of a hydrogen bonded water network and van der Waals bonded inert gas atoms, making them an excellent model system to study charge transfer processes between a dopant and water. We performed a detailed multi-coincidence analysis with a site and process selective experimental scheme, and observed an effective charge transfer from Ar to water.

Surface composition of pure inorganic sea salt aerosols and sea salt aerosols spiked with organics was probed using XPS [2]. A differential mobility analyser was used to size-select 150, 250 and 350 nm in situ generated particles. We observed enrichment of magnesium at the particle surfaces in all aerosols tested, across all particle sizes. Interestingly, the magnitude of this enrichment depended on the type of organic present in the solution as well as the particle size. Our results suggest that the observed enrichment in magnesium is an inorganic effect which can be either enhanced or diminished by the addition of organic substances.

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X-ray induced dynamics in molecules and liquids

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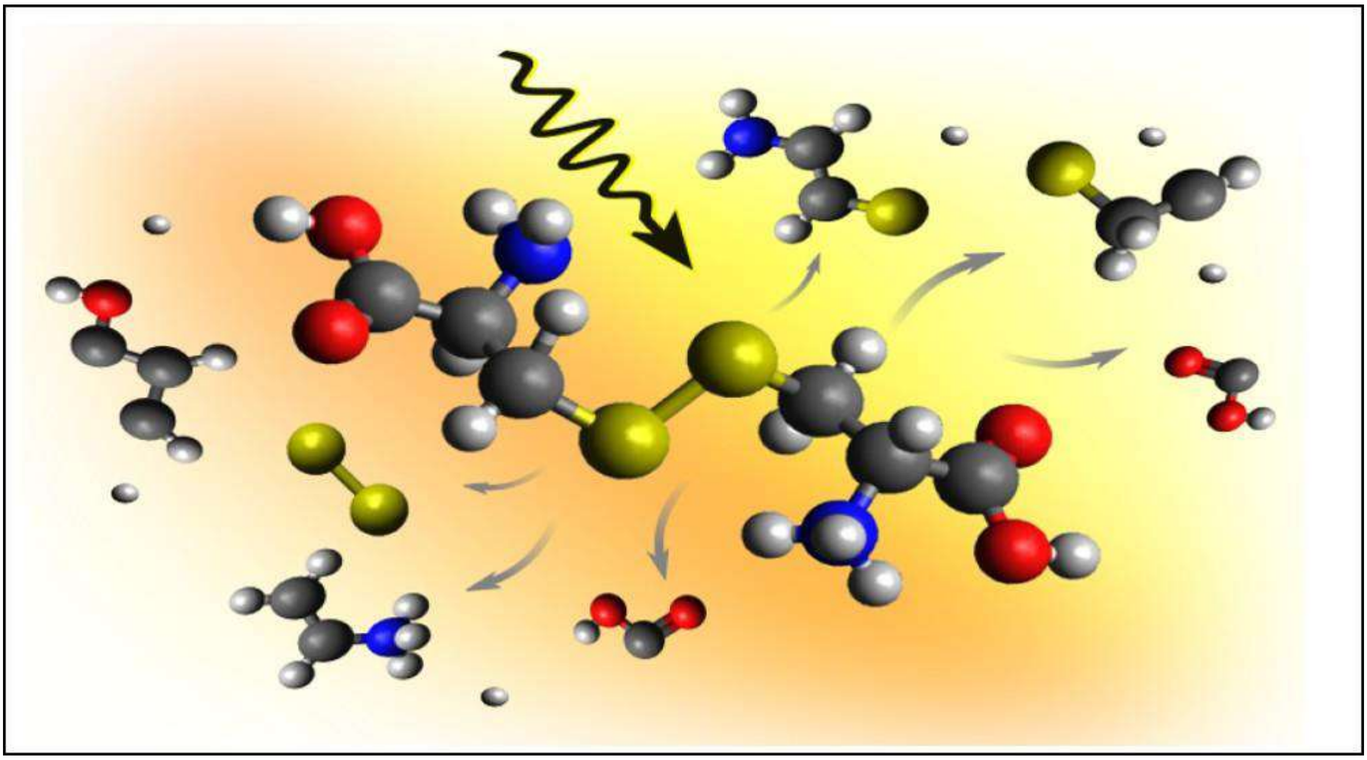
X-ray-induced dynamics of free and solvated systems is connected to the use of X-rays in both medicine and science. In all these cases, radiation damage is either an unwanted side effect or a primary mechanism. In this presentation I will discuss the x-ray-induced electronic and nuclear dynamics, i.e. the first steps of radiation damage, in selected model systems ranging from free molecules to solvated ions and biomolecules. The main questions are what happens when a molecule is irradiated by an x-ray photon, and how this is affected by solvation? This includes the dynamics of the localized core excitation/ionization process itself, and in which way and on what time scale the deposited energy is dissipated by the coupled electronic decay processes and nuclear dynamics, including molecular fragmentation, and how these processes are affected by solvation.



ARPES study of the anomalies at the Dirac point in graphene and it's hole doped compositions

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Study of graphene attracted enormous attention due to its rich physics and application in the next-generation electronic devices. Curiously, angle-resolved photoemission spectroscopy (ARPES) studies show anomalies at the Dirac point suggesting presence of energy gap with unusual in-gap intensities, plasmaron excitations, electron correlation and electron-phonon induced effects, etc. We studied the properties of the Dirac states in pristine and hole-doped graphene employing ARPES and density functional theory. Employing symmetry-selective ARPES measurements for each band, we discover dispersive linear energy bands crossing at a distinct Dirac point within the anomalous region. No gap is observed even after 5% boron substitution that reduced the carrier concentration significantly suggesting protection of the internal symmetries even after boron substitutions. We show that apparent anomalies at the Dirac point appear due to the lifetime and momentum broadenings. The substitution of boron at the graphitic sites essentially leads to a band renormalization and a shift of the Dirac point towards the Fermi level. These results suggest that SiC-graphene is a good platform to realize interesting science as well as advanced technology where the carrier concentration, mobility, etc. can be tuned keeping the Dirac Fermionic properties protected.

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Direct Measurements of Energy Levels in Next Generation Nitride Phosphors

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I will focus on Eu-doped nitride semiconductors used in lighting applications. The *global* energy savings achievable with modern pc-LEDs are very large.

This research presents direct measurements of rare earth energy levels, critical to the color and efficiency of LED phosphors. Modern phosphors use the $5d^1$ to $4f^{n+1}$ transition of Eu^{2+}, which is an excited state since Eu^{2+} has no 5d electrons in the ground state. The 5d states are very sensitive to the surrounding crystal and therefore key Eu^{2+}luminescence parameters like wavelength and efficiency can be tailored by the choice of host lattice.

We are able to experimentally directly determine the energetic separation of the Eu 5d state and the conduction band. We also directly observe conduction to valence band and 4f to valence band transitions in X-ray excited optical luminescence spectra of a series of cutting-edge phosphors.

Electronic structure, magnetic interactions, and charge order in low valence nickelates probed by RIXS

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After a 30-year quest, researchers recently succeeded in realizing superconductivity in low valence nickelates [1]. This ignited a vigorous debate regarding the essential electronic properties of these materials and their similarity to cuprates. Some important questions include: Do these materials have appreciable oxygen charge-transfer character and superexchange akin to the cuprates or are they in a distinct Mott-Hubbard regime where oxygen plays a minimal role and superexchange is negligible? Given that cuprates have a propensity to host proximate competing phases such as charge and spin order, one might ask whether the nickelate's phase diagrams also host competing orders and to what extent they are similar to those in cuprates? In this talk, I will give a perspective of where we are with these questions, including our studies of the trilayer low valance nickelate $La_4Ni_3O_8$ [2-5].

Acknowledgments

Department of Energy Basic Energy Science.

Exploring the Electronic and Atomic Structure of the Surfaces of 2D materials using Photoelectron Spectroscopy and Diffraction

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The so-called *2D materials* such as graphene, h-BN, borophene, and transition metal dichalcogenides (TMDs) emerged in the last decades as an exciting new area for research that discovered new physics phenomena with plenty of room for technological applications. For instance, graphene has been an essential platform for designing new optic-electronic devices based solely on 2D materials. In this sense, graphene has been functionalized in different ways to drive its properties, for instance, by atom and molecule intercalation and by forming new heterostructures with other *2D materials*. Here we will show some results on metal intercalation on graphene and how to explore in detail its electronic, magnetic, and crystallographic structure by using a combination of surface science techniques such as scanning tunneling microscopy (STM), and synchrotron-based high-resolution X-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy/dichroism (XMCD), and photoelectron diffraction (XPD).

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Acknowledgments

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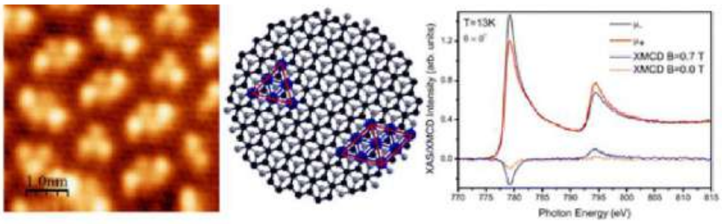
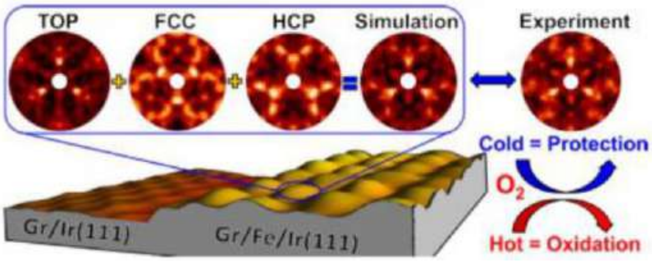
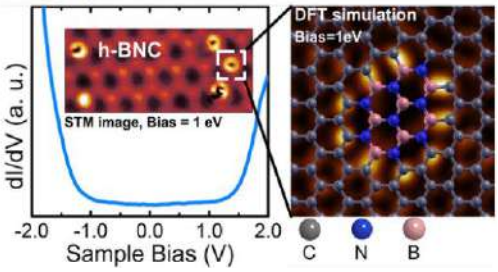


patterning magnetic Co clusters under graphene





Exploring the nature of excitons in 2D materials with time resolved micro-ARPES

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The discovery of 2D semiconductors has revolutionized the study of excitonic physics and optoelectronic technologies. However, even in the simplest materials, such as in monolayer TMDCs, there is a zoo of many different excitonic species. Given that a majority of them are dark excitons, excitons that cannot probe directly with light, either because they are spin-forbidden or momentum-forbidden, it is very difficult to follow their formation pathways and we also cannot see how critical these dark excitons could impact the material's optoelectronic properties.

Time-resolved ARPES is an ideal tool to explore the nature of these excitons within their complex momentum and energy landscape. Here we will discuss the development of our table-top TR-XUV-µ-ARPES technique, which combines a home-built MHz repetition rate high order harmonic XUV light source with a momentum microscope. This technique has enabled us to make direct observation of dark exciton and study their formation dynamics [1]. Additionally, it allows us to make the first observation of the hallmark signatures of exciton in photoemission experiments [2]. Furthermore, it led to the discovery of unexpected tight confinement of interlayer excitons in 2D heterostructures [3].

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High-spatial-resolution ARPES study of kagome superconductors

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Kagome lattice, consisting of 3d transition metal ions with two-dimensional (2D) network of corner-sharing triangles, provides an excellent platform to explore novel quantum phenomena originating from geometrical frustration in real space and nontrivial band topology in reciprocal space. The recent discovery of new family of kagome superconductors AV_3Sb_5 (A = K, Rb, and Cs) has attracted great interest. Intensive research uncovered various exotic phases in AV_3Sb_5, including large anomalous Hall effect without long-range magnetic order, unconventional charge-density wave (CDW) potentially involving time-reversal symmetry breaking, nematic ordering, and topological surface states. To clarify the electronic states responsible for these exotic phases, we have performed angle-resolved photoemission spectroscopy with micro-focused synchrotron beams and photoelectron momentum microscopy on AV_3Sb_5. Here we report our recent progress in these studies [1-5].

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How exchange-energy thresholding of electron-phonon spin-flip scattering governs ultrafast (de)magnetization: Selective determination from core-hole-clock RIXS

Alexander Foehlisch[1,2], Regis Decker[2], Artur Born[2], Kari Ruotsalainen[2], Robert Haverkamp[2], Annette Pietzsch[2], Karl Bauer[2], Robby Buechner[2], Stefan Neppl[2], Christian Strahlman[2]

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For ferromagnets there has been a surprisingly large range of ultrafast time scales of demagnetization from time resolved pump-probe approaches over past decades. This reflects the fact that a multitude of effects contribute to these time traces, such as the sample morphology dependent super-diffusive spin transport, optical effects as well as the Elliott-Yafet electron-phonon spin-flip scattering. Since a change in the magnetic moment of a macroscopic magnet sets this body to rotate in the Einstein-de-Haas effect, the Elliott-Yafet electron-phonon spin-flip scattering rate on the atomic level is crucial to identify the foundational drivers without the influence of the sample dependent aspects. We have thus created a purely local probe to the Elliott-Yafet electron-phonon spin-flip scattering rate with a core-hole-clock approach of resonant inelastic X-ray scattering [1]. With this, we determined selectively the atomic spin-flip scattering rate [1,2,3]. We find a thresholding of the Elliott-Yafet spin-flip scattering in elemental and multi-sublattice magnets as essential to the ultrafast demagnetization time constants [2]. This has also direct consequences for the degree of electronic localization of different electronic states as shown in transition metals, rare earths and alloys [2,3]. Our findings put existing models of ultrafast demagnetization into perspective to the underlying aspect of angular momentum transfer to the lattice.

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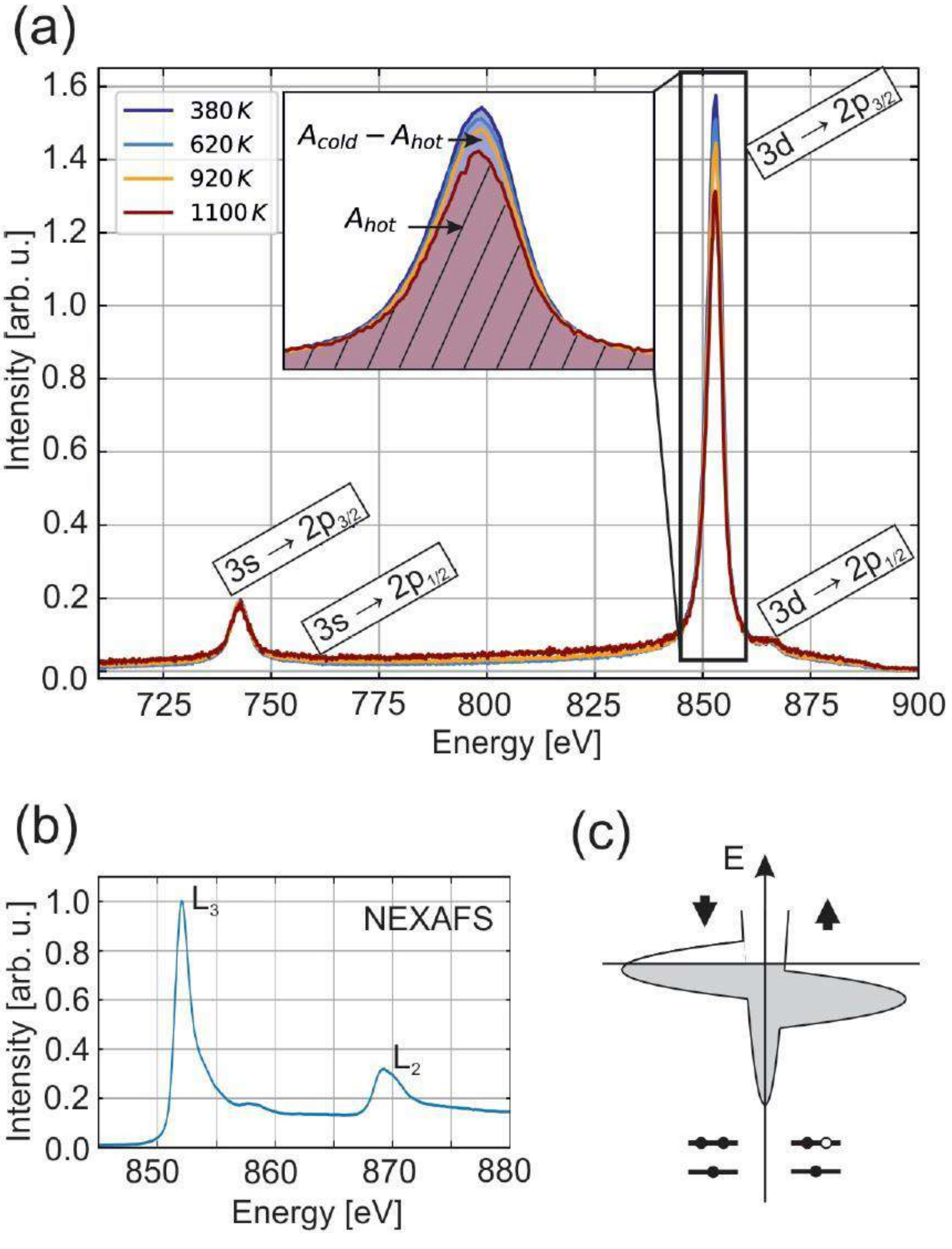
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3d → 2p$_{1/2}$
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Intensity [arb. u.]
Energy [eV]
1.0
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850
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870
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L$_3$
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Impact of vibronic coupling on the electronic structure of organic semiconductor crystals

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Understanding the impacts of weak electronic interaction on the electron delocalization is required to discuss the rich functionalities of organic materials. Moreover, effects of the strong coupling of phonon and/or local molecular vibration to electron must be unveiled. The HOMO-band features can offer a wide variety of key information, that is essential to comprehend charge-hopping transport in the ordered monolayer film [1] as well as to coherent band transport in the molecular single crystal [2,3]. However, detailed experimental studies by photoelectron spectroscopy have not been progressed till recently [4] due to difficulty in the sample preparation, damages upon irradiation, and so on. We present recent findings regarding the precise measurements of electronic fine features found for rubrene single crystal by using low-energy-excited and high-resolution ARUPS. We demonstrate how the HOMO band is observed differently against the theory [5]. To understand the effects of polaron formation on the electronic structure, a partially dressed polaron model that accounts for the electron–intramolecular vibrational interaction with frequency-dependent coupling constants was proposed recently [6]. The precise experiments of the 2D momentum scan in the ARUPS shed light on the issue for describing characteristics of the electronic structure of organic materials and would provide a perspective of designing the organic semiconductor devices.

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Multiple strong topological gaps and hexagonal warping in Bi4Te3

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The electronic topology of Bi4Te3, composed of alternating Bi2 and Bi2Te3 layers, is investigated by density functional theory, scanning tunelling spectroscopy and angle-resolved photoemission spectroscopy. We report on the successful synthesis of a crystal of the strong topological insulator Bi 4 Te 3 and the study of its surface electronic response.

We find, remarkably, that there are three adjacent strong topological gaps with associated protected surface states within a 2-eV range of the Fermi level. The existence of three consecutive Dirac cones in k space gives promise for alternative phenomena and applications, e.g., production of single photons with different energies (in the infrared and visible ranges) for multichannel transport of quantum information as well as multiple degrees of freedom in electron pumping for lasers. Additionally, a surface-state Fermi surface with strong hexagonal warping is observed.

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Time-resolved Resonant Inelastic X-ray Scattering at SCS instrument, European XFEL – first high-throughput and high-resolution studies with Heisenberg RIXS spectrometer

Justine Schlappa[1], Giacomo Ghiringhelli[2], Benjamin van Kuiken[1], Martin Teichmann[1], Natalia Gerasimova[1], Pieter Miedema[1], Giuseppe Mercurio[1], Robert Carley[1], Jan Torben Delitz[1], Luigi Adriano[1], Serguei Molodtsov[1], Yingying Peng[2], Stefan Neppl[3], Friedmar Senf[3], Christian Weniger[4], Annette Pietzsch[4], Torben Reuss[5], Simone Techert[5], Tim Laarmann[5], Andreas Scherz[1], Alexander Foehlisch[4]

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The European XFEL enables research with free-electron laser radiation of unique properties. The accelerator delivers up to 27,000 electron bunches per second that generate ultra-short and coherent x-ray pulses of high brilliance [1]. European XFEL hosts seven instruments for soft and hard x-ray studies. The Spectroscopy and Coherent Scattering (SCS) instrument was designed for soft x-ray spectroscopy and diffraction.

The User Consortium Heisenberg RIXS (hRIXS) spectrometer was built in order to explore high-resolution dynamic RIXS, close to the transfer limit of a monochromatic FEL source. RIXS is a powerfull probe for the study of complex materials, being sensitive to charge, spin, orbital and nuclear degrees of freedom. At FELs their dynamics can be studied, as was shown by pioneering experiments that also suffered from low throughput [2,3].

The high repetition rate of European XFEL, together with the properties of the SCS instrument, provide ideal conditions to host a high-resolution RIXS spectrometer [1,4,5]. SCS and hRIXS offer sample environment for quantum materials and chemical systems/liquid jets. First time-resolved results, obtained in close collaboration with user communities, demonstrate the feasibility of time-resolved RIXS down to 100 fs and 100 meV resolution. In the presentation I will focus more closely on results from photodoped quantum materials, showing emergence of rich dynamics. I will conclude with summarising the current performance and outlook.

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Topological proximity effect in a heterostructure comprised topological insulator and 2D materials studied with angle-resolved photoemission spectroscopy

Cheng-Maw Cheng[1], Su Shu Hsuan[2], Pei-Yu Chuang[3], Shih-Chang Weng[4], Chao-Kuei Lee[5], Ming-Chi Chou[6], Chih-Wei Luo[7], Chien-Ming Tu[7], Tay-Rong Chang[2], Jung-Chun Andrew Huang[2]

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Three-dimensional topological insulators (TIs) are materials that exhibit an insulating gap in the bulk and gapless helical states on the surface, making them highly interesting for their electronic structures. When TIs are used in heterojunctions with other materials, proximity effects can create emerging quantum phenomena of Dirac fermions at the interfaces. In this study, we investigated the electronic structure of nanostructures made of 2D semiconductors such as antimonene and bismuthene, as well as topological insulators, using techniques such as angle-resolved photoemission spectroscopy (ARPES) and density functional theory (DFT) calculations. We provide strong evidence for a 2D topological state in large-area and well-ordered antimonene or bismuthene, delivered through hydrogen etching on $(Bi_{1-x}Sb_x)_2Te_3$ TIs. Spectroscopic evidence of a new topological state or large Rashba splitting states were confirmed in these systems with ARPES and DFT calculations. Our findings suggest that different types of band alignment, such as type II, can dramatically affect the spin texture, leading to Rashba splitting states and a new topologized system in these semiconductor/topological insulator (SE/TI) nanostructures. These results offer a novel phenomenon termed the topological proximity effect, which occurs between a 2D material and a three-dimensional topological insulator. This phenomenon opens up a route to create quantum spin Hall systems in monolayer-substrate heterostructures.

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X-ray induced charge transfer in conjugated polymers by core-hole-clock spectroscopy

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When charge transfer (CT) processes involve complex systems with non-negligible nuclear and electron dynamics, X-ray sources, which allow for element-specific core-excitation, are essential. X-ray spectroscopy offers thus a glimpse into ultrafast dynamics processes in such systems. The core-hole clock spectroscopy (CHCS) method relies on high resolution, monochromatic X-ray radiation to give an insight into processes shorter than the core-hole lifetime [1]. Core-excitation and decay events, in which e.g., Auger electrons are emitted, occur within such a time span, and serve as a probe into the dynamics on the same timescale. Site-specific electron dynamics enables us to investigate CT in solid-state systems through resonant Auger spectroscopy (RAS). We measured resonant sulfur KLL Auger spectra at the GALAXIES beamline of the SOLEIL French synchrotron facility, below the S1s threshold of the π−conjugated polymers polythiophene (PT, powder), where CT is possible only along the polymer chain, and P3HT (thin-film), where CT is possible both along and between chains. An earlier study of PT powder using RAS found no evidence of CT [2]. A following study of PT thin-film showed the presence of CT through RAS in the low fs regime, where the dynamics were ascribed to interaction between the chains [3]. Our results show hallmark features of CT in both PT and P3HT, indicating a predominant CT mechanism along the chain. Our work is in good agreement with real-time TD-DFT calculations.

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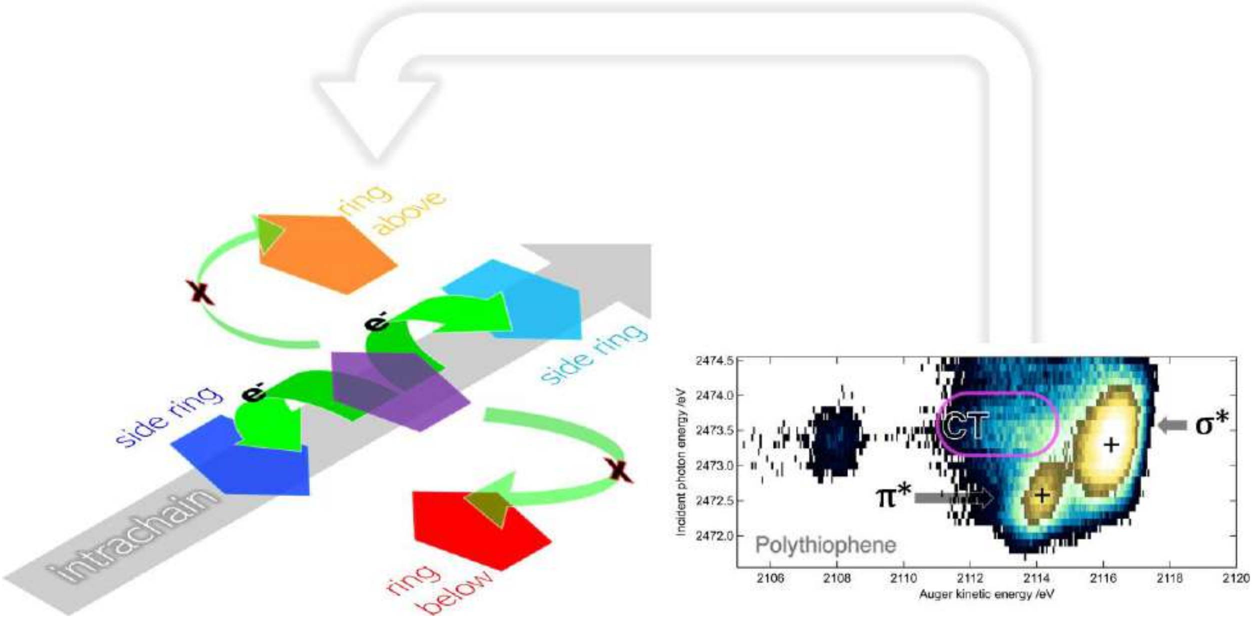

A sight in the Metal-organic frameworks characterization with ambient pressure soft-XAS

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The low penetration depth of soft X-ray (<2.5keV) and the required vacuum limitation of the experimental setup has slowed down the development of in situ/operando XAS experiment in the soft X-ray regime. Nowadays, the XAS in the hard X-ray range is well established and is an indispensable tool for materials characterization under working conditions. [1] However, the $L_{2,3}$ ($M_{2,3}$)-edges of the first (second) row transition metals, which investigate mainly the unoccupied s- and d-DOS, could provide information complementary to those obtained at the K-edges, which provide insights mainly on the unoccupied p-DOS. The d-DOS is of great importance in elucidating the nature of the chemical bonds between the active metal site and the ligands, comprising pure ligands in the metal coordination sphere, the coordinated reactants and the support. The soft-XAS in total electron yield mode is capable to give invaluable information for a complete understanding of the mechanisms of phenomena taking place at material surfaces and interfaces, such as catalysis, adsorption, electrochemistry, etc. In this context, an advanced setup for in situ/operando ambient pressure soft-XAS located at APE-HE beamline at the Elettra synchrotron will be described.[2] Some scientific cases which involve the application of ambient pressure soft-XAS to the world of the metal-organic framework will be presented. In particular, an intensive investigation of the defective sites exhibiting Cu(I)/Cu(II) dimers in HKUST-1 MOFs will be reported. Here, we would like to show new insights into the formation of Cu(I) defective metal sites on the surface of HKUST-1 and their interaction with CO_2. [3] The correlation between the crystal size and the defects formation will be also explored. These studies will lead to an increased understanding of the surface properties of HKUST-1 and pave the way for its rational use in CO_2 separation and uptake processes. Another selected example will focus on the direct observation of the spin transition of iron sites in Fe-MOFs based materials by changing the temperature or the gas environments. These experimental cases will provide an overview of the potentiality of APE-HE beamline.

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Electronic and Structural Properties of Ru complexes with polypyridine ligands as Water-splitting Catalyzes

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Most molecular ruthenium catalysts are based on polypyridine ligands, which can tolerate harsh oxidation conditions and present high stability towards hydrolysis. Changing one of the pyridine ligands for a water molecule, leads to the formation of the class of Ru/aqua complexes that can easily lose electrons and protons to form reactive high oxidation state Ru=O species. Then, these Ru/aqua complexes have been widely used as redox catalysts in the water-splitting reaction, producing clean fuels as products, like H_2 and O_2 [1,2]. The understanding of the electronic properties of these complexes in different oxidation states and in different protonation conditions is a fundamental task for a better description of the artificial water-splitting reaction. We studied the five derivative complexes of $[Ru^{II}(H_2O)(pyridine)(bipyridine)_2]^{2+}$. We have applied a multi-scale method, a sequential QM/MM approach to calculate several electronic properties, such as the solute polarization due to the solvent, the energy of the valence orbitals that affects the oxidation process, the excitations energy of the valence electrons that describe the light harvest process and the excitation energies of the core electrons that identify the chemical environment of each atom of the catalyst [3]. Our results are compared with experimental data of pKa, redox potential, UV-visible absorption spectrum and X-ray photoelectron spectroscopy (XPS) and presented a good agreement.

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Low-temperature luminescence and X-ray spectroscopy to explore defects of inorganic hybrid system ($BaTiO_3$-CaF_2) applicable in solar cells

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In this work, a luminescence investigation of intrinsic and extrinsic defects at room and low-temperature of undoped and Eu-doped inorganic compounds was performed. The materials were synthesized using an eco-friendly method at one minute of plateau time, which can promote defects and interaction of Eu ions with both matrices of a hybrid compound $BaTiO_3$@CaF_2 [1]. Firstly, luminescence analyses under VUV excitation showed that undoped $BaTiO_3$@CaF_2 has an emission band centered at 430 nm attributed to the F center, which is more stable when measured at 60 K. For Eu-doped samples, while CaF_2 isolated showed the $4f^6 5d^1$-$4f^7$ characteristic transition of Eu^{2+}, $BaTiO_3$@CaF_2, can have the association of two defects: emissions related to F center as well as Eu^{2+}. Evidences are supported by the intensity inversion of these bands in function of the temperature. Another difference observed was the presence of the 4f-4f transitions associated with Eu^{3+}. Emission spectrum analysis of these transitions can indicate structural changes in the compounds. The discussions were corroborated by XAS results in the pre-edge and EXAFS regions. These measurements suggest that Eu ions interact with the two hosts, $BaTiO_3$ and CaF_2, therefore, strongly dependent on the synthesis method. The system was mixed with TiO_2 particles and used to enhance the photovoltaic parameters in solar cells. The combination achieved a better fill factor and efficiency when compared to pattern TiO_2 solar cell.

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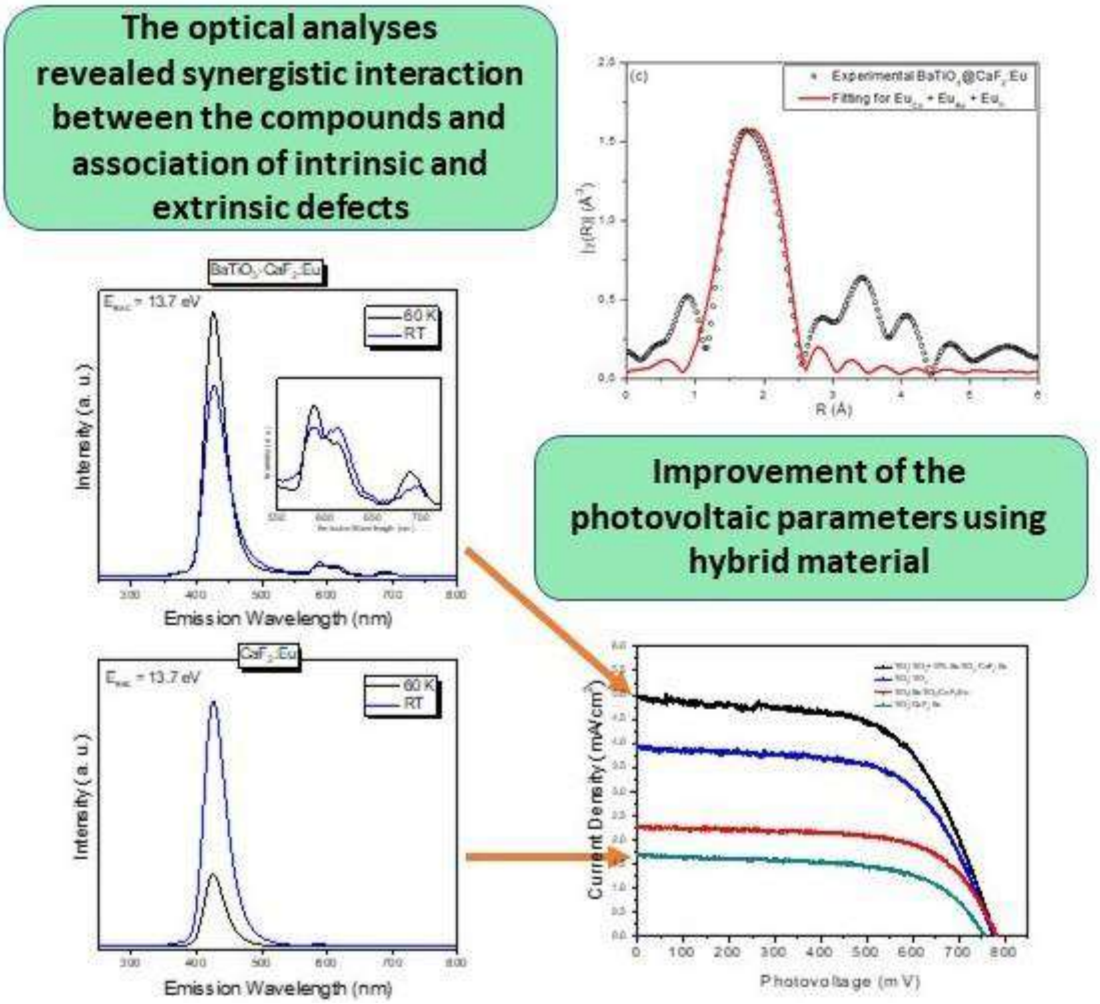

The optical analyses revealed synergistic interaction between the compounds and association of intrinsic and extrinsic defects

Improvement of the photovoltaic parameters using hybrid material

Operando soft x-ray spectroscopy investigation of interfacial chemical transformation of energy materials

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Synchrotron based x-ray spectroscopic techniques offer unique characterization in many important energy materials and catalysis in regards to the functionality, complexity of materials architecture, chemistry and interactions among constituents within. In the in-situ/operando soft x-ray spectroscopy characterization of interfacial phoenomena in energy materials and devices, it has been found that the microstructure and composition of interfaces as well as the microstructure evolution process have a great influence on the performance in energy conversion and energy storage materials, chemical and catalytic processes. This presentation will show how to best use the in-situ/operando soft x-ray spectroscopy techniques, including soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS) to investigate the real electrochemical mechanism during the operation. The experimental results show how in-situ/operando soft x-ray spectroscopy can uncover the phase conversion, chemical and environmental change of elements and important information of solid/gas and solid/liquid interfaces in real time, thus enhance the understanding of real reaction mechanism.

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Opportunities for sodium ion battery research in high-resolution RIXS

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Na-ion battery cathodes are typically materials that are based upon metal oxides and are envisioned as replacement for today's widely used Li-ion battery technology. The purpose of a battery is to store energy densly, reliably, as well as cheaply and environmentally sustainably. Since the cathode is the limiting factor for energy storage capacity in batteries, there is an intense quest for finding the next generation materials that fulfill these requirements. Several promising classes of materials have been explored, such as high-voltage Li-rich, high-energy density cathodes and Na-ion cathodes, based on earth-abundant materials. However, they still fall short on at least some of these accounts. It is therefore imperative to achieve an improved understanding of the underlying energy storage processes and find out where improvements can be made and which are the limiting factors. Since the advent of high-resolution beamlines (<0.1eV resolution) vibrationally-resolved resonant inelastic x-ray scattering (VR-RIXS) has been used to analyze small molecule vibrations in gases. The identification of vibrational signatures using RIXS has already led to the discovery the presence of trapped oxygen molecules in a solid. More systematical investigations using VR-RIXS of various Na-ion battery cathodes battery materials are presented and discussed here. Some of the findings regard the observation of vibration modes belonging to other oxygen species such hydroxides that are a possible degradation products.

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Structural and chemical X-ray probe to study complex systems under ambient conditions.

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In the last two decades, Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) has established itself as a go-to technique to study heterogeneous and complex materials under reaction environments. Multimodal approaches, which correlate information from two or more complementary techniques, are currently one of the forefronts of the APXPS development [1]. In the past three years, the ALS contributed one such setup: a combined Ambient Pressure PhotoEmission and X-ray Scattering (APPEXS) instrument commissioned and operated at beamline 11.0.2 [2]. The combination of the two in-situ techniques allows correlating structural and chemical information. By using APPEXS, we observed dynamics of the exsolution process of catalyst metallic nanoparticles [3]. To expand the capabilities of APPEXS further, we introduced a new platform using arrays of patterned nanoparticles to study the evolution of catalytic systems under reaction conditions [4]. Future developments of the technique(s) will be also discussed.

