SILS Conference 2023

Rome, August 30th - September 1st

SILS Società Italiana Luce di Sincrotrone

SAPIENZA UNIVERSITÀ DI ROMA

SILS 2023

Annual Meeting of the
Italian Synchrotron Radiation Society

Rome 30 August-1 September 2023

Sapienza University

Book of Abstracts

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Plenary Lecture 1. Synchrotron measurements on planet-forming materials at high pressure and high temperature: the key to understanding planetary diversity

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The discovery of an ever-increasing number of exoplanets raises a number of societal questions, ranging from "Are we alone in the universe?" to "Do other forms of life exist?". The past, present or future habitability of planets and satellites in the solar system, and of extrasolar objects, as well as the definition of a habitable zone around a given star, and the existence of a link between habitability and the astronomically observable characteristics of the star and planets, are major scientific questions. One of the first clear conclusions of this planetary quest is that planets are much more diverse than expected, and that Earth is far from the norm. The ability to move from astrophysical and geophysical observations to models of planetary composition, structure and dynamics, requires knowledge of the physical and chemical properties of the constituent materials under the relevant thermodynamic conditions. In this respect, synchrotron measurements play a central role. In this talk, I will give examples of how X-ray diffraction, absorption, scattering, imaging and tomography measurements on high-pressure, high-temperature planet-forming materials can be used to determine phase diagram, equation of state and thermoelastic properties, and, in turn, help to understand planetary observations and improve our comprehension of planetary diversity.

MS2 - Advanced accelerator-driven radiation sources and their applications (XFEL-IR)

KN1. Free-electron lasers: state of the art and opportunities for advanced accelerators

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X-ray free-electron lasers have revolutionized X-ray science, increasing the available X-ray peak brightness by ten orders of magnitude with respect to the previous state of the art.
The ongoing development of plasma-based X-ray free-electron lasers promises another leap forward in the field, dramatically increasing the availability of XFEL sources and providing a path towards brighter and shorter pulses.
In my talk I will discuss the physics of free-electron lasers and highlight their strengths and limitations.
I will then review the state of free-electron lasers and the ongoing R&D effort at the Linac Coherent Light Source and other FEL facilities worldwide.
Finally, I will discuss my perspectives on advanced XFELs driven by plasma-based accelerators, the unique scientific opportunities that they can enable and the potential pitfalls in the quest for the next generation of XFELs.

O1. A compact plasma-based betatron X-ray source: the EuPRAXIA Advanced Photon Sources (EuAPS) project

A. Curcio[1], M. P. Anania[1], R. Assmann[1], L. Avaldi[2], A. Balerna[1], A. Biagioni[1], P. Bolognesi[2], E. Chiadroni[3], J. Chiarinelli[2], A. Cianchi[4], P. Cirrone[5], G. Costa[1], L. Crincoli[1], A. Del Dotto[1], M. Del Giorno[1], Z. Ebrahimpour[1], A. Falone[1], D. Francescone[3], A. Frazzitta[3], M. Galletti[4], A. Ghigo[1], L. Giannessi[1], A. Giribono[1], L. Gizzi[6], L. Labate[6], A. Mostacci[3], M. Opromolla[1], V. Petrillo[7], G. Petringa[5], R. Pompili[1], S. Romeo[1], A. R. Rossi[7], F. Stellato[4], F. Stocchi[4], C. Vaccarezza[1] and M. Ferrario[1]

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The EuPRAXIA Advanced Photon Sources (EuAPS) project, led by INFN in collaboration with the CNR and the University of Tor Vergata, involves the construction of a laser-driven “betatron” X-ray user facility at the SPARC_LAB laboratory of the LNF. EuAPS also includes the development of high power (up to 1 PW at LNS) and high repetition frequency (up to 100 Hz at CNR Pisa) laser drives for EuPRAXIA.
In this talk we first examine the physics behind the dynamics of accelerated electron betatrons in plasma accelerator cavities: the betatron oscillations of relativistic electrons at very short scale lengths are responsible for the emission of ultrashort X-ray bursts.
Next, we present the current status of the experimental activity at the LNF, finally discussing the relevant results for the EuAPS project, highlighting the expected performance of the source for user applications.

O2. Terahertz-driven dynamics in liquid water

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On the microscopic scale, water molecules in the liquid phase make hydrogen bonds with tetrahedral structures that fluctuate on the picosecond (ps) timescale. On the macroscopic scale, thermo-dynamic properties of water, such as density and compressibility, are anomalous as they scale non-continuously. However, it is unclear how the macroscopic behavior emerges from the microscopic properties. An inherently powerful spectroscopic tool to study water is terahertz (THz) radiation because it can reveal the fluctuations of the liquid network on the picosecond time scale, which are of the same order of magnitude of the relaxation time constants. In fact, THz radiation between about 1 and 25 THz is strongly absorbed by the intermolecular collective modes of liquid water.
In order to quantify the coupling between these different modes and their anharmonicity, intense THz sources are needed. Here I detail recent advances in non-linear THz spectroscopy on liquid water performed with accelerator-based sources emitting radiation at about 1 or ~12 THz with repetition rates of 50 Hz and ~10 MHz, respectively. After disentangling thermal and acoustic effects, all these experiments revealed large optical nonlinearities from water, which could be rationalized as the resonant reorientation of hydrogen-bonded water molecules by the THz fields.

[1] F. Novelli et al., *Materials*, 2020, **13**, 1311.
[2] F. Novelli et al., *J. Phys. Chem. B*, 2020, **124**, 4989.
[3] F. Novelli et al., *Appl. Sci.*, 2020, **10**, 5290.
[4] F. Novelli et al., *Phys. Chem. Chem. Phys.*, 2022, **24**, 653.
[4] F. Novelli et al., *AIP Advances*, 2022, **12**, 115319.

O3. Developments of X-ray absorption spectroscopies at FXE instrument

Yohei Uemura[1], Peter Zalden[1], Xinchao Huang[1], Frederico Alves Lima[1], Fernando Ardana-Lamas[1], Martin Knoll[1], Paul Frankenberger[1], Siti Heder[1], Hao Wang[1], Han Xu[1], Doriana Vinci[1], Yifeng Jiang[1], Mykola Biednov[1], Sharmistha Paul Dutta[1], Hazem Yousef[1], Diana Jakobsen[1], Dmitry Khakhulin[1] and Christopher Milne[1]

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X-ray Absorption Spectroscopy (XAS) is one of the essential techniques for materials characterisation. Since XAS can be applied to various kinds of systems, such as solid state materials or molecules in solution, XAS has been employed to study photoexcited states of materials at X-ray Free Electron Lasers[1,2]. The Femtosecond X-ray Exeriments (FXE) instrument is dedicated to the study of photoexcited states of materials using a pump-probe methodology. At FXE non-resonant x-ray emission spectroscopy (nr-XES) has been employed to track photoexcited states of molecules in solution. Due to the intrinsically stochastic x-ray spectral features of the self-amplified spontaneous emission (SASE) process, using monochromatic x-rays at XFELs has been historically challenging. Since nr-XES does not require monochromatic x-rays nor energy scanning, measuring non-resonant XES was straightforward, especially when using a von Hamos dispersive X-ray emission spectrometer geometry. At FXE, 16 von Hamos analyser crystals with 50 cm working distance can be used simultaneously, providing a very large solid-angle coverage. Owing to the setup, different emission lines such as K_α and K_β lines can be measured at the same time. Since non-resonant XES is a photon-in-photon-out measurement, using more incident x-ray photons improves the data quality. Much more x-ray photons are available due to the burst mode operation at European XFEL which makes XES measurements more efficient. Even weak signals such as K_β or valence-to-core (VtC) lines can be measured at FXE. [3]

Recently we have been focusing on x-ray absorption fine structure (XAFS) measurements. Although it is not easy to normalise incident x-ray fluctuations at XFELs, XAFS measurements have been done at other facilities. The XAFS capability is important for our user community. As mentioned above, more x-ray photons are available at FXE owing to the burst mode which should translate into XAFS spectra with a good signal-to-noise (S/N) ratio. In addition, advanced x-ray spectroscopic measurements such as high energy resolution fluorescence detected x-ray absorption spectroscopy (HERFD-XAS) are also available if the XAFS measurement at FXE is established. Such advanced techniques can give detailed information about the photoexcited states of materials. XAFS measurements will extend the ultrafast X-ray spectroscopy scientific scope of the instrument at the European XFEL. In Fig. 1, the XAFS measurement setup at FXE is displayed. X-ray is monochromatized using a Si (111) monochromator and the incident and fluorescence x-ray intensities are measured using photodiodes. In order to adjust the signal level from the photodiodes to the digitizer input range, we use two fast current amplifiers (FEMTO DHPCA-100). We measured pump-probe XAFS of $Cu(dmp)_2$ molecules using a liquid jet and we obtained transient XAFS with a decent S/N. We will present our recent achievements about XAFS at the FXE instrument.

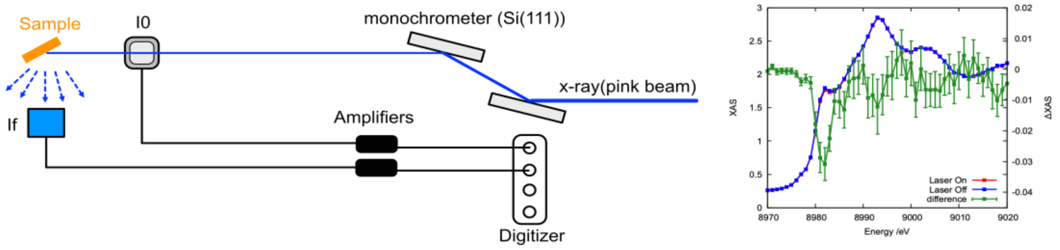

Figure 1. A schematic drawing of the XAFS measurement setup at FXE beamline (left), and pump-probe XAFS of 50 mM $Cu(dmp)_2$ with a 200 μm jet.

[1] Y. Uemura, T. Yokoyama, T. Katayama, S. Nozawa and K. Asakura, *Appl. Sci.*, 2020**, 10,** 21**,** 7818.

[2] D. Khakhulin, F. Otte, M. Biednov, C. Bömer, T. K. Choi, M. Die, A. Galler, Y. Jiang, K. Kubicek, F, A. Lima, A. R. Fernandez, P. Zalden, W. Gawelda and C. Bressler, *Appl. Sci*,. 2020, **10**, 3, 995.

[3] https://www.xfel.eu/facility/instruments/fxe/current_capabilities_of_fxe/index_eng.html

O4. The EuAPS betatron photon beam: ultra-bright light pulses for imaging and spectroscopy

Francesco Stellato[1] on behalf of the EuPRAXIA collaboration

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The EuPRAXIA Advanced Photon Sources (EuAPS) project, led by INFN in collaboration with CNR and the University of Rome Tor Vergata, foresees the construction of a laser-driven “betatron” X-ray user facility at the LNF SPARC_LAB laboratory [1]. EuAPS has received financial support from the Italian PNRR plan for the creation of a new research infrastructure.
While the EuPRAXIA@SPARC_LAB facility [2] will provide the Laboratori Nazionali di Frascati (LNF) with a unique combination of a high-brightness GeV-range electron beam accelerated by a state-of-the-art X-band RF linac, a 0.5 PW class laser system and an ultimate soft X-ray FEL light source [3] driven by a plasma accelerator, the EuAPS project, still using the plasma acceleration, will move in the direction of a pulsed X-ray beam having a continuous energy spectral range from soft to hard X-rays [4,5].
The foreseen applications of the betatron photon source [6], which include ultrafast, time-resolved imaging and spectroscopy measurements on a variety of samples, both biological and inorganic, providing information about their structure and dynamics will be described.

[1] https://euaps.infn.it/
[2] M. Ferrario et al., *Nucl. Instrum. Methods Phys. Res. Sect. A*, 2018, **909**, 134-138.
[3] A. Balerna et al., *Condensed Matter*, 2019, **4**, 30.
[4] A. Curcio et al., *Phys. Rev. Accel. Beams*, 2017, **20**, 012801.
[5] A. Curcio, et al., *Nucl. Instrum. Methods Phys. Res. Sect. B*, 2017, **388**.
[6] F. Stellato et al., *Condensed Matter*, 2022, **7**, 2.

O5. The Sabina Terahertz/Infrared beamline at SPARC-Lab facility

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The SABINA project was developed by INFN at the SPARC_LAB research facility with the aim of creating an electromagnetic radiation source in the important Terahertz (THz)/MIR spectral region. This project is part of a broader framework [1] that for decades has aimed to innovate the techniques for generating, manipulating and detecting THz radiation, the importance and application of which have been severely limited in recent decades by the lack of technologies and techniques that are already widely used and refined in other spectral ranges. Among the frontiers of research in this field, it is important to include the realisation of high-intensity, ps-long, THz and Infrared (IR) sources that are going to become a fundamental spectroscopy tool for probing and control low-energy quantum systems ranging from graphene and Topological Insulators to novel superconductors and magneto/electric excitations [2-4].

In this framework, the SABINA project has the practical goal of realising a FEL beamline operating as a user facility that produces quasi-monochromatic radiation over a wide spectral range from 3 THz up to 30 THz, with time duration pulses on the order of ps and energies in the mJ range. The core of the beamline consists of a series of three undulators based on the APPLE-X design that allows the emission of high intensity synchrotron radiation and the manipulation of high electric fields (~10 MV/cm) by controlling their polarizations (linear, circular and elliptical). The beamline also includes the transport of the produced radiation to an 'open to user' laboratory through a total optical path of approximately 25 m. This laboratory will be equipped with the appropriate optical set-up necessary to perform a wide variety of scientific experiments concerning non-linear and time-resolved optical spectroscopy. Indeed, the laboratory will be equipped and synchronised with a fs laser to allow pump-probe experiments with different combinations of THz, IR and Vis radiation, and will be supplied with a magnetic cryostat to perform temperature measurements with magnetic fields up to 5T.