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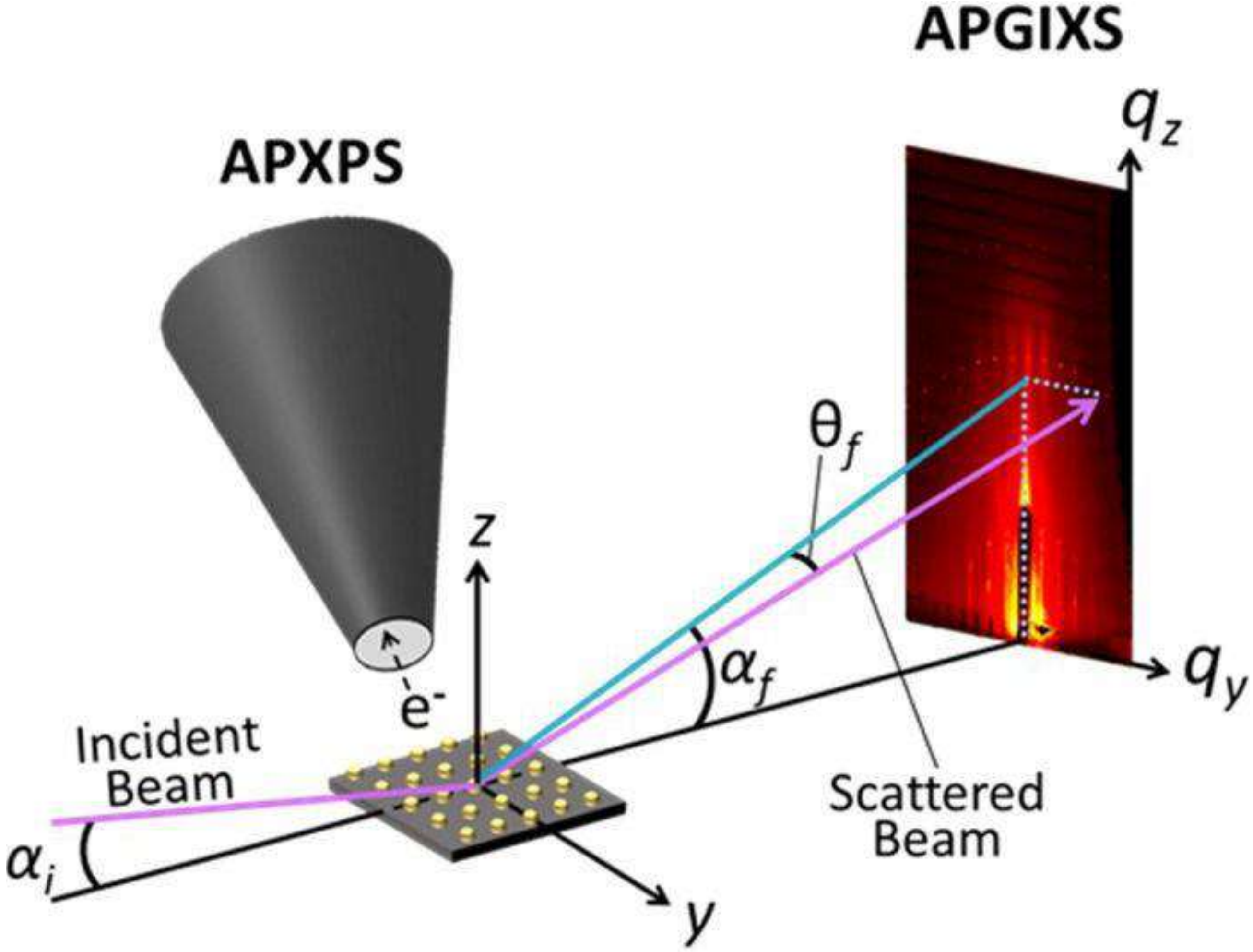
APGIXS
q_z
APXPS
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e⁻
Incident Beam
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The Role of Soft X-ray Imaging and Spectroscopy in Multimodal Analysis of Biogeochemical Processes in Soils

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Soils are hierarchical porous media comprising various types of minerals, organic matter, biomass, and residues in heterogeneous spatial arrangements. Mechanisms that regulate soil nutrient and contaminant behavior involve interactions between physical, chemical, and biological processes such as biologically catalyzed redox reactions under water-saturated conditions. We aim to determine whether such interactions contribute to slowly reversible phosphate binding inside soil microaggregates. Microaggregates of 20 - 50 microns were fractionated from a highly weathered tropical soil, reacted with aqueous orthophosphate, and analyzed using spatially resolving techniques at various beamlines of the Sirius synchrotron. Tender-to-hard X-ray coherent diffraction imaging (CDI) and scanning transmission X-ray microscopy (STXM), X-ray fluorescence tomography (XFT). and FTIR microscopy were used to image physical nanostructure, chemical distributions, and biological structures inside microaggregates. Generally, CDI and STXM showed spatially isolated areas of low and high electron density, and XFT revealed the three dimensionality of chemical hotspots. Soft X-ray analyses of organic carbon spatial distributions and phosphorus speciation could additionally reveal the role of organic matter on any redox processes affecting phosphate binding inside microaggregates. Collectively, such results would our advance knowledge about mechanisms of microaggregate formation and any phosphate entrapment.

Acknowledgments

Contributors include T.R. Ferreira, C.C. Polo, R.S. Rabelo, H.C.N. Tolentino, O.M.M. Menezes, H. Westfahl Jr., E. Miqueles, I.D. Barcelos, L.O. Romão, F. da Silva, T. Roose, and other LNLS staff and students. Funding was provided by the Brazilian Ministry of Science, Technology, and Innovation.

Contributed Talks

High repetition rate beamline for time- and angle-resolved photo-emission spectroscopy with high harmonics

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Time- and angle-resolved photoemission spectroscopy (Tr-ARPES) with high harmonic probe pulses has enabled studies of electron dynamics in a range of 2D materials, e.g. [1]. Many novel materials cannot be produced over large areas or have small domain sizes (<10 µm), and require a suitably small XUV spot to probe their dynamics. However, reducing spot size requires a reduction in the number of electrons generated (and hence number of photons per shot) to reduce space-charge effects that degrade the measured angular and spectral resolution. In order to obtain suitable statistics within a reasonable time, it is necessary to substantially increase the repetition rate. We have designed and commissioned a new beamline for Tr-ARPES running at 100 kHz repetition rate.

Our beamline is based on an optical parametric chirped pulse amplifier pumped by a Yb-doped laser, delivering 50 fs duration pulses at 1700 nm with 200 µJ energy per pulse at 100 kHz [2]. The laser or its second harmonic are focused into argon to produce high harmonics. A single harmonic is selected using a grazing incidence time-preserving monochromator [3], and the exit slit is imaged with demagnification using an aberration compensated double-toroid [4], giving a FWHM spot size of 35 µm. We measured Tr-ARPES from a graphene sample at ~36 eV probe energy and compared the results to measurements from our 1 kHz beamline. The new beamline has much finer angular resolution due to reduced space-charge.

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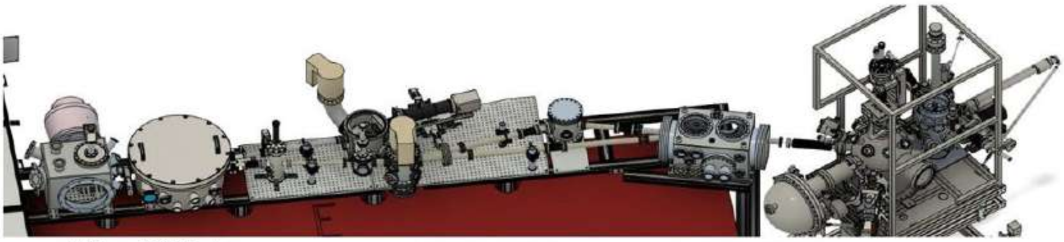
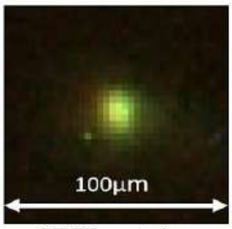
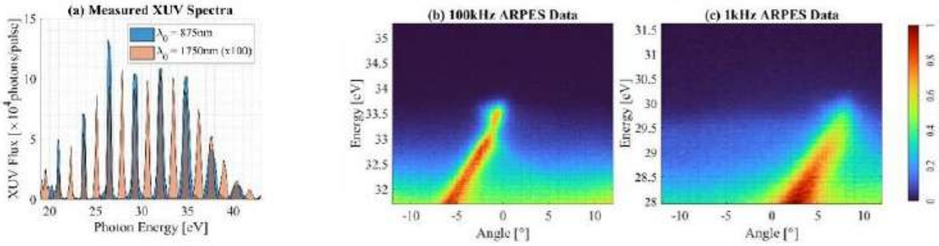




XUV spot size



Low energy edges X-ray spectroscopy under extreme conditions at Sirius

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X-ray Raman spectroscopy (XRS) is a synchrotron technique, which uses hard X-rays for investigating the electronic and structural properties of materials at edges up to ~1000 eV. It provides detailed information about the local environment around specific atoms or groups of atoms, making it an essential tool for the study of complex materials in extreme sample environments [1]. The ability of XRS to analyze materials in extreme conditions, including high pressure and high temperature, makes it a valuable tool for researchers in many different fields. In this talk, I will discuss the wide-ranging applications of XRS in areas such as paleontology, batteries, glasses, molecular analysis, and catalysis. Additionally, I will highlight the potential of the XRS instrument currently under commissioning at the EMA beamline [2], which will enable researchers to study a wide range of material, leading to new discoveries and innovations in materials science and engineering.

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Acknowledgments

Vacuum ultraviolet time-resolved luminescence at P66 at DESY: instrument characteristics and applications

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In October 2023, P66 vacuum ultraviolet (VUV) time-resolved luminescence beamline marks two years of successful operation. Inheriting its main features from previous SUPERLUMI beamline at DORIS III storage ring [1], P66 is requested by leading scientists from more than 30 scientific groups around the world. Excitation and emission energy scans of the luminescence intensity within a unique excitation range of 3.7-40 eV, enabled by the ultrahigh vacuum conditions and added the time resolution down to circa 50 ps, employing the pulsed nature of the synchrotron radiation at PETRA and fast detectors and electronics, make the setup a singular instrument to probe impurity/defect states, to determine the bandgap of dielectric materials and to unravel the energy relaxation and recombination mechanisms after VUV excitation. Absorbed by nearly all materials, VUV is a universal tool to study matter, in particular surfaces (the penetration depth of this radiation is circa 100 nm). An integrated cryostat provides a possibility to cool samples down to 12 K with the use of liquid helium, so even the weakest luminescence is enhanced, cutting away thermal relaxation processes. The applications of the method range from material science to fundamental physics: scintillators for medical imaging and LEDs [2], persistent luminophores for safety signs and phosphors for color display panels are studied next to the first principles spectroscopy of nanophosphors [3].

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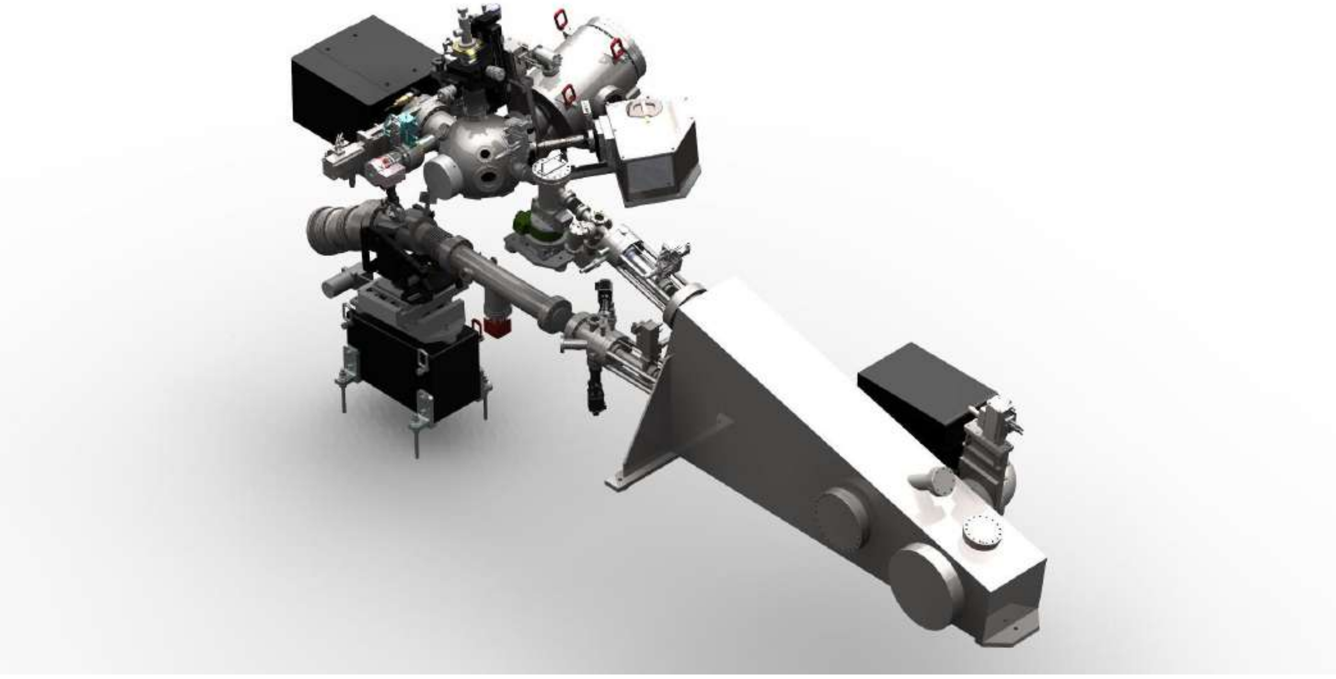

Bulk vs Surface intensity of aqueous samples of atmospherically relevant amino acids.

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Atmospheric aerosols affect the global radiative balance, directly by scattering of sunlight and thus increasing Earth’s albedo, and indirectly by being a major source of condensation nuclei for the formation of clouds. It is estimated that the aerosols counteract the green house effect by ≈1/3, but the effects of aerosols are identified by IPCC as a key uncertainty in predicting climate change. The surface is important for aerosols due to their small size, but surface effects are not taken into account in current climate models. To include surface effects in climate models, it is paramount to improve our molecular level understanding of atmospheric surface phenomena and processes (*1*).

Amino acids from decomposition of biomaterial constitute an important fraction of the water-soluble organic nitrogen compounds in both marine and continental aerosols, and have in laboratory tests been confirmed as effective cloud condensation nuclei materials. Molecular dynamics simulations predict the surface propensity of amino acids to vary with their molecular structure (*2*).

We used XPS on liquid micro-jet to study aqueous solutions of the amino acids (3). By comparing the relative intensities of the different amino acids in XPS spectra, we are able to determine their respective surface propensities, thereby critically testing the predictions based on molecular dynamics, and contributing to understanding the surface of atmospheric aerosols.

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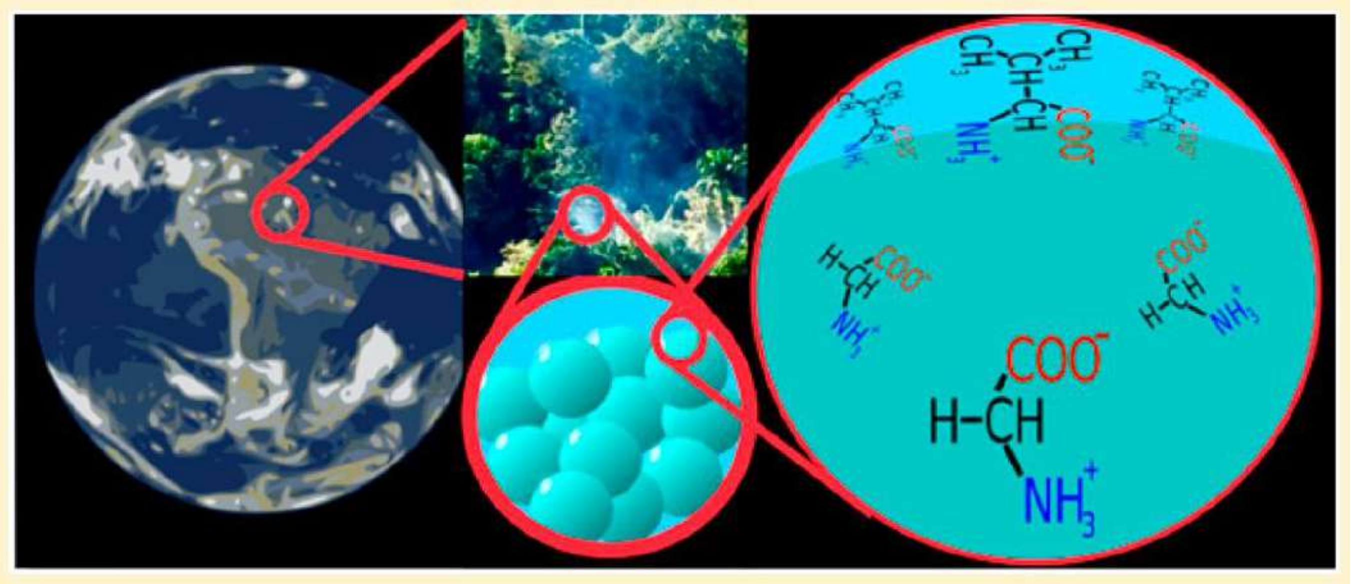

Chemical shifts between the carbon core-levels of ethanol in water-ethanol mixtures

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Spectroscopic signatures in the X-ray range are useful to probe several molecular properties, since inner-shell electrons provide information about the chemical environment. In this context, we here report a theoretical and experimental study of the carbon 1s core-level of ethanol in ethanol-water mixtures at different ethanol concentrations. Both X-ray photoelectron spetrum (XPS) and resonant Auger spectra have been recorded and the measurements were supported by ab initio calculations, where we focused on the differences between the signatures arising from the -CH3 and -CH2OH carbons. In addition, we present the differences regarding the chemical shifts from the bulk and the surface of the sample. The C1s intensities establish a connection between the vapor composition of binary liquid mixtures and the liquid molecular surface in general.

Our results not only characterize the carbon shifts for the bulk and the surface environment but also show how this quantity depends on the ethanol concentration[1]. Also, it was observed an interesting inversion of the signal broadening regarding the two carbons, when compared to the gas phase[2], in the XPS spectrum. The calculations supporting the measurements were conducted combining molecular dynamics and quantum chemistry based on both DFT and RASPT2 level of theory.

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Electronic State Spectroscopy of Nitromethane and Nitroethane

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High-resolution photoabsorption cross-sections in the 3.7–10.8 eV energy range are reinvestigated for nitromethane (CH_3NO_2), while for nitroethane ($C_2H_5NO_2$), they are reported for the first time [1]. The clarification of the processes involved in the interaction of these molecules with photons requires detailed knowledge of the electronic state spectroscopy of both neutral and ionic species. The aim of this work is to obtain the electronic excited states for those molecules through theoretical quantum chemical calculations using the time-dependent density functional theory (TD-DFT) level [2], with GAMESS-USA (The General Atomic and Molecular Electronic Structure System) package [3]. The results for both molecules are compared with the high-resolution photoabsorption cross-sections of nitromethane and nitroethane, obtained at the ASTRID-2 Synchrotron, in Aarhus, Denmark. New absorption features are observed for both molecules which have been assigned to vibronic excitations of valence, Rydberg and mixed valence-Rydberg characters. Also, relevant internal state conversion from Rydberg to valence character is noted for both molecules, while the nuclear dynamics of CH_3NO_2 and $C_2H_5NO_2$ along the C–N reactive coordinate have been evaluated through potential energy curves obtained at the TD-DFT level of theory, showing that the pre-dissociative character is more prevalent in nitromethane than in nitroethane. This work has been published in *The Journal of Physical Chemistry A* [1].

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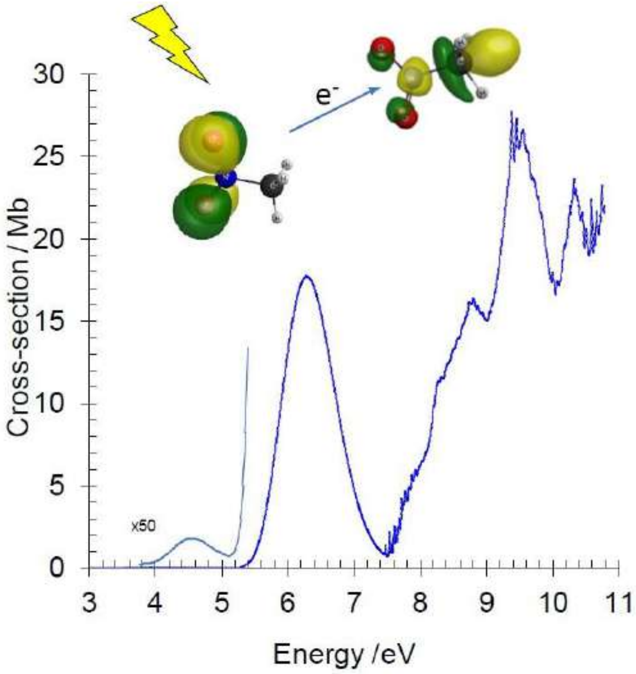
e-
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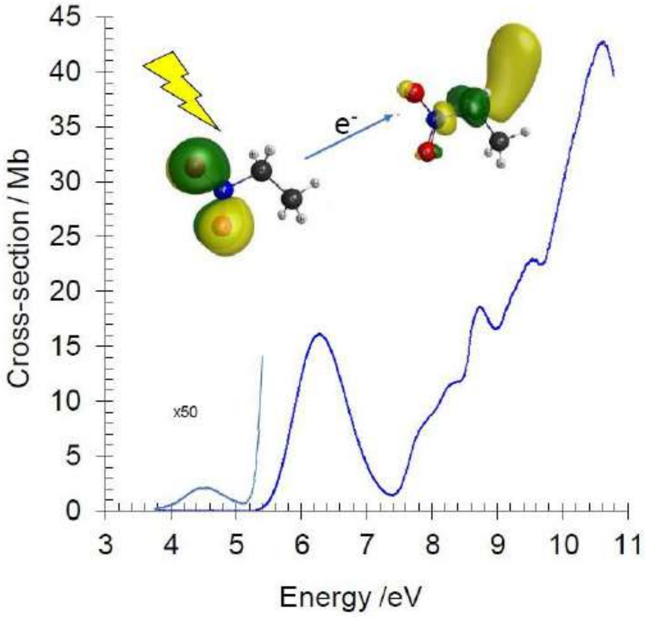
Energy /eV


e-
Cross-section / Mb
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40
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8
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10
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Energy /eV

First principle approach to the simulation of attosecond XUV pump XUV probe spectra for small organic molecules

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The recent availability of intense sub-fs soft X-Ray (SXR) pulses at the LCLS X-Ray free electron laser (XFEL) [1] paved the way for currently undertaken first realizations of attosecond-resolved pump-probe measurements of the molecular electron-nuclear dynamics using all sub-fs SXR pulses. To decipher the obtained transient spectra, first-principle modeling of the observable is desirable. However, simulating the individual steps, i.e., (i) ionization by the sub-fs SXR pump, (ii) coupled electron-nuclear dynamics, and (iii) interaction with the sub-fs SXR probe are extremely challenging tasks on their own already. We present here a protocol that balances computational cost and accuracy to allow complete, (i)-(iii), simulations of sub-fs pump-probe spectra in the XUV to SXR photon energy range for small organic molecules. Therein, the molecular bound and continuum states are described with the CASPT2 and static-exchange B-spline DFT methods, respectively, and the interactions with the pump and probe pulses are simulated explicitly. Further, the electron-nuclear dynamics after the pump is modeled with the trajectory surface hopping method, launching an ensemble of trajectories in every populated electronic state [2].

We demonstrate our approach by evaluating attosecond-resolved transient photoionization spectra of molecular charge dynamics using sub-fs SXR pulses that are accessible at the present XFEL at the LCLS, as well as with lower XUV photon energies.

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Investigation of the molecular structures and VUV induced dissociative photoionization dynamics of chlorinated organic molecules by *ab initio* theories and Photoelectron-Photoion Coincidence Spectroscopy

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The molecular structures and dissociative photoionization dynamics of two related chlorinated organic molecules, chloroacetone (C_3H_5OCl) and 1,2-dichloropropane ($C_3H_6Cl_2$), in the gas phase, were investigated. Vacuum ultraviolet (VUV) synchrotron radiation in the range from 10 to 21.50 eV was employed as ionizing agent, and the resulting ion products were analyzed by using time-of-flight mass spectrometry in the photoelectron-photoion coincidence mode. The appearance energies for the most relevant cation fragments produced in this energy range have been determined, and the most likely fragmentation pathways leading to the formation of the cation species have been proposed and discussed.
The mass spectra show that the most dominant VUV photodissociation cation product for the chloroacetone molecule appears at *m/z* 43 and has been assigned to the $C_2H_3O^+$ species, while for the 1,2-dichloropropane molecule the fragment of m/z 63, assigned to $C_2H_4Cl^+$ dominates in most of this VUV energy range.
By combining the experimental and theoretical data we have been able to determine the corresponding enthalpies of formation (ΔfH°0K) for the most important neutral and cation species from these molecules.
In addition to the experimental data analysis, the structural and energetic parameters for the neutral and cation species associated with these molecules, and photodissociation pathways, also have been examined on the basis of high-level (*ab initio* and DFT) quantum chemical calculations.

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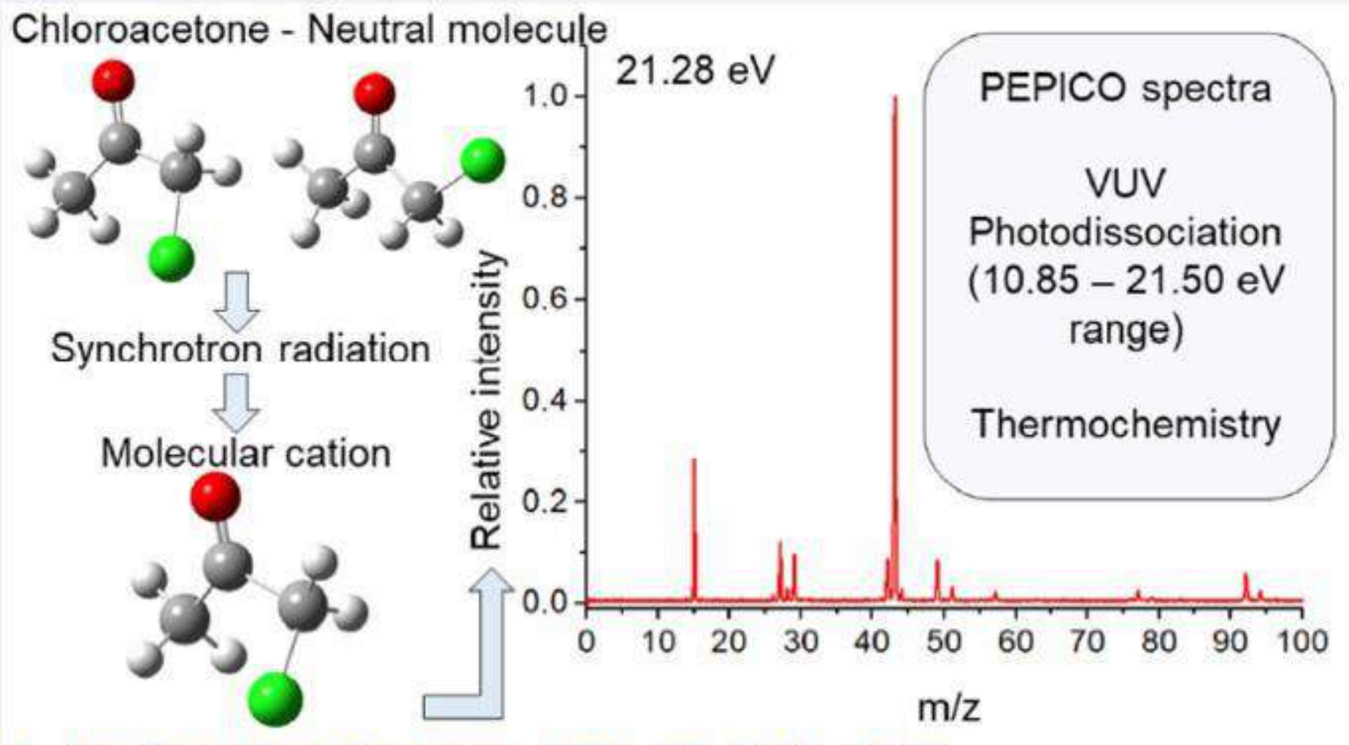

J. Am. Soc. Mass Spectrom. 2021, 32, 2186–2195

Machine-learning-based decomposition for X-ray spectroscopy

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A liquid or an amorphous system allows for the movement of interacting molecules or atoms, which leads to a broad distribution of possible configurations. These individual configurations have been computationally observed to have significantly different X-ray spectra, only the ensemble mean of which predicting the experimentally observed spectrum. Even though interpretation of these spectra may not always be straightforward, they are a widely used probe for structural information. We approach the problem stepwisely, first identifying structural degrees of freedom with spectral sensitivity, and second carrying out a structural reconstruction in terms of them.

We will present our ongoing work with interpretation of X-ray spectra (such as XPS,XAS and XES) in terms of underlying atomistic structure. We study simulated data and present a machine-learning-based algorithm for dimensionality reduction in the structural space so that explained spectral variance is maximized [1]. With this algorithm it is possible to find structural degrees of freedom with most spectral dependence and filter the insignificant degrees of freedom out. We then proceed with a case study where the algorithm is used to transform the inverse problem from spectra to structure into a low-dimensional, easier solvable, one [2]. We find that ensemble mean distances of from the active Ge site can be reconstructed from the ensemble mean Ge Kβ emission spectrum of amorphous GeO_2 at elevated pressures.

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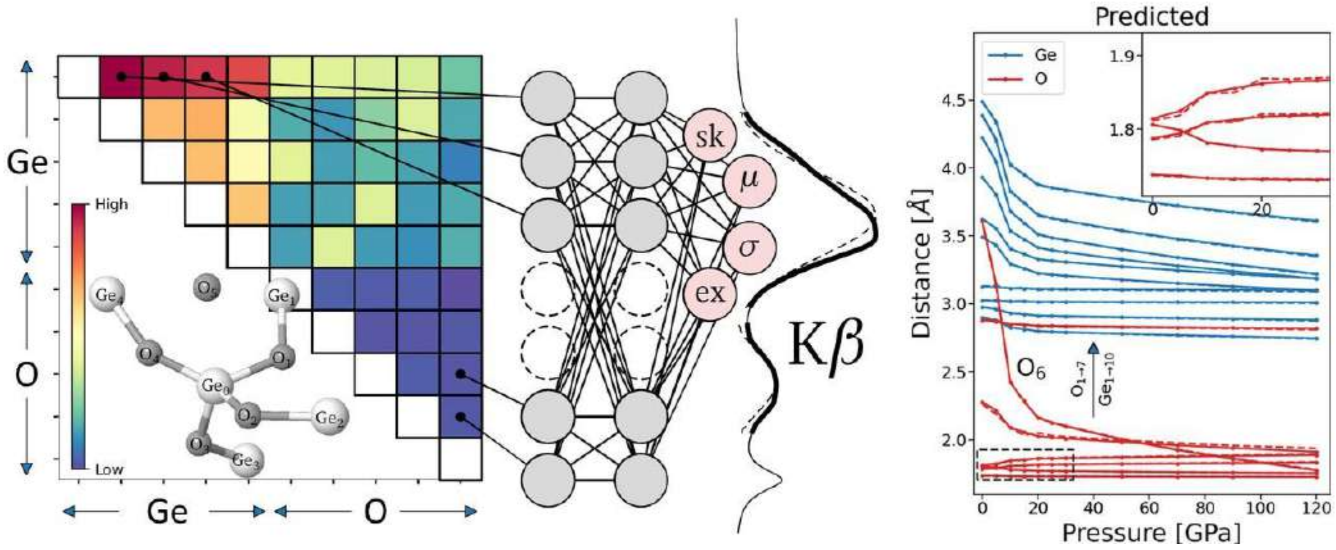
Ge
O
Ge
O
High
Low
Ge4
O5
Ge1
O4
O1
Ge0
O2
Ge2
O3
Ge3
sk
μ
σ
ex
Kβ
Predicted
Ge
O
Distance [Å]
Pressure [GPa]
O6
O1→7
Ge1→10
4.5
4.0
3.5
3.0
2.5
2.0
0
20
40
60
80
100
120
1.9
1.8

Micro-jet X-Ray Photoelectron Spectroscopy applied to surface studies of alcohol-water mixtures

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X-Ray Photoelectron Spectroscopy (XPS) has been applied to studies of gases and solids for many decades. Still, for the liquid phase, only the relatively recent development of liquid micro-jets [1,2] has allowed practical studies of liquid-vapour interfaces.

Alcohols are used in many applications, such as fuel or starting materials for organic synthesis and as a general solvent. Several applications involve the solvation of alcohols in an aqueous solution where the amphiphilic properties of the ethanol molecule must be considered.

In this presentation, we plan to show recent results for ethanol-water mixtures obtained with the application of an electric potential to the solutions, which removes the contribution of the gas phase in the spectra and allows a more accurate analysis. These measurements were performed on the FlexPES - MAX IV (Sweden) and P04 - PETRA III (Germany) beamlines. These studies will be complemented by reviewing our recent publications [3-5] based on results with cylindrical microjets (Fig. 1), including determining ethanol surface orientation as a function of concentration and an atomistic explanation of the ethanol-water azeotrope.

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Soft X-ray fingerprint of reactive transition metal-oxygen cations

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Discovering compounds that present transition metals with unusual oxidation states or reactive oxygen species (superoxide, peroxide and oxygen centered radical) is of great scientific and technological interests, as they have key applications as oxidizing agents, catalysts, or reaction intermediates, and can improve the performance of energy materials.[1,2]

Here, we use X-ray absorption spectroscopy (XAS) at the oxygen K and metal L_3, M_3 or N_3 edges of $[MO_n]^+$ molecular ions (M = transition metal, n = integer) to identify the spectroscopic signatures of oxygen ligands and assign the oxidation state of the metal.[3] The $[MO_n]^+$ species in the gas phase are produced by argon sputtering of a metal target in the presence of oxygen. The cationic species are mass selected and accumulated in an ion trap. X-ray absorption spectra are then recorded in partial ion yield mode.[4] Our ion trap instrument is installed at the undulator beamline UE52-PGM at the Berlin synchrotron radiation facility BESSY II operated by the Helmholtz-Zentrum Berlin.

Reactive species, such as oxygen-centered radicals and species containing high-valent transition metals, are analysed in stable conditions in the ground state inside the cryogenic ion trap. This method is here demonstrated to be an important tool to identify the character offoxygen ligands, offering direct access to element specific electronic structures.

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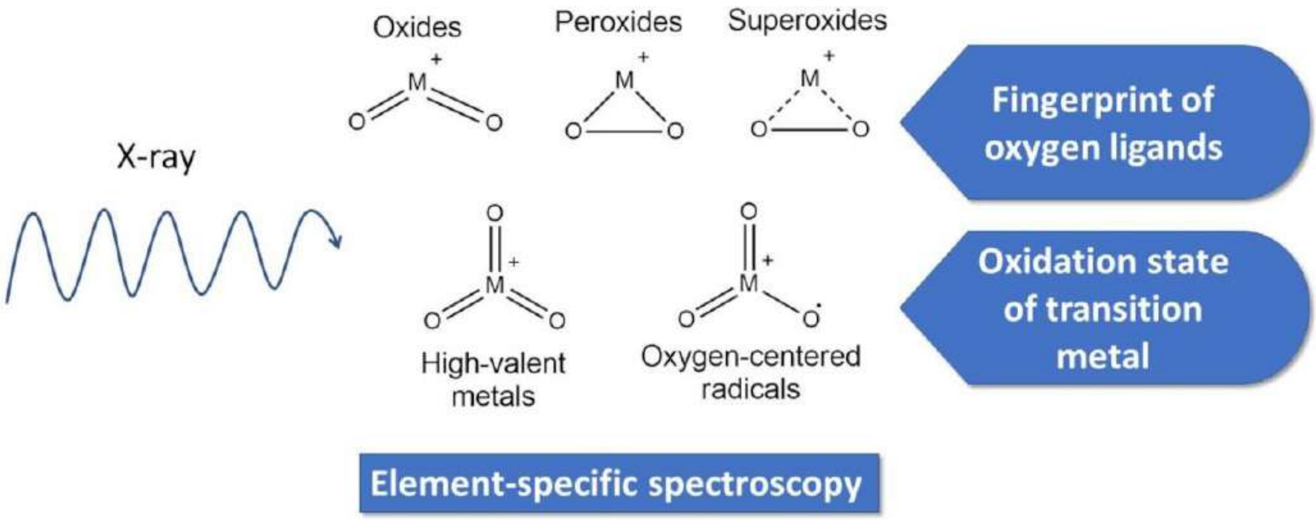

Valence and Inner-Shell Photoionization Cross-Sections of Free and Adsorbed Molecules Using CCSD and TDDFT Methods

Marco Antonio Chaer Nascimento[1], Alexandre Braga Rocha[1], Bruno Nunes Cabral Tenório[2]

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e-mail: chaer01@gmail.com

Photoionization cross-sections are very important to understand a large number of phenomena, such as optical refractivity and for interpreting the photoelectron spectra of free and adsorbed species. The main difficulty in calculating photoionization cross-sections resides in the continuum wave functions. This problem can be circumvented by constructing an approximation to the complex dynamic polarizability which contains both the absorptive and dispersive information about the system, using a discrete basis set L^2 to represent both the bound and the continuum states of the system[1], which is then used in an analytical continuation procedure with Padé approximants[1]. The spectral moments to build the approximation to the complex dynamic polarizability were obtained from coupled cluster damped linear response theory based on the asymmetric Lanczos algorithm at the coupled cluster singles and doubles level (CCSD) and TDDFT methods. Kauffman et. al.[2] Gaussian primitives were used to reproduce some properties of the continuum region. In this talk we present results for valence and inner shell photoionization cross sections for several free and adsorbed molecules[3]. Dunning's correlation consistent aug-cc-pVTZ basis set plus additional Kauffman[2] type continuum-like Gaussian basis functions placed on the center of mass of the molecule with quantum numbers ranging from 3 to 10 have been employed. The calculations were carried out at the experimental equilibrium geometries.

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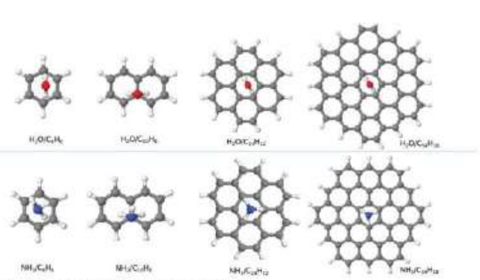

Figure 1. VdW complexes optimized at the DFT-D3 PBE0/def2-TZVP level.

A little bit of Information: Leveraging the interface Spin-Crossover Molecule thin-film interfaces to control the spin state.

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The physics of organic molecule thin films has opened up the field of molecular spintronics research. Organic molecules are coveted as the active ingredients for novel spintronic and electronic devices due to their versatility and energy efficiency, but also for their inexpensive ingredients and much reduced processing cost compared to conventional circuitry. Bi-stable spin-crossover molecules are promising candidates for memory and logic devices, while at the same time a number of fascinating fundamental questions regarding their switching mechanism remain to be explored.

I will present our recent work on spin-crossover and valence-tautomeric molecules. We investigated a number of ways to change the energetics of the transition between the spin states, primarily by choosing and manipulating the interface of a molecular thin film with its support and lay out a path to spin-crossover molecule based devices [1,2]. We probe the spin state and its transition by means of x-ray spectroscopy and spectromicroscopy with x-ray photo-electron microscopy (x-ray PEEM)[3].