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O6. **Towards hard X-ray transient grating spectroscopy**

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Optical-domain transient grating (TG) spectroscopy is a versatile background-free four-wave-mixing technique used to probe vibrational, magnetic and electronic degrees of freedom in the time domain. The newly developed coherent X-ray free-electron laser (XFEL) sources allow its extension to the X-ray regime. X-rays offer multiple advantages for TG: their large penetration depth allows probing the bulk properties of materials, their element specificity can address core excited states, and their short wavelengths create excitation gratings with unprecedented momentum transfer and spatial resolution. Here, we demonstrate TG excitation in the hard X-ray range at 7.1 keV using a single XFEL pulse exploiting the Talbot effect, in contrast with the usual crossing beam setup, since it becomes very challenging in the hard X-ray range. In bismuth germanate (BGO), the non-resonant TG excitation generates coherent optical phonons detected as a function of time by diffraction of an optical probe pulse. This experiment [1] demonstrates the ability to probe bulk properties of materials and paves the way for ultrafast coherent four-wave-mixing techniques using X-ray probes and involving nanoscale TG spatial periods.

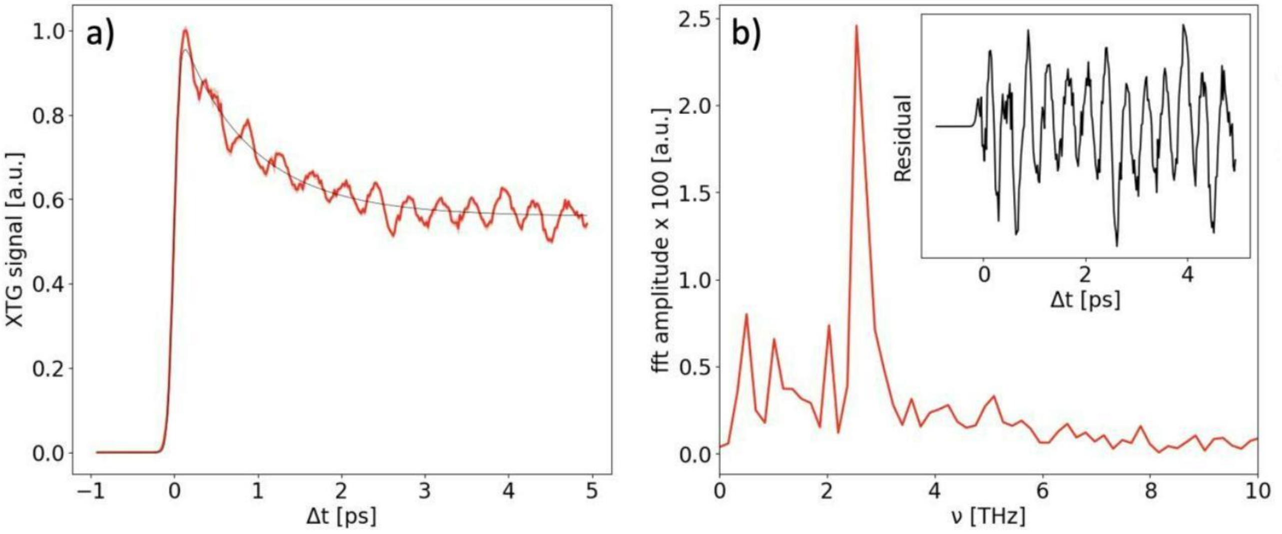

Figure 1. XTG signal from BGO at 7.1 keV with an excitation grating pitch of 770 nm. Panel a) shows the normalized time trace at short times (< 5 ps). The non-oscillatory decay of the signal is fitted (in black) with a single exponential. The fast oscillations are attributed to optical phonon coherence [2]. The Fourier transform of the fast-oscillatory component is presented in panel b) (residuals from the fit in a are shown in the inset).

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O7. Structure and electronic properties of excited states in cerium oxide: recent results obtained at the FXE instrument of Eu-XFEL

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The possibility to assess the electronic and structural modifications induced by photoexcitation in photocatalyitic materials can be of great help to understand the functionality of such materials. Ultra-short and ultra-intense free electron laser (FEL) pulses, tunable in energy in the x-ray energy range, can provide information on the dynamics of photoinduced modifications of the local electronic and atomic structure around the individual atomic species via pump-probe X-ray absorption spectroscopy (XAS) with a time resolution below 100 fs. The technique was applied to cerium oxide, a material with important applications in catalysis and photocatalysis. In typical photocatalysts, based on a high mobility of photoexcited charge carriers, the localization of photoelectrons or photoholes, due to the coupling with structural distortions into the so-called small-polaron states, can significantly limit the photoactivity of the material. On the contrary, since the functionality of cerium oxide is based on the reversible exchange of oxygen ions with the reactants, the self-trapping of excited charge may actually enhance the material reducibility, and as a consequence the photoinduced activity of the catalyst. Moreover, possible structural deformations, correlated with the localization of photoexcited charge, may also further decrease the oxygen vacancy formation energy and have a beneficial effect on the photoinduced redox functionality of the compound. The use of pump-probe XAS using ultrashort pulses allows to investigate the dynamics of the element-specific electronic modifications and correlate it with the structural modifications, providing a detailed picture of the out-of-equilibrium processes which take place in the material after photoexcitation.

We show here the preliminary results of a pump-probe XAS experiment that we recently performed at the FXE instrument of the European X-FEL. The experiment was carried out on a 50 nm polycrystalline CeO_2 film, grown by reactive magnetron sputtering on a sapphire substrate. The measurements were performed at grazing incidence, to minimize sample damage and maximize the sensitivity of the method to the thin film investigated. The CeO_2 film was excited using a laser pump with energy above the band gap (4.6 eV) and probed by XFEL pulses with energy across the Ce L_3 edge (5.73 keV). The sample did not show any detectable damage induced by the pump or by the probe: the XANES signal shape and intensity were unmodified after prolonged exposure and the sample surface under an optical microscope did not show any visible beam trace. We successfully measured pump-probe Ce L_3-edge XAS spectra in the total fluorescence yield acquisition mode in the near and extended energy range at different delay times and we measured the dynamics of the observed variations at different photon energies within a delay time range extending up to 250 ps, with a resolution of 100 fs. The availability of a Von Hamos type spectrometer on the outgoing beam allowed also to acquire pump-probe Ce L_α X-ray emission spectroscopy (XES) spectra at different photon energies across the Ce L_3 edge, as well as pump-probe high-energy resolution fluorescence detected X-ray absorption near edge spectroscopy (HERFD-XANES) – exciting the Ce L_3 edge and detecting the Ce $L_{\alpha1}$ XES intensity – at different delay times. HERDF-XANES allowed us to resolve the pre-edge features, expected to be directly sensitive to 4f occupation. The data show clear dynamic changes in the electronic properties and in the local atomic structure as a function of the delay time between the pump and the probe.

MS5 - Equilibrium and dynamic properties of surfaces and nanostructures

KN1. Charge and Exciton Dynamics in Hybrid Materials Probed by Time Resolved Soft X-Ray Spectroscopies at ELETTRA Synchrotron

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In the fields of optoelectronics and photochemistry there is growing interest in studying the response to optical excitation of organic molecules, films and interfaces, as these systems are of fundamental relevance for the development of the next generation of environmentally sustainable optoelectronic devices and catalysts. In order to probe the charge and exciton dynamics in such materials down to the sub-nanosecond timescale we developed a setup at the ALOISA beamline of the Elettra synchrotron that exploits the chemical selectivity of X-ray absorption spectroscopy (XAS) and X-ray photoemission (XPS) in an optical pump/X-ray probe experiment. In this talk, I will present our recent results on tracking triplet dynamics in pentacene and perylene thin films. The role of the film morphology will be discussed by comparing the response of perylene molecules with different terminations. Finally, I will show how the developed setup can follow a structural transition in 2H-MoTe2 initiated by the illumination of the organic molecules adsorbed on top.

O1. Sub-femtosecond electron dynamics in ZnO studied by Resonant Photoemission Spectroscopy

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ZnO has emerged as a highly attractive material for many applications, such as sunlight driven photo-electro-catalytic cells, photocatalysis, solar energy conversion, etc. To gain full control on the characteristics of the ZnO based devices, it is mandatory to quantify the charge transfer times, and to fully understand the electron dynamics as influenced by different electronic excitations. This experimental work aims to gather fundamental knowledge of the ZnO ground and excited electronic states that is the basis of a correct description of the optical properties of any material. We provide a deep insight in the spectroscopy of the highly excited states underlying ultrafast charge transfer processes in a ZnO, which may lead to improved functionality of materials derived from this oxide. The reported investigation complements pump-probe experiments, such as time-resolved-XAS or pump-probe XPS, for which the time resolution is limited by the laser-pump pulse duration. Resonant Photoemission (RESPES) spectra are measured on ZnO polycrystalline thin films [1] at the Zn L_{23} and M_1 thresholds, in a core-hole-clock spectroscopy fashion [2]: the core-hole lifetime is used as a time reference clock to estimate, with element selectivity, the charge transfer dynamics occurring to screen the core-hole itself. L_{23} results (Figure 1) compare well with the literature [3]; in particular, it is found a charge transfer (CT) time that ranges between 3 and 6 fs for L_3 and L_2, respectively. Experiments were performed at BESSY II, CoESCA station, with linearly polarized photon range (110-1900) eV, by exploiting the high luminosity Angle Resolved-Time of Flight spectrometers that are inherently energy multichannel and allow for reasonable acquisition time. The present results confirm RESPES as an effective tool to determine CT times in the fs domain and open the road to new experiments that correlating in time photoelectrons and Auger-electrons allow for time resolved experiments with the core-hole acting as the pump and Auger decay as the probe [4].

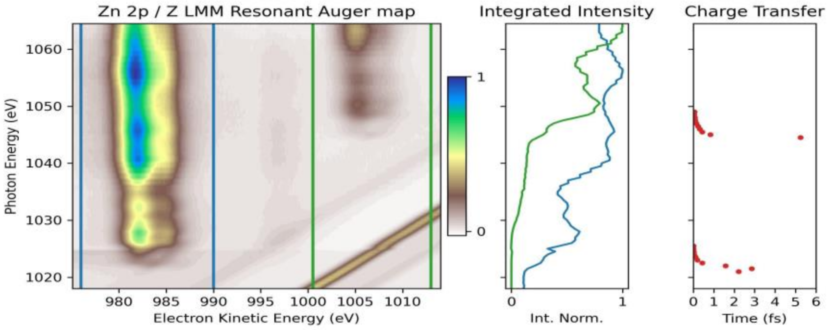

Figure 1. Zn L_{23} Auger-resonant Raman scattering: (left panel) 2d maps measured on ZnO polycrystalline thin films; (center panel) photoelectron energy distributions; (right panel); charge transfer time.

Acknowledgements: We are grateful to the technical staff of the COESCA beamline for valuable support.

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O2. Investigating the water/MgO and water/MgCl$_2$ interfaces through Ambient Pressure soft X-ray Absorption Spectroscopy

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Achieving accurate chemical knowledge on the mechanisms of surface processes is of interest both for fundamental understanding and for applications. Surfaces, in fact, provide unique platforms for the success of desirable reactive or nonreactive pathways, for instance by acting toward them as efficient energy-dissipating heat baths and by altering their symmetries significantly if compared to those in the gas or condensed phases [1].

The metal oxide–water and metal-chloride interfaces are of considerable importance in catalysis, materials science, biology, corrosion, geochemistry, and interstellar and atmospheric chemistry. In this regard, magnesium oxide and magnesium chloride have been frequently investigated as model systems. The interaction of a number of MgO surfaces with water has been studied both experimentally and theoretically at various temperatures and pressures in the range between high vacuum and ambient conditions, with the MgO(001) slab being one of the most popularly evaluated by researchers. While it is known that for low water coverage on the MgO(001) surface water forms a layer where 1/5 and 1/3 of the water molecules are dissociated at low (100–180 K) and higher (185–221 K) temperatures, respectively, for water coverages beyond a monolayer, the picture is less definite [2]. In the latter case the standard model of a fully hydroxylated MgO(001) surface has been put into question. The extent of MgO(001) surface hydroxylation has not in fact been settled by the numerous experiments conducted at ambient water conditions, and recently it has been found that reconstructed surfaces, involving hydrated/hydroxylated Mg(II) ions above the MgO(001) surface, are more stable than the fully hydroxylated ones [3]. In addition, MgCl$_2$ plays a central role in the stereoselective polymerization of propylene, where it acts as the active support for Ziegler-Natta catalysts. For this reason, the adsorption properties of a number of catalytically relevant MgCl$_2$ surfaces have been investigated by theoretical and experimental methods, with a particular emphasis on the coordinatively unsaturated ones. Notably, recent dispersion-corrected periodic density funcionaly theory (DFT-D) calculations suggested that in well-formed MgCl$_2$, in the absence of adsorbates, the unsaturated (104) surface exhibiting 5-coordinate Mg cations is the energetically favoured one [4]. Moreover, despite significant theoretical efforts, a limited number of experimental techniques have been employed so far to track the MgCl$_2$ surface modifications upon interaction with gas-phase molecules in realistic conditions, and spectroscopic data concerning water adsorption on MgCl$_2$ surfaces are almost nonexistent.