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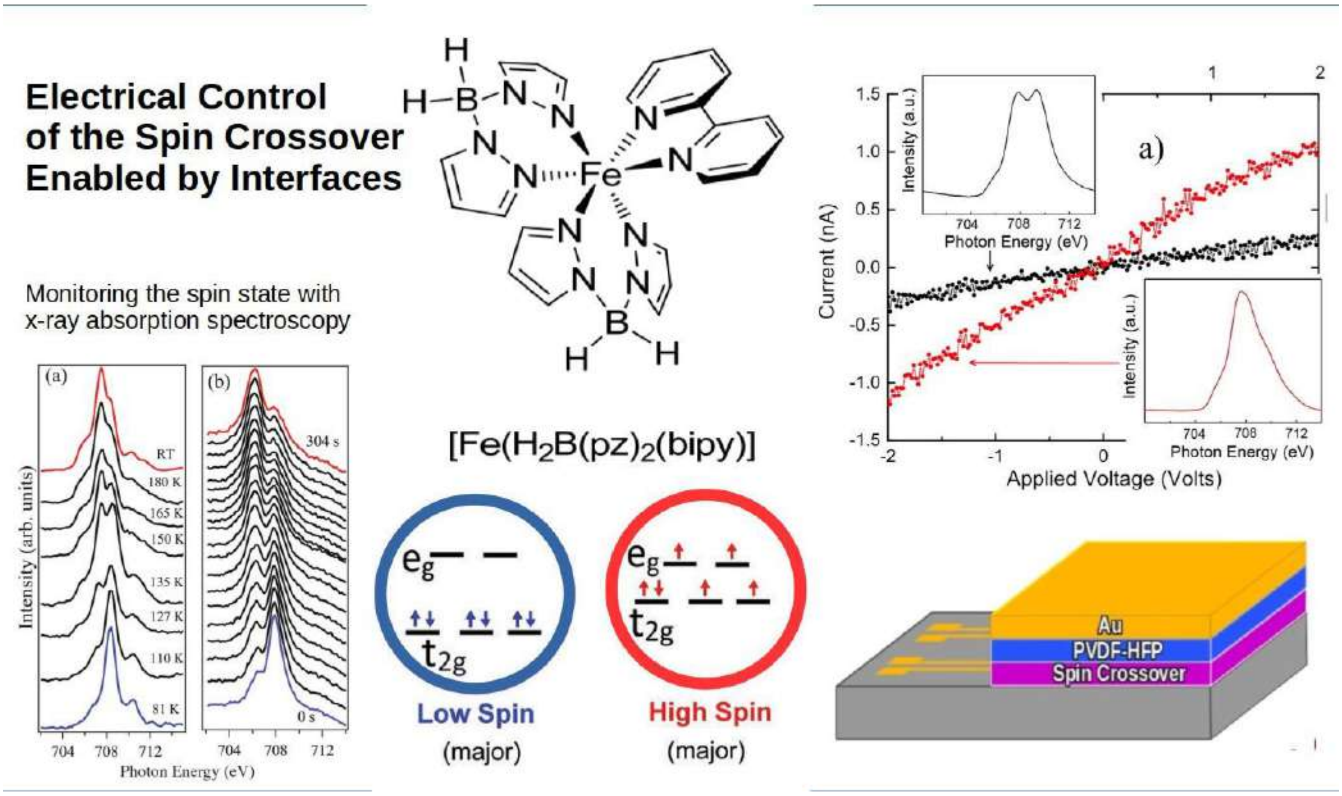

Electrical Control of the Spin Crossover Enabled by Interfaces

Monitoring the spin state with x-ray absorption spectroscopy

$[Fe(H_2B(pz)_2(bipy)]$

Low Spin
(major)

High Spin
(major)

ARPES STUDIES ON WEYL SEMIMETAL CANDIDATES PrAl(Ge,Si)

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In this work we study the Weyl semimetals PrAlSi and PrAlGe through Angle Resolved Photoemission Spectroscopy (ARPES) technique with the objective of investigating the role of the magnetic properties of these compounds and its interplay with the topology of the system. With the ARPES technique, a systematic study was conducted combining measurements with VUV and soft X-rays. We observed that the central pocket of PrAlSi is larger than that of PrAlGe, as these central bands possibly shifted to deeper binding energies in PrAlSi, since there was no major change in its shape between the compounds. It is possible to visualize an asymmetry in the Fermi surface (FS) of the two compounds when comparing the Γ-X and Γ-Y directions, therefore, it is indicative of a break in the time-reversal symmetry due to the ferromagnetic ordering of the system. When comparing the central pocket of both compounds, we saw a slight asymmetry that probably happens due to the displacement of the bands. Thus, as a primary approach, we conclude that PrAlSi and PrAlGe have similar FS, but with the differences coming from a possible band shift. We were also able to see through the bandmaps the existence of Weyl nodes with their characteristic linear dispersion.

References

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Bayesian framework for analyzing dynamic processes observed via time-resolved X-ray diffraction

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Clarifying dynamic processes of materials is an important research topic in materials science. Time-resolved X-ray diffraction (Tr-XRD) is a powerful probing technique for such dynamics. To understand dynamics through Tr-XRD, it is essential that analysts use appropriate time-evolution models and precise start times (t_0) of dynamics. However, conventional analyses based on least-squares fitting [1,2] have difficulty both evaluating time-evolution models and estimating t_0.

In this study, we establish a Bayesian framework including time-evolution models. The Bayesian framework enables the selections of the most plausible time-evolution model among possible models. In addition, the framework enables us to estimate t_0 directly from Tr-XRD data.

To demonstrate the effectiveness of the Bayesian framework, we investigate the Ar gas adsorption process of CPL-1 observed at SPring-8 BL02B2. In the analyses, we consider two different time-evolution models, i.e., Model 1 and Model 2. We clarified that the Model 2 is much better than Model 1 by comparing Bayes free energies. The information about the time-evolution model and t_0 enables us to understand the adsorption process more accurately and to approach practical applications of adsorption materials. The Bayesian framework is highly versatile, can be applied to other dynamic processes such as chemical reactions and phase transitions, and is expected to be utilized in various areas of materials science.

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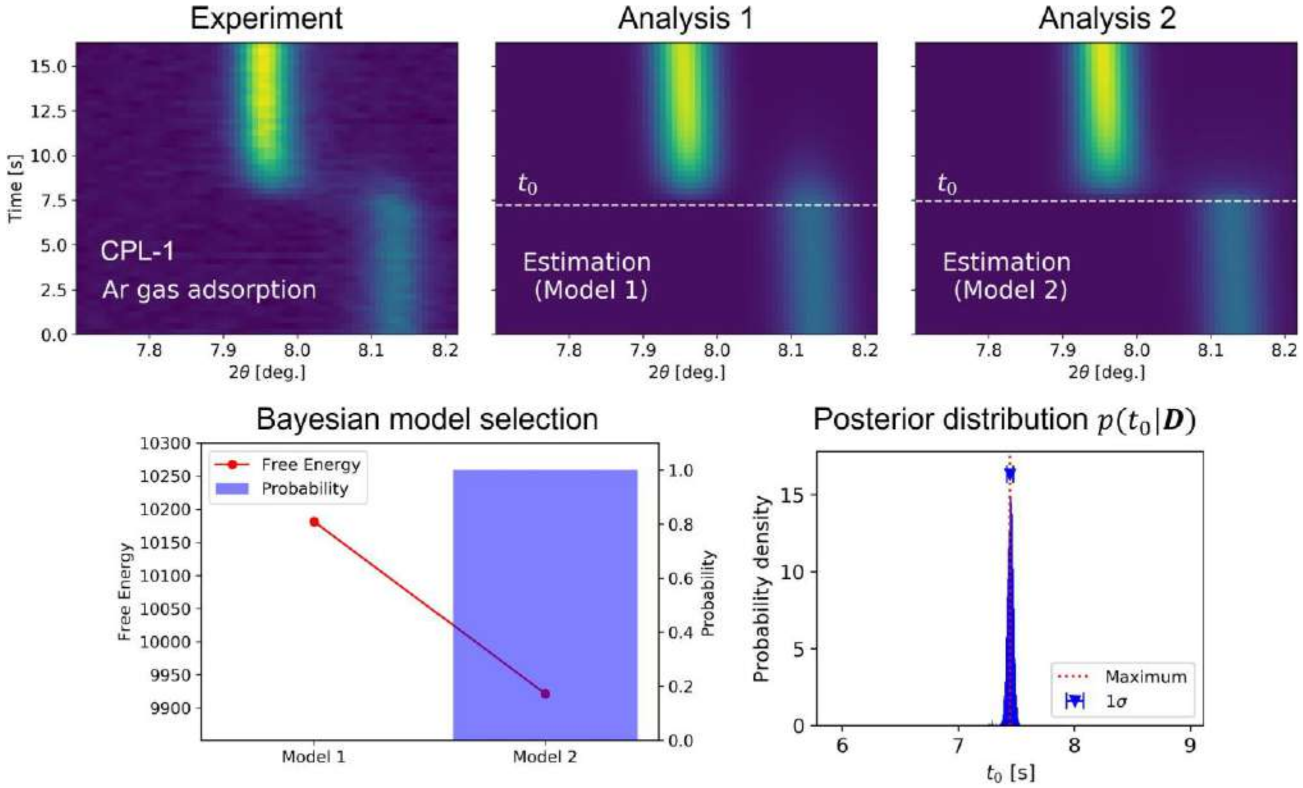
Experiment
Analysis 1
Analysis 2
Time [s]
15.0
12.5
10.0
7.5
5.0
2.5
0.0
CPL-1
Ar gas adsorption
t_0
Estimation
(Model 1)
Estimation
(Model 2)
7.8
7.9
8.0
8.1
8.2
2θ [deg.]
Bayesian model selection
Free Energy
Probability
10300
10250
10200
10150
10100
10050
10000
9950
9900
1.0
0.8
0.6
0.4
0.2
0.0
Model 1
Model 2
Posterior distribution $p(t_0|\boldsymbol{D})$
Probability density
15
10
5
0
Maximum
1σ
6
7
8
9
t_0 [s]

Complex depth dependent magnetic profiles probed by SXRMR

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Soft X-ray resonant magnetic reflectivity (SXRMR) experiments exploit the magnetization sensitivity and the x-ray polarization dependence of the atomic scattering factor (ASF) at an absorption edge. As the ASF depends on the transverse (m_{tran}), longitudinal (m_{lon}), and polar (m_{pol}) components of the magnetic moment with different dependence on the respective scattering angles, it is able to probe the changes of the orientation of the magnetization within different magnetic layer forming the multilayer. We intend to present the basic fundamentals of this important element selective technique and its power to probe the magnetization profile across complex heterostructures with subnanometer spatial resolution [1,2]. As an example, we present the SXRMR results for ferromagnetic (FM)/antiferromagnetic (AF)/FM trilayers obtained at the RESOXS setup at the SEXTANTS beam line at SOLEIL/Paris/France [3] using linear p and circular polarized light at the Co, Fe, Mn and Ni $L_{2,3}$ edges. The analysis using the Dyna code [4] led to rather homogeneous profile in the Co and NiFe FM layers (except at the interfaces) and revealed a very complex magnetic profile with a non-monotonous spiral domain wall inside the AF material and nearly orthogonal couplings between the FM/AF moments at both the interfaces.

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Acknowledgments

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Effects of Dimensionality on the Electronic Structure of the Ruddlesden-Popper Series $Sr_{n+1}(Fe/Ni/V)_nO_{3n+1}$

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The so called Ruddlesden-Popper series consists of stacks of basic crystalline structures, whose different arrangements can lead to several chemical and physical behavior. In the case of $Sr_{n+1}(Fe/V)_nO_{3n+1}$, one has *n* strontium ferrite/vanadate $Sr(Fe/V)O_3$ perovskites, of conductive nature, intercalated between 2D films of strontium oxide SrO, of insulating nature. For different *n* one observes interesting properties such as magnetorresistance, conductor-insulator transitions, cycloidal magnetic arrangements and negative charge transfer regimes, for example. The iron $n = \infty$, 2, 1 and vanadium $n = \infty$, 1 materials were simulated by Density Functional Theory (DFT) calculations using the solid-adapted Perdew-Burke-Ernzerhof and modified Becke-Johnson approximations for the exchange and correlation potential, as implemented in the WIEN2K package. For $n = 2$, the substitution of one iron atom for a less magnetically active nickel atom was also studied. The projected density of states (PDOS) for the ferromagnetic ground states of the structures was obtained and analyzed considering different oxygen crystallographic positions. For all materials, a significant dependence on the oxygen positions was observed, which indicates that the presence of the 2D films can greatly change the covalent behavior of the bonds between the atoms in the materials. This in turn impacts the physical properties they exhibit, such as their magnetic moment and orbital localization.

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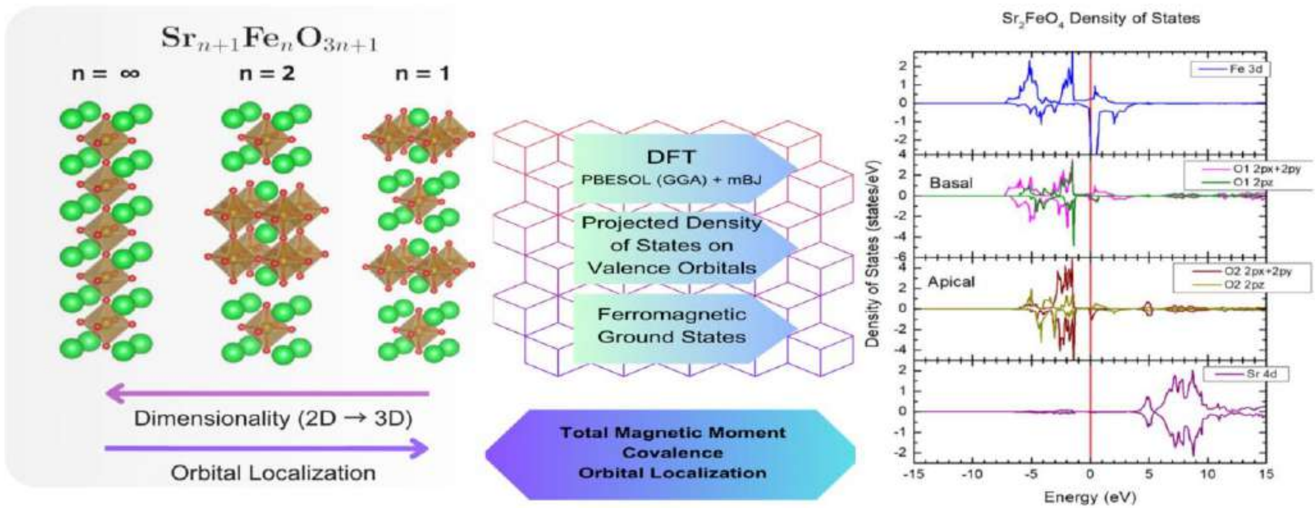
$Sr_{n+1}Fe_nO_{3n+1}$
n = ∞
n = 2
n = 1
Dimensionality (2D → 3D)
Orbital Localization
DFT
PBESOL (GGA) + mBJ
Projected Density of States on Valence Orbitals
Ferromagnetic Ground States
Total Magnetic Moment
Covalence
Orbital Localization
Sr_2FeO_4 Density of States
Fe 3d
Basal
O1 2px+2py
O1 2pz
Apical
O2 2px+2py
O2 2pz
Sr 4d
Density of States (states/eV)
Energy (eV)
-15
-10
-5
0
5
10
15

Electronic characterization of the manganese oxide thin film on metal substrates

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Manganese oxides have been extensively employed in applications related to battery devices, non-volatile memories, and water-splitting photocatalytic processes. These applications are generally related to its surface properties connected to their wide variety of valence states and structural forms [1,2]. In this study, we are interested in disentangling the role of the substrates (i. e.: Ag(001), Cu (111) and Au (111)) in determining the electronic properties of the film. The substrate surfaces differ in plane lattice parameter (4.07 Å (Ag); 2.56 Å (Cu); 2.84 Å (Au)) and surface work function (4.64 eV(Ag); 4.7 eV(Cu); 5.31 eV (Au)). Our preliminary characterization of Mn oxides film on these substrates, using low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) evidences different stability and structural phase diagram. The LEED analysis have shown that Mn_3O_4 thin film grows as (110) orientation on Cu (111) and (001) on Au (111) and Ag (001). X-ray linear dichroism experiments revealed the sensitivity of the 3d orbital occupancy and their intensity ratio ($d_{2-\;2}/d_{3\;2-\;2}$) to the surface orientation. The variation of relative 3d occupation as a function of strain was quantified by using the XLD sum rules [3].Moreover, we have tried to identify the contributions to the valence band originated from the Mn_3O_4 thin film by analysing the resonant photoemitted (RPES) electron excited at Mn $L_{2,3}$ and O K edges.

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Enhancing Electron Correlation at a 3d Ferromagnetic Surface

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Understanding the physics of interfaces that involve ferromagnetic transition metal surfaces is pivotal for designing novel spintronic devices with exotic properties and unmatched performances [1]. By combining spin-resolved momentum microscopy with state-of-the-art theoretical calculations that go beyond the one-electron approximation, we unveil that a chemisorbed oxygen layer strongly enhances electron correlation at an iron (Fe) surface [2]. As a result of this enhancement, the Fe d-bands near the Fermi energy are severely narrowed and their exchange splitting is reduced. Furthermore, electronic correlations lead to a spin-dependent broadening of the adsorbate-related bands at higher binding energies, due to the influence of emerging satellite features that are a direct manifestation of many-electron behavior.

Overall, adsorption and interface formation can be used to access different intermediate correlated regimes, which would otherwise not be accessible and possibly offer unique electronic and magnetic properties. Our results show that the concepts developed to understand the physics and chemistry of adsorbate-metal interfaces, ubiquitous in spintronics and catalysis, need to be reconsidered with many-particle effects being of tremendous importance, as they may affect chemisorption energy, spin transport and magnetic order, and even play a key role in the emergence of ferromagnetism at interfaces between non-magnetic systems [3].

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Acknowledgments
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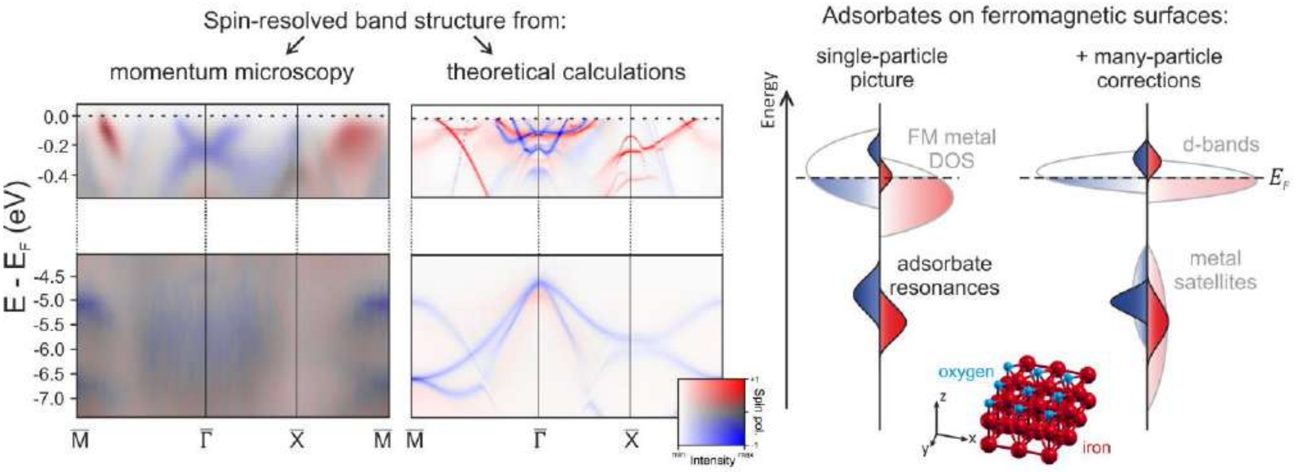
Spin-resolved band structure from:
momentum microscopy
theoretical calculations
E - E_F (eV)
0.0
-0.2
-0.4
-4.5
-5.0
-5.5
-6.0
-6.5
-7.0
M̄
Γ̄
X̄
M̄
M̄
Γ̄
X̄
Spin pol.
+1
-1
min
Intensity
max
Adsorbates on ferromagnetic surfaces:
single-particle picture
+ many-particle corrections
Energy
FM metal DOS
d-bands
E_F
adsorbate resonances
metal satellites
oxygen
iron
z
y
x

From infrared to X-ray: synchrotron radiation as a powerful probe to study 2D silicate minerals

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In an effort to increase the list of naturally abundant layered materials (LMs) that could become an alternative low-cost source of two-dimensional (2D) materials over its synthetic counterparts, recent research has been carried out in the group of phyllosilicate minerals which are wide bandgap insulators that can be mechanically exfoliated down to monolayers[1]. The challenge in using naturally occurring LMs is related to the existence of impurities/defects that can strongly affects their optoelectronic properties[2,3]. Furthermore, phyllosilicates are hydrated minerals. Theoretical studies suggest that substitutional ions in the atomic structure of phyllosilicates modulate how water confines in the interlamellar space[4]. In this sense, understanding the role that impurities play in the macroscopic properties of phyllosilicates and their capillary capacity is crucial to applying these minerals in 2D technologies from nanotransistors to microfluidic devices and sensors. This work presents several synchrotron techniques that can be used as powerful tools in the characterization of ultrathin phyllosilicates. We investigated the distribution of impurities using nano-XRF. We established their oxidation states and coordination using nano-XANES. Through SINS, we can overcome the classical diffraction limit of standard techniques to access the local opto-chemistry of phyllosilicates[5]. We also investigated possible arrangements of interlamellar water in phyllosilicates by CTR analysis.

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Acknowledgments

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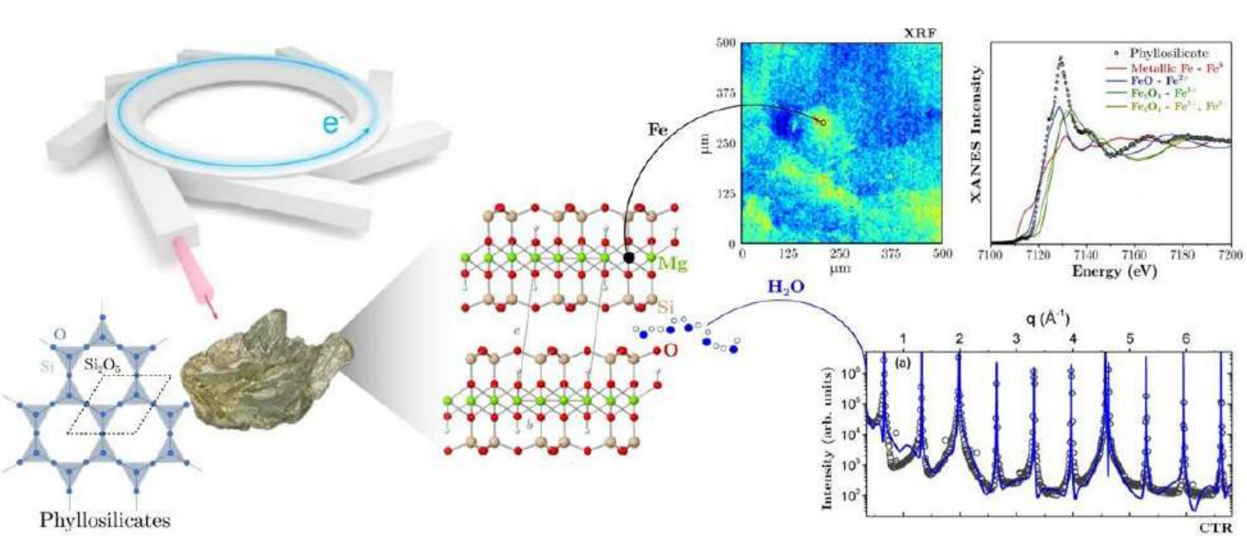
e-
O
Si
Si_2O_5
Phyllosilicates
Fe
Mg
Si
O
H_2O
c
b
XRF
500
375
250
125
0
μm
0
125
250
375
500
μm
XANES Intensity
Phyllosilicate
Metallic Fe - Fe^0
FeO - Fe^{2+}
Fe_2O_3 - Fe^{3+}
Fe_3O_4 - Fe^{2+}, Fe^{3+}
7100
7120
7140
7160
7180
7200
Energy (eV)
q (Å^{-1})
1
2
3
4
5
6
(a)
Intensity (arb. units)
10^6
10^5
10^4
10^3
10^2
CTR

Investigating magnetic anisotropy in the system Au/Co-Staircase/Au by XMCD

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Ultrathin films grown on metal surfaces may exhibit a variety of interesting magnetic phenomena [1-2]. Of particular technological relevance is the strong perpendicular magnetic anisotropy (PMA) often observed in ultrathin magnetic films grown on metal surfaces. Such systems are also of relevant scientific interest, as they allow the investigation of relevant magnetic phenomena, such as the origin of magnetocrystalline anisotropy (MCA) [3-4].

In this work, we investigated, through of the anisotropy in the orbital moment, the influence of the magnetocrystalline anisotropy in epitaxial Cobalt ultrathin films grown on the surface Au. The aim of this study was to apply the X-ray magnetic circular dichroism (XMCD) technique to determine the influence of the magnetocrystalline anisotropy in the *spin* reorientation transition (SRT), in the system Au/Co-Staircase/Au. The preparation of the surface Au were characterized using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM).

The analysis of the XMCD measurements as a function of the thickness of the ultrathin Co film (range from 5 ML to 11 ML) in the Au/Co-staircase/Au system reveals a considerable orbital-moment anisotropy along the thinnest region (5 to 7 ML range). Above 9 ML, nearly isotropic orbital magnetic moment is observed, indicating a small influence of the MCA and a greater influence of shape anisotropy, which tends to induce in-plane magnetic anisotropy (IMA).

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Acknowledgments

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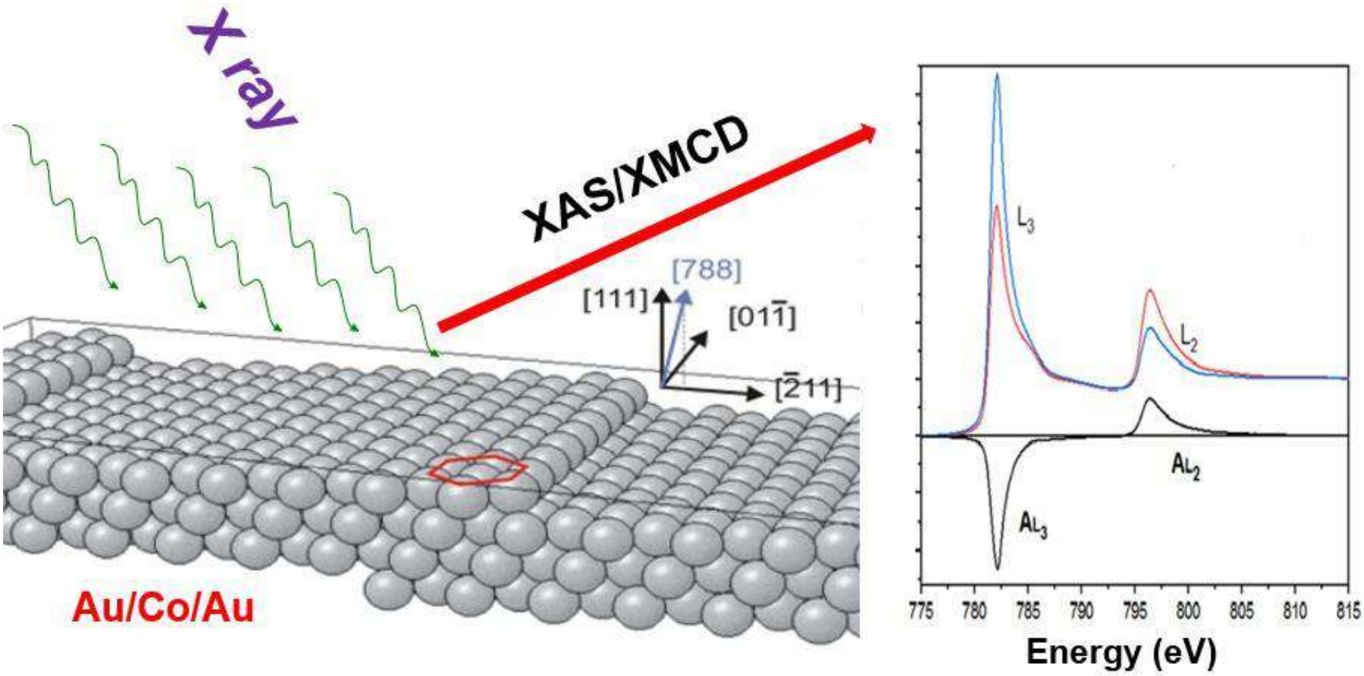

$L_{2,3}$ X-ray absorption spectra of transition metal oxides (Mn, Fe, Co): The influence of covalence effects

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Transition metals (TM) present a plethora of physical properties, which makes their study very interesting for theoretical and experimental purposes. To study these properties, we make use of the x-ray absorption spectroscopy (XAS). This method is based on electronic transitions between core and empty conduction states, which can be very sensitive to the local chemical environment. Therefore, we consider the full multiplet effects on the nominal valence of the analyzed compound, for a more complete analysis. Further, we take into account the covalence between different TM and their ligands, which is often mistreated. If not considered correctly, this effect can affect the interpretation of the results. In this work, we analyze the XAS of different TM oxides, namely, manganese, iron and cobalt, with different nominal valences of 2+, 3+ and 4+. By using atomic multiplet, ligand and crystal field theories, we obtained the ground state energy, 3d band electron count, and the TM 2p XAS spectra of all these systems, considering different number of electronic configurations (EC). From the analysis of our results, we found that, to correctly describe the electronic structure of these materials, the required number of EC are usually greater than one expects from the direct comparison with the experimental data. Also, this effect is heavily dependent on the TM valency. Thus, the covalent effect between TM and ligand ions is of great importance to correctly interpret the XAS technique.

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Acknowledgments

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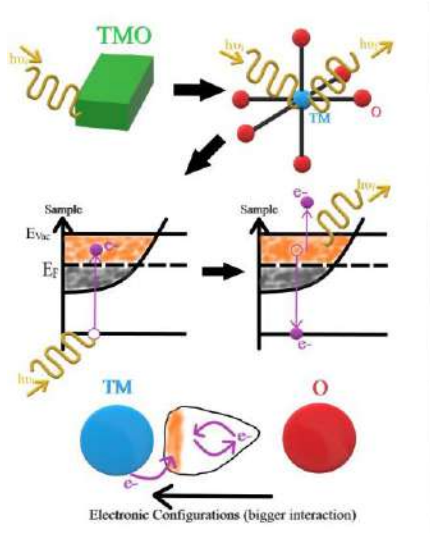
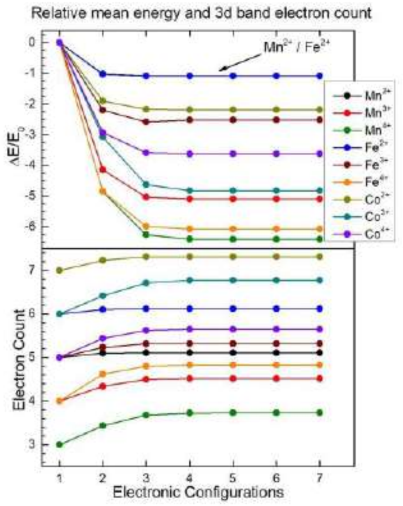

TMO
hν
TM
O
Sample
Sample
E_Vac
E_F
e-
e-
e-
TM
O
e-
e-
Electronic Configurations (bigger interaction)


Relative mean energy and 3d band electron count
Mn2+ / Fe2+
ΔE/E0
Electron Count
Electronic Configurations
Mn2+
Mn3+
Mn4+
Fe2+
Fe3+
Fe4+
Co2+
Co3+
Co4+
0
-1
-2
-3
-4
-5
-6
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6
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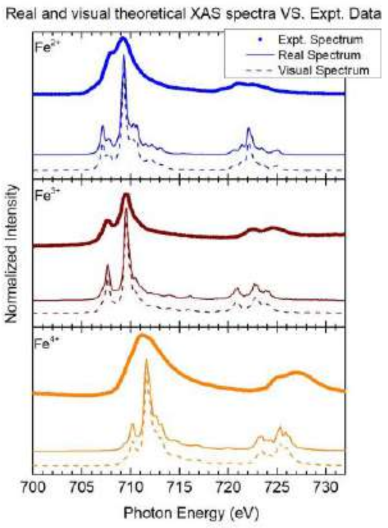
1
2
3
4
5
6
7


Real and visual theoretical XAS spectra VS. Expt. Data
Expt. Spectrum
Real Spectrum
Visual Spectrum
Fe2+
Fe3+
Fe4+
Normalized Intensity
Photon Energy (eV)
700
705
710
715
720
725
730

Multispectral studies of metal halide perovskites: simultaneous x-ray ptychography, x-ray fluorescence, and x-ray excited optical luminescence experiments

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Among new photovoltaic materials, metal halide perovskites (MHP) (ABX_3, where $A=CH_3NH_3^+$, $CH(NH_2)_2^+$ or Cs, $B=Pb^{2+}$, $X= I^-$ or Br^-) are the most promising for solar cells and detectors owing to their process of fabrication and material properties.[1] Despite that, several aspects of morphology, chemical composition, and optoelectronic properties are still uncovered from the micro to the nanoscale. X-ray nanoscopies available at the CARNAUBA beamline (SIRIUS/LNLS)[2] reveal the correlation among its morphology (x-ray ptychography), chemical distribution (x-ray fluorescence - XRF), and optoelectronic response (x-ray excited optical luminescence - XEOL).[3,4] We report x-ray nanoscopy experiments, including coherent diffractive imaging (CDI) in fly-scan mode.[5] Ptychography in phase contrast (14 nm pixel size @10 keV) reveals morphological aspects not visible in traditional scanning transmission. XRF maps correlate wrinkled morphology to variations in Br:Pb stoichiometry, which agrees with shifts in the XEOL. The possibility of measuring in fly-scan mode and N_2 atmosphere was essential to mitigate damages, typically the main limiting factor to applying the CDI in such samples. Our multispectral images of MHP are a pivotal step in developing and applying the technique in beam-sensitive samples for high-resolution imaging, especially in the case of heterogeneous and hierarchical functional materials in which the multiscale properties determine final device performances.

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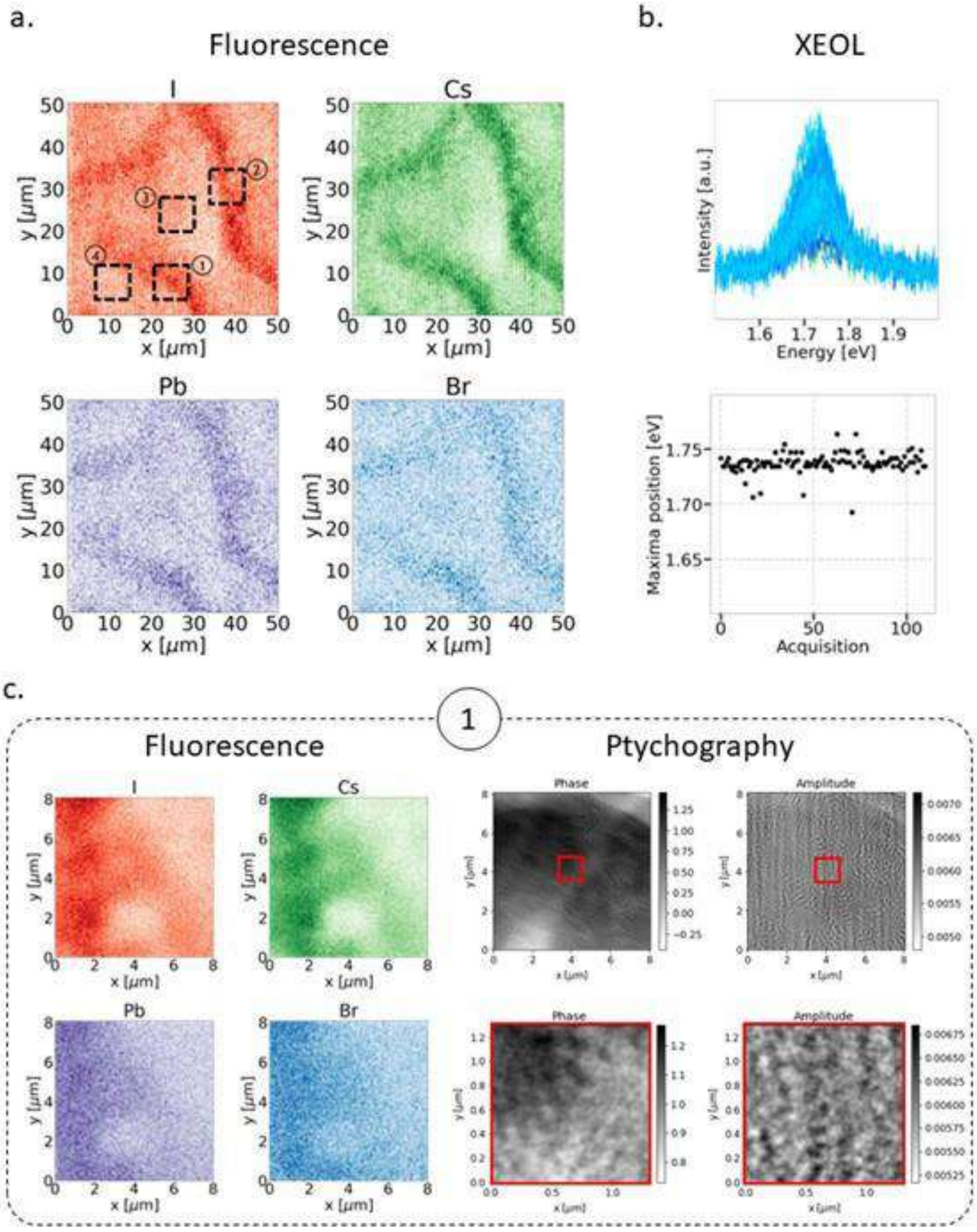
a.
Fluorescence
I
Cs
Pb
Br
y [μm]
x [μm]
0
10
20
30
40
50
①
②
③
④
b.
XEOL
Intensity [a.u.]
Energy [eV]
1.6
1.7
1.8
1.9
Maxima position [eV]
1.65
1.70
1.75
Acquisition
0
50
100
c.
1
Fluorescence
Ptychography
Phase
Amplitude
x [μm]
y [μm]
0
2
4
6
8
1.25
1.00
0.75
0.50
0.25
0.00
−0.25
0.0070
0.0065
0.0060
0.0055
0.0050
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0.5
1.2
1.1
1.0
0.9
0.8
0.00675
0.00650
0.00625
0.00600
0.00575
0.00550
0.00525

Orbital-specific correlations in Cr substituted BaFe2As2 probed by ARPES and DMFT

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In Cr-substituted $BaFe_2As_2$ (CrBFA) materials, the absence of superconductivity (SC) [1] has been speculated to be related to electronic correlations induced by Cr. Upon Cr substitution, the magnetic ordered ground state changes from an itinerant orthorhombic spin density wave (SDW) to a localized tetragonal G-type antiferromagnetic order [2]. Cr doping thus leads to the coexistence of magnetic fluctuations of distinct symmetries, that compete for the formation of the ground state throughout the phase diagram. However, the importance of the putative Mott localization for the $BaFe_2Cr_2As_2$ and its interplay with the Hund metal phase is still an open question [3].

In this work, we present a comprehensive investigation of the electronic structure of CrBFA using angle-resolved photoemission spectroscopy (ARPES). Our results show that electronic correlation increases with Cr content and that, although it compares to Mn substituted samples in terms of electronic disorder, Cr indeed introduces hole doping into the system while Mn does not. Our findings are supported by density functional calculations combined with dynamical mean-field theory calculations (DFT+DMFT) and with RIXS results, pointing to the importance of Hund interactions and orbital-specific correlation and localization effects. We conclude that SC is lacking in CrBFA mainly because of magnetic pair breaking and suppression of the itinerant spin fluctuations which promote SC.

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Probing Electronic Sturucture of materials with ARPES and Synchrotron Radiation at SAPÊ beamline in SIRIUS

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In this presentation I will provide information about SAPÊ (Angle-resolved PhotoEmission) which is one of SIRIUS beamline dedicated to angle-resolved photoemission spectroscopy (ARPES) experiments, with high energy and momentum resolution, in the vacuum ultraviolet (VUV) spectrum range. Such experiments allow the analysis of the electronic structure of crystalline materials and are an essential tool for the study of the frontier of new materials, with special emphasis on topological materials and 2D materials.

The UV extraction is done from a B2 dipole and provides a photon flux, in the sample, of up to 1×10^{12} ph/s/100mA at 40 eV and energy resolution of 1 meV at 10eV. The operating energy range of SAPÊ is between 8 and 70eV and the micrometer beam in the main chamber will allow carrying out ARPES experiments with high energy and momentum resolution on samples with size of 5×20 μm^2 [1].

I will also provide information about the experimental endstation of the beamline which the samples will be loaded, handled and prepared before the ARPES experiments. The main objective of the SAPÊ beamline is to provide the scientific community a tool capable of probing the band structure of new materials and unveiling phenomena that may arises from it.

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Probing the Spin Waves in the Ferromagnetic Topological Metal Fe_3Sn_2 by Resonant Inelastic X-ray Scattering

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Magnetic metals with kagome structure can host various topologically non-trivial spin or electronic states, providing an extraordinary platform for studying both the fundamental topological physics and potential technological applications. The metallic kagome ferromagnet Fe_3Sn_2, which has large spin-orbital coupling, shows considerable interplay between magnetism and non-trivial electronic states[1, 2]. The material has a host of anomalous bulk properties, including a first-order spin reorientation transition[3], a large anomalous Hall effect[4], skyrmionic bubbles[5], and field tunable nematic states[1]. Here, using circularly polarized X-Rays in resonant absorption (XAS) and inelastic scattering (RIXS), we report the unambiguous isolation of magnetic signals of a flat spin wave band and large (compared to elemental iron) orbital moment in Fe_3Sn_2. The flat mode energy is consistent with the high Curie temperature ($T_C \approx 640$ K) as well as the strong acoustic mode dispersion, implying, together with the substantial spin-orbit coupling indicated by the large orbital moment, that the mode is topological. The measured properties of the spin waves are highly unconventional, and include very severe damping as well as a flat mode amplitude, which is maximized in the long wavelength limit where it is ordinarily expected to vanish. Our results illustrate how the magnetic circular dichroism analysis enhances the sensitivity of RIXS to magnetic excitations in ferromagnetic materials.

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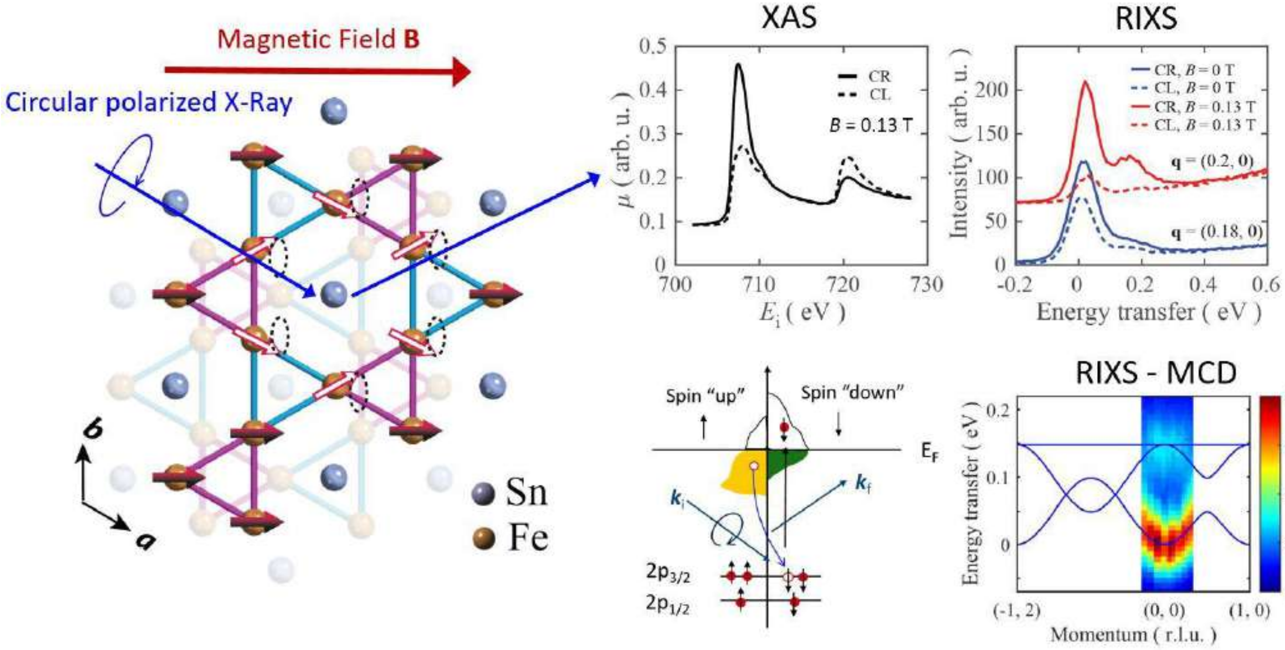

Probing the surface polarization of ferroelectric thin films by X-ray standing waves

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Ferroelectric materials consist of noncentrosymmetric unit cells with permanent electric dipole moments leading to a macroscopic spontaneous electric polarization. Uncompensated charge at the surface of a ferroelectric material is responsible for its chemical reactivity and can influence the polarization itself. Therefore, revealing the polarization at (and near) the surface of a ferroelectric material is important not only from a fundamental point of view, but also to obtain a deeper insight into its surface chemistry and learn how to exploit it for technologically relevant catalytic reactions [1].

In this study, we investigated $BaTiO_3$ ferroelectric thin films grown on three different scandate substrates, with a bottom electrode ($SrRuO_3$) in between. The interference between the incident and Bragg-diffracted X-ray wave generates an X-ray standing wave (XSW) [2]. The structural sensitivity of the XSW technique combined with the chemical specificity of X-ray photoemission spectroscopy (XPS) reveals the atomic positions of Ba and Ti atoms within the top unit cells. As a result, the off-center displacement of Ti atoms, thus the local ferroelectric polarization, can be determined at different depths from the surface. These results are discussed in the light of oxygen-related adsorbates measured by XPS.

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Acknowledgments

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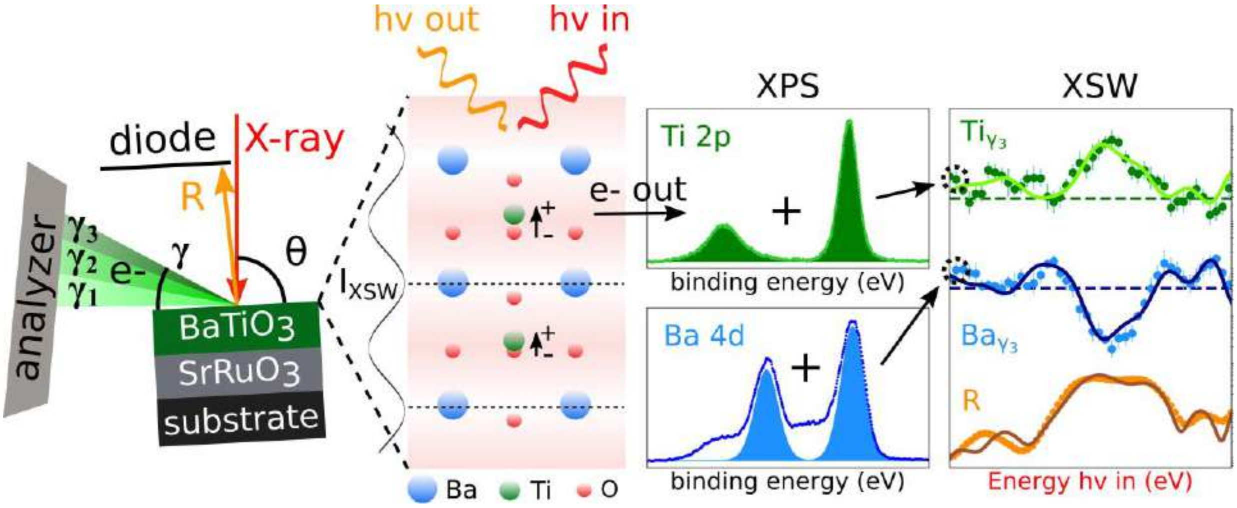
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Proximity-Induced Novel Ferromagnetism and Metallicity in $NdNiO_3$ Heterostructure

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Anna Zakharova[5], Cinthia Piamonteze[5], Milan Radovic[5]

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Rare earth nickelates ($RENiO_3$) possess a rich phase diagram where a metal-insulator transition (MIT) is accompanied with a paramagnetic (PM) – antiferromagnetic (AFM) transition. The MIT temperature (T_{MIT}), as well as the Néel temperature (T_N), can be tuned changing the tolerance factor of the perovskite structure, i.e. changing the rare earth element. In $NdNiO_3$ (NNO) TMIT and TN coincide, emphasizing the intimate connection between magnetic and electronic properties in the nickelates family (1).

Growing thin NNO films on a ferromagnetic manganate ($La_{0.67}Sr_{0.33}MnO_3$ - LSMO), we demonstrate through X-ray Magnetic Circular Dichroism (XMCD) that proximity effect can induce a new ferromagnetic phase in NNO. Moreover, using Angle Resolved Photoemission Spectroscopy (ARPES) and electric transport measurements, we can visualise how growing NNO on LSMO affects the nickelate electronic structure, with a suppression of the temperature induced MIT and a persisnt density of states at the Fermi level. Finally, with the help of momentum-resolved density fluctuation calculation (MRDF), we link the suppression of the MIT with the emergent ferromagnetism in NNO (2).

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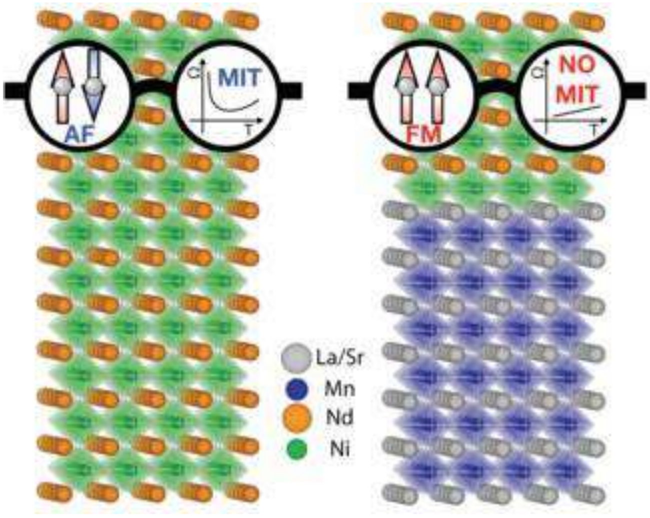
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T
La/Sr
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Nd
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Quantum critical scaling of charge order in $La_{2-x}Sr_xCuO_4$ revealed by high-resolution RIXS

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The pseudogap (PG) and strange-metal (SM) phases observed in cuprates above the superconductivity transition temperature are enigmatic. Quantum phase transitions, which are driven by nonthermal fluctuations at absolute zero temperature, play a crucial role in shaping the phase diagram of high-temperature cuprate superconductors. Understanding the PG and the SM phases might hinge on the influence of quantum criticality at finite temperatures. Recently, quantum fluctuations of charge-density waves (CDW) were observed in different families of cuprates [1-4]. In this study, we investigated the high-resolution resonant inelastic x-ray scattering (RIXS) of $La_{2-x}Sr_xCuO_4$ to unravel the quantum fluctuations of CDW in different doping. Our findings provide the spectroscopic signature of quantum critical scaling in cuprates, in which the PG and SM phases correspond to the renormalized classical and quantum critical scaling regimes, respectively. In addition, the characteristic energy Δ of the CDW fluctuations at zero temperature determines the crossover temperature T* between the PG and the SM phases, i.e., $T^* \sim \Delta$.

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Resonant Inelastic X-ray Scattering Investigation of 2D Magnets

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The discovery of ferromagnetism down to the monolayer in two-dimensional van der Waals chromium trihalides CrX_3 (X=Cl, Br, and I) has gained research attention because of their interesting electronic and magnetic properties[1,2]. The strong spin-lattice interaction and the hexagonal stacking order, the magnetic properties of CrX_3 depend sensitively on the number of layers. Spin ordering can be manipulated by electric and magnetic fields, pressure and strain. On the other hand, the magnetic ground states are sensitive to the degree of ligand−metal hybridization and relevant modulations in the Cr *d*- orbital interactions. These properties make CrX_3 prime candidates for spintronics and optoelectronics applications and highlight the importance of correctly determining the essential energy scales to understand the physics of CrX_3. We have measured Cr *L*-edge soft X-ray absorption spectroscopy (XAS) and resonant inelastic scattering (RIXS) for all CrX_3 under different conditions[3]. With the assistance of quantum many-body script language QUANTY, we have reliably extracted the energy scales of CrX_3 and reproduced the RIXS spectra better than those methods found in the literature[4]. This systematic study shows that our approach has yielded a set of well determined parameters for building a base Hamiltonian for CrX_3. Furthermore, the atomic part of the Hamiltonian has been used very satisfactorily in ligand field theory for the interpretation of optical data of these magnetic compounds.

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Spin-orbital excitations encoding the magnetic phase transition in the van der Waals antiferromagnet $FePS_3$

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Magnetic van der Waals (vdW) materials have provided exciting new opportunities in the studies of functional exotic magnetic phases of various symmetry-breaking ground states and collective behavior. [1] Recent studies utilizing primarily optical spectroscopy have demonstrated the sensitivity of the phonon spectral response to the magnetic state down to the few-layer limit. [2] $FePS_3$, whose interlayer exchange interaction is very small, is an S = 2 zig-zag quasi-two-dimensional antiferromagetic insulator with a honeycomb lattice. [3] The electronic structure resolved by x-ray absorption spectroscopy (XAS) suggests how the local crystalline environment shapes the anisotropic electronic structure. [6] Here we performed resonant inelastic X-ray scattering (RIXS) at Fe L_3-edge as a function of temperature across the magnetic transition to elaborate the spin-orbital excitations of $FePS_3$ and their relation to magnetism. The identified multiplets have a large sensitivity to the spin state. By comparing with ligand field theory calculations, we establish the essential role of the trigonal lattice distortion and negative metal-ligand charge transfer to explain the low-energy spin-orbital excitations in the presence of magnetic order. This establishes a generalized approach, shown here for a vdW magnet, that is ideal for studying magnetic functional materials, and the relation between their low-energy electronic properties and the magnetic state.

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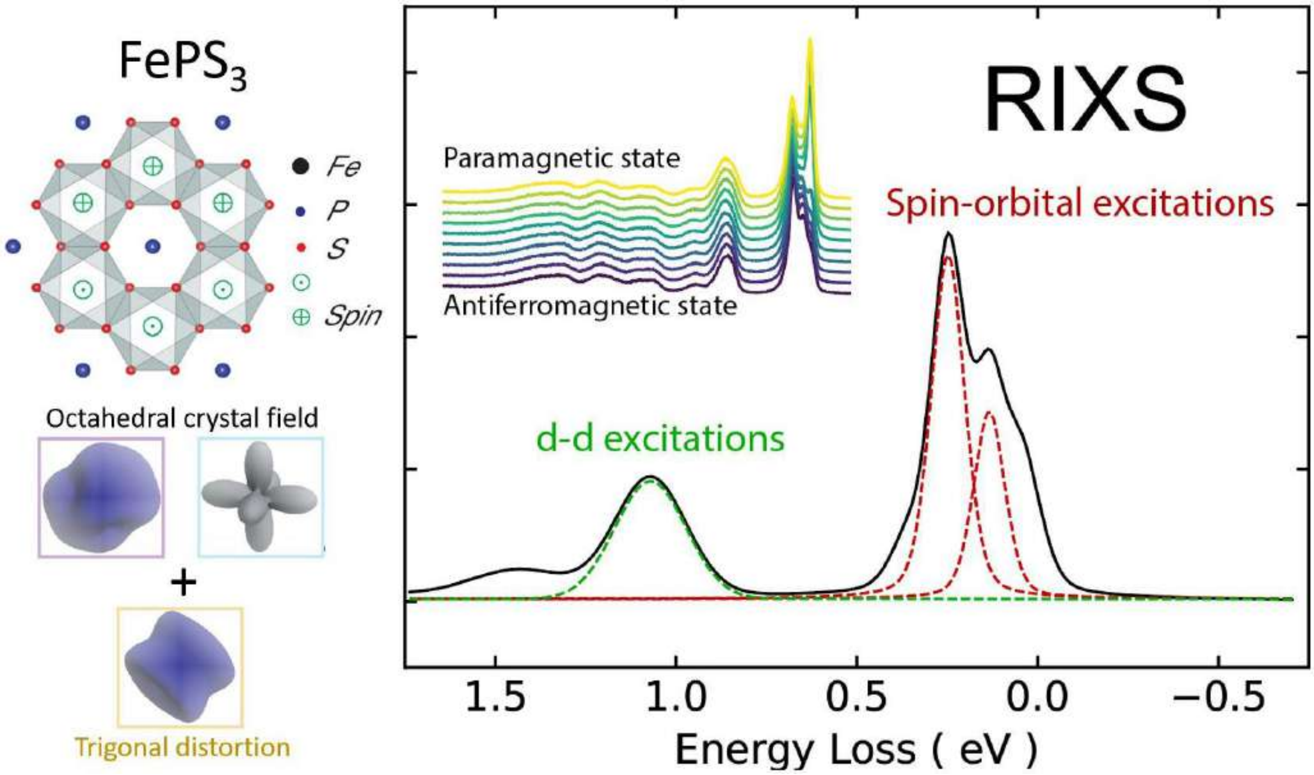

The Brazilian RIXS endstation on the IPE beamline at Sirius: commissioning results and perspectives

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The IPE beamline at Sirius is dedicated to high-resolution resonant inelastic X-ray scattering (RIXS), X-ray absorption (XAS), and X-ray photoelectron spectroscopies (XPS) in the soft X-ray range (100 – 2000 eV). The soft X-ray RIXS is particularly useful for studying transition metals and light elements in strongly correlated electron systems, quantum materials, molecular complexes, catalysts, and metalloenzymes, among others. While the XPS branch has been opened for regular proposals early in 2023, the RIXS endstation commissioning is ongoing. With a 6 m long spectrometer and a spot size of 0.8 x 3.4 μm^2 (v x h), the Brazilian RIXS is designed to deliver a combined resolution of 30 meV at 930 eV. The sample chamber has a 120° continuously rotatable port for momentum-resolved experiments and a high precision 4 DOF manipulator that allow one to scan micrometer-sized samples such as Van der Waals materials flakes with good stability. The station's versatility allows for various sample environments, such as low temperature (~14 K) for solids, 4+2 DOF for single crystals, high temperature, membrane-based liquid cells, uniaxial strain devices, electric field, and other customized environments. In this presentation, we will show results obtained during the commissioning, the actual status, and perspectives.

The role of the dopant on electronic structure of Er-doped oxides for quantum memory

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Rare earth ion defects in solid-state hosts are excellent candidates for applications in quantum communication technologies as qubit systems, due to their inherent spin-photon interface and long coherence times. [1] Er^{3+} is an especially promising candidate due to its $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition in the telecom C-band. This classically-forbidden telecom transition is made accessible by placing Er^{3+} ions within a crystal host, which makes the transition sufficiently bright to use for quantum communication. Oxides are an excellent class of hosts for rare-earth ions due to their straightforward growth even at high purity and expected overall good coherence times when hosting defects. [2] Here, we show that linewidths in photoluminescence excitation spectra vary with dopant concentration and growth conditions. However, the causes for this variation are unclear. X-ray absorption spectroscopy (XAS) is an element-specific technique broadly applied for local electronic structure characterization in materials. In this work, we performed XAS at the Advanced Photon Source to probe the electronic structure of Er-doped oxides as a function of the doping level. This information is crucial for controlling the tunability of excited state lifetimes and rare-earth defect linewidths in such systems.

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Ultrafast and steady-state X-ray investigation of CuInS2 quantum dots

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[1]IMDEA nanociencia (*Ultrafast X-ray Science*) , [2]Universidade Estadual de Campinas (\"*Gleb Wataghin\" Institute of Physics*) , [3]Universidade Estadual de Campinas, [4]Universidad Complutense de Madrid (*Facultad de Química, Departamento de Química Física*) , [5]PAL XFEL Pohang Accelerator Laboratory, [6]Japan Synchrotron Radiation Research Institute (*SACLA*) , [7]Universidade Federal de São João Del Rei (*Departamento de Ciências Naturais*) , [8]Universidad Autónoma de Madrid (*Chemistry*)

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The interest in $CuInS_2$ (CIS) quantum dots (QDs) has increased significantly in the past few years. CIS QDs have been studied for many applications like photodynamic therapy or solar cells[1]. They show exciting optoelectronic properties, such as broad photoluminescence (PL) with a large Stokes shift and long charge carrier lifetimes. Several mechanisms for the radiative recombination in CIS QDs have been proposed.

In this work we aim to understand and confirm the possibility of radiative recombination resulting form an electron in the conduction band and a hole in a so-called confined hole state (CHS),[2-3]. The range of such possible states would explain the broad PL and large Stokes shift. In addition, we aim to understand the effects of stoichiometry and Zn doping on the passivation of the QDs and the formation process of the CHS [4].

The element and oxidation state specificity of X-ray techniques can serve to more directly observe such processes. We approached these questions through a combination of laser, synchrotron and XFEL techniques with our recent beamtimes at SACLA XFEL and ALBA. We focused on following the oxidation state of Cu through time-resolved Cu K-edge XANES and comparing the structure of the different samples through steady-state XANES and EXAFS at the Cu, Zn and S K-edges. This allowed us to gain insights into the structure, the surface passivation and the Zn incorporation through different synthetic routes. This is then complemented by optical studies.

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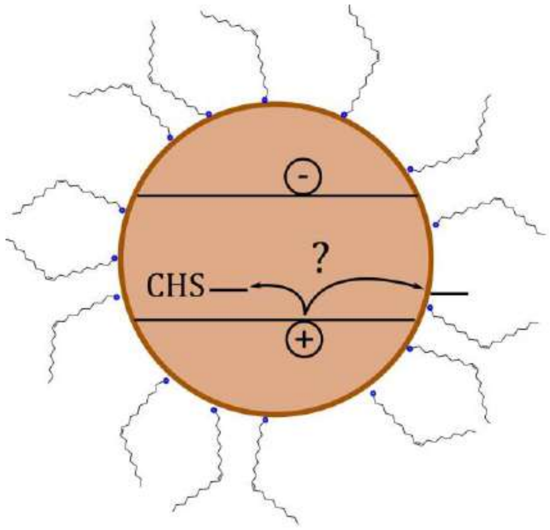
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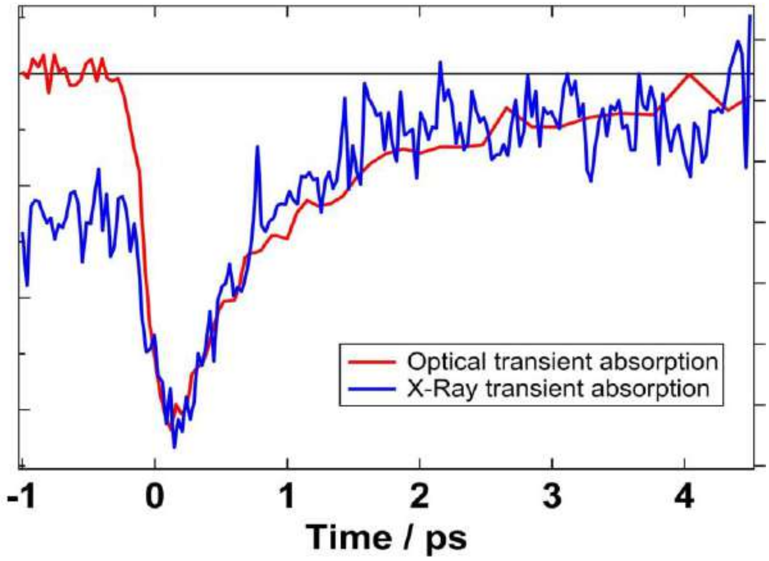
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Unusual orbital configuration and possible low-energy orbital excitations in a copper oxide with trirutile structure

Carlos William Galdino[1], Eduardo Granado Monteiro da Silva[2], Túlio C. R. Rocha[3], Thiago J. A. Mori[4], Thorsten Schmitt[1], Yuan Wei[5], John Neumeier[6]

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The electronic configuration of Cu (3d9) ions in low-dimensional cuprates is such that the electron hole is generally found in the eg x2−y2 like orbital instead of the 3z2−r2. This is due to the strong tetrahedral distortion of the octahedral environment which lifts the x2−y2 like orbital. Remarkably, the quasi-1D Mott-insulator CuSb2O6 with trirutile shows fairly regular CuO6 octahedra that seem to promote a close competition between the 3z2−r2 and x2−y2 levels. In this compound, tight-binding model calculations indicate that the orbital ground state of the Cu 3d hole appears to be 3z2−r2 [1]. However, such unusual ground state and the presumably small Cu eg orbital splitting has never been experimentally verified. Additionally, this unusual orbital configuration may provide new pathways for electron-phonon interaction in cuprates. Indeed, recently published Raman scattering spectra displays possible low-energy electronic excitations in CuSb2O6 single crystals that strongly interact with phonons of similar energy [2, 3]. In this work we shall explore the unusual structure of CuSb2O6 to investigate the microscopic mechanism of orbital/electron-phonon coupling. We will show resonant X-ray inelastic scattering (RIXS) spectra together with multiplet simulations that confirm the small split between the two eg levels and a mixed character orbital configuration. The possibility of low lying orbital excitations that couples with the phonons is discussed.

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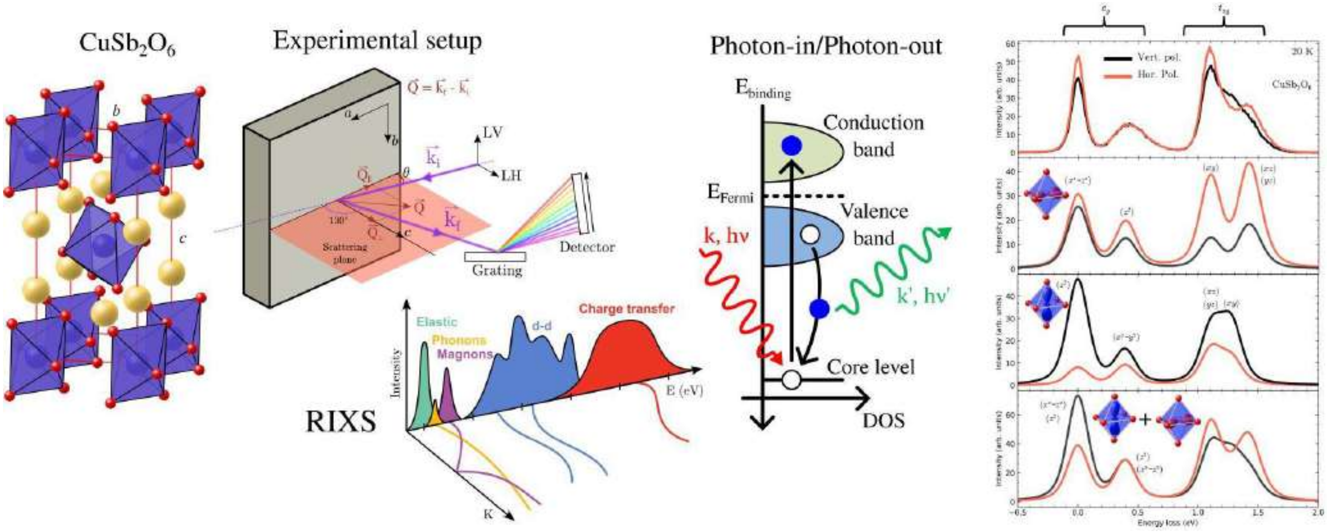
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(yz)
(x^2-y^2)
Energy loss (eV)
-0.5
0.0
0.5
1.0
1.5
2.0

Zn-vacancies as Hydrogen Trap Sites in Polar Surfaces: A New Stabilization Mechanism for the ZnO(0001)-(2x2) Surface Reconstruction

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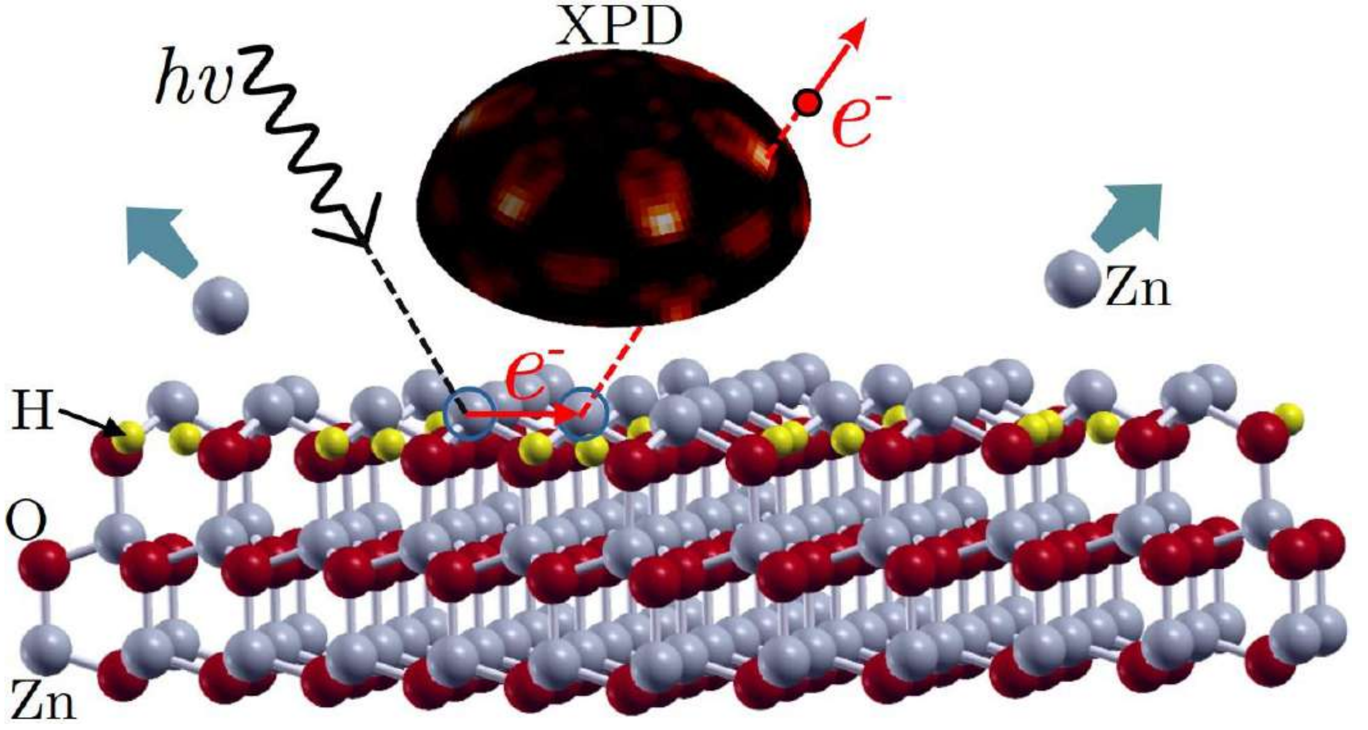
The (2x2) reconstruction of the ZnO(0001) surface has been investigated by x-ray photoelectron diffraction (XPD). Comparing the XPD measurements with multiple-scattering simulations, the single Zn vacancy per (2x2) surface unit cell model is confirmed, and structures with O adatoms are ruled out. The analysis indicates an outward relaxation of the topmost Zn layer, in contrast to the usually reported results by density-functional theory (DFT) calculations. Based on DFT, we describe a new stabilizing mechanism of the polar ZnO surface through surface reconstruction where the Zn vacancies are occupied by three hydrogens atoms. The DFT surface relaxation of the proposed model is in excellent agreement with the XPD findings. Our DFT simulations also strongly indicate that the migration of hydrogens atoms to the surface, coming from the bulk, may influence the desorption of the surface Zn atom to create the vacancy.



Ambient Pressure X-ray Photoelectron Spectroscopy Combined with Polymer Membrane-based Electrochemical Liquid Cells for Electrochemistry Applications

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Ambient pressure X-ray photoelectron spectroscopy (APXPS) has been considered one of the important in-situ and operando surface science technologies to study the chemical state and elemental composition evolution of the materials' surface during heterogeneous reactions. Here, we will present two scientific results by using APXPS combined with polymer membrane-based liquid electrochemical cells for the liquid-solid heterogeneous reaction in electrochemistry applications. The first result reveals the surface oxide species (Pt^{d+}, Pt^{2+}, and Pt^{4+}) evolution on Platinum catalysts in an electrochemical redox reaction under an acid solution. Incorporating depth-profiling studies enabled us to uncover the mechanism of oxide species evolution between the surface and subsurface of the Pt catalyst during a redox reaction. The second result investigated the reaction mechanism for the zinc substitution iron cobaltite-based spinel structure ($Zn_xFe_{1-x}Co_2O_4$) with a different amount of Zn substitution ($0 < x < 0.6$ with steps of 0.2) under an alkaline environment. In operando APXPS results show the highest Co (IV) percentage in Co 2p, approximately 56%, and an increase of superoxide on the surface in O 1s. We proposed that the Co (IV) and superoxide species are the important intermediates in the OER for iron cobaltite-based spinel structure catalyst to produce oxygen. More detailed results will be presented in this meeting.

Controlling the integer charge transfer at the pentance/MgO/Fe interface.

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Novel molecular multi-spinterfaces can be useful in engineering devices capable of storing quantum information using the molecular spin state [1]. Recently, it has been shown that the large changes in work function (WF) induced by ultrathin magnesium oxide (MgO) film grown on Ag(100) can modify the electron energy level alignment for molecular adsorbates, promoting charge transfer *via* tunneling. Since the fractional charge transfer is hindered due to the lack of hybridization, only integer charge transfer is expected to be possible [2]. We have extended this approach to a truly spinterfaces implemented in tri-layer configuration consisting of an iron substrate coupled to a molecular system through a MgO thin layer. Here, by means of photoemission orbital tomography experiments, supported by X-ray photoemission spectroscopy measurements, we show that the integer charge transfer occurs at the interface formed by depositing 1 layer of Pentacene (5A) atop 2 monolayers (ML) of MgO grown on the Fe(100) surface. We are able to fully populate the lowest unoccupied molecular orbital (LUMO) of 5A with two electrons, injected *via* tunneling from the ferromagnetic substrate underneath. Moreover, by tuning the WF of the MgO film, we can control the energy position of the LUMO in a wide energy range. Changing the growth conditions of the MgO film allow us to place and oxygen interlayer between the MgO and the Fe(100) that quenches the charge transfer at the interface.

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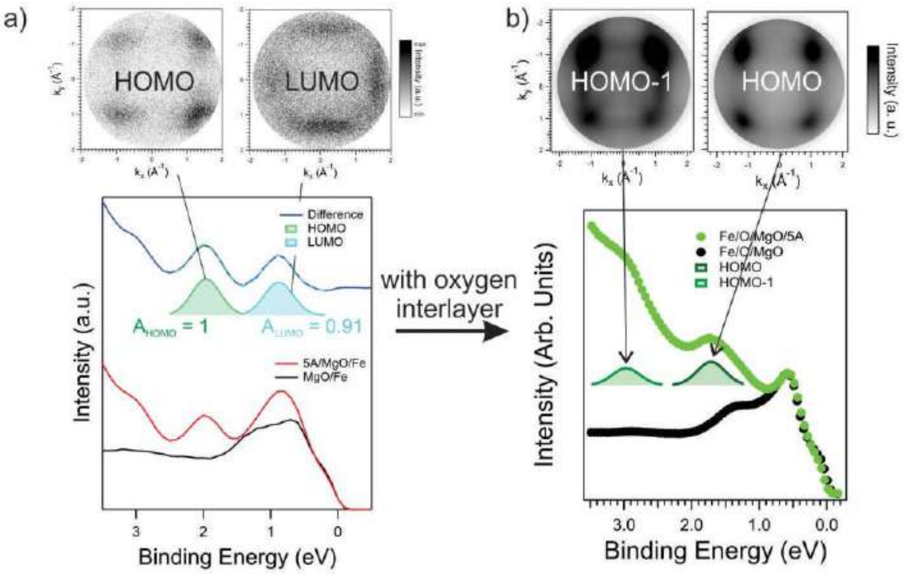

Fig. 1. a) Momentum-integrated valence band for the 5A/MgO/Fe(100) interface. The HOMO and LUMO can be identified with the photoemission tomography approach from their clear momentum fingerprints (top). b) Momentum-integrated valence band for the 5A/MgO/O-Fe(100) interface. Here there is no sign of the occupation of the LUMO.

Electronic structure of hydroxyl at Ag(100) and Ag(110) under near ambient conditions.

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The interaction between water and hydroxyl with metal surfaces is one of the most studied adsorption cases in surface science [1] since they are of utmost importance in heterogeneous catalysis, electrochemistry and corrosion. Although the O-Ag adsorption phase have been extensively studied in previous works, OH adsorption has been much more elusive, perhaps due to the difficult in identifying the hydroxyl in presence of other adsorbates. Moreover, hydroxyl represents a key intermediate on many surface reactions. It is a by-product of total oxidation, and it was proposed to have an active role in partial oxidation reactions [2].