In this contribution, we will show that surface-selective X-ray absorption spectroscopy (XAS) at ambient pressure may be combined with multivariate curve resolution, molecular dynamics and XAS theoretical methods to track in real time and accurately describe the interaction between water vapor and both the MgO and MgCl$_2$ surfaces. Specifically, we leverage soft-XAS at the Mg K-edge to evidence in real time the occurrence of Mg(II) hydration solvation at the water/MgO interface, to show that the Mg(II) surface ions undergo a reversible hydration process, and to demonstrate the formation of octahedral $[Mg(H2O)_6]^{2+}$ intermediate hydrated species. Further, by exposing MgCl$_2$ to water vapor at temperatures between 595 and 391 K, we prove that water is preferentially adsorbed on 5-coordinated Mg(II) sites in an octahedral configuration, confirming previous theoretical predictions, and find that MgCl$_2$ is capable of retaining a significant amount of adsorbed water even under prolonged heating up to 595 K. The unique surface, electronic, and structural sensitivity of the developed technique may be beneficial to access often elusive properties of low-Z metal ion intermediates involved in interfacial processes of chemical interest.

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O3. Inverse ball milled CeO_2/CuO catalyst for partial methane oxidation: a combined *in situ* DRIFT and *operando* NEXAFS study

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Nowadays, methane (CH_4) is a precious resource and its valorization represents an important objective for the imminent energetic transition. The research for successful catalysts able to efficiently activate the CH_4 molecule and convert it to partial oxidation products such as methanol (CH_3OH) is particularly challenging. One emerging material is the so called "inverse" CeO_2/Cu(111) catalyst, that has demonstrated CH_4 conversion to methanol with high selectivity [1]. In this system, a Cu_2O monolayer formed at the interface between CeO_2 and Cu(111) seems to have a key role for the activation of CH_4; however, the synthetic method employed in the study is not suitable for large scale applications. In this work we present a facile, scalable and green synthetic approach, namely ball milling, for the synthesis of an inverse CeO_2/CuO composite which demonstrated to activate methane at the temperature of 250°C. Through a multitechnique investigation involving *in situ* DRIFT, *operando* Soft X-Ray NEXAFS and DFT calculations, we have been able to associate this peculiar activity to the presence of interfacial Ce^{4+}/Cu^{+} redox couples, generated by a charge transfer from Ce^{3+} to Cu^{2+} atoms promoted by the mechanical energy provided by the synthesis. The DRIFT investigation showed that methane is chemisorbed on the catalyst surface in the form of methane oxidation intermediates (mainly methoxy and formates), while NEXAFS spectra showed that at the same time part of Cu^{2+} sites are reduced to Cu^{+} (Fig. 1). When the catalyst is exposed to an oxidizing agent, gas products are desorbed in the form of CO_2, H_2O, CH_2O and CH_3OH, detected by the micro-GC directly connected to the *operando* NEXAFS reaction cell developed at the APE-HE beamline of Elettra Synchrotron [2]. The product desorption promoted by O_2 restores the initial electronic configuration of the catalyst surface, therefore making it possible to perform more catalytic cycles without deactivating the catalyst. The spectroscopic investigation at real catalytic conditions coupled with DFT calculations allowed to identify the reaction active sites, i.e. oxygen atoms located in proximity of the CeO_2/CuO interface, able to activate the CH_4. These results demonstrate the effectiveness of the synthetic technique of creating peculiar interfaces and pave the way for the optimization of CeO_2/CuO catalysts as potential candidates for industrial applications.

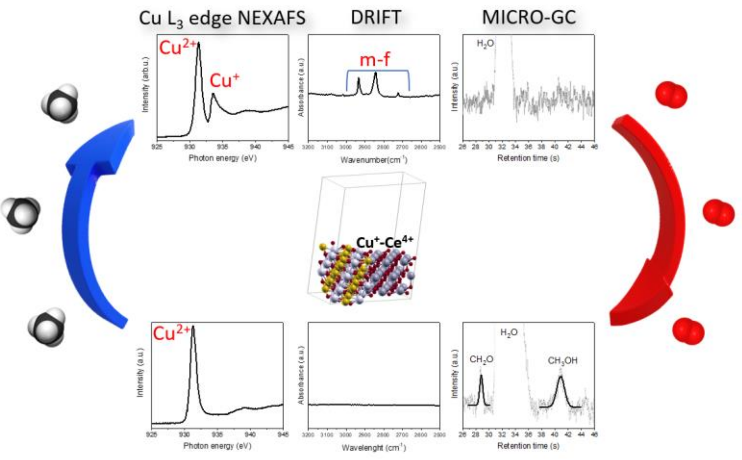

Figure 1. Cu L_3 edge NEXAFS spectra (left), DRIFT spectra (center), and micro gas chromatograms acquired while cyclically exposing a ball milled CeO_2/CuO composite to CH_4 (upper panels) and O_2 (lower panels) at 250°C. *m* e *f* labels in DRIFT spectra are referred to methoxy and formates species respectively.

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O4. Anomalies at the Dirac point in pristine and substitutional doped graphene

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The properties of the Dirac state in graphene on 6H-SiC(0001) and its changes induced by different atomic species (B, N ...), substituted via low energy (25eV) ion bombardment, were investigated via angle-resolved photoemission spectroscopy (ARPES) at the BaDElPh beamline of the Elettra synchrotron light laboratory. The symmetry-selective measurements for the Dirac bands reveal their linearly dispersive behaviour across the Dirac point which was termed as the anomalous region in earlier studies. No gap at the Dirac point of graphene is observed even after 5% of B and N substitution. The anomalies at the Dirac point are attributed to the spectral width arising from the lifetime and momentum broadening in the experiments. The internal symmetries appear to be preserved in graphene on SiC even after significant B and N substitutions. These results provide new insight to tune the carrier properties of graphene while keeping the Dirac fermionic properties protected, which is important for exploring its technological applications [1].

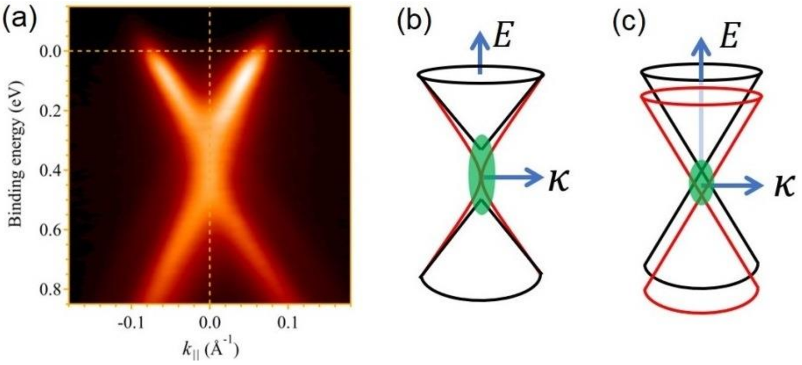

Figure 1. (a) Typical ARPES spectra of graphene on SiC along the ΓKM direction of the Brillouin zone; the origin of the momentum axis is shifted to K point. Schematic of (b) anomalous region and (c) plasmaron scenario around the Dirac point. Red curved lines in (b) show bands in the presence of electron correlation. Red Dirac cone in (c) is due to plasmaron bands.

*These authors contributed equally to this work.

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O5. Single-Atoms on Crystalline Carbon Nitrides for Selective C-H Photooxidation

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The field of catalysis involving single atoms systems (SAs) holds great significance in modern science, as it possesses a remarkable capacity to merge the domains of homogeneous and heterogeneous catalysis. Natural iron and manganese metalloenzymes have demonstrated their effectiveness in C-H oxidation reactions, which has motivated researchers to replicate their active sites in artificial catalytic systems [1]. In this study, a simple and versatile cation exchange method was successfully employed to stabilize single iron and manganese atoms in poly(ep-tazine imides)(PHI) [2], and their high selectivity for the photooxidation of toluene to benzaldehyde, a crucial compound for the chemical industry, was demonstrated. The Fe-PHI can produce superoxide radicals and toluene under neutral conditions, with extremely low yields. However, it has been shown that to achieve high selectivity for benzaldehyde, the reaction should not involve radical formation. Obviously, the photogenerated electrons and holes are still produced by the semiconductor and are crucial, as without light, the reaction proceeds with lower amounts of product. In the case of Mn-PHI, no reaction occurs in the absence of irradiation, and as observed for Fe-PHI, high concentrations of hole scavengers (e.g. IPA) inhibit the photocatalyst activity. This characteristic highlights the importance of photogenerated holes in the selective oxidation of toluene to benzaldehyde through the formation of oxo M=O species generated by the oxidation of the metal center [2]. However, it appears that at low concentrations, IPA acts as an electron promoter in the conduction band to form H_2O_2, thus avoiding premature oxidation of toluene by holes. The similar reaction mechanisms of Fe and Mn were further investigated through in operando conditions XAS analysis operating in the presence of oxygen, oxygen and water, and light irradiation. These experiments demonstrate the initial presence of Fe(III) and Mn(II) in the pristine materials. Irradiating the samples with a laser during the flow of a mixture of water and oxygen detects an increase in the population of Fe and Mn in higher oxidation states. The reversible behavior that is observed by turning on and off the laser is evident: the process of turning the light on and off can be repeated, obtaining the same results in the spectra. This result demonstrates and confirms that light irradiation plays a role in promoting the oxidation of metal sites into high-valence species, suggesting that photogenerated holes of carbon nitride interact with Fe and Mn sites and drive the formation of Fe=O and Mn=O species.

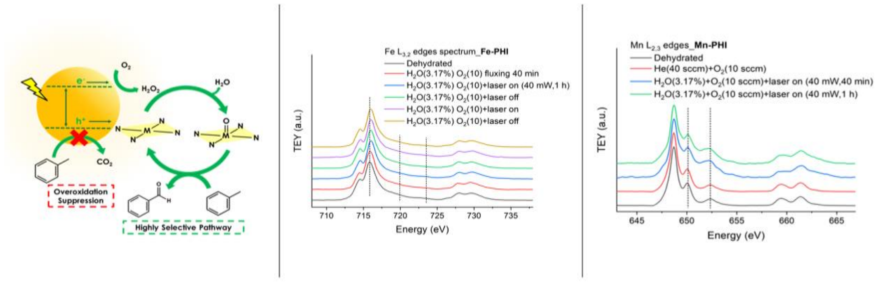

Figure 1. Mechanism of metal oxo species formation and XAS spectra of Fe and Mn $L_{3,2}$ edge

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O6. Relevance of thermal fluctuations in Fe(100)-p(1x1)O in optically-induced ultrafast demagnetization

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Since the first observation of ultrafast demagnetization in a 3d ferromagnet following optical excitation [1], a variety of pump-probe techniques have addressed this challenging aspect of solid dynamics. The comparison with theoretical models has suggested that a Stoner picture cannot explain the observed dynamics [2] and that temperature-dependent spin fluctuations play an important role [3].
To confirm such scenario, here we separately investigate the electronic and spin degrees of freedom in Fe(001)-p(1x1)O after the pump excitation (1.55 eV energy and 50 fs duration), by means of two time-resolved (TR) photoelectron spectroscopies: angle-resolved photoemission (ARPES) with probe energy of 21.7 eV and spin polarization (SP) of the total electron yield at threshold photon energy (4.8 eV).
In the former measurement, we identify the sudden appearance of non-thermal electrons in a specific region of the valence band, and, after few tens of fs, an increase of the electronic temperature across the whole Fermi surface. On the other hand, the average magnetic moment retrieved from SP measurement shows a different temporal behavior: it quenches only after the electron gas is fully heated and the thermalization with the lattice is activated, and then recovers with a slower time constant (see Figure 1).
The interpretation of experimental results with a microscopic 3-temperature model (m3TM) [4], resulting in the fit curves in Figure 1, highlights the role of thermal disorder in the quenching of the average spin magnetic moment and indicates Elliot-Yafet type spin-flip scattering as the main mediation mechanism, with a spin-flip probability of 0.1 and a rate of energy exchange between electrons and lattice of 2.5 K fs^{-1}.

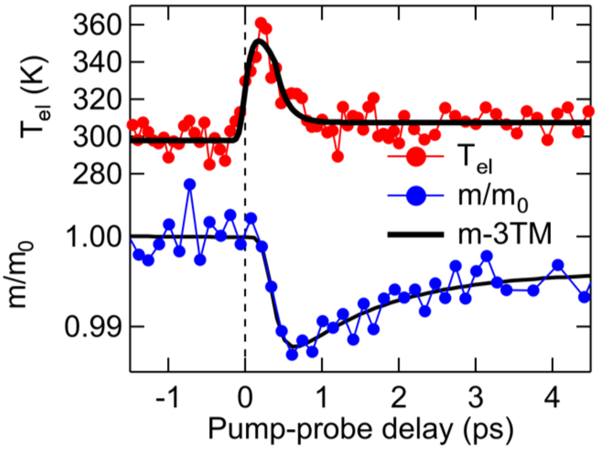

Figure 1. Electronic temperature (top, from the TR-ARPES experiment) and relative magnetic moment (bottom, from the TR-SP experiment). Black lines are fits based on the m-3TM model.

Acknowledgements: This work has been performed in the framework of the Nanoscience Foundry and Fine Analysis (NFFA-MUR Italy Progetti Internazionali) facility.