In this work we study the hydroxylation of an oxygen covered silver surface under reaction conditions and provide a complete description of the spectroscopic features, electronic structure and bonding configuration. Starting from a well defined oxygen covered Ag surface with O-p(2x1) reconstruction, we prepared a fully hydroxylated surface phase in equilibrium with water and oxygen in the gas phase at near ambient conditions [3]. Combining in situ soft x-ray spectroscopic at near ambient conditions, by synchrotron radiation facility BESSY II and Elettra, with density functional theory we show that OH adsorbate states have higher binding energies relative to the Fermi level of Ag and a larger energy splitting than the states for O adsorbate.

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Electronic Structure of La0.6Sr0.4MnO3 Films in Water Vapor Using in situ RIXS Spectroscopy

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Oxygen evolution reaction (OER) has attracted much attention over the past decades. One of the major challenges is the control of the multi-electron transfer processes during the OER of water. [1] It is of fundamental importance to understand the various active sites, active states, and intermediate states during water OER. We use element-specific multidimensional *in-situ* grazing incidence resonant inelastic X-ray scattering (RIXS) spectroscopy to monitor the Mn-O coordination and Mn valence of the perovskite $La_{0.6}Sr_{0.4}MnO_3$(LSMO) as a model catalyst.[2] We will introduce novel RIXS techniques that combine in-situ and operando capabilities for identifying various Mn states in this contribution, exciting and Mn L-edge. Crucially, our method allows for identifying the short-living intermediate species upon water-vapor exposure, mimicking the OER conditions in LSMO films. We further explored the LSMO catalyst by probing the O K -edge, revealing low-energy features potentially associated with polaron formation in the surface and bulk of the LSMO. These low-energy features exhibit excitation energy and angle dependence. Our method enables the characterization of perovskite surfaces and will help tune the perovskite structures for better catalytic applications.

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Acknowledgments

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Femtosecond TR-XAS of solvated Biomolecule with a Water Window HHG Source

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Light induced dynamics is essential for various bio-chemcial processes, i.e. vision [1]. However, it is experimentally challenging to follow the ultrafast reaction process in real time. In this work, we present femtosecond time resolved X-ray absorption spectroscopy (trXAS) of aqueous urea (CH4N2O) solution utilizing a high-harmonic-generation (HHG) source covering the essential carbon and nitrogen edges as depicted in Figure 1. The inherently broadband HHG pulse allows to probe both edges simultanouesly and is therefore ideal for XAS [2]. XAS is an element and site specific method and very popular in investigating the electronic properties of matter including intermolecular dynamics in a liquid environment [3]. Another advantage is that the pump and probe pulse are derived from the same source and therefore principally time jitter free. Furthermore, we utiliuzed a sub-µm thin flat jet to record artefact free XAS in transmission mode [4]. Our experimental results indicate spectral features appearing after ~200 fs and lasting up to around 700 fs before it stabilizes, which we attribute it to nuclear rearrangement after multiphoton ionization.Theoretical simulation and XAS calculations of several urea dimer and ureawater geometries support the experimental findings and can reproduce the main spectral features. The theoretical results indicate charge dynamics changing the structural arrangement and leaving geometric specific spectral fingerprints on the electronic properties.

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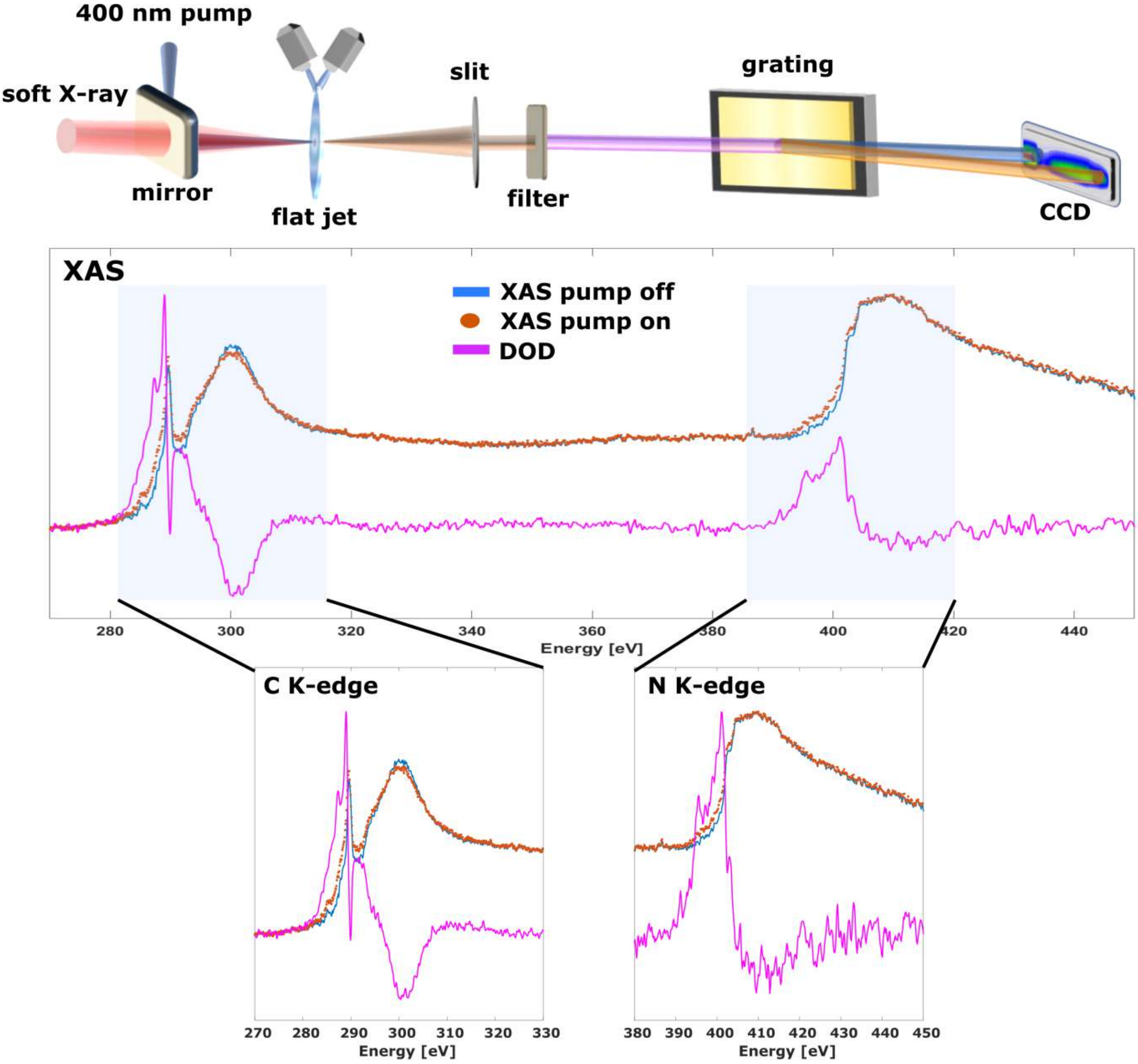
NCCR-MUST of Swiss National Science
Foundation. Z.Y. ETH Career Seed Grant SEED-12 19-1/1-004952-00.
Y.S. IMPRS-UFAST.
L.I. and R.S. DFG-EXC 2056-project ID 390715994



Hydrogen Spillover and Storage on Graphene with Single-Site Ti Catalysts

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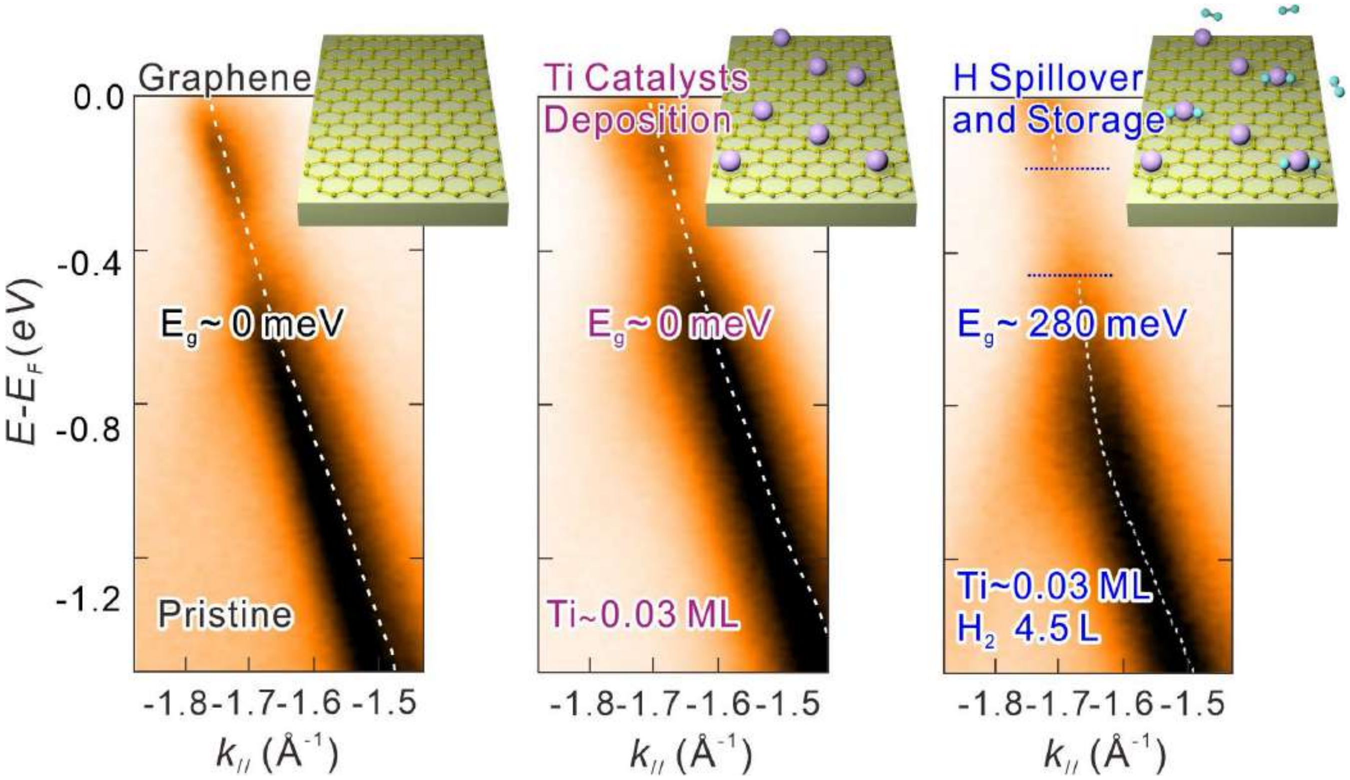
Hydrogen spillover and storage for single-site metal catalysts, including single-atom catalysts (SACs) and single nanocluster catalysts, have been elucidated for various supports but remain poorly understood for inert carbon supports. Here, we use synchrotron-radiation-based methods to investigate the role of single-site Ti catalysts on graphene for hydrogen spillover and storage. Our *in situ* angle-resolved photoemission spectra results demonstrate a band gap opening, and X-ray absorption spectra reveal the formation of C−H bonds, both indicating partial graphene hydrogenation. With increasing Ti deposition and H_2 exposure, the Ti atoms tend to aggregate to form nanocluster catalysts. Our results demonstrate how a simple spillover process at Ti SACs can lead to covalent hydrogen bonding on graphene, thereby providing a strategy for the rational design of carbon-supported single-site catalysts.


Graphene
Ti Catalysts Deposition
H Spillover and Storage
0.0
-0.4
-0.8
-1.2
E-E_F (eV)
E_g ~ 0 meV
E_g ~ 0 meV
E_g ~ 280 meV
Pristine
Ti~0.03 ML
Ti~0.03 ML
H_2 4.5 L
-1.8 -1.7 -1.6 -1.5
-1.8 -1.7 -1.6 -1.5
-1.8 -1.7 -1.6 -1.5
k_// (Å^-1)
k_// (Å^-1)
k_// (Å^-1)

Investigating liquid water with X-ray emission spectroscopy using XFEL

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The complexity of the hydrogen-bond network makes understanding the bulk water structures and properties an unsolved problem. Currently, water is assumed as a dynamical mixture of two local motifs (high-density (HDL) and low-density (LDL) liquid) near the liquid-liquid critical point.[1] However, direct observations of these motifs under ambient conditions are still missing. We present high-resolution resonant inelastic X-ray scattering (RIXS) results of liquid jet water under ambient conditions. The experiments have been performed at the SCS beamline of European XFEL that delivers <15 fs pulses around the oxygen K-edge. Figure 1A shows the spectra below the pre- (533 eV, blue) and post- (550 eV, orange) region. In both, features attributed to the three outer valence orbitals of water are visible: the $1b_2$ at ~520.8 eV, the $3a_1$ at ~524.8 eV, and the $1b_1$ at ~526eV.[2,3] While below the pre-edge excitation, the $1b_1$ presents one peak, with the post-edge excitation, the 1b1 splits in two bands, assigned to the HDL and LDL motifs.[2] Fluence-dependent measurements, reported in figure 1B, shows a relative decrease in intensity of the LDL peak compared to the HDL peak with increasing FEL fluence. Previous works explain this effect as a temperature-induced morphology change,[2] which are unlikely here due to the ultrashort XFEL pulses. Preliminary interpretations predict this as an ultrafast effect from ionized neighbouring molecules resulting in complex hydrogen bond interactions.

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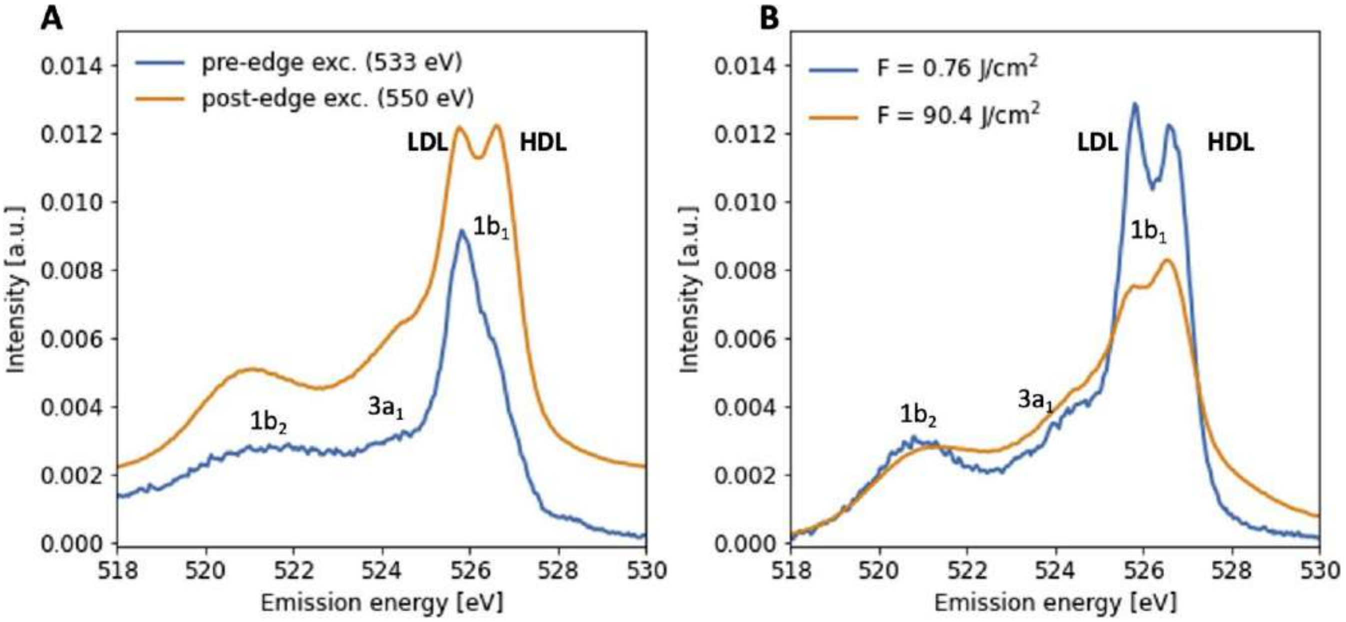

Investigation of the influence of methylammonium chloride on formation and properties of wide-bandgap hybrid perovskites using synchrotron radiation techniques

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Perovskites have been receiving great attention because they have excellent photovoltaic performance.[1] For tandem cell applications, Br-rich perovskites with a wide-bandgap are required. However, these compositions have greater compositional heterogeneity.[2] Methylammonium chloride (MACl, MA = $CH_3NH_3^+$) is often added to the perovskite precursor solution to improve optoelectronic properties and performance. However, the effect of MACl additive on Br-rich perovskites is poorly known.[3] For this, we characterized thin films of perovskites with different amounts of Br and MACl. Grazing-incidence wide-angle X-ray scattering (GIWAXS) and photoluminescence spectroscopy (PL) were measured simultaneously during the formation of perovskite films at Advanced Light Source synchrotron (Berkeley). The results allowed the establishment of a hypothesis for the formation of perovskite in the presence of MACl: Cl^- destabilizes the intermediate phases and favors the formation of the more crystalline perovskite phase initially rich in Br and Cl and with preferential orientation in the [001] direction. X-ray fluorescence (XRF) mapping at the Carnaúba/Sirius/LNLS beamline identifies changes in the distribution of elements by reducing the size of domains richer or poorer in Br of the samples produced with MACl. In summary, we showed the formation mechanism of wide band-gap perovskites in the presence of MACl and its effect on the distribution of halides on a sub-micrometer scale.

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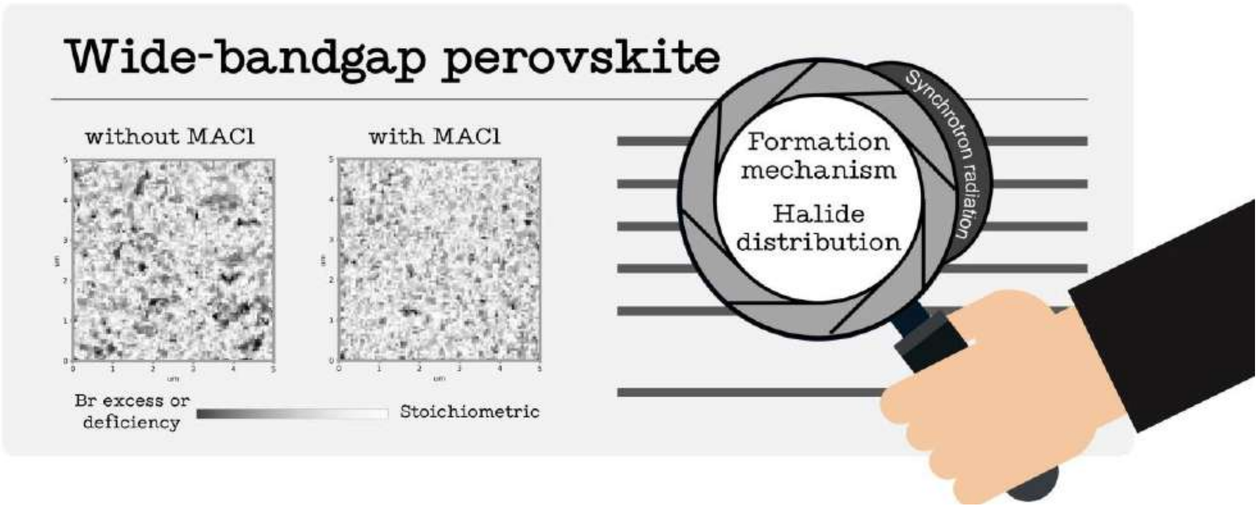
Wide-bandgap perovskite
without MACl
with MACl
Br excess or deficiency
Stoichiometric
Formation mechanism
Halide distribution
Synchrotron radiation

Pump-probe spectroscopy study of the ligand substitution reaction of chromium hexacarbonyl in 1-pentanol

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In the context of development of synthetic organic chemistry, transformative metal catalysts greatly improved the conditions for producing desired organic products and brought many advancements in the areas of medicinal chemistry, drug discovery and material sciences, among other areas [1]. With the discovery that organometallic compounds could act in selective activation without prior pre-functionalization, the often generated hazardous waste was minimized showing that inner-sphere C-H activation driven by metal bond functionalization represents an environmentally attactive tool in organic synthesis [3]. One of the first organometallic class to be throughly studied was the class of metal carbonyls. Chromium hexacarbonyl is a typical model system that helps us to understand the role of metal carbonyls as activator of organic reactions. The solubility of this apolar complex in organic solvents grants the complex a special spot in the group of catalysts for selective site activation. When excited in a MLCT transition, the unsaturated pentacoordinated species interacts with even the most inert of bonds as we will show in this work. Here, we aim to present the photosolvation of Cr(CO)6 in 1-pentanol solution using time-resolved x-ray absorption spectroscopy data. By analyzing the ligand O K-edge and metal Cr L3-edge, we aim to explore the photoreaction mechanism and discuss the indications of ligand rearrangement that are highlighted by the time-dependent absorption dynamics.

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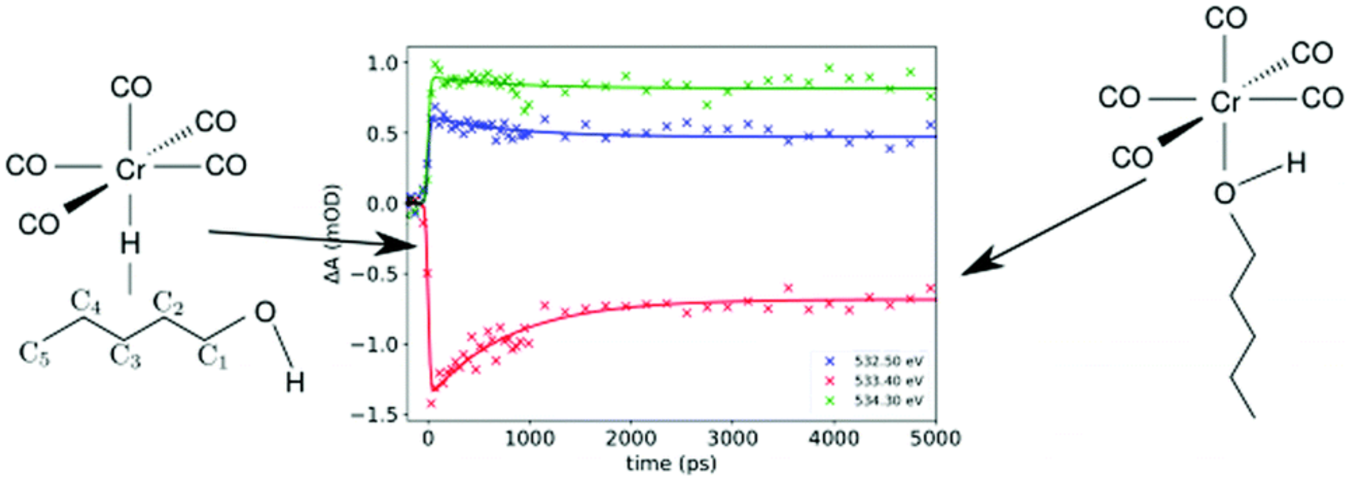
synchrotron radiation beamtime.



Synchrotron-based X-ray Photoelectron Spectroscopy (XPS) for probing the surface composition of a CoFe Prussian Blue Analogue catalyst with electrochemically formed vacancies

Rafael Lavagnolli Germscheidt[1], Túlio C. R. Rocha[2], Juliano Alves Bonacin[1]

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Prussian blue analogues (PBA - $M_{1(x)}[M_2(CN)_6]_{(y)}$,) stand out as catalysts for water oxidation (WO) due to their great performance in neutral pH. Although having a great activity, the low number of active sites is the main drawback, thus, the creation of vacancies is the best strategy to increase active sites and improve the catalyst activity.[1-3] X-ray Photoelectron Spectroscopy (XPS) allows the composition of a material to be determined, providing insights into the metals oxidation state.[4] Herein, we report a methodology to synthesize CoFePBA and promote the improvement of its properties on OER by electrochemically formed vacancies (ACoFePBA). Moreover, synchrotron-based XPS, performed at IPÊ beamline of the synchrotron light source Sirius, was used to probe the surface composition and Co and Fe speciation of the films, performed using different excitation energies and different depths in the surface. The results show that ACoFePBA has an outstanding activity toward the WO. XPS analysis shows the same general elemental composition, identifying Co 2p (782 eV), Fe 2p (708 eV), O 1s (531 eV), Sn 3d (485 eV), N 1s (397 eV), and C 1s (284 eV). However, it is possible to observe some differences when comparing the Co^{2+}/Co^{3+} and Fe^{2+}/Fe^{3+} composition, especially when looking at the results with different kinetic energies. We believe this can help us to have a better understanding of the material composition and can give insights on how this affects the catalysis.

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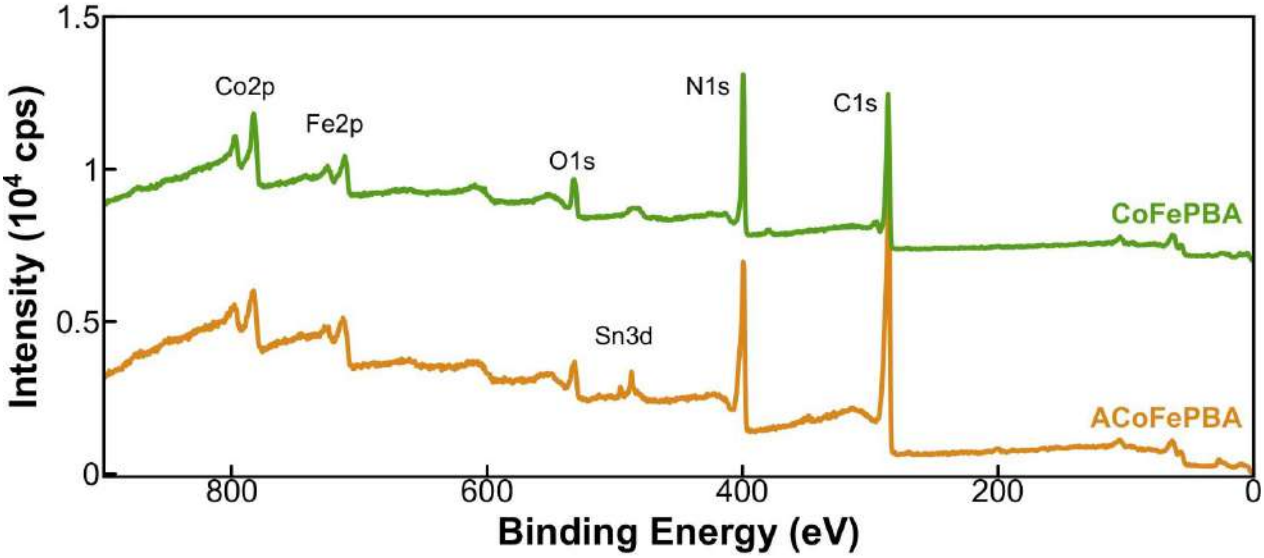

Unravelling excited-state dynamics in molecular dyads using ultrafast X-ray spectroscopy

Wojciech Gawelda[1], Michal Nowakowski[2], Tae-Kyu Choi[3], Marina Huber-Gedert[2], Jakob Steube[2], Aleksandr Kalinko[4], Dmitry Khakhulin[5], Frederico Alves Lima[5], Natalia Pierunek[6], Ahmet Kertmen[6], Jacek Kubicki[6], Matthias Bauer[2]

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The conversion of sunlight into chemical fuels is a key technology for a sustainable future. Hydrogen production via photocatalytic proton reduction with sunlight is a prominent example of this strategy. Base metal photoactive compounds are sustainable alternatives to their noble metal counterparts. Bimetallic assemblies of the later are often used for direct conversion of sunlight into chemical energy carriers like H_2. The transition to base metal dyads as active compounds is partially hindered by the s missing understanding of the working principle of such complexes, which is required to improve their photocatalytic performance. Therefore, more detailed investigation of the ultrafast photoinduced electron transfer is of utmost importance on the way towards fully functional base metal dyads.

Such an ambitious aim requires the knowledge driven design of photoactive complexes, which in turn relies on the application of cutting-edge spectroscopic methods. We will underline the advantage of employing ultrafast X-ray emission spectroscopy to obtain the transient electronic structure changes in transition metal-based photosensitizers and functional bimetallic dyads. We will report on our recent results investigating the novel family of Fe-Co molecular dyads using combined optical pump/ X-ray probe experiments at X-ray free electron lasers to track the electron transfer dynamics in a bimetallic assembly, connecting an Fe photosensitizer to a Co catalyst.

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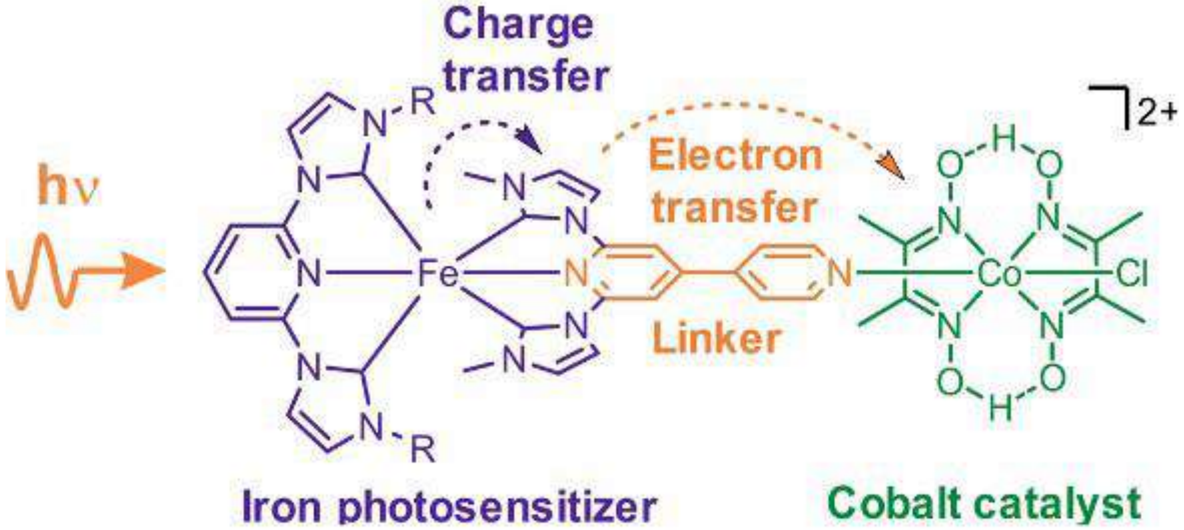
Charge transfer
hν
Electron transfer
Linker
2+
Fe
Co
Cl
R
Iron photosensitizer
Cobalt catalyst

X-ray nanoscale imaging and spectroscopy of perovskite oxides for electrocatalysis

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With the current world crisis related to global warming, pollution and depletion of fossil fuels, the need for sustainable energy sources are already a set reality. Electrocatalysis is a field that can majorly contribute with new energy sources; however the widespread usage of noble metals can economically hinder its wide application [1]. In this context, perovskite oxides are gaining attention as non-rare metal catalysts which have already been used for the oxygen evolution reaction (OER) [2] and biomass electro-oxidation (such as methanol and glycerol) [3].

However, since the overall objective using these materials is their application in energy-related devices (electrolyzers and fuel cells), we must understand the mechanisms by which their operate to improve the efficiency of the electrochemical process involving them. In order to do that, herein we analyzed these materials in situ using nanoimaing and nanospectroscopy to account for heterogeneities at the nanoscale, which are crucial for electrocatalysts [4].

We performed X-ray fluorescence and X-ray absorption maps to image the material morphology and oxidation state distribution. Moreover, we tracked the changes in the B metal site oxidation state using XAS during glycerol oxidation using perovskite oxides with different compositions.

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Acknowledgments

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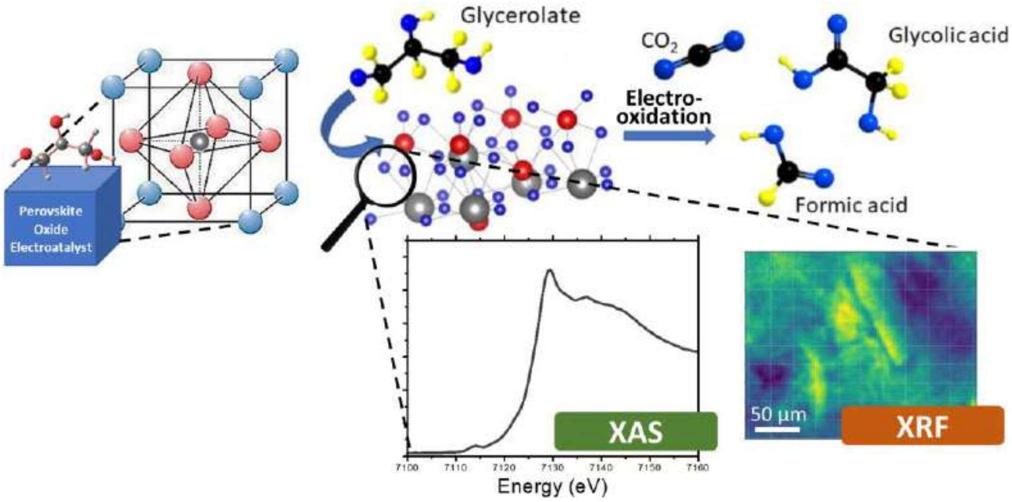

Poster Presentations

Automated alignment of optics and sample precession correction at the IPE beamline of Sirius

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The IPE beamline at the Sirius synchrotron light source is currently in the commissioning phase and is set to become a vital tool for material research. To optimize alignment tasks and reduce downtimes and errors, it is necessary to develop automated procedures. One example is automating the beam switch between the two experimental stations RIXS and XPS. We developed an iterative method based on optimizing the photon flux through the exit slit by making angular scans the mirror for successively smaller slit apertures. However, due to the long distance between the mirror and the exit slit, the mechanics of the mirror translation, based on the sliding of large granite bases, introduced significant errors in the mirror

Acknowledgments
This work was developed with the support of the IPE group team.

COMMISSIONING AND FIRST EXPERIMENTS AT THE XPS/IPÊ ENDSTATION

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The soft X-ray IPÊ (Inelastic and PhotoElectron spectroscopy) beamline at Sirius/LNLS (100 to 2000eV) serves two endstations: XPS and RIXS. The XPS endstation has been operating for technical commissioning since October 2021 and opened to users in June 2022.

The spectroscopies available in the XPS endstation are X-ray Photoelectron (XPS), using a Specs Phoibos 150 electron analyzer with 9 channeltrons, and X-ray absorption (XAS) measuring in different detection modes (Total Electron Yield, Fluorescence Yield, and Auger yield). Both techniques (XPS and XAS) allow for studying electronic and chemical composition in materials. In addition, the endstation is equipped with a flood gun for XPS analysis in non-conductive samples and argon sputtering.

The beamline’s current performance has reached the following parameters: photon flux of 3.3×10^{11} ph/s @ 930 eV and focus size close to $16\times8\ \mu m^2$.

The upcoming presentation will show technical commissioning results and noteworthy scientific cases that were studied using the XPS endstation. By sharing these results, we hope to demonstrate its capabilities and potential for further scientific inquiry.

EBL2 Beamline: A Cutting-Edge EUV Research Facility for Semiconductor Industry using assisted discharge-produced plasma (LDP) source

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TNO is a leading research organization in the semiconductor industry, driving innovation and technological advancements.
EUV lithography machines have sensitive optical components that may be affected by plasma interactions. The EBL2 beamline reproduces EUV lithography-relevant conditions, featuring a high-brightness EUV source that provides accelerated tests for next-generation lithography and investigates EUV-induced plasma phenomena.
The facility offers an efficient alternative to synchrotron sources, capable of handling a diverse range of samples, including EUV photomasks and multi-layer mirrors. The EBL2 beamline

References

High-radiance LDP source: clean, reliable and stable EUV source for mask inspection - Yusuke Teramoto
On the opportunity of liquid metal rotated anode for high brightness X-ray source - A. Ushakov
EBL2: An EUV (Extreme Ultra-Violet) lithography beam line irradiation facility - Herman Bekman

Acknowledgments

Teramoto, Y , Ushakov, A., Bekman, H., van Veldhoven, J., Wu, C.-C., van Putten, M., Storm, A., Meijlink, J., Molkenboer, F., and the all EBL2 team

Efficacy of a light-emitting diode at 280 nanometers on Staphylococcus aureus colonies

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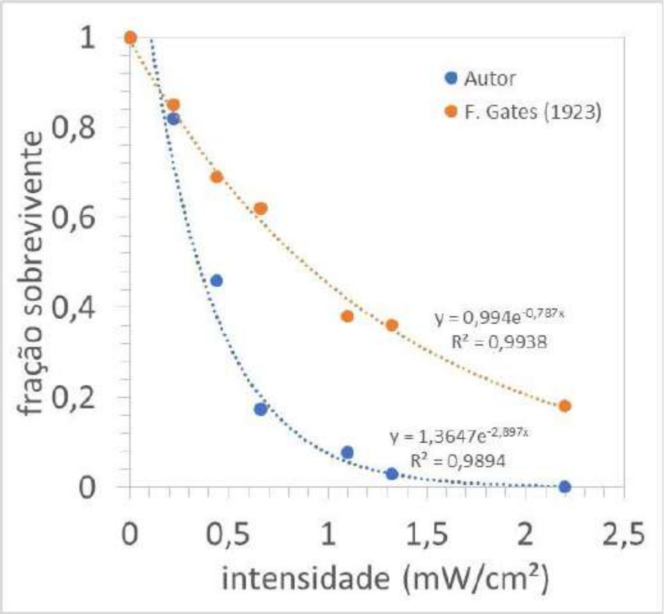
Ultraviolet Germicidal Irradiation (UVGI) involves utilizing ultraviolet (UV) wavelengths within the germicidal range (200-320 nm). The 200-280 nm range within UVGI, known as UVC, is highly effective in germicidal applications due to its ability to damage the genetic material of microorganisms. The common literature claiming the effectiveness of the germicidal peak at around 260-265 nm, due to actions on bacterial DNA, is not entirely accurate since it is not the only deleterious effect. Proteins exhibit a UV absorbance peak at 280 nm due to the absorption of the amino acids' tryptophan and tyrosine. Therefore, LEDs emitting light at 280 nm could potentially damage proteins, increasing germicidal efficacy, despite not directly acting on DNA.

The objective of the present study is to determine a set of coefficients for the bactericidal action of UVC at 280 nm. Previous studies conducted by Gates (1929) established a single stage decay model for microbes exposed to UV irradiation as: $S = e^{-kD}$, with S = Survival fractional (%), k = UV rate constant (cm^2/mJ), and D = UV exposure dose (fluence), mJ/cm^2, for S. aureus with UVC at 266 nm. Although less energetic, our studies reveal a k= -2,899, much slower than suggested by Gates, implying a faster decay and a rapid disinfection.


1
0,8
0,6
0,4
0,2
0
fração sobrevivente
0
0,5
1
1,5
2
2,5
intensidade (mW/cm²)
Autor
F. Gates (1923)
y = 0,994e-0,787x
R² = 0,9938
y = 1,3647e-2,897x
R² = 0,9894

Possibilities for ARPES Using the 4th Generation Brazilian Synchrotron – the SAPE Experimental Station at Sirius

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Angle-resolved photoemission spectroscopy (ARPES) is a powerful technique to probe the electronic structure of materials based on photoelectric effect. Such experiments provide the direct measurement of the kinetic energy and emission angle distributions of the emitted electrons from a crystalline solid submitted to ultraviolet radiation. This is a fundamental tool to study topological and two-dimensional (2D) materials, contributing to the understanding of their properties[1]. The experiment is performed in an ultra-high vacuum (UHV) environment to prevent the scattering of emitted electrons and protect the surface of the sample[2]. In addition, special care must be taken with sample handling to avoid surface contamination by adsorption and oxidation processes. As a solution to the scientific community, SAPE beamline will provide a fully equipped facility to perform ARPES measurements with in-situ sample preparation capability. The beamline experimental station is composed of a set of UHV chambers where the samples will be incorporated, handled and prepared before the ARPES experiments. In this presentation, we will show the possibilities for ARPES experiments at SAPE experimental station using a high-flux synchrotron ultraviolet radiation produced by the brazilian 4th generation synchrotron light source – Sirius at LNLS. We will provide details about the instrumentation, sample preparation processes and endstation parameters to conduct those experiments at SAPÊ.

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Sample environment for extreme thermodynamic conditions integrated with X-ray technique at EMA Beamline

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Achieving thermodynamic quantities boundaries such as pressure, temperature and magnetic field is important for a wide range of research fields in both fundamental and applied science. In this context, the Extreme condition Methods of Analysis (EMA) beamline at Sirius [1], a hard X-ray beamline (5.5-30 keV), shines in delivery a versatile sample environment to integrate extreme thermodynamical conditions with X-Ray Diffraction, Spectroscopy and Imaging techniques coupled with visible Raman spectroscopy. To explore extreme combinations of pressure, temperature, and magnetic field, specialized instruments must be developed or adapted. At EMA, we can achieve hydrostatic pressures up to 300 GPa using Diamond Anvil Cells (DACs). We have a commercial piezocell to provide uniaxial strain and an in-house device to apply biaxial strains on flexible substrates. We can cover temperatures from 2 K to 300 K using a DAC compatible He4 cryostat, and temperatures down to 0.3 K can be achieved by a He3 evaporator insert. For high temperatures, we have available a double-sided laser heating setup (1000K-8000K). Further, a DAC compatible filament lamp furnace (300K-1000K) is being developed. In terms of magnetic field, we have both an electromagnet (max. 1T) and a superconducting magnet (max. 11T). This presentation aims to showcase the sample environment instrumentation available at the EMA beamline and to encourage open discussions with the community about new developments for the future.

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Status of Sirius Carcará-X Diagnostic Beamline

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Carcará-X is a diagnostic beamline of the temporal structure and emittance of the Sirius electron beam. In its optical design, the beamline uses a toroidal multilayer mirror that refocuses 1:1, with 11 KeV energy emitted from the source (magnetic dipole). In the focal position, the beam has micrometer dimensions. By checking such dimensions, it is possible to continuously analyze the status of the Sirius beam through a DVF (Beam Verification Device, in Portuguese).

We report recent activities of commissioning and performance on Carcará-X. diagnostic beamline at Sirius.

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Acknowledgments

We would like to thank all technical Groups of Sirius.

Temperature control sample enviroment comissioning for RIXS endstation at Sirius

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Resonant inelastic X-ray scattering is a photon-in/photon-out technique that measures the energy and momentum change of photons scattered by a sample. The energy and momentum loss in the inelastic process leads to intrinsic excitations inside the material under study, providing detailed information about the electronic structure of the material. The RIXS endstation at CNPEM consists of an in-house developed soft X-ray spectrometer connected to a main chamber with a differentially pumped rotatable flange that allows continuous rotation under ultra-high vacuum. The high-precision manipulator with 4 axes (X, Y, Z, Rz) allows for the positioning of samples in the X-ray beam and rotation to control the momentum transfer direction. To carry out more challenging experiments, it is necessary to develop sample environments that allow control of the thermodynamic variables of the sample (temperature, strain, fields), as well as rotation on the x and y axis. Since these are not commercial instruments, it is imperative to design, build, and characterize each enviroment. In this work, we report the commissioning of a cryogenic insert based on a commercial open-cycle cryostat using a transfer line, both from ColdEdge, and controlled by a LakeShore 336. We will show the design and commissioning results, discuss the current limitations, including temperature control and overshoot, as well as future upgrades. Furthermore, we will discuss the possible implementation of other environments.

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I would like to extend my sincere thanks to the Brazillian Center for Research in Energy and Materials (CNPEM) for the internship at the IPÊ beamline at Sirius. I am also grateful for the guidance I recieved from everyone at the beamline, specially Felipe Custódio, Luiz Borges and Flavio Vincentin.

The SABIÁ soft X-ray beam line at SIRIUS

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The SABIÁ beam line is at SIRIUS is a facility optimized to study magnetism and magnetic materials employing soft X-rays. It covers the energy range from 100 to 1600 eV, with full polarization control, allowing users to access the L_{23} absorption edges of 3d transition metals and M_{45} absorption edges of lanthanides. The beam line offers two end stations. One branch is equipped witha superconductor magnet which can apply up to 9 T along the beam, for X-ray Magnetic Circular Dichroism measurements, or 4 T perpendicular to the beam for X-ray Magnetic Linear Dichroism. The magnet allows to fast magnetic field sweeping, optimizing the use of the beam time. In this end station the sample temperature can be controlled from 5 up to 450 K.

A second branch is equiped with a Photoemission Electron Microscope (PEEM) which allows to obtain images of the sample surface based on contrasts given by the X-ray absorption process. In this case, using dichroic signal it is possible to obtain details of the magnetic domais at the sample surface with resolutions down to few tens of nanometers in most cases.

The SABIÁ beam line can receive thin films from the Laboratory for In-Situ Growing - LCIS, another facility at SIRIUS, using vacuum suit cases to avoid sample surface contamination.

The SABIÁ beam line is under final phase of its commissioning and should be available for the user community along 2023.

Using Data Science Techniques to Analyze SAXS patterns.

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SAXS is a useful technique to analyze the physical structure of colloids formed by proteins, polymers, and nanomaterials, among others[1]. The success of SAXS lies in the ability to choose the appropriate mathematical model that allows obtaining physical information about the analyzed system [2] [3]. Nowadays, with the advance of informatic tools such as Machine Learning (ML), Data Science (DS) and Artificial Intelligence (AI), it is possible to obtain physical information from data by comparing with thousand of SAXS results by applying ML and DS. By this way, in this work the evaluation of metaheuristic algorithms: Particle Swarm Optimization (PSO) and Global Best Harmony Search (GHS), as an alternative to the adaptive genetic algorithm of discrete variables (AGA) used in the "Computational Reverse Engineering Analysis for Small-Angle Scattering Experiments" (CREASE) is presented. CREASE is a method recently developed to analyze results from SAXS experiments [4], [5]. Results show that it is possible to reconstruct the morphology of the scattering object by analyzing a SAXS curve, using the appropriate mathematical model (size distribution, form factor and structure factor) and by applying CREASE to validate results using data science techniques.

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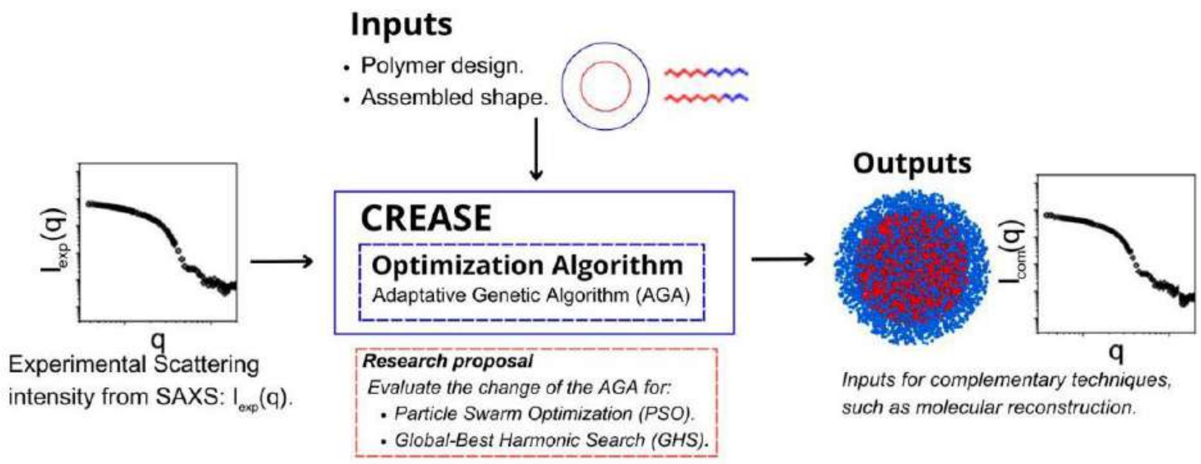
Acknowledgments

The authors would like to thank the University of Cauca



CREASE workflow, case study: amphiphilic polymer chains in self-assembled micelles [5].

X-ray diffraction and reflectometry in a simple in-operando Lead-acid Electrochemical Cell

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An *in-operando* analysis, based on X-ray diffraction and X-ray reflectometry, on a lead-acid electrochemical cell is proposed. The electrochemical cell is designed to be simple and inexpensive, consisting of a 3D printed structure (Espinola *et al.*, *in press*), with a rectangular lead electrode, a platinum counter electrode, a mercury/mercurous sulfate (Hg/Hg_2SO_4) reference electrode and polypropylene windows. The cell works by applying a constant current (galvanostatic) and by measuring the potential response using a low-cost potentiostat. The entire process will be followed by X-ray diffraction and reflectometry. Mixing these techniques, it is possible to follow the evolution of the corrosion/discharge product in different transient stages, from very thin films to $PbSO_4$ crystal growth. For this, we always start from the same initial condition, applying an electrochemical cleaning method to eliminate mechanical polishing products on the Pb. The correlations between galvanostatic electrochemical processes and x-ray results at the $Pb/PbSO_4/H_2SO_4$ interface will be presented, which will help in understanding the mechanisms in lead acid batteries.

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Damage induced by synchrotron radiation in sulfur containing biomolecules: a spotlight on oxidized glutathione (GSSG)

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Biomolecules in general are very sensitive to synchrotron radiation, undergoing deep chemical transformations under relative exposure [1]. The samples studied in this work are sulfur containing biomolecules: oxidized (GSSG) and reduced glutathione (GSH). In GSH, sulfur is present in a reduced form as a thiol (-S-H). In molecules like GSSG, sulfur is present in an oxidized form (-S-S-). Due to its oxidation form, GSH spectra present only one peak associated with the S1s → σ* (S-C) transition and were used as reference. GSSG spectra present two peaks attributed to S1s → σ* (S-S) and S1s → σ* (S-C) transitions [2]. The samples were prepared in two distinct forms: solid and liquid solution for comparison purposes and analyzed at the Brazilian Synchrotron facility (LNLS).

In GSSG solid samples no significant alteration was seen in the NEXAFS spectra. In GSSG liquid solution, however, it is possible to verify drastic peak changes around the S1s edge. After continuously collecting ten spectra of GSSG it was not possible to observe the two clearly resolved peaks previously observed in the first spectrum, assigned to S1s → σ* (S-S) and S1s → σ* (S-C) transitions. In order to confirm structural modifications in the biomolecules caused by synchrotron radiation, we have taken advantage of the NEXAFS technique. The photoabsorption spectra obtained around the sulfur K-edge show clear modifications which can be related to breakage of disulfide bridges in GSSG, an essential molecule.

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Acknowledgments

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How does solvation affect molecular ultrafast dissociation?

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X-ray-induced molecular fragmentation is an important process in radiation chemistry and radiation biology. One such phenomenon is molecular ultrafast dissociation (UFD), in which a core-excited molecule dissociates during the core-hole lifetime of a few femtoseconds.

UFD has been extensively studied for gas phase molecules via the core-hole Auger decay [1,2], which may occur anytime throughout the dissociation process.

For the few cases where UFD has been studied in both gas phase and condensed phase, the effects go in opposite directions.

Here we have aimed to investigate to how solvation affects UFD in chloroform. The resonant Auger spectrum (RAS) was recorded as a function of photon energy around the Cl2p edge as shown in figure 1. In the case of the gas phase, the atomic states appear as narrow peaks, while broad features are associated with “non-dissociated” final states.Although these characteristics in the liquid cannot be seen, we can see corresponding peaks at the resonance energy. The relative intensity of these peaks compared to the features from non-dissociative states is clearly lower than in the gas phase, indicating a suppression of the dissociation in the condensed phase for chloroform. The detailed analysis is in progress, and we hope that the knowledge obtained from model systems such as this can be transferred to more complex systems of relevance to radiation chemistry and radiation biology.

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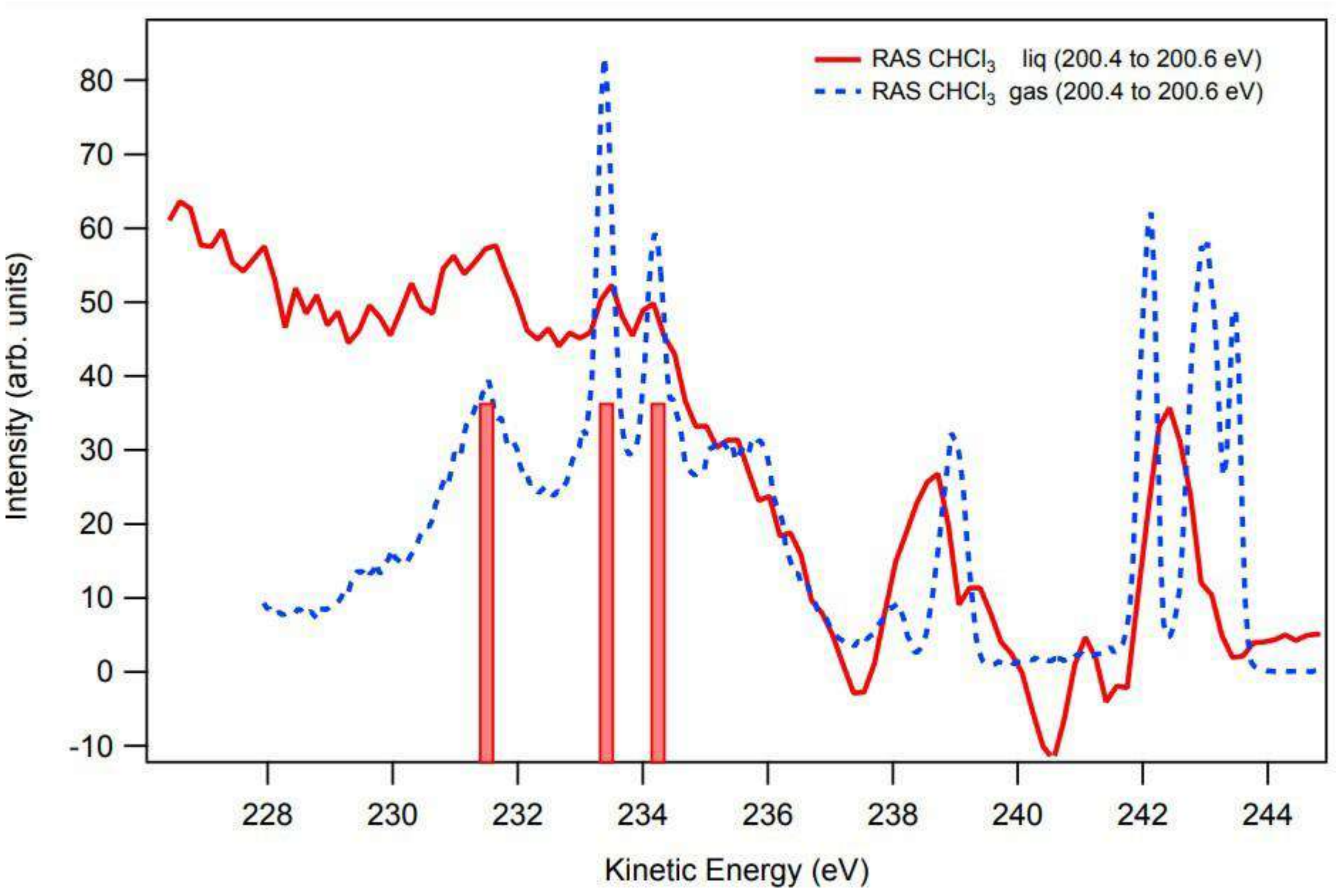
RAS $CHCl_3$ liq (200.4 to 200.6 eV)
RAS $CHCl_3$ gas (200.4 to 200.6 eV)
Intensity (arb. units)
80
70
60
50
40
30
20
10
0
-10
228
230
232
234
236
238
240
242
244
Kinetic Energy (eV)

Impact of the XFEL shot-to-shot variation onto soft X-Ray pump-probe studies of attosecond charge migration in molecules

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Recently, the production of sub-fs soft X-Ray pulses became possible at the LCLS X-Ray free electron laser (XFEL) [1]. These pulses exceed the intensity of high harmonic generation sources by many orders of magnitude, allowing the first realizations of attosecond nonlinear X-Ray spectroscopies of electronic dynamics. However, the pulses, being generated by self-amplified spontaneous emission, bear a stochastic shot-to-shot variation resulting in different induced charge dynamics. Hence, measuring transient spectra averaged over an ensemble of pump pulses may diminish the dynamical features.

In this contribution we show by means of first-principle CASPT2 and static-exchange B-spline DFT calculations, explicitly modeling the molecular bound and continuum states, that the shot-to-shot variation in an ensemble of 100 sub-fs soft X-Ray pulses, obtained from simulating the XFEL at the LCLS, reduces the charge fluctuation amplitudes in the p-aminophenol molecule by no more than 35% [2]. We found this to be much weaker than the influence of the initial nuclear wave function that we represent by an ensemble-average over molecular geometries, resulting in a damping of the charge dynamics within the first 3 fs following the pump to about 20% of their initial amplitude. These results suggest that attosecond soft X-Ray spectroscopies at XFELs are not restricted by the inherent shot-to-shot variation and may be reliably used to investigate early stage charge dynamics.

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Acknowledgments

Submission on behalf of the LCLS Attosecond Campaign Collaboration:

https://lcls.slac.stanford.edu/depts/amo/asc

Ion-neutral coincidence experiments to characterize the photofragmentation of cyclo-dipeptides

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Mass spectrometry in gas phase is a powerful tool to shed light on the molecular composition and the chemical-physics processes taking place in several environments from the deep space to the human body. The aim of the technique is to unveil the fragmentation paths resulting from the ionization of the target molecule. This is not a simple task because of the numerous undetected neutral moieties. Ion-neutral coincidence experiments are a powerful tool to provide information on all the actors of a metastable fragmentation, even when subsequent processes take place. Here we show that a time-of-flight spectrometer can enable also the detection of the neutral moiety in coincidence with the charged partner.

The technique is applied to the study of the VUV fragmentation of three cyclo-dipeptides (c-Alanine-Alanine, c-Glycine-Alanine and c-Glycine-Glycine). As an example, the ion-neutral coincidence map for the fragmentation of the cyclo-alanine alanine (cAA) molecule1 by VUV radiation is shown in Fig. 1. The sequence of successive fragmentations starting from the parent ion as well the existence of competing channels are clearly identified in the map.

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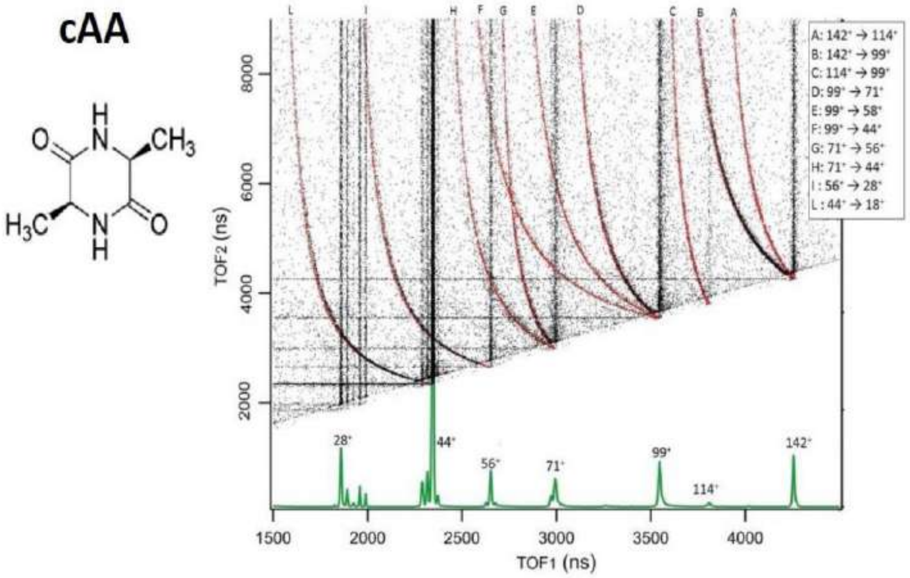

Figure 1. The mass spectrum (green) and 2D coincidence map obtained of the VUV photofragmentation of cAA molecule. The traces due to ion-neutral coincidences of metastable fragmentations are highlighted in red while the involved ionic moieties are reported in the inset.

Small angle X-ray scattering applied in the study of drug delivery systems encapsulating lysozyme and curcumin

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The study of drug delivery systems has gained a lot of attention in recent years due to the advantages of using such systems, such the possibillity of controlling the amount of drug delivered to the recipient organism. Cubosomes, cubic lipidic nanoparticles, show promise within this perspective. The objective of this work is to understand how the interaction of lysozyme and curcumin occurs within the nanoparticle, since they have different characteristics such as hydrophilicity and hydrophobicity, respectively. Through the curves obtained by the analysis of the Small Angle X-ray Scattering data in the MAX IV synchrotron, it is possible to understand that both drugs do not significantly alter the structure of the cubosome when compared to the blank cubesome, indicating that the interaction between both is minimal. This result is positive because the drugs occupy different spaces inside the cubosome due to their characteristics. Soon, these results will be used for comparison with other techniques such as Transmission Electron Microscopy and Nanoparticle Tracking Analysis.

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CNPEM, USP, CAPES, FAPESP, CNPQ

Study of Encapsulation of Antineoplastic Drugs in Nanostructured Systems: Structural Characterization and Synergistic Effect of Drugs

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Nanotechnology field has been growing in the past decades, improving studies of several compounds. Among these technologies, the *drug delivery* systems are being largely used, whose objective is increase pharmaceutical substances efficacy, and this may includes a more selective distribution within the sick organism, the molecules liberation time fine tuning and/or attenuation of adverse effects. To make this possible, drugs are nanoencapsulated within synthetic origin or biodegradable structures, necessarily compatible with the active principle. Among the nanoparticles responsible for this systems are cubosomes, which are complex nanostructures that successfully encapsulate hydrophilic and hydrophobic actives. The main objective is to study the effect of the antineoplasic actives against cervical cancer cells (HeLa) and human epidermal keratinocyte (HaCat), the synergic/antagonic effects of drugs, cubosomes synthesis and characterization for further encapsulation of actives inside them. The chosen molecules are cisplatin, vemurafenib and curcumin. In this research project, we will broaden knowledge of antineoplastic activity of these compounds, testing them on HeLa and HaCat cells, quantifying the post-exposure cell viability. The cubosomes were synthesized with phytantriol and tested by dynamic light scattering (DLS), nanoparticle tracking analysis (NTA), small angle x-ray scattering and cell viability test.

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Sub-micrometer X-ray imaging with a spherical multi-crystal Laue monochromator: a trial characterization with 3D printed parts

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Hard X-ray imaging with single spherical Laue crystal has been studied either, theoretically [1] and experimentally [2]. Polymer-based substrates have been used for mounting cylindrical bent analyzer crystals [3] and multi-crystal spherical analyzers [4] for spectroscopy applications. In this work, we show the project and characterization of a short-working distance spherical multi-crystal Laue Si 220 monochromator (curvature radius of 62.5 mm) mounting on a 3D printed convex-concave substrate to work at 8.4 keV (WLα_1) for sub-micrometer X-ray imaging purposes (Fig. 1). The characterization was carried out with a Microfocus X-ray source (**Kevex** PXS5-927) at 44 kV and 54 mA (X-ray source size with diameter of 5 mm) and includes multi-crystal misorientation and thickness requirements, thermo-mechanical stability, focus size and image acquisition. The use of such a device as focusing optics for coherent diffraction imaging purposes is envisaged.

Fig. 1 (a) Convex-concave substrate design. (b) Mounting of the multi-crystal Laue Si 220 monochromator on the 3D printed convex-concave substrate. (c) Alignment procedure of the central crystal with the microfocus X-ray source and a collimator. (d) Schematic representation of the focus size and image acquisition characterization by using the microfocus X-ray source without the collimator.

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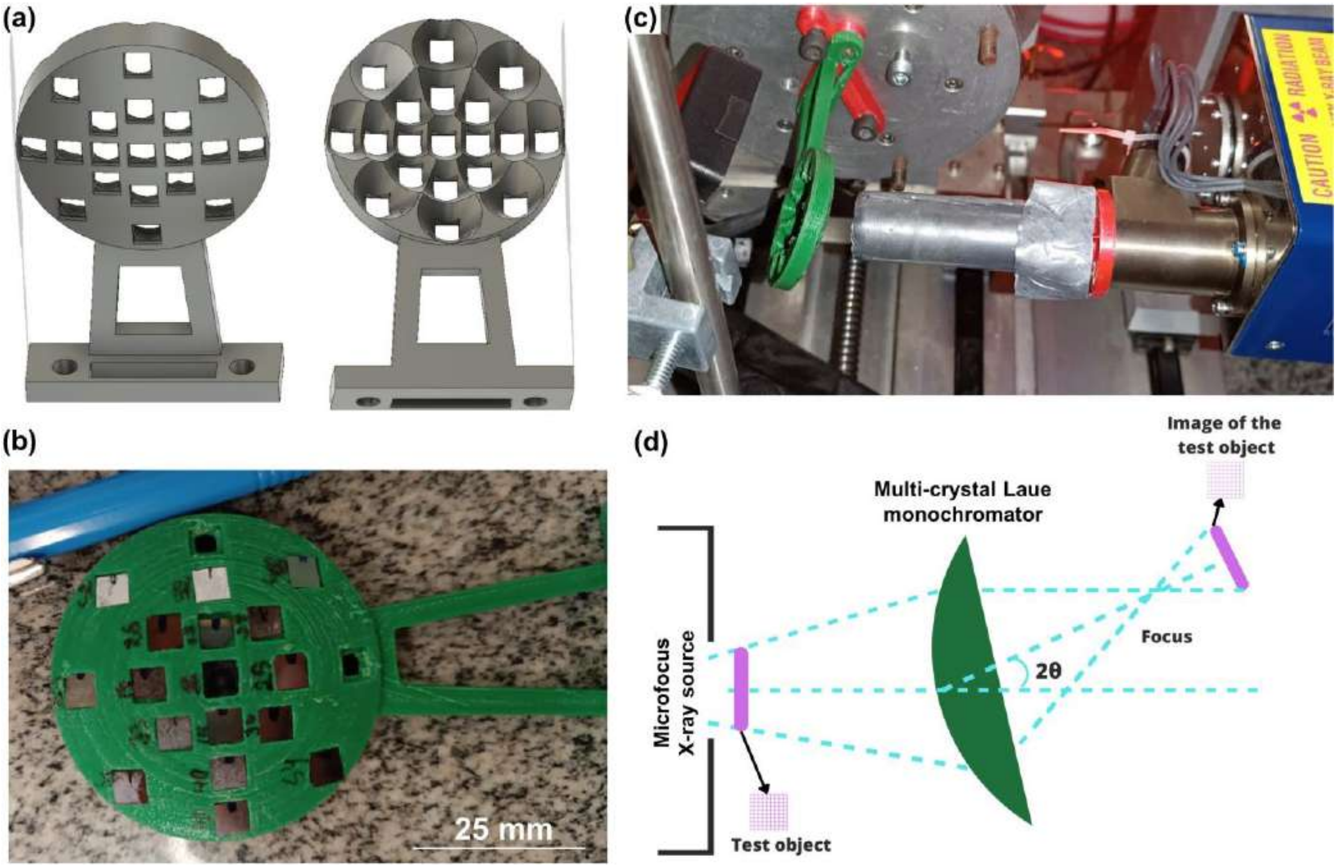
(a)
(b)
25 mm
(c)
CAUTION RADIATION
(d)
Image of the test object
Multi-crystal Laue monochromator
Focus
2θ
Microfocus X-ray source
Test object

Surface structure characterization of Fe nanoparticles grown on strontium titanate (100) by x-ray photoelectron diffraction

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The surface composition and structure of Fe nanoparticles (NPs) grown on strontium titanate (100) single crystal were evaluated by x-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and x-ray photoelectron diffraction (XPD). The (1x1) reconstructions of Fe NPs on $SrTiO_3$ (100) surface was characterized by XPD. The comparison between the experimental and theoretical XPD results that used multiple-scattering calculation of diffractions (MSCD) simulation combined with the genetic algorithm suggests that the nanoparticles grow with bcc-type packing.

Symmetry breaking in core-valence double ionisation of allene

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By combining an electron-electron coincidence technique with the use of soft X-radiation, we have measured a double ionisation spectrum of the allene molecule in which one electron is removed from a C1s core orbital and one from a valence orbital, well beyond Siegbahn's established X-ray electron spectroscopy method. Allene, which in its neutral form belongs to the D2d symmetry point group, is a highly interesting molecule both from a fundamental and from an applied point of view. Whereas its electronic structure in singly ionised form is well understood since the 1970's, not much is known until today about its doubly ionised form especially when an inner shell/core electron together with an outer shell/valence electron is removed. The core-valence double ionisation spectrum shows the effect of symmetry breaking in an extraordinary way when the core electron is ejected from one of the two outer carbon atoms. To explain the resulting spectrum we have implemented a new theoretical approach combining the benefits of a full self-consistent field approach with those of perturbation methods and multi-configurational techniques, thus establishing a powerful tool to reveal molecular orbital symmetry breaking on such an organic molecule, going beyond Löwdin's standard definition of electron correlation.

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XPS Study in situ of the Diluted Perovskite Nanocrystals Surface's Stability and Stoichiometry

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Here we present an investigation of these Lead-Halide Perovskites Nanocrystals (NCs) from two synthetic methods: Protesescu et al. [1] and Yassitepe et al. [2]. NCs showed slow colloidal and phase stability in the first method. The labile bond nature of the OLA+, as well as a non-bind nature of the OA/oleate species, are pointed out as responsible for the low colloidal and phase stability of perovskite NCs. Thus to solve these problems Yassitepe et al was developed named as Amine-free where only oleic acid was used as a surface ligand. Although the improvement in the colloidal stability of Amine-free CsPbX3 NCs seems to be related to the absence of OLA+ species on the NCs surface, there is still a lack of surface chemistry for the material obtained under this condition. So far only the OLA+ method has been studied by X-ray electron spectroscopy (XPS) applied on solid samples. In this work we employed XPS microjet study of perovskite NCs diluted in a mixture of toluene and hexane aiming to shed light on the surface chemistry of the amine-fee CsPbBr3, providing valuable information that will benefit the development of new experimental strategies that can enhance nanoparticle stability. In addition, we introduce experimental evidence supporting that not only Cs are substituted but also Br atoms are substituted in either of the two syntheses. Along with DFT calculations and high-resolution electron microscopy to unambiguously access the surface structure of the NCs.

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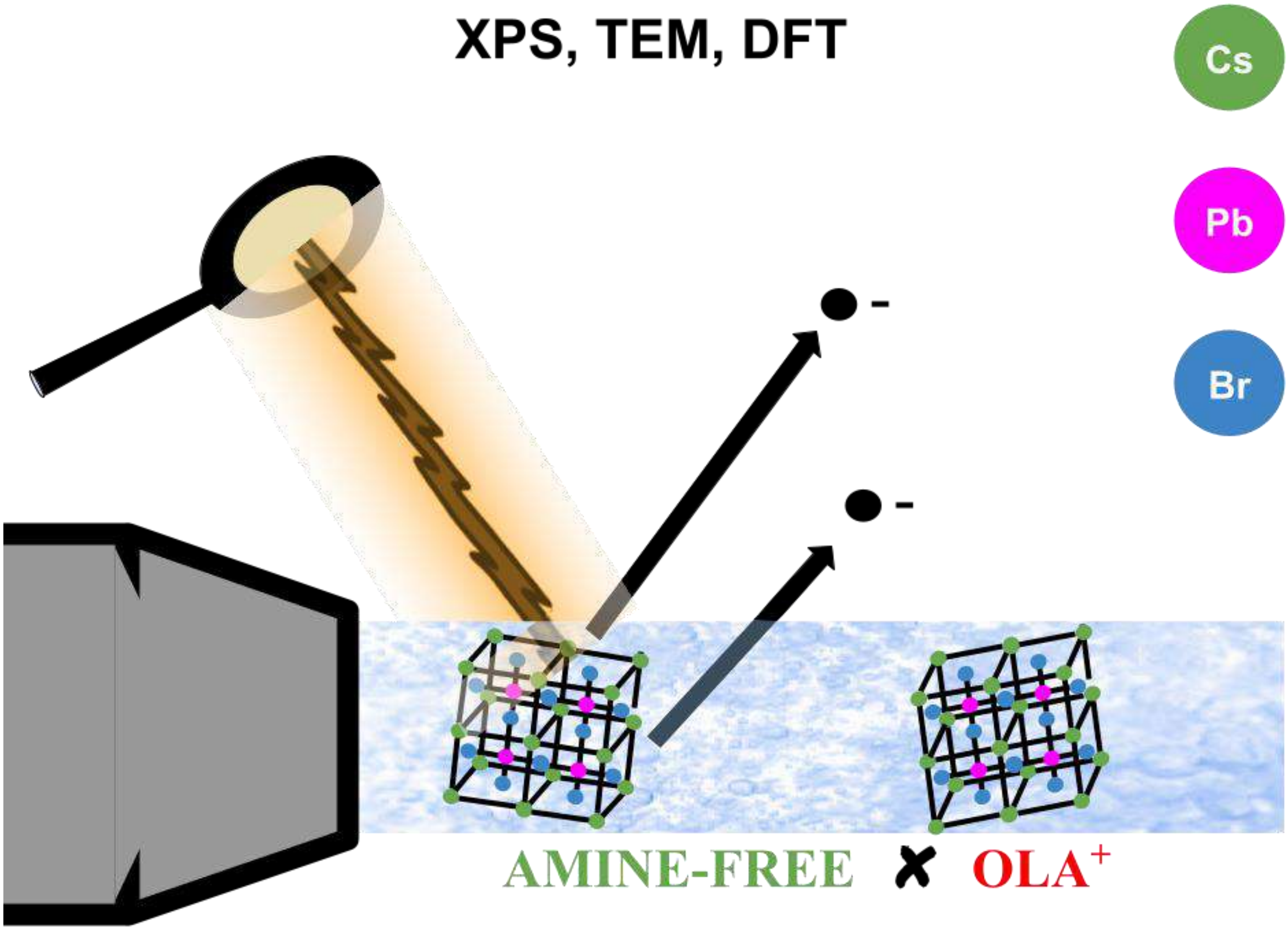

Atomic and electronic structure of vicinal Ag(977) surface

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We conducted a comprehensive investigation of the Ag(977) vicinal surface using various techniques such as low energy electron diffraction (LEED), scanning tunneling microscopy (STM), angle resolved photoemission spectroscopy (ARPES), and ab initio calculations. Our findings show that the Ag atoms located at the step edge undergo an inward relaxation, as expected for this type of vicinal surface. Moreover, we observed an anisotropic electronic dispersion around the Γ point, which strongly suggests the presence of a two-dimensional electron gas (2DEG) interacting with the potential barrier of the superlattice.We also studied the band structure of the surface and bulk-like atoms, as well as the closure of the L-neck gap and the presence of minigaps in the conduction band due to a band-folding effect. Comparing the contributions of the surface atoms in Ag(111) with those in Ag(977), we found that the surface atoms in the latter have a significantly higher mean contribution to the band structure.

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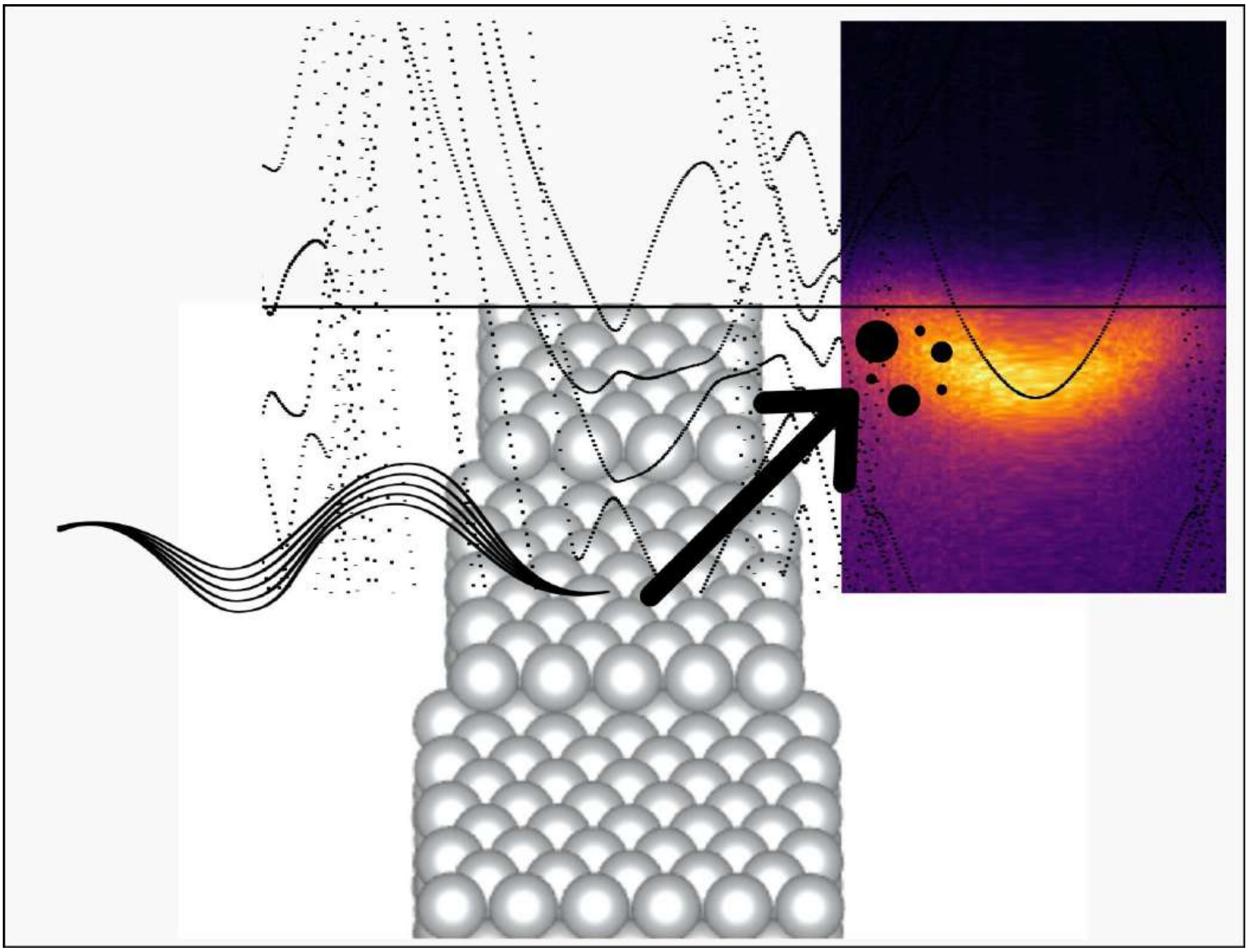

Characterization of fluoroperovskites synthesized via microwave-assisted hydrothermal method

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The NaMgF3 (NMF) belongs to fluoroperovskite family although presents an orthorhombic structure. This happens because the traditional cubic perovskite structure is distorted when A and B atoms differ significantly in ionic radii size. NMF is traditionally obtained via solid-state synthesis that produces unnecessary contamination by oxygen [1]. In this work, undoped and Eu-doped NMF samples were synthesized by microwave-assisted hydrothermal method (MAHM) that has produced fluorite compounds with low oxygen and hydroxyl contamination, short synthesis time and low synthesis temperature. The crystal phase was confirmed via X-ray diffraction measurements (XRD). The Rietveld refinement was used to identify the strain effect in the crystal lattice due to dopant presence. Photoluminescence (PL) studies in the vacuum ultraviolet (VUV) and visible (VIS) range were also performed to investigate the luminescent properties of the europium ion inserted in this new chemical environment. PL results showed a dominant $^5D_0 \rightarrow {}^7F_2$ transition (centred around 613 nm), for excitations with photons with energies smaller than the bandgap energy (Eg = 12 eV [2]), resulting in typical Eu^{3+} red emission spectra. The prevalence of $^5D_0 \rightarrow {}^7F_2$ transition suggests that the Eu^{3+} ion is in a chemical environment of low symmetry [3]. However, when the material is excited above the band gap energy, the emission spectra switch to a violet colour due to the appearance of the Eu^{2+} blue band (centred around 378 nm).