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O7. Unique adsorption configuration of M(II)-tetraphenylporphyrins (M = Co, Ni, Cu, Zn) on the r-TiO_2(110) surface

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The efficiency of interfacial charge transfer for photovoltaic and photocatalytic applications of metal-porphyrins on rutile TiO_2(110) is governed by the molecular adsorption site and configuration. Here we present a combined experimental and theoretical study of the adsorption configuration of metal(II)-tetraphenylporphyrins, M(II)-TPPs, on the r-TiO_2(110) surface for molecules with different transition metals, namely Co, Ni, Cu, Zn. Although each metal in its oxidation state (II) displays a different tendency to axial coordination at the porphyrin center, we found [1] that all molecules adsorb on the Obr rows with the same molecular conformation (saddle-shape) and orientation. All M(II)-TPP species display a large mobility at room temperature (RT) yielding molecular aggregation into a commensurate phase with the same (2x4)-oblique symmetry, independently on the metal species. Such a homogeneous behaviour of different M(II)-TPPs is correctly reproduced by density functional theory (DFT) computation of the porphyrin equilibrium configurations. According to calculations, the tendency to axial coordination determines the hierarchy of the molecular adsorption energy (where Co-TPP displays the largest one) and the preference for adsorption either atop one Obr atom (Co- and Zn-TPP) or on bridge between two Obr atoms (Ni- and Cu-TPP). In the latter case, the adsorption site is driven by the optimization of the molecular backbone H-bonds to the Obr rows rather than by metal coordination to the substrate rows.

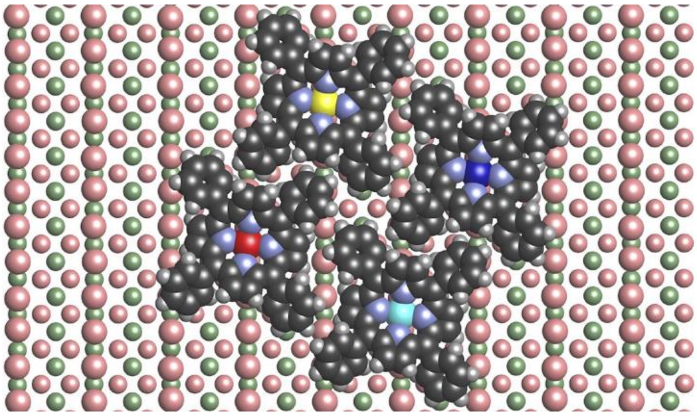

Figure 1. Adsorption configuration for the Co, Ni, Cu, and Zn tetraphenyl porphyrins on the r-TiO_2(110) surface.

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Plenary Lecture 2. Terahertz nonlinear electrodynamics of Dirac materials

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Due to their peculiar band dispersion, Dirac materials present intrinsic nonlinearities in the terahertz range giving rise to a wealth of fascinating phenomena, from saturable absorption to plasmon softening and terahertz harmonic generation [1]. These properties – which are highly demanded for the development of novel terahertz technologies – stem from the absence of parabolicity at the bottom of the band dispersion resulting in massless Dirac carriers. Due to the similarities in their low-energy band structure, both graphene and topological insulators display similar nonlinear terahertz properties. Remarkably, we have recently found that another technologically relevant material as black phosphorus displays very significant terahertz saturable absorption properties, while presenting a finite band mass at ambient pressure.

After an introduction on the TeraFERMI facility [2] at the FERMI free-electron-laser facility we will review our research on the terahertz nonlinear properties of the topological insulator Bi_2Se_3 [3,4]. We will show how a thermodynamic model which was already successfully employed in graphene, can account for the properties of Bi_2Se_3 as well. Finally we will present the terahertz saturable absorption properties of black phosphorus [5]. We have found that in the case of black phosphorus, the key to its very unconventional behaviour lies in its peculiar band structure, which mimics that of massive relativistic Dirac fermions. Black phosphorus therefore represents a unique platform for the study of the high temperature thermodynamics of a relativistic Fermi gas.

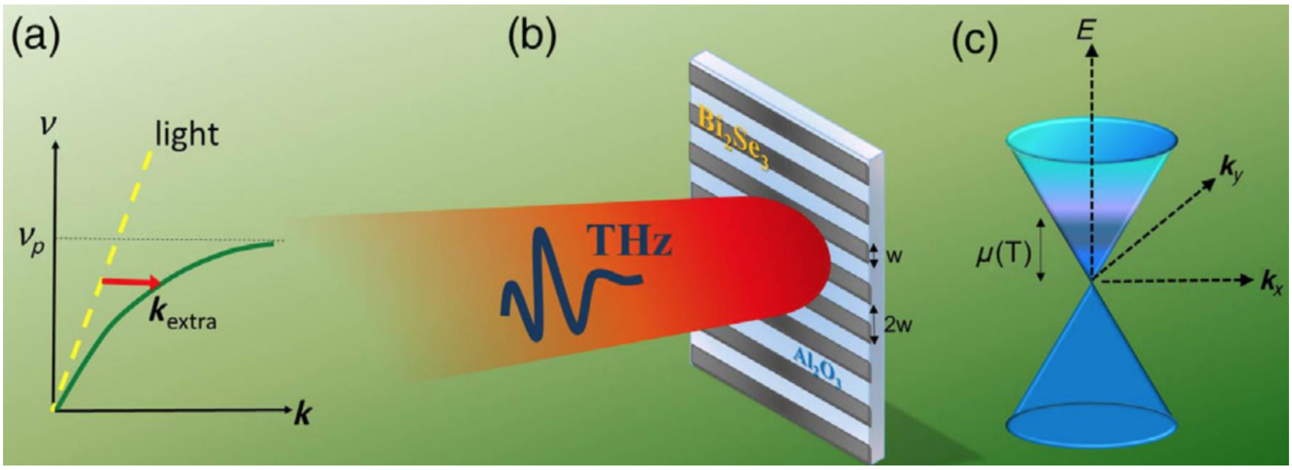

Figure 1. Terahertz plasmons in a topological insulator. Plasmons are collective oscillations of electrons that can be directly excited by light in the presence of an extra momentum provided by the periodic patterning of the sample. The massless Dirac fermions of topological insulators show a natural nonlinear optical behaviour in the terahertz range.

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MS6 - Advanced data analysis methodologies

KN1. Handling heterogeneity: Approaches to separate signals using multiple spaces

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Material properties depend sensitively on the atomic structure, and on the local structure. The local structure may be a symmetry breaking in a crystal, an explicit nanocrystalline or nanoporous sample or even an amorphous or liquid material. We now have powerful tools for studying such materials, many based on the atomic pair distribution function analysis (PDF) of x-ray, neutron and electron diffraction data. This approach has traditionally leaned heavily on the assumption that the average scattering is isotropic, and any heterogeneities in the sample are averaged over. In this talk we explore extensions to the method to allow it to be used to understand the heterogeneities. The most obvious is the ability to carry out spatially resolved PDF measurements, which we have been able to do for some time now. I will review these developments, spending more time on a recent advance that allowed us to to make spatial PDF maps in an electron microscopy with a lateral resolution of around 10 nm. Also challenging is if the sample has orientational heterogeneities, for example, it is a powder sample but with some preferred orientation. We have developed the equations that propagate the orientational distribution function (ODF) through the Fourier transform allowing us to study the ODF in real-space and to obtain a real-space equivalent of a pole figure. Finally, if we allow ourselves to imagine that material whose structure depends on the time-scale that it is probed on is a kind of temporal heterogeneity, we have also demonstrated an approach, variable-shutter PDF (vsPDF), that allows us to probe the structure with different time-resolutions. I will illustrate this with the example of GeTe, a not-so-simple binary compound.

KN2. Advances in modelling X-ray absorption spectroscopy data using reverse Monte Carlo

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X-ray absorption spectroscopy (XAS) has become a standard technique for studying materials under different ambient conditions, with dedicated beamlines at synchrotron facilities. In particular, analysis of the EXAFS region permits to obtain information on the local structure around the photo-absorbing element. The standard fitting procedure for the oscillating EXAFS signal consists in using few model contributions from nearest-neighbours shells, usually described with a simple Gaussian distribution, and optimize their parameters through a least-square fitting procedure. This method works well for simple cases, like crystals with well-defined shells, but it has shortcomings when dealing with amorphous materials and in the presence of distortions, such as in nano-materials [1]. The use of Reverse Monte Carlo (RMC) can overcome some these limitations and permits to obtain additional information about the structure.

RMC is a modelling method, initially developed to fit diffraction data [2], but that can be generalized to any experimental technique for which the experimental signal can be calculated starting from the atomic coordinates. At every step, an atom is moved randomly, the signal is recalculated and compared with the experimental one: if the agreement is improved, the new position is retained, otherwise it is discarded. Repeating this step multiple times, we obtain in the end a three-dimensional model that is compatible with our data within experimental uncertainties.

In this presentation, we show various examples of applications done in recent years using our RMC program based on the GnXAS software package, together with recent developments and general considerations [3].

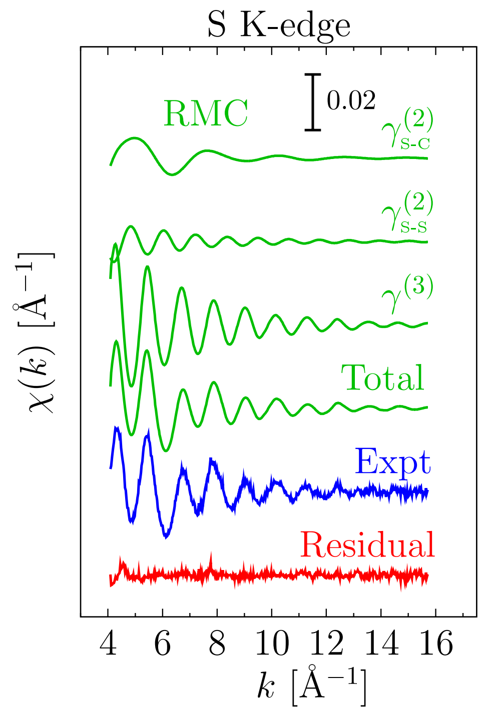

Figure 1. Experimental EXAFS signal of molecule CS2 fitted by RMC.

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O1. Local structure of solid and liquid Au as a function of temperature by EXAFS

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Accurate Au L-edge EXAFS (Extended X-ray Absorption Fine Structure) spectra have been collected and analyzed in a wide temperature range (80 K-1400 K) for solid and liquid phases. Suitable samples for high-temperature measurements in the liquid phase were obtained by in-situ reduction of an organic precursor. Data-analysis was carried out using GnXAS software [1,2], a reliable for multiple-scattering calculations including relativistic corrections[3,4], especially important for this heavy element. Simultaneous L_1, L_2 and L_3-edge refinements were performed and local structural results were compared with those obtained in previous studies based mainly on x-ray diffraction experiments. In the solid phase, increasing temperatures led to an increased asymmetric distribution of first-neighbors while the average distance is found to be compatible with present thermal expansion data. The structure refinement of liquid Au was carried out considering the short-range contribution to the pair distribution function g(r), using available x-ray diffraction data[5,6] as a constraint for long range order. We have shown that EXAFS is extremely sensitive to local structure and that the g(r) of liquid Au is characterized by a clear shift of the foot of the g(r) and a slight shortening of the position of the maximum as compared with previous data. Moreover, present data provided a test for MD calculation (Molecular Dynamics) based on EAM (embedded atom models)[7,8].

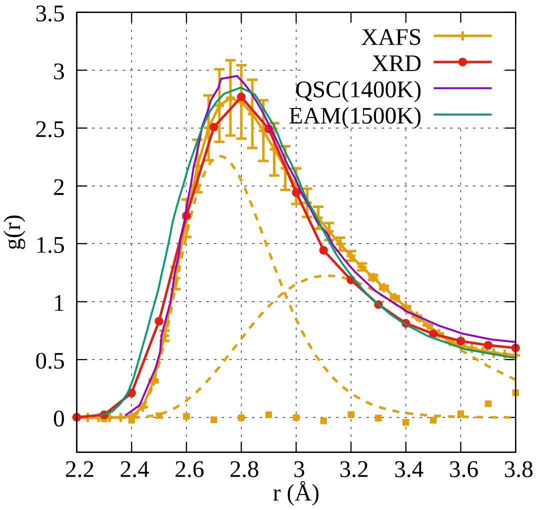

Figure 1. Reconstruction of the liquid Au (solid orange line) pair distribution g(r) obtained by XAFS compared with: XRD data [5,6] (red dots), MD simulation with (Quantum Sutton-Chen) QSC potential [7] (solid purple line) and with EAM potential [8](solid green line). The individual contributions to the first g(r) peak reconstructed by XAFS are also shown (orange dashed lines and dots).

Acknowledgements: This work has been funded through the PNRR MUR Project No. PE0000023-NQSTI.

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O2. An effective approach to the structural analysis of complex molecules: combining DFT and EXAFS

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EXAFS data analysis is a complex procedure from which information about the average local structure around the absorbing atom can be obtained. To achieve a reliable quantitative data analysis a suitable model of the expected average local coordination cluster around the absorber is required in order to individuate the relevant signal to be used in the fitting of the data and calculate the photoelectron amplitude and phase scattering functions required to calculate the theoretical curves[1-2]. Usually, crystallographic structures provide suitable models for the local structure, but when dealing with complex molecules and organic complexes the crystallographic structure is often unavailable. In these cases optimization algorithms and Ab-initio methods, such as Quasi-Newton and DFT, can be used to obtain satisfactory models of the local clusters with relatively simple steps, and help to individuate the relevant scattering paths and disambiguate specific signals having similar amplitudes and length (i.e. a coordination shell where species of similar Z are present).
Here we present a real-life scenario where this approach proved to be effective and time saving, it is the study on a series of bis(pyrazol-1-yl) acetate Cu complexes that were prepared, characterized with complementary techniques (XAS, XPS and NEXAFS) and tested for their antitumoral activity [3]. These complexes depict a number of different contributions from both single and multiple scattering paths originating from the Carbon and Nitrogen neighbours that making the Cu-K edge EXAFS analysis a difficult task. The coordination clusters were built considering the additional information from the Cl 2p XPS data analysis that individuate the dimerization, leading to a reliable refinement of the EXAFS signals.