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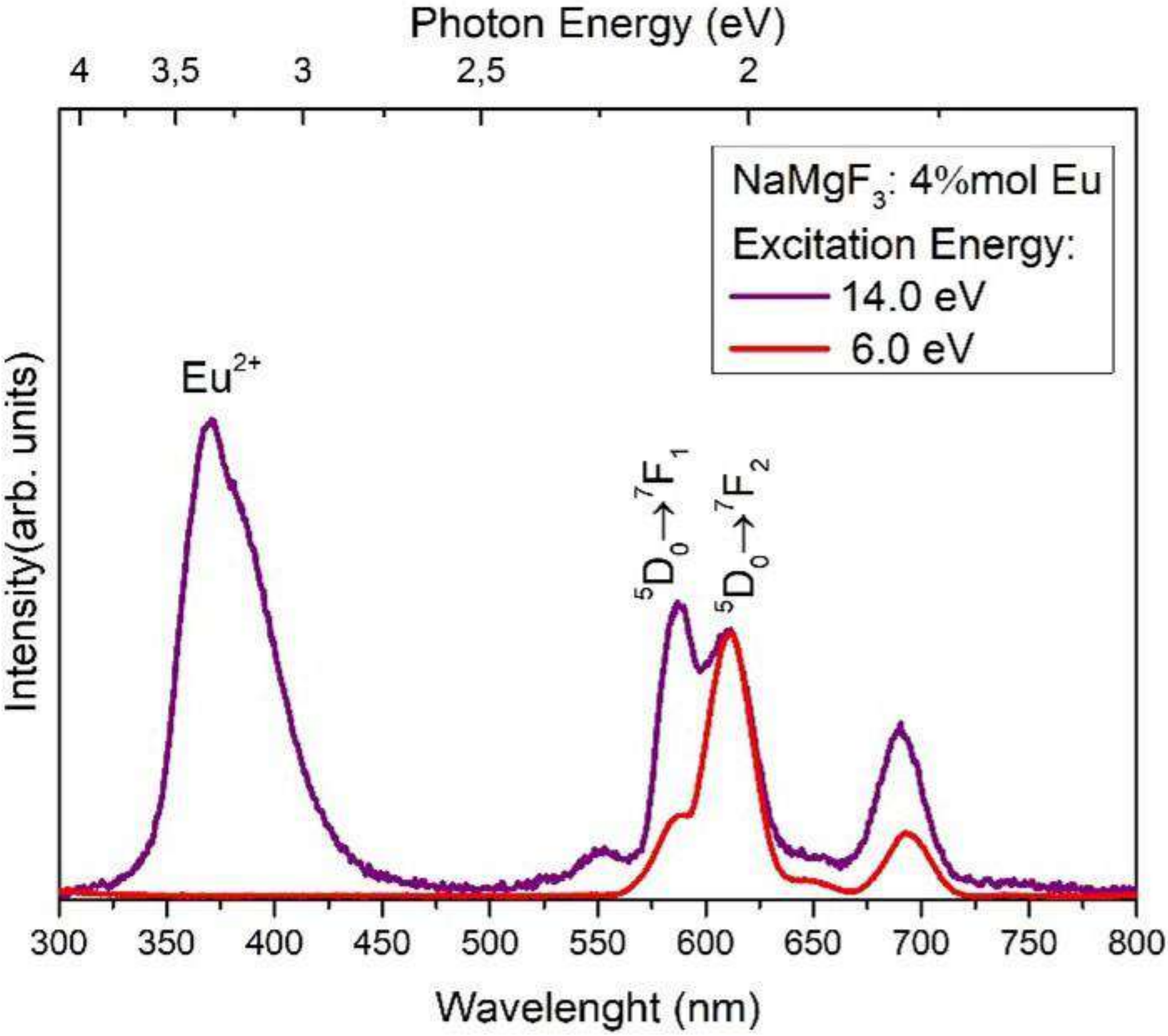
Photon Energy (eV)
4
3,5
3
2,5
2
NaMgF$_3$: 4%mol Eu
Excitation Energy:
14.0 eV
6.0 eV
Eu^{2+}
$^5D_0 \rightarrow {}^7F_1$
$^5D_0 \rightarrow {}^7F_2$
Intensity(arb. units)
300
350
400
450
500
550
600
650
700
750
800
Wavelenght (nm)

Development of a novel Ti-based alloy for use as knee prostheses

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Used biomaterials are mainly used to repair or replace damaged tissues in the body. Single-axis knee prosthesis is used as a healthcare device for amputees, with mechanical properties, wear and main problems related to failure and discomfort. In addition, weight and cost are also considered factors, as they can impact the availability and adaptability of the prosthesis for people living in underdeveloped countries. 304 stainless steel is the primary choice for manufacturing this prosthesis due to its lower cost. However, its properties still need to be adjustable for all the biomechanical functions of the human body. This study aims to develop a new Ti-based alloy for the fabrication of single-axis knee prostheses using lightweight and low-cost materials. Samples of Ti--(0 - x) AlxV (x0, 2% by weight) were directed to an argon melting furnace and structural analysis, for some thermomechanical treatments, microstructural chemistry, composition = arc mechanical strength and electrochemical analysis. The results indicate that, as properties, they were dependent on the phase and chemistry of the combinations, with Ti-10Al having the best composition of properties for the application.

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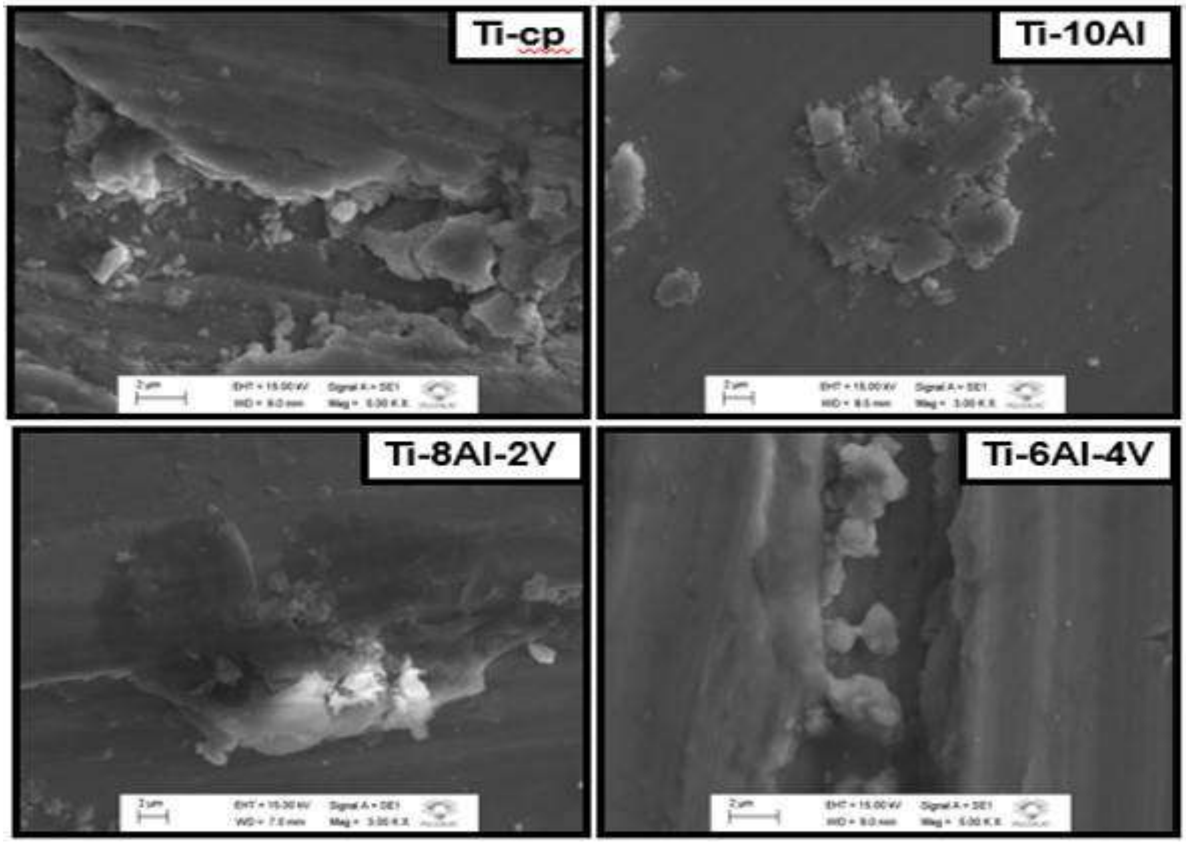
Ti-cp
Ti-10Al
Ti-8Al-2V
Ti-6Al-4V
2 µm

Growth of ZnS ultrathin films on Ag(111): A combined XPS, XPD, LEED and STM study

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Zinc Sulfide (ZnS) is an important semiconductor compound studied in materials science with several applications like sensors, photocatalysis, light emitting devices, etc [1]. Bulk ZnS crystallizes in either zincblende (ZB) or wurtzite (WZ) structures, with the cubic ZB form being the more stable phase at ambient conditions. In an attempt to modify the properties of regular ZnS bulk materials, the synthesis, and growth of various nanostructured ZnS have attracted considerable interest. However, in the literature, there are only a few reports of ultrathin film growth [2] and theoretical investigations [3].

In this study, a single layer of ZnS consisting of one atomic layer of ZnS(111) plane has been grown on Ag(111) using the gas source molecular beam epitaxy (GSMBE) technique. The ultrathin film was characterized using X-ray photoelectron spectroscopy (XPS), X-ray photoelectron diffraction (XPD), low-energy electron diffraction (LEED), and scanning tunneling microscopy (STM). In XPS a small shift in Zn $2p_{3/2}$ core-level indicates the formation of ZnS. XPS was also used to investigate how the system evolves thermodynamically with increasing temperature, demonstrating that ultrathin film ZnS/Ag(111) is stable until it reaches 280 °C. In addition, LEED measurements indicate the superstructure of ZnS-(3x3)/Ag-(4x4). Furthermore, STM measurements propose the coexistence of two ZnS-phases. Finally, investigations using XPD suggest the existence of Zn-vacancies in the first layer.

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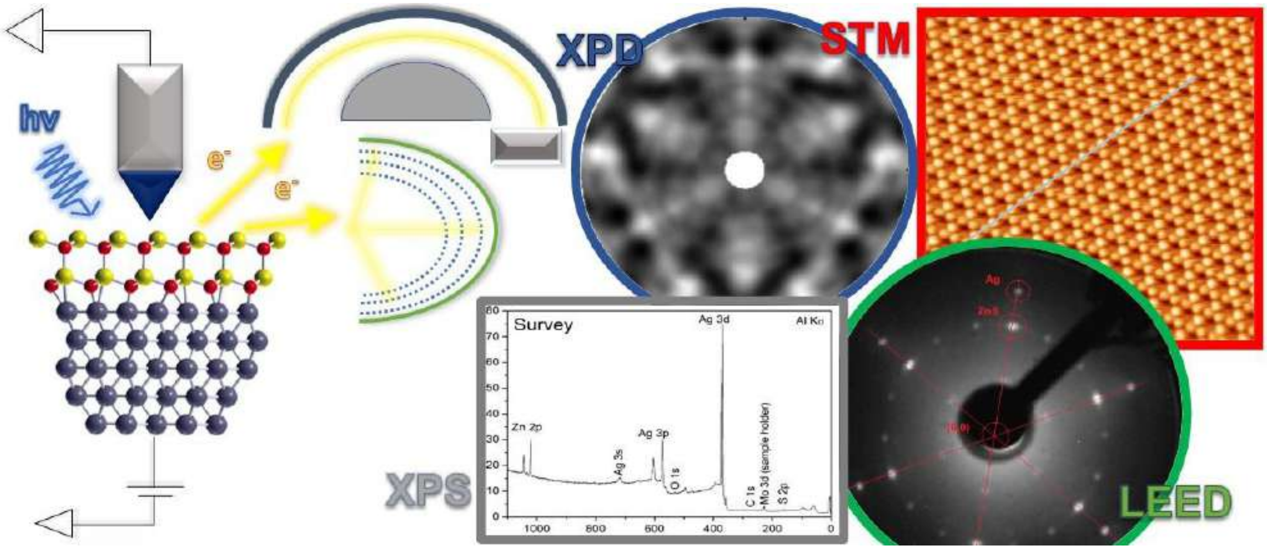
hν
e⁻
e⁻
XPD
STM
XPS
LEED
Survey
Al Kα
Zn 2p
Ag 3s
Ag 3p
O 1s
Ag 3d
C 1s
Mo 3d (sample holder)
S 2p
80
70
60
50
40
30
20
10
0
1000
800
600
400
200
0
Ag
ZnS
(0,0)

Luminescence enhancement of red emission of Ce3+ and Bi3+ co-doped LiLaP4O12 phosphor

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Red light-emitting scintillators are important to applications in detectors with maximum efficiency at a red portion of electromagnetic spectra [1]. X-ray irradiation in some bismuth-doped phosphates compounds is able to induce a red emission from divalent bismuth ions through valence changes from Bi^{3+} to Bi^{2+} caused by the interaction with X-rays photons. The $LiLaP_4O_{12}$ host was shown to be useful as scintillator material when doped with some rare earth and with bismuth ions [2,3]. Good charge transfer from host to dopant ions and capability to accommodate relatively high concentrations of dopants without quenching effects is one of the characteristics that make this host useful in application in light emission [4]. However, despite the characteristics of bismuth emission in the $LiLaP_4O_{12}$ host already studied, the process of bismuth valence change induced by X-rays is not known, as well as if a rare-earth ion can transfer electrons to bismuth, as occur in some hosts, and if this can be a mechanism to potentialize the bismuth emission. To study the mechanism of interaction between the Ce^{3+} and Bi^{3+} ions in the $LiLaP_4O_{12}$ host, doped and co-doped samples were synthesized. The luminescent properties were studied with photoluminescence emission, excitation at vacuum ultraviolet range at LNLS, and radioluminescence. The results indicate that Ce^{3+} can transfer electrons to Bi^{3+} ions, and enhance the red emission from Bi2+ when the material is exposed to X-rays.

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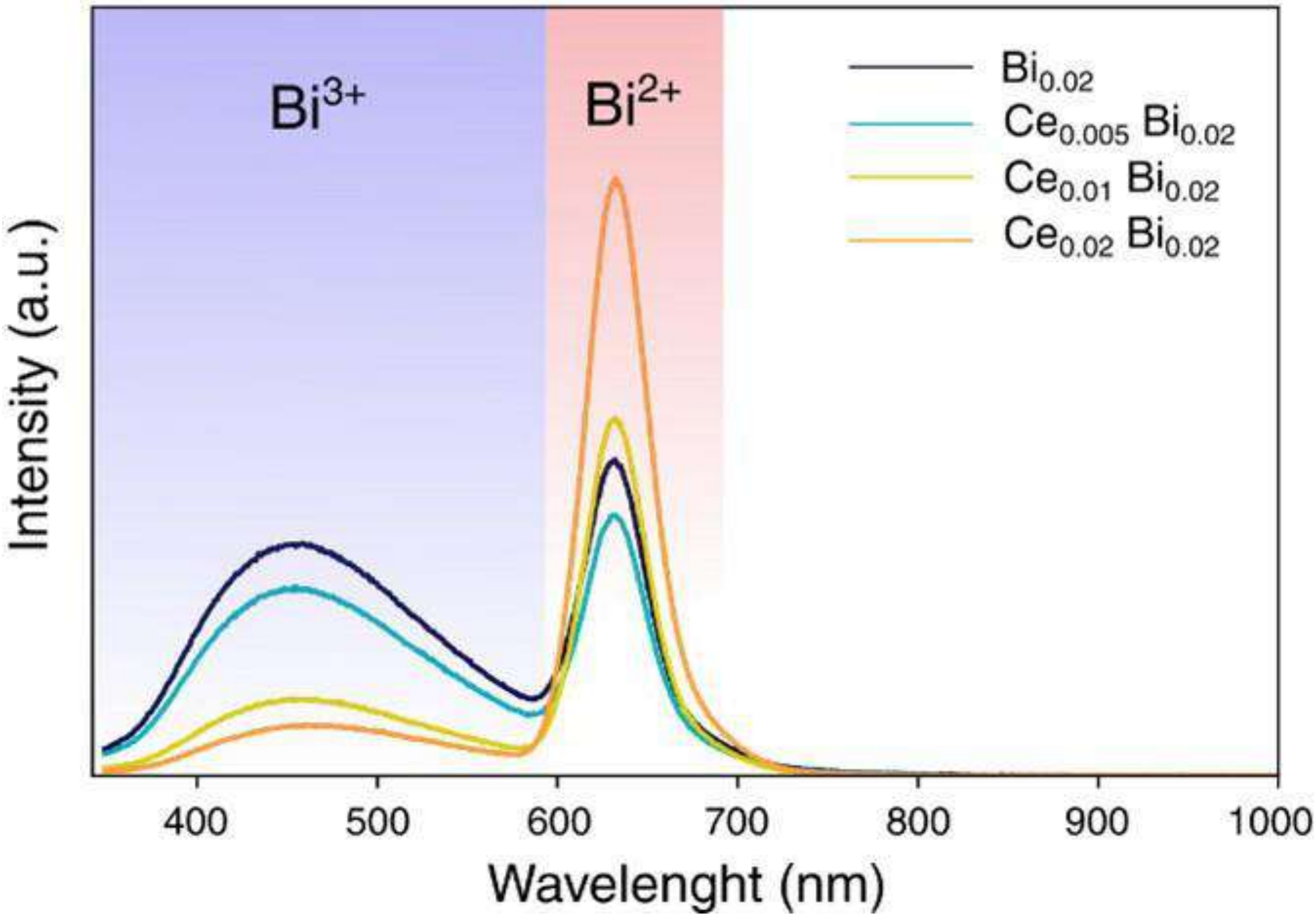
Bi^3+
Bi^2+
Bi0.02
Ce0.005 Bi0.02
Ce0.01 Bi0.02
Ce0.02 Bi0.02
Intensity (a.u.)
400
500
600
700
800
900
1000
Wavelenght (nm)

Microstructure and selected mechanical properties of new biocompatible non-equiatomic high entropy alloy

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High entropy alloys (HEAs) have been developed for many applications and recognized for their superior strength, ductility, and corrosion resistance, which has attracted the attention of the biomedical industry [1, 2]. This work aims to thermally treat and characterize HEAs with admittedly non-toxic elements for potential use as load-bearing orthopedic implants. The samples of the alloys were produced in non-equiatomic proportions, following some ab initio design predictions. The alloys were cast by arc-melting and subjected to a heat treatment for microstructural homogenization. Then, thermal aging treatments were performed at 300 ºC, 400 ºC, and 500 ºC for 6 hours. The samples exhibited the BCC crystalline structure with the precipitation of the HCP and BCC crystalline structures. The semi-quantitative analysis by punctual EDS indicated segregation of the elements in a micrometric scale. The TiZrNbTaMo Aged 500 °C condition had the lowest module (87 GPa) due to the influence of the aging temperature. The samples of the TiZrNbTaMn alloy showed values between 76 and 80 GPa. The alloys presented microhardness superior to the Ti-6Al-4V alloy, following what was predicted by the literature. In this study, a new HEA alloy composed of admittedly non-toxic elements was studied after heat treatments, contributing to studies of biocompatible biomaterials with potential to be applied to the orthopedic area.

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FAPESP (grants #2018/24931-7), CNPq and Capes for the financial support.

On the epitaxial growth and surface structure characterization of monolayer 1T-HfS_2 on Ag(111)

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In the last few decades, a series of 2D materials have attracted the scientific community. In particular, the transition metal dichalcogenides (TMDs) have a range of extremely interesting electrical, optical, and mechanical properties [1] to potentially outperform and complement the existing semiconductor technology [2] with atomically thin van der Waals materials. The HfS_2 has a calculated indirect electronic bandgap of 1.2 eV and presents a large mobility of carriers at room temperature, high optical absorption coefficient, and high photoluminescent response from the monolayer [3]. However, this material presents limited literature owing to the synthesis and implementation difficulty for devices development. In this work, we use the gas source molecular beam epitaxy (GSMBE) technique to grow HfS_2 on Ag (111) substrate. This growth method consists of a surface-mediated reaction of metal atoms on substrate and the chalcogen provided by a precursor gas, H_2S, and was effectively applied by our group [4]. HfS_2 was successfully grown in a monolayer regime with only 1T structural phase and explored in UHV and after air exposure for the oxidation effect. We analyze the system in both conditions with characterization techniques for their structural, chemical, and electronic properties performed by low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy/spectroscopy (STM/STS), and angle-resolved photoemission spectroscopy (ARPES).

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Phase transition in biomedical stainless steel 304 induced by alloying chemical depletion during PEO treatment

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Due to their lower cost and good mechanical and corrosion properties, ferrous materials, such as stainless steels (SS), are commonly used as biomaterials, mainly as surgical instruments and implants. Surface treatments, such as plasma electrolytic oxidation (PEO), can be a valuable tool to increase corrosion resistance and enhance the biocompatibility of metallic materials [1]. In this scenery, the current study evaluated the effect of electrolyte composition on the surface of SS304 submitted to plasma electrolytic oxidation (PEO). The variation in the amount of KOH and TaOH promoted significant changes in surface characteristics. The PEO-treated substrates were depleted of some alloying elements (Cr, Ni, and Mn), which, allied to the Ta-enrichment, affected the roughness, wettability, phase stability, and corrosion resistance. Chemical analyses indicated that Ta successfully enriched the Fe oxide coatings, depleting the substrate of some alloying elements (Cr, Ni, and Mn). As a result, the bulk's phase composition changed from biphasic (α +) to single -Fe. The KOH and TaOH content affected the surface roughness and wettability and promoted distinct corrosion behaviors in saline solution. The study shows that it is possible to induce chemical and phase composition changes in SS304 by controlling the electrolyte in PEO treatment.

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This work was supported by CNPq (#407251/2018-9), FAPESP (#2021/13921-3), and LNNano (#20210364).

Predominant surface states of the multiple topological material Sb4Te3

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Topological materials are well-known for their surface states with different electronic properties [1-6]. Recently, we have calculated the electronic structure of Sb4Te3. Remarkably, we have found that this compound possesses several topological states due to complex structure as well as different surface terminations. The goal of this experiment is to determine the predominant surface states of Sb4Te3. We have identified three strong topological gaps in Sb4Te3 , via DFT calculations, that are adjacent to each other, at different energies, and below the Fermi level. These gaps are related to three TSS Dirac cones. The possible energy alignment of electronic states from different structural terminations opens up the possibility of information transfer at the surface of these materials. The atomic structure of Sb4Te3 can be described as a stack of Sb2Te3-Sb2Te3-Sb2-Sb2 layers. The insertion of bilayers in topological insulators creates new surface electronic states . We performed a DFT calculation for these terminations and it is possible to observe different TSS in the band structure. Arpes measurements were performed at BLOCH line in MAX IV synchrotron to verify these states and observe how this material can change properties depending on which termination.

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Acknowledgments

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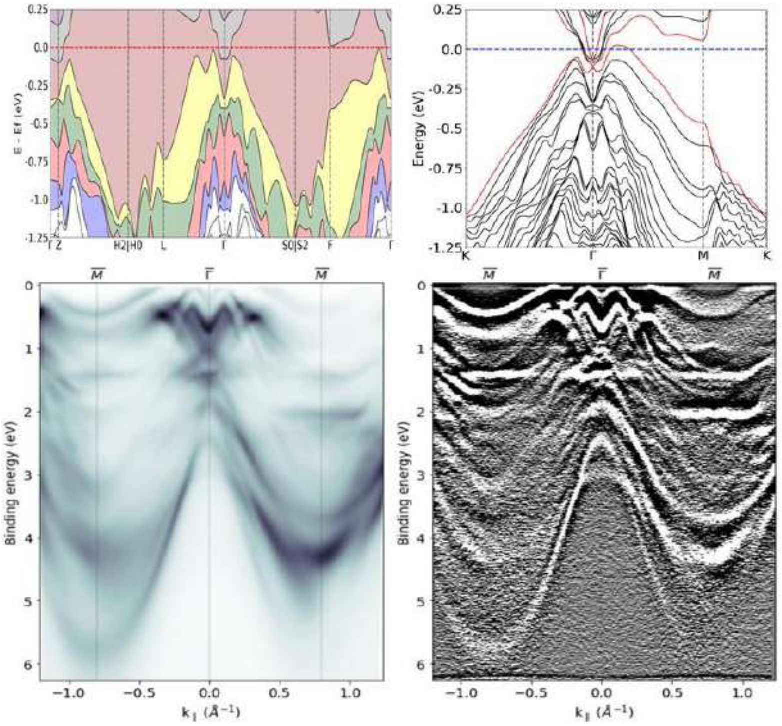
MAX IV


0.25
0.0
-0.25
-0.5
-0.75
-1.0
-1.25
E - Ef (eV)
Γ Z
H2|H0
L
Γ
S0|S2
F
Γ
Energy (eV)
K
Γ
M
K
$\overline{M}$
$\overline{\Gamma}$
$\overline{M}$
Binding energy (eV)
0
1
2
3
4
5
6
−1.0
−0.5
0.0
0.5
1.0
$k_{\parallel}$ ($\AA^{-1}$)

Probing the surface electronic structure of SrTiO3 self-doped with oxygen vacancies

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The interface between SrTiO3 (STO) and other oxides or semiconductors has been shown to exhibit unique quantum states that are absent in the bulk, resulting in intriguing macroscopic phenomena. Recently, it has been reported that pure STO surfaces also exhibit 2DEG, polarons, and ferromagnetic order, which have been attributed to the presence of oxygen vacancies. STO has a conventional band insulator with a 3.2 eV band gap and a crystal field splitting of 2.4 eV between eg and t2g states. However, in its oxygen-deficient form, STO becomes a grey-colored conducting crystal due to changes in the valence of Ti and the appearance of in-gap states. Although STO interfaces have been widely studied,still not having a model describing the diverse symmetry-broken quantum phases at these interfaces. The IPE beamline provides techniques such as XPS, XAS, and RIXS, which can be applied to high-quality single crystals with increasing amounts of oxygen vacancies to explain the intriguing interface quantum phases of STO. In this study, we report on the atomic and electronic structure of STO single crystals with varying amounts of vacancies using synchrotron soft X-ray spectroscopy. We use the variable surface sensitivity of soft X-rays to probe the depth distribution of vacancies and examine variations in stoichiometry (O:Ti) and Ti speciation (Ti4+/Ti3+). Our results may help to test the hypotheses and predictions of models that describe the phenomenology of STO interfaces.

Production of highly oriented NiSi2 nanoplatelets, and morphological characterization by Grazing Incidence Small-Angle X-Ray Scattering

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The study of Nanocomposites formed by $NiSi_2$ nanocrystals embedded in single-crystalline silicon have attracted the attention of a plethora of researches due to the potential of this material in applications for low-power memory devices (nanospheres), electrical transport (nanowires) and, also highly oriented nanoplatelets could have applications by the magnetic properties of NiSi2 nanostructures. The formation of the nickel-silicates are done by a technique that uses the reduction of a thin layer of $Ni(NO_3)_2.6H_2O$, generated by a spin coating technique of a solution of the Nickel(II) Nitrate Hexahydrate dissolved in ethyl alcohol, in a H2+He controlled atmosphere, followed by a thermal treatment in different temperatures. Finally, the morphological characterization of the produced nanoplatelets is made by an *ex-situ* GISAXS analysis. By using 1.54 Å X-ray radiation, it was performed a preliminary analysis of the GISAXS result, thus, obtaining the formation of nanoplatelets in the studied range of [340-700] ºC. An ongoing analysis of the GISAXS obtained data, is the morphological characterization of nanoplatelets, then, perform a quantitative analysis of the density of the nanoplatelets in the silicon subtract.

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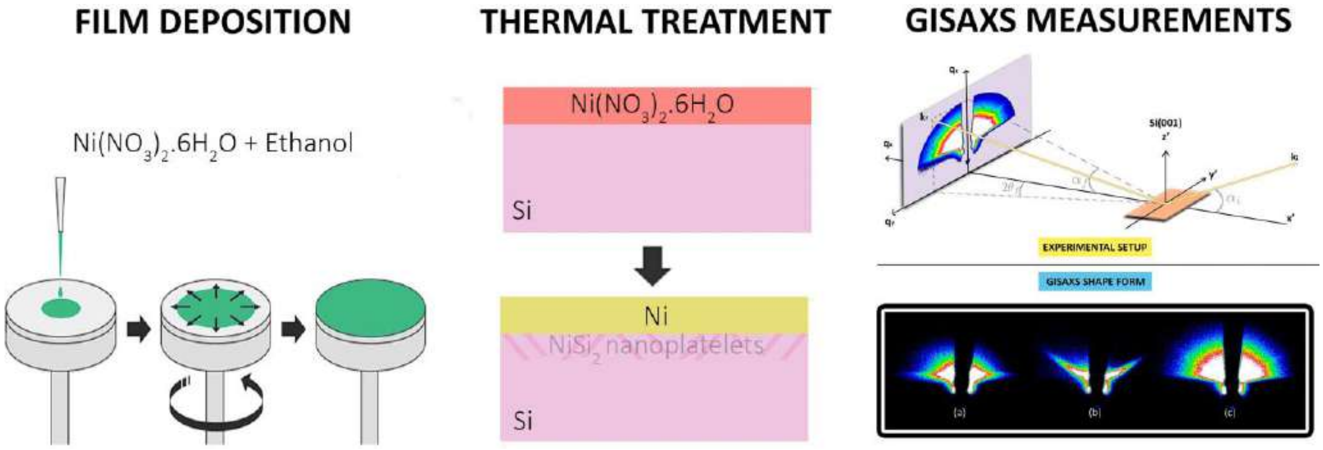
FILM DEPOSITION
THERMAL TREATMENT
GISAXS MEASUREMENTS
Ni(NO$_3$)$_2$.6H$_2$O + Ethanol
Ni(NO$_3$)$_2$.6H$_2$O
Si
Ni
NiSi$_2$ nanoplatelets
Si
Si(001)
EXPERIMENTAL SETUP
GISAXS SHAPE FORM
(a)
(b)
(c)

Simulations on spin wave dynamics in ultrathin ferromagnetic films: first steps towards studying THz magnetic excitations by RIXS

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Resonant Inelastic X-ray Scattering (RIXS) allows the detection of THz spin waves (SW) in thin films, which cannot be detected by techniques such as Inelastic Neutron Scattering (INS). With a new RIXS spectrometer being commissioned at the IPE beamline at the Sirius syncrothon light source, simulations on SW dispersion and damping are important to plan experiments for measuring low energy magnetic excitations. In this work, we simulated THz spin wave dispersion in ultrathin ferromagnetic Fe films along different crystalographic directions. We also investigated the SW damping via Stoner excitations. The SW dynamics follows the Heisenberg hamiltonian and the damping follows the Stoner criterion for ferromagnetism. Two different unit cells with three different dispersion directions were explored.

Serving as a basis for future studies at the IPE beam line, these calculations were the first step towards using the new Brazilian RIXS as a tool for studying THz spin waves. In this sense, we discuss also the perspective of focusing on the generalization of the simulations and of using RIXS to probe magnetic excitations.

Spacial distribution of $LiYF_4$:Ce,Tb scintillator in polystyrene matrix using STXM, X-ray fluorescence and XEOL mapping

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In this work, composite films based on lithium yttrium fluoride ($LiYF_4$) particles co-doped with Ln^{3+} (Ln = Ce, Tb) and polystyrene (PS) have been investigated as possible candidates for X-ray detection with high efficiency. The luminescent properties of the films were analyzed by photoluminescence (PL) with excitation at ultraviolet and visible (UV-VIS) range. Scanning Transmission X-ray Microscopy (STXM), X-ray fluorescence (XRF) and X-ray excited optical luminescence (XEOL) 2D mapping were performed at Coherent X-ray Nanoprobe Beamline (Carnaúba) to investigate the dispersion of the constituent elements in the polymer matrix. The results showed that the PS precursor solution concentration directly affects the particles distribution on the film body influencing, consequently, the efficiency of emission process. In addition, the images reveal that for some compositions the powder is mainly deposited at on one side of the films more than the other and this leads to different photoluminescent response obtained to the sides excited. The films show visible emission in the green region of the spectrum, that is suitable to the spectral sensitivity of charge coupled device (CCD) image sensor. The results obtained so far indicates that the $LiYF_4:Ln^{3+}$ – PS composites are potential candidates for use in scintillator devices.

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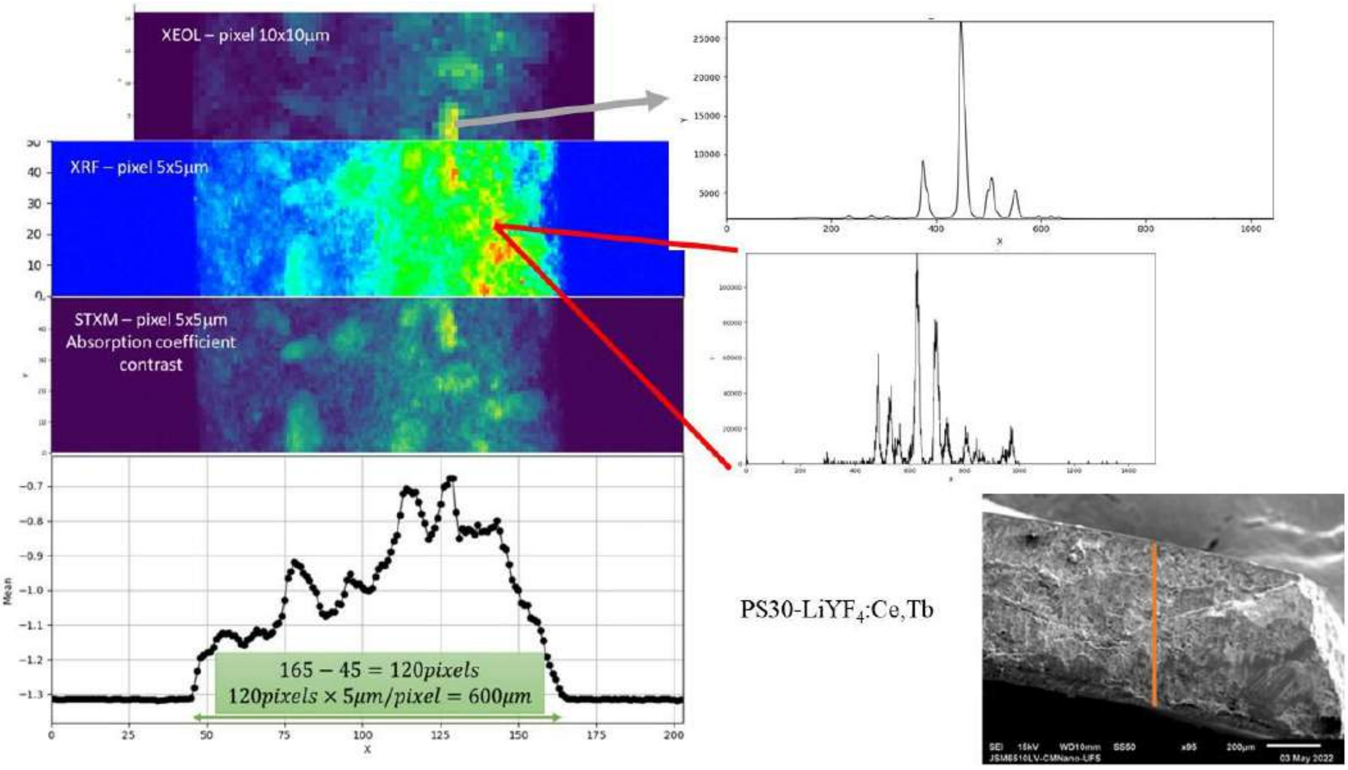

PS30-$LiYF_4$:Ce,Tb

Study of porous films formed in High Entropy Alloys by micro-arc oxidation

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Titanium and its alloys are good choices for biomedical implants due to their excellent mechanical properties. In the same way, high entropy alloys (HEA) are an emerging class that has attracted the attention of biomedical applications by their high strength, ductility, and corrosion resistance [1,2]. Micro-arco oxidation (MAO) is a surface treatment based on the surface

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Acknowledgments

FAPESP, CNPQ, and CAPES for the financial support

Study of the intrinsic defects responsible for the diversity of the emission colour of undoped CdSiO3 at different pH values for contactless thermometers applications in the cryogenic range

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The photoluminescence of $CdSiO_3$ were investigated to identify the defect centres that generate the PL emission and how the sample preparation conditions can tune the PL emission for practical proposed devices. The samples were synthesized via sol-gel route varying the pH and calcined at 1000°C/3h in open atmosphere. The behaviour of the PL emission showed that the intrinsic luminescence of $CdSiO_3$ is composed by 4 emission channels centred around 2.10 eV, 2.66 eV, 3.07 eV and 3.48 eV. The temperature effect shows that peaks 1 and 2 are due to charges trapped in Cd and O vacancies and peaks 3 and 4 are due to STE, generated after excitation and pinned at Cd vacancies and O vacancies, which link two Si tetrahedra. The tuneability of the emission colour according to the pH is crucial to the PL emission. Another application arises from the temperature effect on the PL emission, that presents a variation of the fluorescence intensity ratio of about 2 orders of magnitude when the samples are cooled from room temperature down to 62 K. This quite interesting result indicates that $CdSiO_3$ can be explored as a contactless fluorescence thermometer for cryogenic applications.