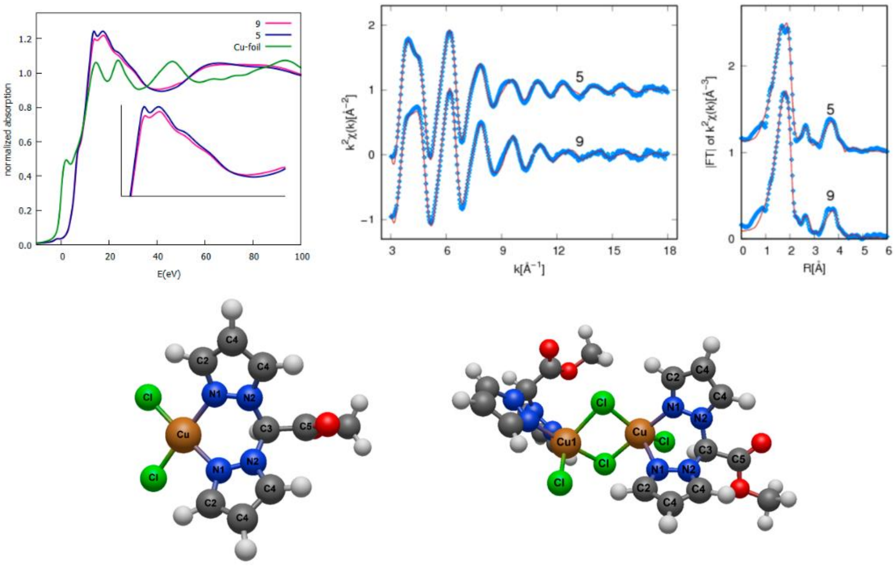

Figure 1. Cu K edge XANES region (left panel), EXAFS experimental (blue dots) and best fit (full black lines) results in k (central panel) and R (right panel) space for two investigated complexes. Optimized monomeric and dimeric structures for the Copper complex 5 (bottom).

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O3. CrystalMELA: Advancing Crystallographic Structure Solution Using Machine Learning and Powder Diffraction Data

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A powder diffraction pattern is primarily influenced by overlapping peaks, challenges in accurately estimating the background, the presence of preferred orientation effects, and limited experimental resolution. These factors make the process of solving the structure complex. One of the critical initial steps, such as pattern indexing and determining the space group, becomes difficult, especially when multiple chemical phases are present. However, an incorrectly defined unit cell does not lead to a structural solution. Despite the availability of automatic indexing software like DICVOL [1], N-TREOR09 [2], and ITO [3], these challenges persist. In recent years, significant advancements in data-driven models and the abundance of experimental data from various sources have facilitated the application of Artificial Intelligence (AI) in materials science, particularly in the analysis of diffraction data using machine learning (ML) algorithms.

To address the difficulties encountered in the structure solution process using powder diffraction data and complement traditional indexing approaches, a new ML-based web platform called CrystalMELA (Crystallographic MachinE LeArning) [5] has been developed. Its purpose is to classify crystal systems. The platform focuses on the seven crystal classes and currently utilizes three different ML models: Convolutional Neural Network (CNN), Random Forest (RF), and Extremely randomized trees (ExRT). These models have been trained using theoretical powder diffraction patterns from over 280,000 crystal structures of inorganic, organic, organo-metallic compounds, and minerals collected in the POW_COD database [6]. The classification accuracy of CrystalMELA is 70%, which improves to 90% when considering the top-2 accuracy.

CrystalMELA is freely available to the scientific community and can be accessed through its homepage (Fig. 1). The platform offers powerful and user-friendly classification options, supported by a graphical interface.

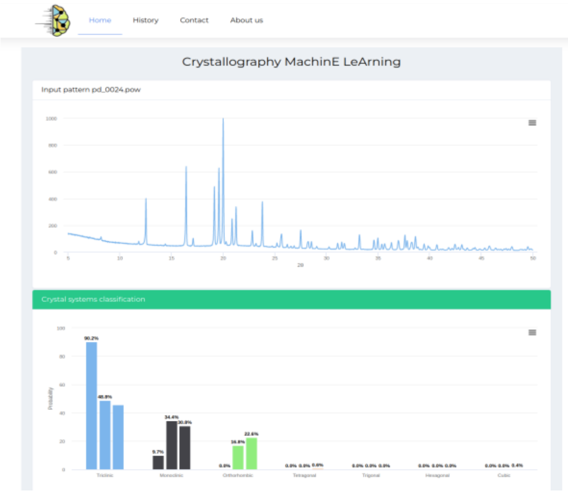

Figure 1. Screenshot of result page.

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O4. XAS investigations related to the Magnetic response of Magnetic Zeolite Synthesis from Polluted Mt. Etna Volcanic ash

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Magnetic zeolites are a category of nanostructured materials that find applications in various fields such as water treatment, catalysis, selective magnetic filtration, and more. Natural volcanic ashes (VA), owing to the presence of iron oxides/hydroxides in their chemical composition, serve as suitable precursors for the cost-effective synthesis of magnetic zeolites on a large scale. However, natural materials are often characterized by an intrinsic variability of composition and physical and chemical properties, it is crucial to achieve an accurate description of their local atomic structure, coordination chemistry, and electronic state of the active elements, particularly Fe, which provides the magnetic behaviour. This knowledge is necessary to comprehend the macroscopic properties of the materials and to design optimal synthesis routes for magnetic zeolites. In this regard, X-ray absorption fine structure (XAFS) spectroscopy is a highly suitable technique thanks to its element-selective local probe specificity.

In this study, the magnetic characterization and Fe-K edged XAFS analysis have been combined to relate the average Fe coordination chemistry and valence state, to the magnetic properties of zeolites hydrothermally synthesised from natural volcanic ash collected from Mt. Etna in pure (VA-H) or sea (VA-HM) water [1]. The zeolite formation has been confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The magnetic properties of the natural volcanic ash and zeolites were probed by the field and temperature dependence (ZFC-FC) of the magnetization at 5K and 300K. The Fe-K edge XAFS were analysed in the near edge (XANES) and extended (EXAFS) regions.

The magnetic characterization demonstrated that the formation of zeolite directly affected the magnetic properties of the volcanic ash decreasing the saturation magnetization. Interestingly, the first derivative of M_{FC}-M_{ZFC} of pristine (VA) and zeolite (VA-H) samples point out a sharp pick at around 55K in the spectra of VA (Fig.1a) suggesting an antiferromagnetic-paramagnetic transition [2] that likely associated to olivine phases (fayalite or forsterite) detected in X-ray diffraction patterns and having similar T_N= 55K. The pre-edge spectra (Fe-XANES) demonstrated the local structure of iron in VA samples changing after hydrothermal treatments (Fig. 2b). Quantitative analysis demonstrated the Fe oxidation $Fe^{2+} \rightarrow Fe^{3+}$, associated to a change in Fe-O coordination. This behaviour comes in agreement with the expected changes in evolution of olivine with thermal treatments.

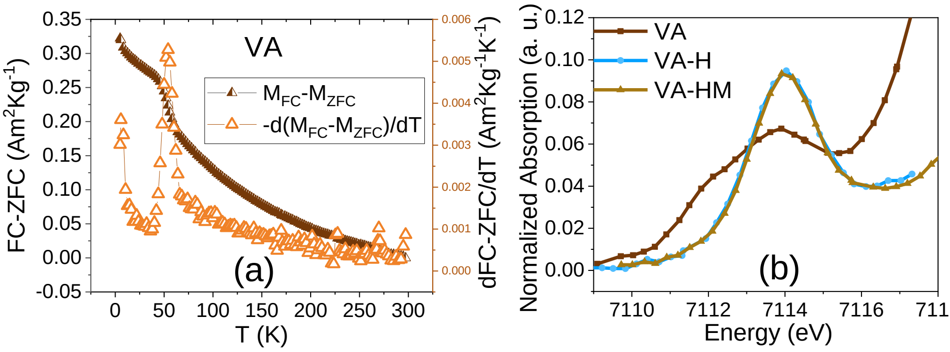

Figure 1. (a). (M_{FC}-M_{ZFC}) and the derivative of (M_{FC}-M_{ZFC}) curves of the volcanic ash and (b). The pre-edge region of the experimental Fe K-edge XAS spectra of the samples.

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MS1 - 4D-microscopy and tomography

KN1. Chasing dynamic processes: the challenges of time-resolved tomographic X-ray microscopy

Marco Stampanoni[1,2] on behalf of the TOMCAT team and its users' community

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Time-resolved tomographic X-ray microscopy (TR-TXM) has emerged as a powerful imaging technique for studying the dynamics of evolving processes in a wide range of scientific fields. By providing high-resolution, three-dimensional snapshots of time-dependent phenomena, TR-TXM enables researchers to unravel the temporal evolution of materials, biological systems, and industrial processes. However, the pursuit of comprehensive understanding through TR-TXM poses numerous challenges, including technical limitations, data management complexities, and synchronization requirements. This talk explores the challenges associated with TR-TXM and discusses potential strategies to overcome them.

TR-TXM combines fast X-ray imaging with tomographic reconstruction algorithms to capture the temporal changes in a sample's microstructure. It offers insights into dynamic phenomena such as phase transitions, growth kinetics, structural deformations, and transport processes. While TR-TXM has made significant strides in improving temporal resolution, capturing fast processes with high fidelity remains a challenge, requiring advancements in both imaging technology and computational methods.

One of the major challenges in TR-TXM is acquiring images with sufficient signal-to-noise ratio. As the temporal resolution increases, the exposure time for each projection decreases, leading to lower photon counts and increased noise levels. This necessitates the development of advanced imaging techniques, such as phase-contrast boosting and efficient data acquisition strategies, to mitigate noise and enhance the quality of reconstructed images.

Additionally, the vast amount of data generated during TR-TXM experiments presents challenges for data handling, storage, and analysis. High-throughput data acquisition demands robust data management systems and sophisticated computational tools for image reconstruction, segmentation, and quantification. Advanced algorithms capable of handling large datasets, accounting for time-dependent changes in the sample's microstructure, and extracting meaningful information are crucial for successful analysis.

Synchronization of external stimuli and imaging acquisition is another critical aspect of TR-TXM. In many dynamic processes, precise control, and synchronization of mechanical, thermal, or chemical stimuli are necessary. Accurate temporal alignment between the applied stimuli and imaging frames is essential to unravel the underlying mechanisms. Developing synchronized experimental setups, precise triggering mechanisms, and real-time feedback control systems are key to achieving reliable and reproducible results.

Despite these challenges, TR-TXM holds tremendous potential for advancing scientific knowledge across numerous disciplines. Overcoming technical limitations through advancements in imaging technology, computational algorithms, and experimental setups will enable the exploration of even more complex and rapidly evolving processes. By addressing the challenges of TR-TXM, we can unlock new frontiers in dynamic imaging, leading to transformative advancements in fields such as materials science, biology, physics, and engineering.

KN2. Multi-modal x-ray imaging and microscopy with intensity-modulated beams - opportunities for dynamic implementations

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Modulation of the x-ray beam intensity through e.g. regular absorbing masks placed before the imaged sample offers two advantages: it makes the spatial resolution dependent only on the size of the apertures in the mask [1], and it provides access to phase-based contrast mechanisms [2]. The latter consist in the direct measurement of x-ray refraction (i.e. the first derivative of the phase shift) and in the extraction of an additional, complementary “dark-field” image, sensitive to sample features smaller than the system’s spatial resolution (i.e., in this case, the mask aperture). Both can be measured either by placing a second mask in contact with the detector, and acquiring multiple frames with different relative displacements of the two masks, or with a detector with sufficient spatial resolution to resolve the individual “beamlets” created by the mask apertures. The latter approach, effectively an x-ray embodiment of the Hartmann wavefront sensor [3], has the advantage that attenuation, refraction and dark-field can be simultaneously retrieved from a single frame, without the need to displace (or even align) the mask; it does though require a small pixel, which imposes field-of-view limitations compared to the two-mask case.

The recently demonstrated ability to manufacture masks with apertures as small as 1 μm [4] was exploited to develop a laboratory-based system capable of producing images with micrometric resolution despite a 350 μm focal spot [5]. This system allows the direct visualization of individual cells and their nuclei; moreover, since the dark-field signal is sensitive to sample features below its resolution, it provides an insight on nanometric features while using standard laboratory instrumentation.

One downside is that, in order to access aperture-driven resolution, either the mask or the sample has to be scanned laterally in steps equal to the aperture size over a mask period. This imposes a step-and-shoot approach which hinders dynamic implementations. The problem was sidestepped by moving the mask continuously, with the detector also acquiring continuously with an exposure time equal to the size of an aperture divided by the mask speed: this effectively allows dynamic imaging with aperture-limited spatial resolution in flyscan mode, although the ultimate time resolution is reduced by a factor equal to the ratio between mask period and mask aperture. The method was used at the Diamond synchrotron to study melting processes in laser-driven additive manufacturing [6] and molten pool dynamics in metals [7], in both cases revealing features undetectable by x-ray attenuation alone. More recently, a first application to the life sciences (circulating contrast agents using a lab-on-the-chip model) was tested at the ESRF, and early results will be presented at the conference; applications to the life sciences are particularly attractive, because a single absorbing mask placed before the sample makes the method 100% dose efficient. Lab translation of this dynamic approach are also underway, and the first results will be shown at the conference. While these early results are 2D + time, options to translate them to 4D through the “cycloidal CT” concept [8] are underway and will also be discussed.

Acknowledgements: AO is supported by the Royal Academy of Engineering through their “Chairs in Emerging Technology” Scheme (CiET1819/2/78). Additional support for this work was provided by EPSRC (grants EP/T005408/1, EP/P023231/1 and EP/M028100/1), NIBIB/NIH (R01EB028829) and from the ATTRACT project funded by the EC under Grant Agreement No. 777222. Beamtime from the Diamond Light Source (MG23760-1 and MG31421-1) and the ESRF (MD-1353) is also acknowledged.

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O1. Complex materials as seen by high resolution X-ray synchrotron techniques

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Dynamical structural disorder at different length scale plays an important role in the functionality of complex materials [1]. Here different topological templates and weak interactions between building units produce phase separation in different ultrastructure configurations with correlated disorder [2-4]. Achieving optimal material performance requires a quantitative knowledge of this functional correlated disorder, as well as its evolution under external stimuli. In this contest we propose new experimental approaches based on high resolution probes, jointly to advanced modelling and statistical tools for big data analysis [5,7]. Examples of complex functional materials can be found in different fields ranging from quantum science to biology [3-7]. Here we discuss the connections between the dynamical correlated disorder at nanoscale and the functionality in recent cases studies.

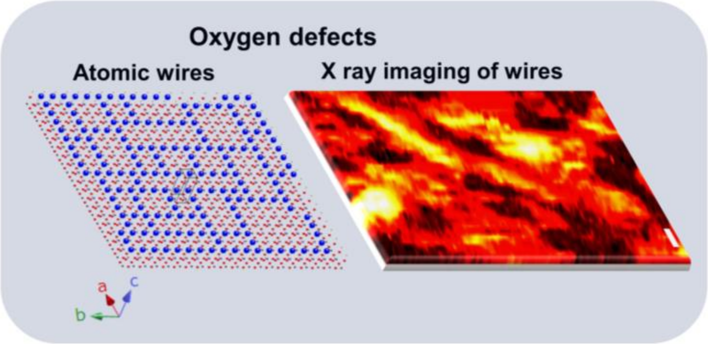

Figure 1. Imaging of scale free arrangement of wires of oxygen interstitial defects in a cuprate superconductor.

Acknowledgements: I thank my long standing coworkers Michela Fratini, Luisa Barba, Alessandro Ricci, Nicola Poccia, Gabriele Ciasca, Manfred Burghammer, Naurang Lal Saini and Antonio Bianconi.

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O2. Laboratory-based X-ray Scanning Microscopy with scattering/absorption contrast for structural characterization in medicine and nanotechnology, supported by Synchrotron data

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Scanning X-ray microscopies provide qualitative and quantitative imaging with lateral resolution, selectively probing different material properties depending on the specific contrast, allowing for multiscale or multiparameter characterization. From the structural point of view, Small (SAXS) and Wide (WAXS) Angle X-ray Scattering provide information at the nano- and atomic scales, respectively, but can be severely affected by the absorption contribution of the investigated objects and/or the embedding matrix. The absorption contrast allows in turn for direct imaging and fast sample screening but can be often blind in case of soft matter samples with low or negligible absorption contrast. Both scattering and absorption contrast can be selectively enhanced: the former by analyzing the X-ray intensity scattered in specific Q-ranges [1], and/or integrating it in specific regions of interest (ROIs) of the sample microscopy; the last by applying suitable algorithms for image post-processing. Three case studies will be presented, carried out by using a high brilliance laboratory X-ray microsource: lipid nanovesicles dispersed in a gel matrix [2]; drug detection in administration beads [3]; CsPbBr3 nanoclusters studied by synchrotron PDF and SAXS/WAXS micro-diffraction [4]. Scanning microscopy data were processed by the freely available software SUNBIM developed in-house [https://www.ic.cnr.it/software/sunbim/].

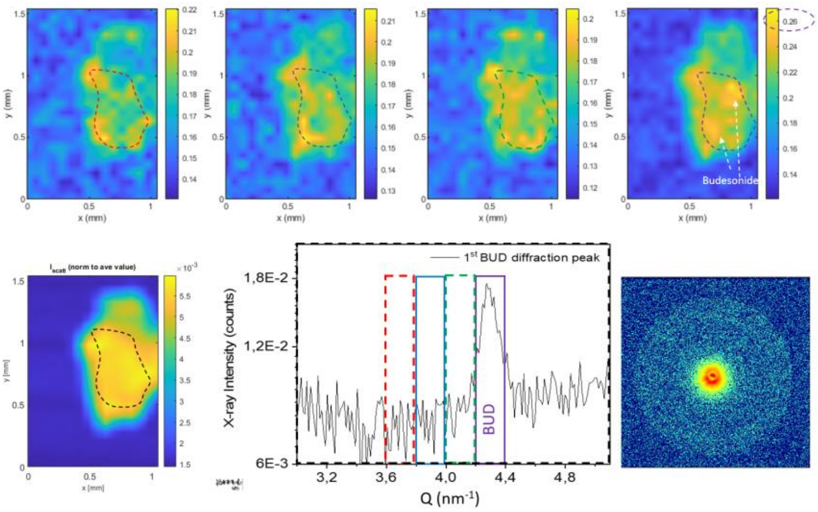

Figure 1. Scanning WAXS microscopies showing Budesonide spatial distribution based on the scattered intensity in selected Q-ranges.

Acknowledgements: the work was partially funded by Ministero Universita` Ricerca as part of the Call PRIN2017 project ‘A system approach for identifying connective tissue degeneration in diabetic analogues - SAPIENT’. Protocol Number: 2017CBHCWF.

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O3. Transverse deflecting cavities for short x-ray pulses at a diffraction-limited storage ring light source: an accelerator-plus-beamlines perspective

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Picosecond-long x-ray pulses of moderate intensity and high repetition rate are highly sought after by the light source community, especially for time-resolved fine spectroscopic analysis of matter in the linear response regime. We investigate the upgrade of the Elettra 2.0 diffraction-limited storage ring light source to radiofrequency transverse deflecting cavities generating a steady-state vertical deflection of selected electron bunches. The study demonstrates the feasibility of sub-picosecond to few picosecond-long x-ray pulses at MHz repetition rate, provided simultaneously to several beamlines and transparent to the standard multi-bunch operation. The short pulse exhibits a total flux at 1–10% level of the standard single bunch emission, and transverse coherence preserved in both transverse planes up to 0.5 keV photon energy. Ultimate performance, limits and operational aspects of the scheme are analysed in an integrated accelerator-plus-beamlines perspective.

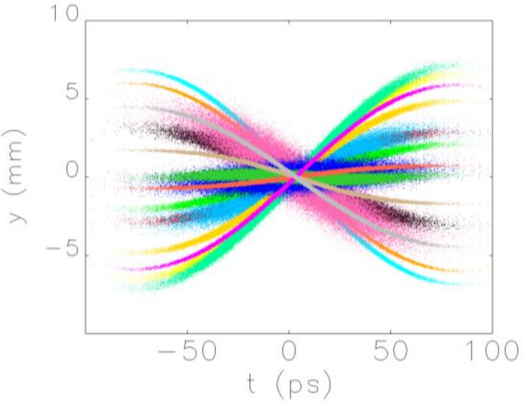

Figure 1. Simulation of vertically tilted photon pulses at the source points of different beamlines of Elettra 2.0, for the production of picosecond-long x-rays.

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O4. X-ray dynamic beam tracking combined with microfluidic to investigate feasibility of contrast-enhanced refraction and dark-field angiography

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Angiography is routinely performed to visualize the circulatory system and it is fundamental in the diagnosis of several vascular pathologies. When performed with X-rays, iodine-based contrast media must be injected into patient's blood stream to increase absorption by the almost invisible vascular system. However, iodine contrast media are known to cause severe allergic reactions preventing subsequent investigations, with a severe impact on the life expectancy of those who need regular examinations. In this talk we present preliminary results into the possible use of X-ray multi-contrast signals as an alternative to the current angiography practice. Multi-contrast X-ray imaging refers to the possibility to obtain refraction and ultra-small angle scattering (or dark-field, DF hereafter) maps in addition to the conventional transmission, originated by the presence of interfaces between different materials both above and below the system resolution. However, circulatory system is expected to produce very limited to none contrast since no X-ray scatterers are naturally present. Therefore, the use of a contrast agent will be required to highlight blood vessels.

We developed an in-vitro model based on a microfluidic chip with channels of decreasing size (from 200 μm to about 50 μm) where has been made flow a solution of water and commercially available microspheres with different concentration to significantly increase both the refraction and dark-field contrast [1]. This microfluidic platform has been combined on a synchrotron beamline with the dynamic beam tracking (BT) multi-contrast X-ray method. BT is based on the use of a single X-ray absorption mask and recently have been successfully extended to time resolved studies [2]. We found that, with a time resolution of about 8 ms, we can track, both in the refraction and DF, the flow of microspheres within the microfluidic channels. As expected, visibility decreases with the concentration of microspheres but can be detected up to about 1%, with an increase in visibility for smaller channels for all the concentrations due to an increase in the packing of the microspheres (Fig.1c). Moreover, the additional contrast maps can provide both information about velocity in each channel and sphere packing when combined with Monte Carlo simulations. It is worth noting that while our work represents a proof-of-concept, the extension of this method to gas microbubbles will make it compatible with human angiography, since microbubbles are already used in ultrasound imaging with significative less adverse reaction compared to iodine-based contrast agents [3].

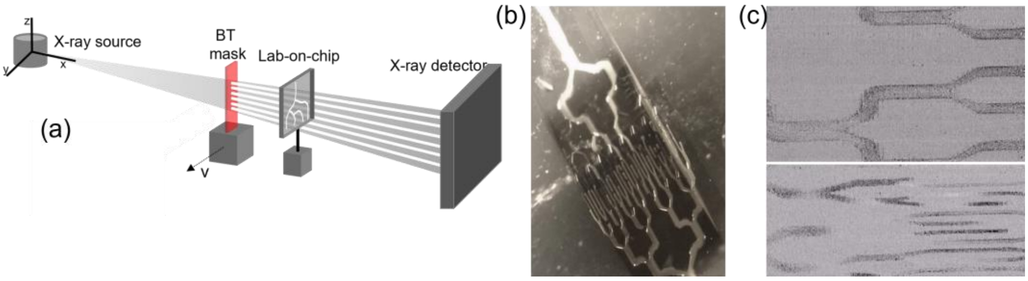

Figure 2(a) Schematic view of the experimental setup (b) real view of the microfluidic chip (c) retrieved X-ray multi-contrast signals for large (top) and narrow (bottom) microfluidic channels

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MS3 - Multi scale approaches for the study of functional materials

KN1. Probing the structure of solid catalysts across scales and their dynamics using X-rays

Paula Abdala[1], Nora K. Zimmerli[1], Lukas Rochlitz[2], Pedro Castro-Fernandez[1], Alexey Fedorov[1], Dragos Stoian[3], Stefano Checchia[4], Wouter van Beek[3], Christophe Copéret[2] and Christoph Müller[1]

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Developing innovative processes that produce environmentally friendly products and by-products, and use, convert or store renewable energy and raw materials is imperative for transitioning to a sustainable, low-carbon society. Catalysis plays a pivotal role in such processes, allowing, for instance, the production of clean fuels, the conversion of waste into energy, or a reduction of greenhouse gas emissions into the atmosphere. Advancing our fundamental knowledge of catalytic materials from the molecular to the nanoscale level is critical to unlock the potential of new materials and processes. In general, we require a better understanding of how catalysts function, the structure/motifs of their active sites, and how a catalyst deactivates to rationally advance the design of new catalysts. However, the inherent complexity of heterogeneous catalysts and their structural dynamics challenge our experimental techniques when deciphering their atomic-scale structure. In this context, in situ/operando X-ray-based studies are a powerful approach to investigating such complex and dynamic systems.[1,2] In this presentation, the complementarity of X-ray powder diffraction (XRD), pair distribution function analysis (PDF) and X-ray absorption spectroscopy (XAS) studies to reveal structure–performance relationships in heterogeneous catalysts and related materials will be discussed. The concerted analysis of these data allows for studying the materials' structure across different length scales, from the atomic level to the nanocrystalline structure, and the changes thereof under relevant conditions.

Acknowledgements: ETH Zürich, ESRF, SNBL.

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O1. Direct insight on crystallization pathways by *in situ* time-resolved SAXS/WAXS: role of space confinement

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Enclosed nanoscale volumes with limited accessibility, i.e., confined spaces, represent a challenging playground for the spatially and phase-controlled synthesis of inorganic materials,[1] albeit their role in determining the synthetic outcome is currently not fully understood. In this regard, synchrotron-based multi-technique approaches offer an exceptional tool to unravel the key stages of inorganic crystallization, especially when the formation of inorganic systems is probed through *in situ* time-resolved experiments simultaneously collecting information over different length scales.