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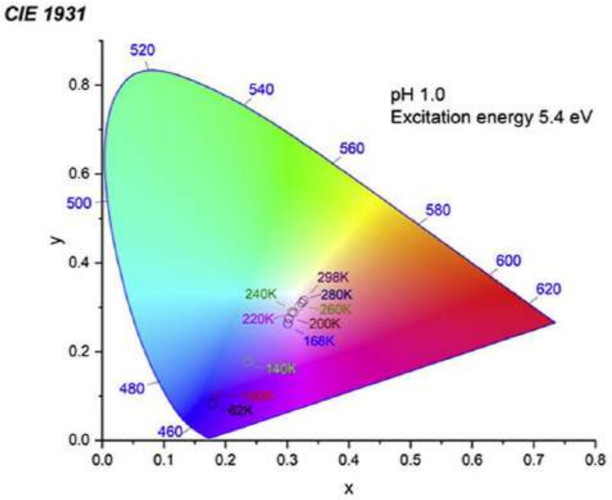
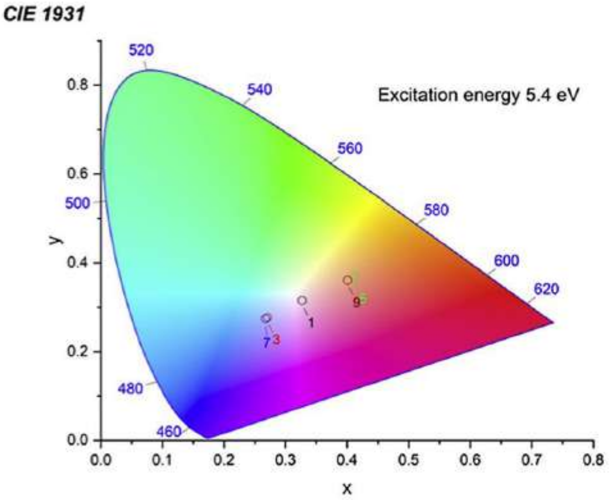
Simone S. Melo, et al. Undoped $CdSiO_3$ for contactless thermometer in the cryogenic range: pH-dependent intrinsic defects and emitting colour, Journal of Solid State Chemistry, Volume 321, 2023, 123908, ISSN 0022-4596

Acknowledgments

This work has been supported by the Brazilian funding agencies CNEN CNPq, CAPES, FINEP and FAPITEC. This research used resources of the LNLS/CNPEM. The TGM beamline staffs are acknowledged for the assistance during the experiments with proposals TGM #20190096 and #20190133



Effect of the temperature on the luminescence response of the $CdSiO_3$ synthesized using pH1.0 and excited at 5.4 eV.



Effect of the pH of the starting solutions in the room temperature luminescence response of the $CdSiO_3$ when excited at 5.4 eV.

Surface Structure studies of 3D Nb-superconducting resonators using in-situ cryo GI-XRD

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Superconducting radio frequency (SRF) Nb-resonators are a key element in the development of new generations of particle accelerators and in the fabrication of circuit QED architectures for quantum computing. Nevertheless, niobium is extremally reactive to light elements such as C, N, O and H, and therefore to impurity ordering under special conditions, e.g., cryogenic temperatures. Since these resonators are put through a series of metallurgical and chemical processes, the number of impurities approaches the tens of ppm regime. At the typical operating temperature of these cavities (2K), Nb becomes vulnerable to H atom ordering, which leads to the nucleation of secondary phases such as Nb-hydrides. These precipitates drive energy dissipation and the superconducting breakdown known as Q-disease and potentially the High-Field Q-slope. In this contribution, we present a detailed structural analysis of these Nb-hydrides with high energy grazing-incidence X-ray diffraction of specimen extracted from 3D Nb-resonators to shed light on the kinetic formation of the resulting secondary phases and their crystal phase identification upon cooling and heating cycles. This work opens new routes to understand the chemical and phase composition as well as crustal and electronic structure of the Nb-surface near typical operating temperatures as a strategy to improve the physical and functional properties of Nb superconducting resonators.

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uThis work has been authored by Fermi Research Alliance, LLC under Contract No. DE-AC02-07CH11359 with the U.S. Department of Energy, Office of Science, Office of High Energy Physics. Award Number ECCS-2025124. Th authors are grateful to the SpLine staff for their valuable help.

Synthesis and characterization study of Bi ferrite nanoparticles prepared by modified sol-gel method

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In this work bismuth ferrite (BFO) particles were synthesized using sol-gel technique[1,2,3], followed by calcined in a tube furnace at different temperatures from 400 °C to 650 ºC. X-ray diffraction (XRD) results showed the formation of small sizes nanoparticles (NPs) with high purity. Structural analysis displayed that calcination at 600 ºC could make BFO NPs be perfectly fitted to rhombohedral space group R3c with a small amount of secondary phase. Transmission electron microscopy (HRTEM) revealed that the sizes of the BFO nanoparticles are distributed in the range from 50 to 100 nm.

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Theoretical Evaporation Protocol for Bulk Heterojunctions in Organic Solar Cells

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Organic solar cells (OSCs) have gained significant attention in recent years due to their potential as a low-cost, renewable energy source [1]. One key component of OSCs is the active layer, which typically consists of a blend of electron-donating and electron-accepting materials in a bulk heterojunction (BHJ) structure [2]. The morphology of the BHJ layer plays a crucial role in the device performance, and the evaporation process is an important step in achieving the desired morphology [3]. In this study, we present a theoretical evaporation protocol that simulates the experimental development of BHJ layers. Simulations are perfomed in the molecular mechanics framework with the aid of quantum mechanical calculations to parameterize the force fields. Specifically, partial charges are determined at the DFT level of theory, while crucial dihedral interactions are described by fitting the coefficients to reproduce the quantum rigid scan profile. The impact of the solvent evaporation protocol is discussed along with the solvent concentration and drying rates. Annealing temperatures are also a key factor, as it is directly related to the packing of organic semiconductors, indicating that higher values increase the grain size and cristallinity, impacting the overall charge transfer processes that integrate the energy conversion chain of events.

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Unraveling the entangled J_{eff} state of Re *5d* electrons in B-site ordered double perovskites

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[1]Universidade Estadual de Campinas (*Instituto de Física Gleb Wataghin*) , [2]Universidade Federal do Espírito Santo, [3]Swiss Light Source, Paul Scherrer Institut, [4]Argonne National Laboratory, Lemont, [5]Universidade Estadual de Campinas (*IFGW*)

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Transition-metal oxides with *5d* electrons are an attractive field of study, as the strong spin-orbit coupling can lead to entangled J_{eff} orbitals. From this entangled electronic state emerges a variety of exotic ground states with multipolar ordering. In this regard, the B-site ordered double perovskite structure $A_2BB'O_6$ is an excellent playground to explore the role of *5d* ions [1]. One example is $Ca_{2-x}Y_xMnReO_6$, which crystallizes with a monoclinic crystal structure ($P2_1/n$). These materials are characterized as spin-orbit-assisted Mott insulators with a non-collinear antiferromagnetic ground state. Such non-collinearity is not compatible with the expected collinear magnetic structure that should derive from a Heisenberg-like interaction between spherically symmetrical half-filled *3d* shell of Mn^{2+}, showing that Re magnetic moments, albeit small, are crucial for understanding this magnetic structure [2,3]. In addition, the undoped sample shows considerable lattice parameter anomalies around the transition temperature, pointing to a possible quadrupolar orbital ordering of Re *5d* orbitals. In fact, Re $5d^1$ electrons in $J_{eff} = 3/2$ electronic state experiencing strong spin-orbit coupling can host multipolar orderings beyond the magnetic dipolar one. Thus, a detailed study of the electronic structure of Re is desired in those samples. With the help of XANES, XMCD, and RIXS experiments, we will try to shed light on the $J_{eff} = 3/2$ spin state of Re.

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Acknowledgments

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Unravelling the surface structure of β-Ga2O3 (100)

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The present work is on a comprehensive surface atomic structure investigation on the *β*-Ga_2O_3 (100). The as-received *β*-Ga_2O_3 single crystal was studied by a structural model system in the simulations and *in situ* characterization via X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED) and X-ray photoelectron diffraction (XPD) allowed for the probing the outermost layers' properties. In situ XPD characterization[1,2] allows us valuable element-specific short-range information from *β*-Ga_2O_3 surface, and the results were compared to a systematic and precise multiple scattering simulation approach. The experiments, characterizations, and simulations indicated strong evidence of considerable structural variations in the interatomic layer

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Combined XAS and XRD “in operando” insights in Li ion intercalation in cathodematerials with spatial resolution.

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Recent Lithium-ion batteries (LIBs) studies are devoted to understanding the interface processes that are crucial in the reversible Li ion uptake. Some of the most promising cathodes for LIBs are based on LiFePO4 (LFP), Mn and Ni spinel’s (LMNO) and Lithium rich layered materials (Li Rich) between others. Those materials arise as candidates because they are safer and cheaper to produce and possess higher energy densities compared with the state-of-the art LiCoO2 (LCO). In general the mechanism of Li ion intercalation is governed by processes that occur in a homogeneous way and in different scales of sizes that go from microns to a few nanometers. For this reason, spatial resolution arises as a need in order to understand

this intricate process. For example, XRD is a widely used technique for the structural characterization of these materials, providing valuable insights into their crystal structure, phase composition, crystallite size. More recently X ray absorption (XAS) arises as being strongly sensitive technique for oxidation state and coordination chemistry characterization of the absorbing atom of interest.

In this work we combine XAS and XRD measurements performed in operando conditions at NOTOS beamline at ALBA to obtain an average characterization of LIB cathode materials. Those materials were also characterized by XRD with spatial resolution of 1 micron in operando during Li ion intercalation at Micro XAS beamline at SLS synchrotron.

Acknowledgments

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Electronic structure and morphology of organic semiconductors with application in photovoltaic devices

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The study of organic semiconductors has grown over the last few decades for applications in solar cells, light-emitting devices, photodetectors, transistors, among others, due to their various characteristics such as lightness, low cost when compared to inorganic ones, semi-transparency, flexibility and easy processing by different techniques [1]. In the case of organic photovoltaic devices, the blend between a non-fullerene small molecule ITIC and the polymer PBDB-T showed higher efficiency [2]. In order to understand this result, it is important to gain insight into its electronic structure and morphology. In this work, XPS and angle-resolved NEXAFS measurements were performed at IPÊ beamline (Inelastic Scattering and Photoelectron spectroscopy) at SIRIUS (LNSL-National Synchrotron Light Laboratory in Campinas-SP/Brazil) which, together with previous UV-Vis and AFM measurements and TDDFT calculations, were used to elucidate the absorption bands and morphology of ITIC, PBDB-T and ITIC:PBDBT thin films. The morphological properties are the ones that change the most between pristine and blend films: pure ITIC forms ordered films, while the blend indicates crystalline disorder.

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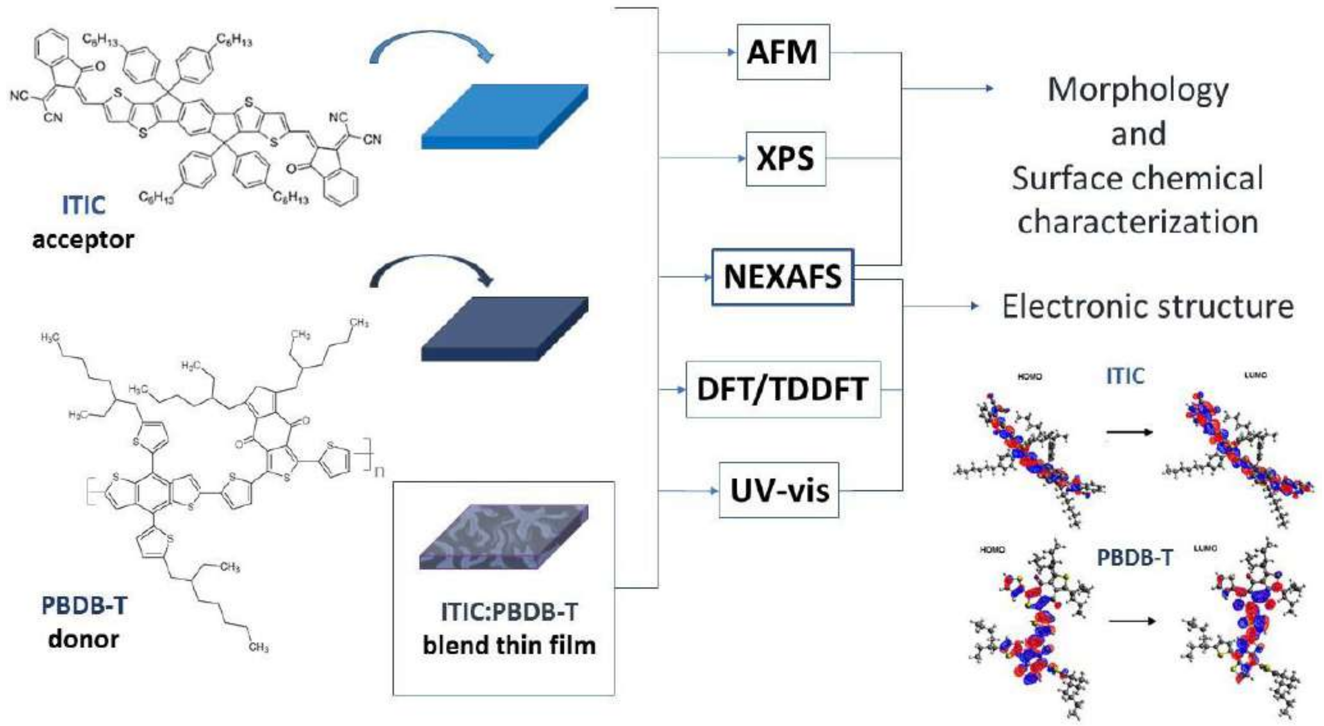
ITIC
acceptor
PBDB-T
donor
ITIC:PBDB-T
blend thin film
AFM
XPS
NEXAFS
DFT/TDDFT
UV-vis
Morphology
and
Surface chemical
characterization
Electronic structure
HOMO
ITIC
LUMO
HOMO
PBDB-T
LUMO

Evaluating the impact of heat treatment, DIO addictive and PMMA on the morphology and femtosecond charge transfer dynamics of F8T2 films

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In the field of OPVs, studying the morphology of solution-born films is crucial to achieve high power conversion efficiencies, as phase separation must reach an optimal degree to increase the contact area between electron donating and acceptor materials while providing a continuous pathway to the selective charge transport to respective the electrodes. We investigated the electronic structure and morphology of thin films of poly(9,9-dioctyl-fluorenyl-*co*-bithiophene) (F8T2), as well as samples with the additive 1,8-diiodooctane (DIO) and subjected to heat treatment. The effects of adding the poly(methyl methacrylate) (PMMA) insulating polymer were also studied. Measurements were carried out using angle-resolved S K-edge NEXAFS (near-edge X-ray absorption fine structure) in TEY and FY detection modes. Two main transitions were observed at the S1s NEXAFS spectra, S 1s → π* and S 1s → σ* (S-C), which indicated a face-on orientation of the polymeric chains. We also observed significant increase in the dichroism behavior for F8T2 with DIO. Resonant Auger decay spectra were measured and analysed through the Core-Hole Clock (CHC) method. Enhancement in the charge transfer process was observed, especially, for samples treated with DIO and with the addition of PMMA, mostly due to an increase in film ordering. The investigated films were also characterized by XPS.

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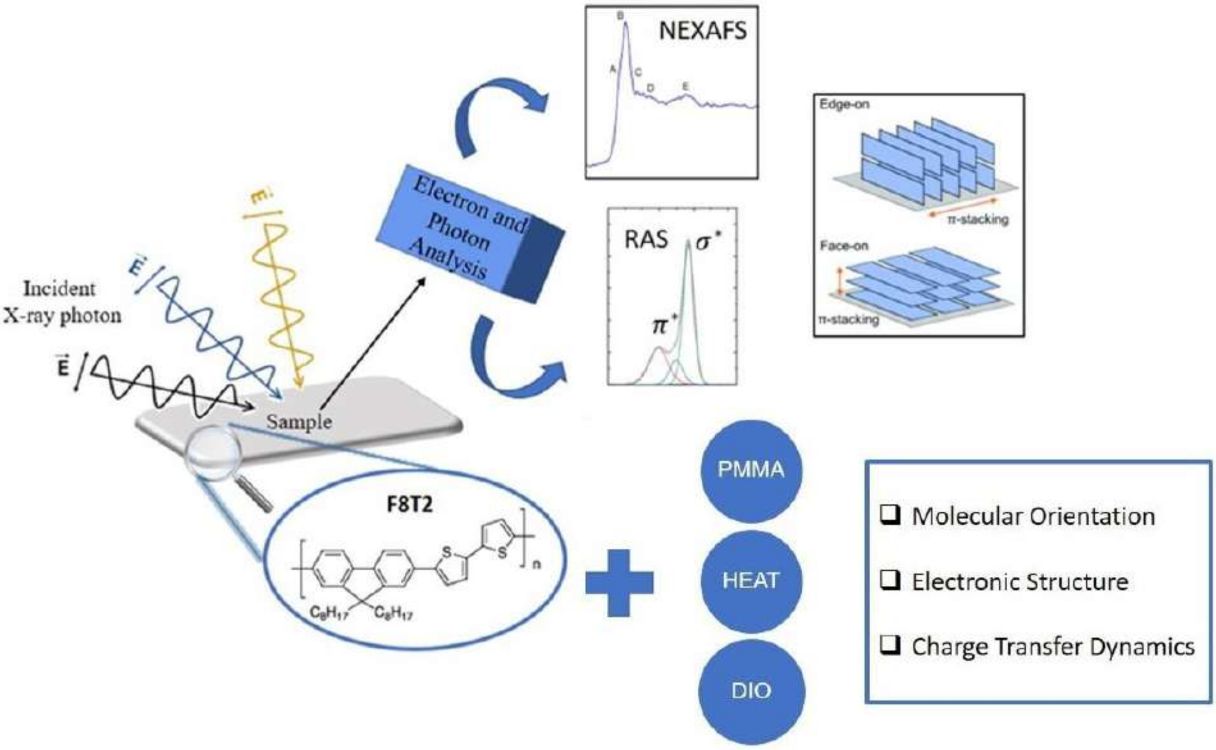

☐ Molecular Orientation

☐ Electronic Structure

☐ Charge Transfer Dynamics

Highly stable all inorganic lead-free nanoparticles by water-assisted mechanical milling

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Solar cells often require expensive and toxic lead-containing materials or low-efficiency materials to convert solar energy into electrical energy. A promising alternative is to use perovskites with the ABX3 structural form (A is a 1+ valence cation, B is a 2+ valence cation, and X belongs to the halogen group), such as the CsSnCl3 perovskite in the cubic phase. This perovskite has electronic properties suitable not only for solar cells but also for LEDs, photodetectors, and sensors.

To produce perovskite layers for devices, a glovebox with a controlled environment is required as most precursor compounds are sensitive to moisture and oxidize when exposed to normal atmospheric conditions. Additionally, the cubic phase is challenging to produce as it is always associated with other phases. We focused on producing CsSnCl3 perovskite through mechanical mixing using water as a reactive medium. We tested different synthesis temperatures and times to form the stable cubic phase, which had chemical stability of three months stored in a desiccator and outside the glovebox. The material had an average stoichiometry of 40 wt.% for the cubic phase and 60 wt.% for the monoclinic phase, both relative to the CsSnCl3 phase. Our findings, including X-ray diffraction, transmission electron microscopy, and bandgap values, will be presented.

Acknowledgments
We thank LINDEN - UFSC for X-ray measurements, LCME - UFSC for electron microscopy images, and CAPES & PGMAT - UFSC for financial support.

Monitoring the Exsolution of Platinum Nanoparticles from Perovskite Oxides using Synchrotron-based XAS, XRD and Nano Diffraction Techniques

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The exsolution of nanoparticles (NPs) from perovskite oxides (PO) has emerged as a promising strategy for synthesizing stable metal nanoparticles with tunable electronic and catalytic properties and minimizing the use of noble metals. It has also garnered significant interest due to its potential applications in various catalytic reactions due to its superior performance explained by its high resistance stabilizing metal-support interaction. In this study, we will induce the exsolution process via electrochemical methods and monitor the process *in situ* using synchrotron-based X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), and nano diffraction techniques. The exsolution occurs via a reduction process, where the B-site of perovskite diffuses to the surface, followed by reduction, nucleation, and growth[1][2]. In situ XAS technique allows us to monitor how the local coordination geometry and electronic properties of different atoms (both PO and exsolved NPs) change during the process. Additionally, XRD will permit monitoring changes in the structure of the PO and the emergence of the metallic NPs. Finally, nano diffraction experiments can provide valuable insights into the degree of strain and defects within the crystal structure. Therefore, X-ray-based techniques are promising tools that might permit to obtain unprecedented information in this field, tracking the exsolution of NPs at ambient temperatures by following their structural and electronic changes.

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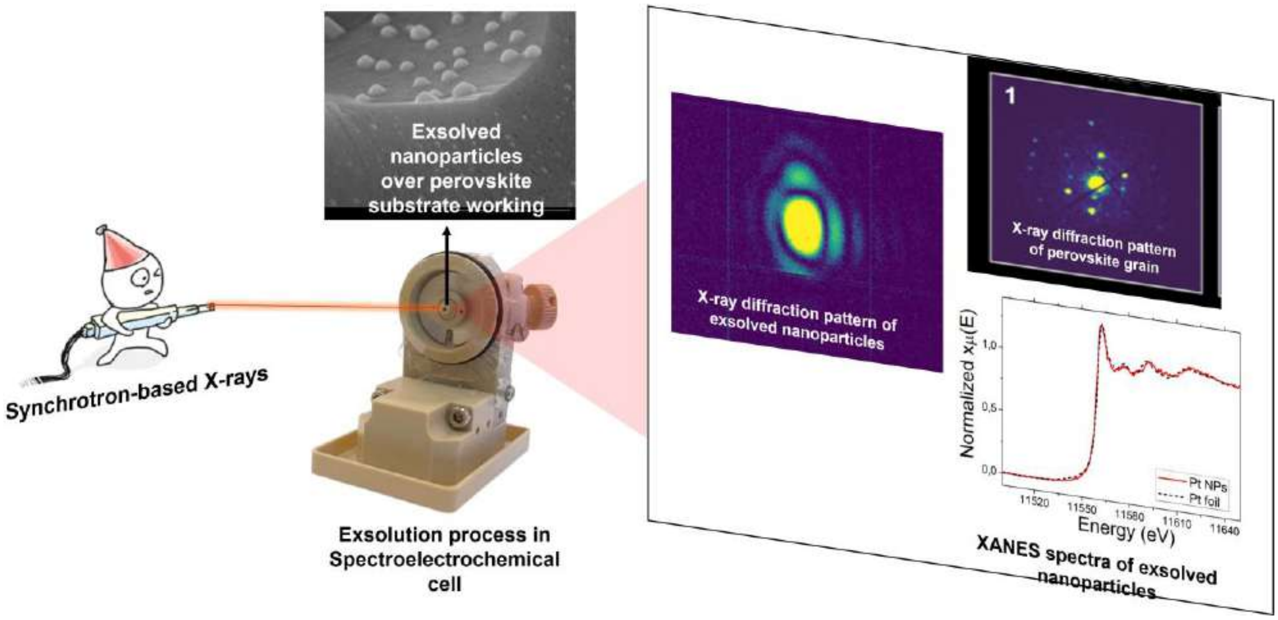
Exsolved nanoparticles over perovskite substrate working
Synchrotron-based X-rays
Exsolution process in Spectroelectrochemical cell
X-ray diffraction pattern of exsolved nanoparticles
1
X-ray diffraction pattern of perovskite grain
Normalized xμ(E)
1,0
0,5
0,0
Pt NPs
Pt foil
11520
11550
11580
11610
11640
Energy (eV)
XANES spectra of exsolved nanoparticles

Nanostructured magnetic systems associated with hexadecafluoro zinc phthalocyanine for photodynamic therapy

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The hexadecafluoro zinc phthalocyanine ($ZnPcF_{16}$) are synthetic dyes, chemically pure and considered photosensitizers (PS) of second generation, currently the use of $ZnPcF_{16}$ has been attracting a lot of attention in the area of photodynamic therapy (PDT), due to its photochemical and photophysical properties. However, one of the disadvantages of $ZnPcF_{16}$ is its impracticable direct administration in biological systems, due to its hydrophobicity, as this property in aqueous media leads to self-aggregation. Furthermore, it is possible to promote the improvement of physicochemical characteristics through coating with nanoparticles, which may result in increased activity. This project aims at the development of magnetic nanoparticles (Fe_3O_4) and phthalocyanine ($ZnPcF_{16}$) for application in PDT. The Fe_3O_4 were synthesized by the technique of co-precipitation of Fe $^{2+}$/Fe^{3+}, chitosan (chi) and ($ZnPcF_{16}$), obtaining the systems Fe_3O_4 and Fe_3O_4@Chi/ZnPcF16. They were characterized by scanning electron microscopy (SEM), X-ray diffraction (XDR) and UV-Vis spectroscopic. Fe_3O_4 and Fe_3O_4@Chi/$ZnPcF_{16}$ showed composite homogeneous morphology and mostly particle agglomerates, XDR analysis showed characteristic peaks of Fe_3O_4 and Fe_3O_4@Chi/$ZnPcF_{16}$. The UV-vis spectrum of Fe_3O_4@Chi/$ZnPcF_{16}$ shows absorption, with a Q band displayed at 686 nm. Therefore, the new nanosystems incorporated with $ZnPcF_{16}$, described here, can be considered as potential for the use of PDT.

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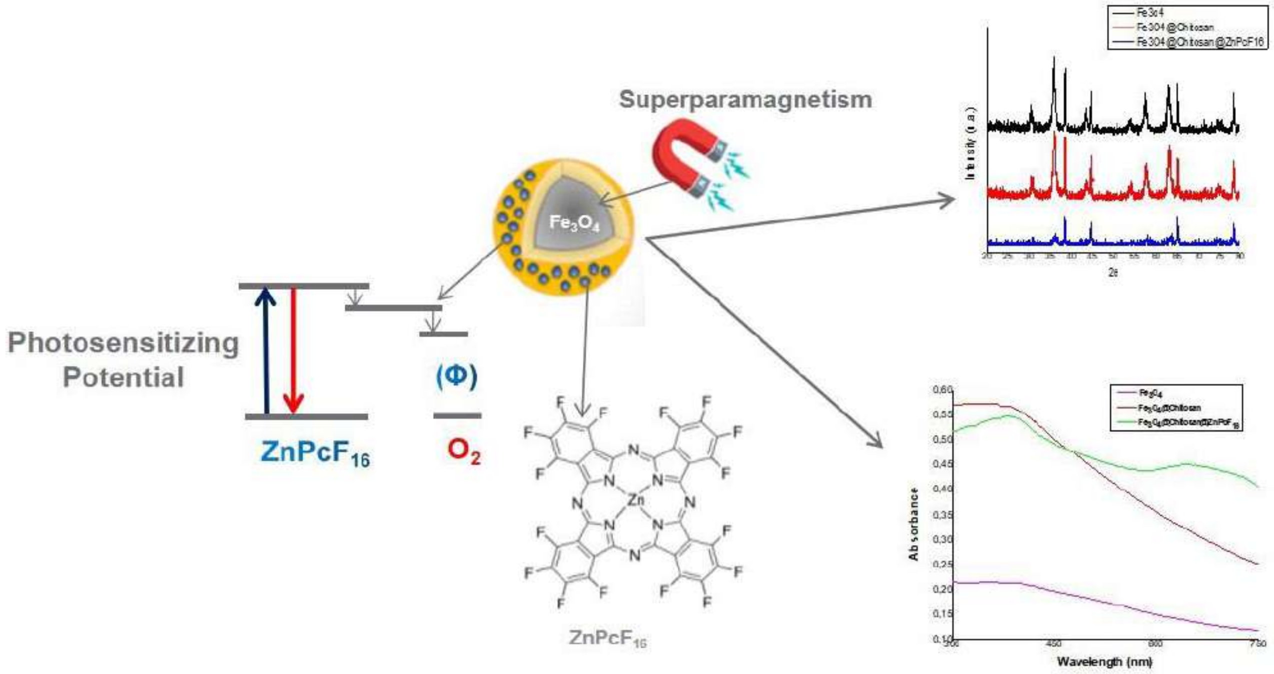

Sulfur chemical speciation in complex samples using XANES spectra: application of statistical tools in data analysis

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Chemical speciation of biological samples can be performed through XANES spectra taken on a selected absorption edge. Due to their complex nature, some biological samples present a challenge to the interpretation of their XANES spectra. Such is the case of the sulfur K-edge spectra of plant samples. These samples may exhibit spectral features around 2471 eV, corresponding to species of reduced sulfur, features around 2474 eV related to intermediate oxidized sulfur species and features around 2480 eV associated with oxidized sulfur species [1].

A procedure to perform speciation makes use of linear combination fitting (LCF) of standards spectra, since total absorption coefficient corresponds to the sum of the absorption coefficients of all species present in the sample. The coefficients of the LCF correspond to the contribution of each species in the total spectrum.

Nonetheless, some questions may arise when performing LCF: How many components are present in the sample and which standard spectra are best candidates to the fitting?

Principal components analysis (PCA) and target transformation (TT) are data analysis tools that combined with LCF may contribute to a better understanding of the sample composition [2]. In the present work, application of these tools to the fitting of the XANES spectra of samples of plants from the Amazonian rainforest will be presented. The validity of our results have been tested through the fitting of the spectra of mixtures of the standards used.

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Synchrotron-based soft X-ray absorption spectroscopy (XAS) for probing the nature of electrochemical formed vacancies on a CoFe Prussian Blue Analogue catalyst

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Prussian blue analogues (PBA - $M_{1(x)}[M_2(CN)_6]_{(y)}$) stand out as catalysts for water oxidation (WO) due to their great performance in a neutral pH. Although having a great activity, the low number of active sites is the main drawback, thus, the creation of vacancies is the best strategy to increase active sites and improve the catalyst activity.[1]–[3] X-ray absorption spectroscopy (XAS) is an element-specific method that allows the probing of different valence states in the elements, providing insights about the electronic state.[4] Herein, we report a methodology to synthesize CoFePBA and promote the improvement of its properties on OER by electrochemically formed vacancies (ACoFePBA). Moreover, synchrotron-based XAS, performed at IPÊ beamline of the synchrotron light source Sirius, was used to probe the composition and the nature of these defects by analyzing Co and Fe L-edges. XAS analysis, performed in different film depths, indicates some differences in the films when comparing the Co^{2+}/Co^{3+} and Fe^{2+}/Fe^{3+} compositions. Furthermore, it is possible to observe that the spectrum for ACoFePBA is shifted in 0.2 and 0.4 eV toward lower energies when compared to the CoFePBA spectra, indicating some CN^- left the structure and was replaced by H_2O. We believe the unique sensitivity of soft X-ray spectroscopy might break the complexity of defect chemistry on earth-abundant catalysts recently exploited for catalysis and energy conversion.

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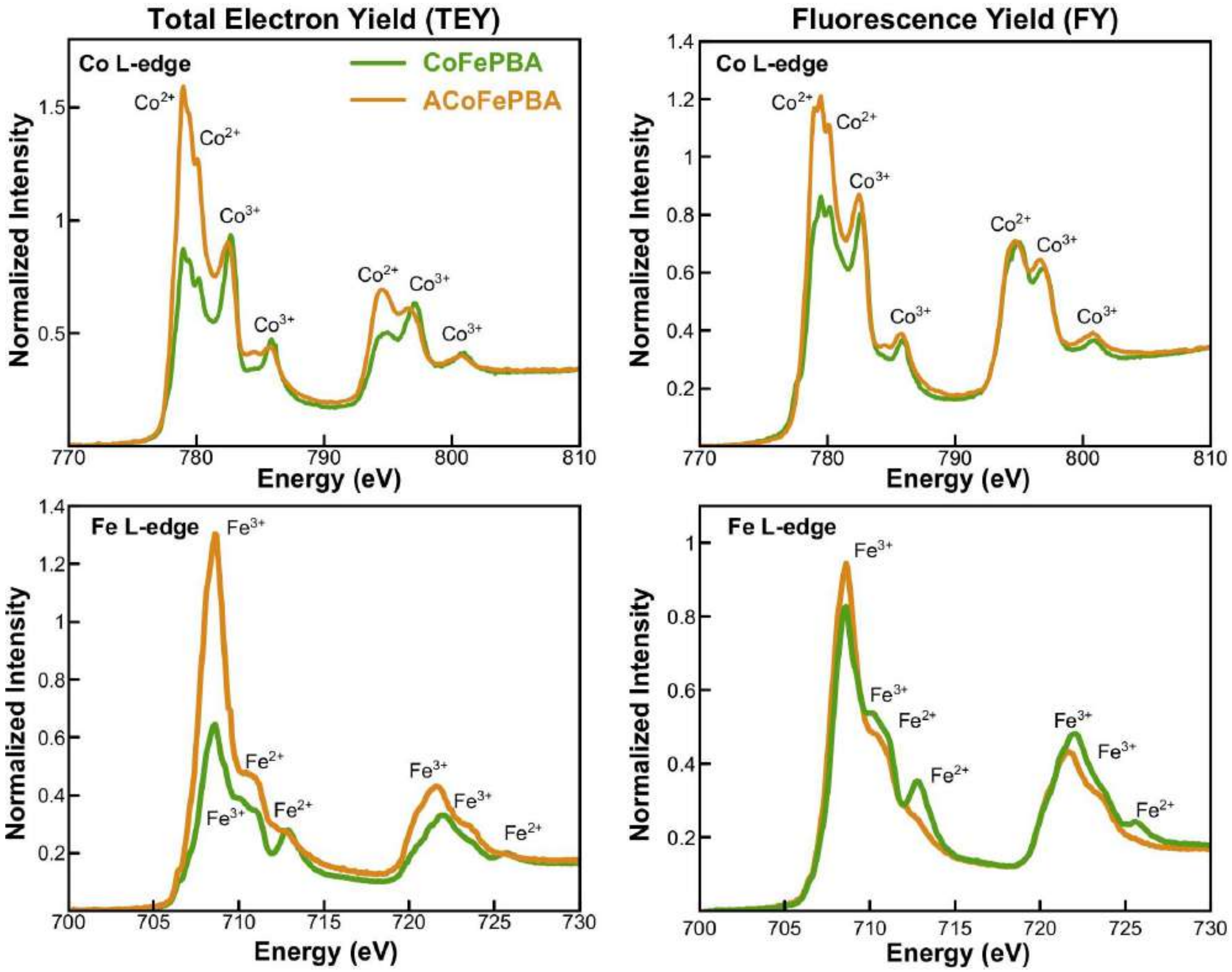

The effect of the cations on the structure of the electrolyte in the electrochemical interface: an in situ FTIR and in situ RIXS approach

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In the field of electrochemistry, it is well established that the electrochemical interface (electrode/electrolyte) determines the kinetics of the electrochemical reactions, hence the stability of the intermediates and/or products that are being produced during the electrochemical reaction.[1-3] In this context, it is important to understand the electrochemical interface, which plays a ubiquitous role in electrochemical reactions by increasing/decreasing the stability of the reaction intermediates and/or of the own surface.

In the present work, we are planning to study the effect of the cations on the structure of the electrolyte in an electrochemical interface. Herein we will show some preliminary results of surface-enhanced infrared absorption spectroscopy in the attenuated total reflectance (ATR-SEIRAS) mode and perspectives, which is related to performing resonant inelastic x-ray scattering (RIXS) at Ipê beamline[4] (SIRIUS – CNPEM) to complement the information obtained by ATR-SEIRAS.

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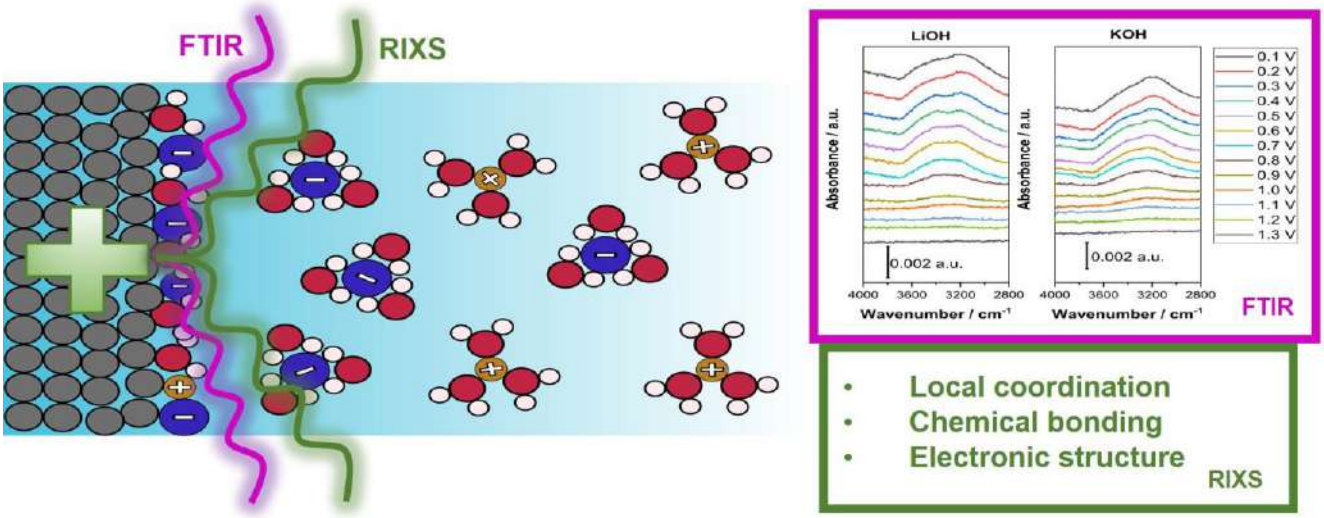
FTIR
RIXS
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0.7 V
0.8 V
0.9 V
1.0 V
1.1 V
1.2 V
1.3 V
0.002 a.u.
4000
3600
3200
2800
Wavenumber / cm⁻¹
FTIR
Local coordination
Chemical bonding
Electronic structure
RIXS

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