Herein, we address the synthesis of MoO_3 nano- and microrods with hexagonal section in the confined space of inverse (water-in-oil) miniemulsion droplets (30-500 nm)[2] and batch conditions (i.e., in a macro-reactor), evaluating the effects of spatial confinement offered by miniemulsion droplets on their crystallization. A direct insight on the crystallization pathway of MoO_3 in both synthetic conditions and as a function of synthetic parameters was provided by an *in situ* time-resolved SAXS/WAXS study, that proved for the first time the role of miniemulsion confined space in altering the stepwise process of the formation of h-MoO_3.[3]

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O2. Direct molecular oxygen-based oxidation of methane to methanol over open Fe(II) sites in a metal-organic framework under mild conditions: a combined operando XAS, XES, RIXS and PXRD characterization

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Achieving the direct oxidation of methane to methanol (MTM) under mild conditions is considered the holy grail of modern catalysis, as the current large-scale methanol production technologies rely on expensive and non-environmentally friendly multi-step processes operated at elevated temperatures and pressures (T>400 °C, P>30 bar) [1]. Natural enzymes efficiently activate molecular oxygen to perform the MTM reaction [2], and have therefore inspired the development of upscalable artificial catalysts able to reproduce this exceptional reactivity. Metal-organic frameworks (MOFs), hybrid porous materials composed of metal nodes and organic linkers, have recently drawn attention as promising candidates to realize the MTM oxidation because of their intrinsically high tunability and porosity. Among these, MIL-100(Fe) is a MOF containing trimeric Fe(III) units and the benzene-1,3,5-tricarboxylate (BTC) linker, which is known to form open Fe(II) sites upon thermal treatment above 200 °C [3]. These open metal sites have been shown to perform the N_2O-based MTM oxidation through a highly reactive Fe(IV)=O intermediate [4-5], but an in-depth spectroscopic characterization of their formation process is lacking. Additionally, the application of N_2O in the MTM process can only be considered of academic interest, as the low availability of this gas limits its industrial relevance. Exploring a more economically convenient process based on molecular oxygen therefore appears of high interest.

In this work, we present a detailed spectroscopic characterization of the direct MTM conversion at ambient pressure and moderate (200 and 100 °C) temperatures over open Fe(II) sites in MIL-100(Fe), using O_2 as the oxidant. We first characterize the thermally induced self-reduction of some Fe(III) sites to Fe(II) (see Figure 1), from both the electronic and structural points of view, with operando high energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD-XAS) and resonant inelastic X-ray scattering (RIXS), determining the intermediate species involved in this process as well as the final Fe(II) abundance. Subsequently, we track the behavior of the MOF under catalytic conditions, highlighting the fate of the Fe(II) sites during the MTM reaction and the propensity of the material towards active site regeneration. As part of our integrated approach, we also identify the species formed upon catalyst deactivation with the help of valence-to-core X-ray emission spectroscopy (VtC-XES). We employ operando powder X-ray diffraction (PXRD) throughout the entire process to monitor the catalyst stability. Finally, we complement this experimental characterization with theoretical calculations steered by the experimental evidence, validating both the proposed activation and MTM reaction mechanisms.

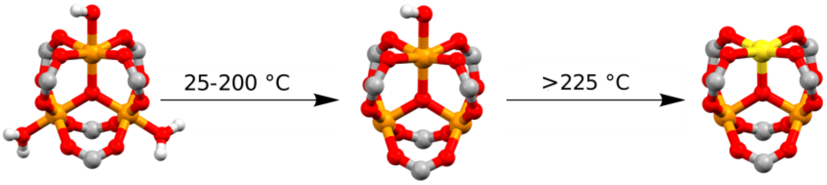

Figure 1. Thermal activation scheme of the MIL-100(Fe) triiron nodes generating open Fe(II) sites. Color code: Fe(III), orange, Fe(II), yellow, oxygen, red, carbon, grey, hydrogen, white.

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O3. Ni/Pt-CeO$_2$ in-situ DRIFT/XAS: accessing metal, Ce^{3+} and coordination species kinetics in one measurement

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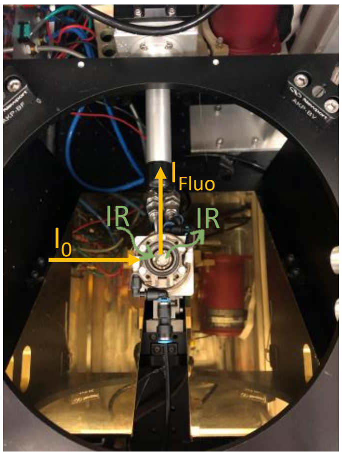
Ce-based catalysts are widely known for their importance in the heterogenous catalysis field.[1] In-situ and operando XAFS measurement have almost become a routine measurement to investigate the catalysts chemistry under relevant reaction conditions. In this contest metal supported CeO$_2$ catalysts (M-CeO$_2$) are deeply studied expecially for undertsanding the M/Ce synergic interaction suspected to be the key factor towards small molecules (CO, CO$_2$, H$_2$) activation. In particular, enginneering of single atom catalysts (SACs) is becoming extremely relavant to reduce the quantity of loaded metal and improve the overall catalytic properties of the material. However, XAFS investigation of SACs is not trivial since it implies monitoring materials with a low absorber concentration (<5%) deposited on an highly absorbing matrix (Ce). Since, the reaction takes place on the catalyst surface XAFS of SACs can track reaction-related variations of the metal however, the spectra of the support will hardly detect surface variations hence making difficult to disclose and associate the M/Ce synergy with the reaction evolution. Neverthless, it is known as DRIFT/XAS can be exploited to track surface species coordination chemistry while parallelly monitoring metal XAFS spectra (Figure 1 left).[2-4] Moreover, we recently reported as CeO$_2$ infrared spectra presents a fingerprint band at 2127 cm^{-1} related to $^{5/2}F_{2g}\rightarrow{}^{7/2}F_{2g}$ electronic transition which can be quantitatively associated to Ce^{3+} concentration.[5-7] This band can then be use to exploit DRIFT/XAS to parallelly monitor metal and Ce oxidation state together with molecular kinetic and catalytic activity within a single experiment. In the presentation I will present the versatility of DRIFT/XAFS towards studying different relevant reactions (CO oxidation, Water Gas Shift and Sabatier Reaction) over Ni-CeO$_2$ and Pt-CeO$_2$ (Figure 1 right). The techcnique allowed indeed to ultimately relate SAC oxidation state, local geometry and structure variations with Ce oxidation state and coordination species (carbonates and hydrides) formation kinetic. Moreover, the cell is coupled with an online Mass Spectrometer allowing quantitative determination of relevant species consumption/formation hence confirming the reproduction of reaction conditions.



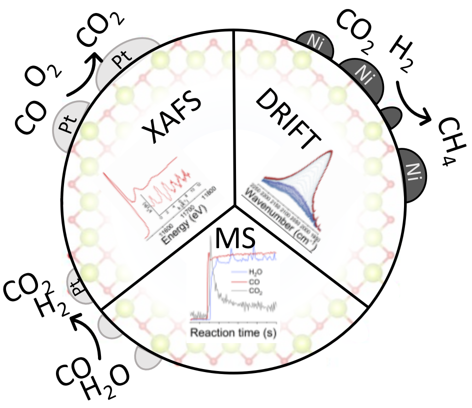


Figure 1. (Left) Top picture of DRIFT/XAS cell set-up. (Right) Sketched representation of results achievable on M-CeO_2 catalysts by in-situ DRIFT/XAS.

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O4. Investigation of charge state heterogeneity inside MnHCF cathode material by synchrotron-based transmission soft X-ray microscopy

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Manganese hexacyanoferrate is Prussian Blue Analogue (PBA), with high specific capacity and redox plateaus at a high voltage against both Li and Na in lithium- (LIBS) and sodium-ion batteries (SIBs) [1]. However, it suffers of capacity fading during the cycling process, and one of the possible causes might be the inhomogeneous distribution of the oxidation state of the metal-sites inside the active material [2]. To access the structural and functional characteristics at the nanometre scale, energy-dependent full field transmission soft X-ray microscopy (TXM), was used, at MISTRAL beamline at ALBA synchrotron facility. On one hand, by using X-rays of the "soft" energy region (<3 KeV), it is possible to access transitions of core level of light elements, such as O, N, F and L-edge of transition metals [3], which provide higher resolution because of the longer core-hole lifetime of the 2p [4]. On the other hand, TXM provides pixel-by-pixel absorption spectrum, making it possible to select groups of pixels and map regions with the similar spectral features [5].
In this study Mn L-, Fe L- and N K-edges were recorded on fresh and ex-situ cycled electrodes. Inhomogeneities within the samples were identified, increasing in the aged electrodes, and more dramatically in the Li-ion system, highlighting the advantages of using MnHCF as a cathode material for the SIBs, rather than LIBs. Furthermore, strong correlation between the Fe L-edge, Mn L-edge and N K-edge suggested a coupling between the redox centres and electron delocalization over the entire host framework.

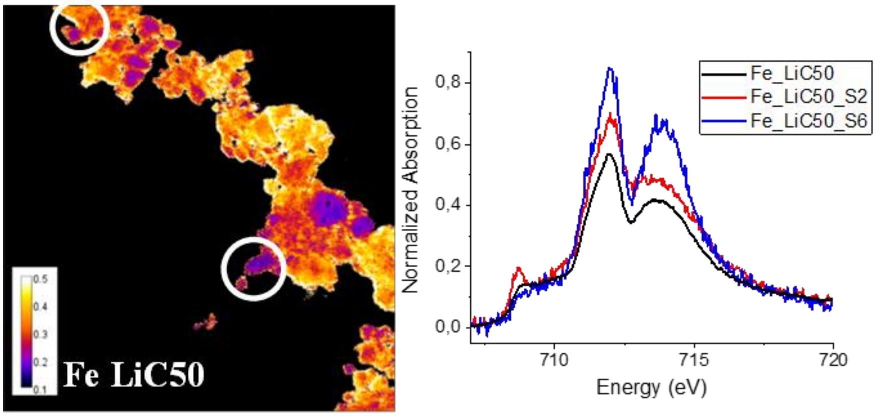

Figure 1. TXM image recorded on Fe L-edge of charged sample after 50 cycles, extracted from LIB, and its corresponding spectra: average one and from marked regions.

Acknowledgements: University of Bologna; ALBA synchrotron facility for providing SR through the project AV–2019093934.

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O5. Fluorination-Induced Asymmetry in Vacancy-Ordered Brownmillerite: Route to Multiferroic Behavior

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Four distinct classes of multiferroics are usually being discussed in the literature, in which ferroelectricity is respectively driven by electronic lone pairs, geometry, charge ordering, and magnetism. Each class has its own shortcomings for technological applications. In the present work, through a combined experimental and theoretical investigation, we propose a mechanism to achieve multiferroicity in a single phase by engineering the anionic network and creating local geometric distortions in fluorinated, vacancy-ordered brownmillerite $Ca_2Mn_2O_{5-x}F_y$ [1]. The brownmillerite $Ca_2Mn_2O_5$ [2] is one such oxygen-deficient perovskite (n = 2, within the generic formula of $A_nB_nO_{3n-1}$ applicable for oxygen-deficient perovskites) where oxygen vacancies are created in an orderly fashion along [001] rows of the cubic perovskite $CaMnO_3$ ($n = \infty$), resulting in an overall conversion of every MnO_6 octahedron into a square pyramid along with the formation of regular void patterns and three inequivalent oxygen sites in the structure (left image to Figure 1). The MnO_5 pyramids of this brownmillerite are supposedly to have polarization. However, an inversion symmetry connects all the Mn, each having antiparallel polarization. The net resultant of the local polarizations of the four MnO_5 pyramids in the unit cell is zero, which makes the parent compound nonferroelectric. Next, the fluoride ion, which is a potential candidate because of its comparable ionic radius (r_{F-} = 1.33 Å) with that of the oxide anion (r_{O2-} = 1.40 Å), has been chosen as the dopant ion for creating a mixed anionic network. Curiously, we observe that filling up the ordered vacancy sites with F–also imposes clear preferences toward certain sites for substitutions, thereby creating an overall O/X ordering. We find that fluorination of the vacancy sites along with preferential substitution indeed lowers the overall symmetry. The MnO_5F or MnO_4F_2 octahedra eventually breaks the inversion symmetry, which was absent in the parent compound, and the system turns into a robust ferroelectric at high temperature. Moreover, this system shows an antiferromagnetic transition at ∼340 K, which along with the developed ferroelectricity provides a good example for achieving multiferroicity through anion doping and geometric distortion.

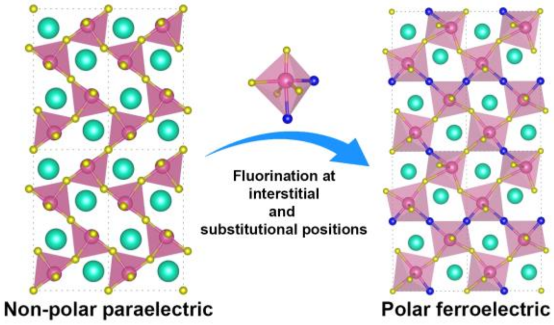

Figure 1. Route showing creation of local asymmetry upon fluorination.

Acknowledgements: The authors acknowledge Indo-Italian POC for support to carry out experiments in Elettra, Italy. The authors also thank Tomas Skala from Materials Science Beamline for his help during the XPS experiments.

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O6. Understanding C-H activation in light alkanes over Cu-MOR zeolites by advanced XAS analysis during temperature-programmed reduction

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The strong C-H bond in light alkanes presents a significant obstacle in preventing the over-oxidation of desired products making, for instance, the direct valorization of methane into valuable oxygenates challenging. In the last years, approaches allowing the direct conversion of methane to methanol (MTM) through a chemical-looping process over Cu-oxo sites in zeolites have been proposed [1]. In this context it is of utmost importance to unravel and understand the impact of Cu speciation on MTM performance, investigating the Cu_xO_y-sites potentially active towards methanol formation. Out of several zeolites system that have shown activity towards MTM, the Mordenite (MOR) topology is among the most promising [2].

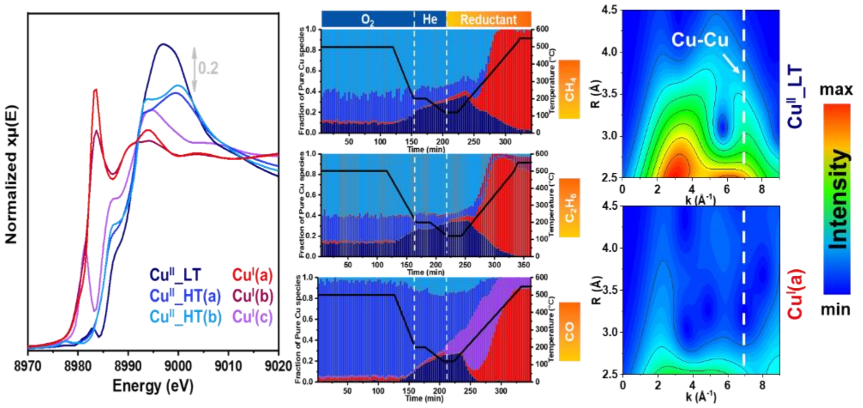

Figure 3. (Left) Summary of MCR reconstruction, including XANES and EXAFS spectra and concentration profiles of pure Cu species. (Right) Representation of WT maps magnified in the 2.5-4.5 Å range.

Herein, we focus on two Cu-MOR samples with different Cu/Al and Si/Al ratio, characterized at beamline BM31 of the ESRF synchrotron by in situ X-Ray Absorption Spectroscopy (XAS) during Temperature Programmed Reduction (TPR), comparing reduction in CH_4, C_2H_6, and CO [3]. Multivariate Curve Resolution (MCR) and Wavelet Transform EXAFS (WT) advanced analysis methods were applied, securing a thorough understanding of the dynamic evolution in Cu-speciation (Figure 1). MCR analysis allowed the identification of four common pure Cu species, with additional, reductant-specific Cu^I components in the case of C_2H_6 and CO. The MCR-derived concentration profiles showed that Cu^{II} species were dominant in the materials pretreated in O_2, albeit with different fractions. It was possible to observe a complete reduction during the TPR step (120-550°C), involving the formation of an extra Cu^I species in C_2H_6 and CO cases. WT analysis indicated that in all Cu^{II} species, Cu-Cu contributions were detectable, leading us to describe these species as dicopper(II) cores. Importantly, these Cu-Cu scattering contribution were completely lost for the identified Cu^I species, corroborating our previous observations and indicating the redistribution of Cu^I ions into different, mutually farther, sites. These results highlight the potential of XAS to quantitatively resolve and characterize Cu-species in zeolites, while guiding in the identification of active sites for C-H bond activation in light alkanes.

Acknowledgements: this work is financially supported by the CuBE ERC-Synergy project (G.A. n° 856446) and by iCSI Centre for Research-based Innovation (contract n° 237922).

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MS7 - Extreme condition science

KN1. Polyamorphism in $GeSe_2$ glass under ultra-high pressures studied by extended x-ray absorption fine structure

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Experimental studies of local atomic structure and electronic properties in the network forming glasses under ultra-high pressures (P >1Mbar) has long been a challenging topic. Experimental data that convincingly describe the evolution of short and intermediate structural ordering and its correlation with changes of electronic properties are essential for understanding the further densification mechanism of the network structures after the primary low to high density amorphous-amorphous transformations which is generally associated with a tetrahedral to octahedral coordination crossover at moderate high-pressure ranges (typically 15-60GPa). Recently, we have investigated pressure behavior of several simple chalcogenide glasses including $GeSe_2$ and GeS_2 under ultra-high pressures up to 160 GPa using x-ray absorption spectroscopy. Quantitative and qualitative information concerning the evolution of local atomic and electronic structures have been obtained with unprecedented details through EXAFS refinements assisted by molecular dynamics simulations.

O1. Exploring liquids under extreme conditions of pressure and temperature with XRD and XAS

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Determining the structure of a liquid as a function of pressure and temperature is crucial to constrain elastic properties, such as compressibility and thermal expansion. Accessing the density of the liquid of materials constituting planetary cores (coupled with the study of melting curves and the determination of the density of the corresponding solid) allows to better constrain the differentiation process of a planet, from the magma ocean to its crystallization regime.

X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) are routinely used techniques to directly explore the atomic structure of materials under extreme conditions of pressure and temperature. When performed in a synchrotron, these two probing techniques coupled with a diamond anvil cell (DAC) and with a laser heating (LH) system allow to probe properties of materials at pressures of few Mbar and temperatures of thousands of kelvin.

XRD and XAS can be exploited not only to determine the solid-liquid phase transition, but also to follow the compressibility of the liquid. Concerning XRD, a recently developed software for the analysis of X-ray diffuse scattering signal, Amorpheus [1], will be here presented. As for XAS, the analytical solutions proposed to determine the compressibility of liquids under extreme conditions [2] (where the data quality loss is significant) will be shown. Moreover, the structural and electronic information contained in the XANES (X-ray absorption near edge structure) can be employed to determine in-situ the composition of a binary alloy [3]. Taking as example Fe-C and Fe-O, we show that chemical migrations induced by the temperature gradients can now be tracked in-situ, with direct consequences in high pressure studies of laser heating of multicomponent complex systems.
New opportunities for high pressure experiments following the Extremely Brilliant Source upgrade at the European Synchrotron Radiation Facility (ESRF) will be presented.

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O2. Femtosecond snapshots of atomic clusters: a new eye on nanomatter and its interaction with light

Alessandro Colombo[1], Mario Sauppe[1], Simon Dold[2], Arezu Sehati[1], Linos Hecht[1], Katharina Kolatzki[1], Carl Frederic Ussling[1], Marcel Mudrich[3], Bernd von Issendorf[4], Paul Tümmler[5], Andre Al Haddad[6], Gregor Knopp[6], Kirsten Schnorr[6], Zhibin Sun[6], Christoph Bostedt[6] and Daniela Rupp[1]

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Coherent Diffraction Imaging (CDI) allows to take pictures of the electronic distribution of isolated samples from the analysis of their diffraction patterns [1]. It is the imaging method of election for experiments at Free Electron Lasers (FELs), which provide extremely intense pulses of femtosecond duration in the soft X-ray regime. CDI at FELs allows to spatially and temporally resolve ultrafast processes in nanomatter, opening a new window on light-matter interaction at the nanoscale. Isolated atomic clusters represent the perfect prototypical system for such investigations [2], thanks to their simple electronic structure and their highly tuneable size and shape. Here we present our recent imaging results on atomic clusters at different FEL light sources in Europe. Snapshots of isolated argon clusters acquired at SwissFEL, in Fig. 1a), show surprising architectures that give insights into their formation process. Reconstructions of heterogeneous argon/xenon clusters reveal unexpected anisotropies, as displayed in Fig. 1b), and the behaviour of their scattering cross-section around the xenon 3d electronic resonance at 670eV is the footprint ultrafast ionization dynamics happening within the 100fs duration of the FEL pulse. Superfluid helium nanodroplets are of great interest in studying the behaviour of dopants inside them [3]. A recent experiment at the European XFEL revealed mesmerizing fractal structures formed by the different dopants and raised questions about how the different materials interact, with and without the presence of quantum vortexes. To get real advantages of the time resolution capabilities of FELs, experiments can be performed in a pump-probe configuration. For example, ultrafast heating and boiling phenomena can be efficiently ignited in silver nanoclusters by tuning the pump photon energy at their plasmonic resonance. Snapshots of the melting dynamics, acquired at the FLASH FEL and more recently at SwissFEL, allow to investigate the phase diagram of silver at conditions never accessible so far [4]. The peculiar features of atomic clusters also make them ideal for pioneering new analysis methods. In this regard, we recently demonstrated the feasibility of full three-dimensional imaging from single diffraction shots [5], by retrieving the three-dimensional morphology of silver clusters from single wide-angle scattering images acquired at FLASH. These studies are the fruit of the recent impressive developments at FELs as well as improvements in the analysis methods and theoretical models, and clearly indicate that ultrafast movies of nanomatter are quickly approaching the status of concrete reality.

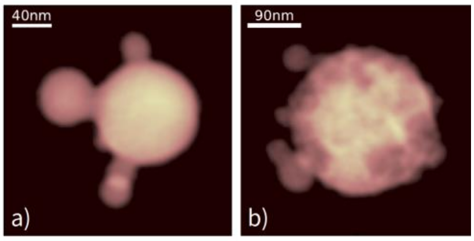

Figure 1. CDI reconstruction of an Ar cluster, in a), and a Xe/Ar cluster, in b).

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O3. First high-resolution pump probe RIXS on prototypical charge transfer insulators at the EuXFEL

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In the last decade, resonant inelastic x-ray scattering (RIXS) has been widely exploited to investigate and understand the physics of various families of quantum materials. Indeed, RIXS spectra exhibit a plethora of excitations that belong to all the intertwined degrees of freedom ruling the physics of these systems. Thanks to the intense efforts in the instrumentation development, best RIXS experiments at synchrotrons have reached 20-30 meV energy resolution allowing the study of excitations in the far-infrared region, like phonons and charge density fluctuations.

With the advent of high repetition rate x-ray free electron lasers (XFELs), x-ray spectroscopies became a very promising candidate to perform pump probe (pp) experiments with unique specificity on the probe side. In this context, the development of hRIXS, a high energy and temporal resolution RIXS instrument at the spectroscopy and coherent scattering (SCS) beamline of the European XFEL, marks a milestone. For the pp-RIXS commissioning we selected two prototypical antiferromagnetic insulators, NiO and La_2CuO_4 (LCO) and pump photon energies larger than the charge transfer gap of the two systems. We measured the L_3-edge RIXS spectra at Ni and Cu, with ≈ 80 meV and ≈ 93 meV resolution respectively. The temporal resolution was ≈ 100 fs. We acquired spectra changing the pump delay between -2 ps and 50 ps, and the laser fluence on the sample between 1 mJ/cm^2 up to 35 mJ/cm^2.

The first important result is the consistency of static RIXS spectra taken at XFEL with those measured at the synchrotron, with comparable resolving power. This means that the short and intense FEL pulses are not altering the RIXS process. The major results are those of ppRIXS: in both samples the RIXS spectra are clearly modified by the optical pump in several spectral regions. A long lasting red shift of the dd peaks is detected in both LCO and NiO, accompanied by an increase of the elastic and quasi-elastic (low energy phonons) intensity. The magnon peak is transiently affected by the optical pump too. Moreover, in the case of NiO the optically-induced charge transfer from oxygen to nickel generates a new excitonic state, evident both in the x-ray absorption spectra and in the RIXS, with new spectral features both in the energy loss and energy gain sides. Our results establish pp-RIXS as a superior tool to investigate transient states with unprecedented sensitivity, opening the route to innovative studies on the transient optically excited states in quantum matter.

O4. Ultrafast plasmon dynamics in an insulating crystal triggered by intense extreme UV free electron laser pulses

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We will present the results of a time-resolved optical transmission experiment performed on a high bandgap insulating crystal, LiF, pumped with ultrashort extreme ultraviolet (EUV) free electron laser (FEL) pulses, and probed with broadband supercontinuum visible pulses, obtained from the FEL seed laser for users at the TIMEX beamline of FERMI (Elettra, TS) [1]. The EUV pumping generated a high-density, high-temperature electron plasma in the LiF sample. The time-resolved transmission experiment revealed an oscillating time dependence of the plasmon mode, well visible in Figure 1 where the effective transmission, as derived from experimental data fitting, is shown. The effect is interpreted as a fingerprint of the electron-ion interaction: the ion motion, shaped by the electron dynamic screening, induces, in turn, electron density fluctuations that cause the oscillation of the plasmon frequency at the timescale of the ion dynamics. Fitting the high-resolution transmission data with an RPA model for the temperature-dependent dielectric function, which includes electron self-energy and electron-ion coupling, confirms the interpretation of the time modulation of the plasmon mode. In line with other research articles in the recent literature [2], our results suggest that the ultrafast excitation of the system by high energy density FEL pulses can promptly bring solid state systems into highly excited out-of-equilibrium states in a much more direct way compared to the conventional optical pumping processes. Indeed, EUV to X-FEL photons dominantly couple to the electron core states, thus triggering different excitation and de-excitation pathways in the system compared to those achieved using optical pump pulses [2,3]. We will discuss the semi-empirical model developed to describe the plasma creation by EUV to X-FEL pulses and present its application to the case study of interest [1] and to other relevant classes of materials [3], focusing on the short (~1 ps) delay window before the electron-ion energy transfer occurs. In particular, we will discuss the differences in the plasma creation process expected in insulating and metallic systems, suggesting potential experimental investigations [3].

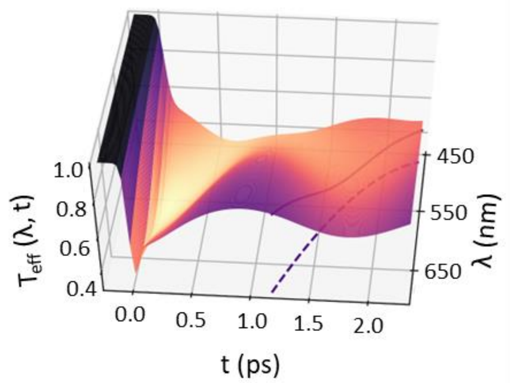

Figure 1. 3d mapping of the LiF transmission $T_{eff}(\lambda,t)$ versus pump-probe delay time as obtained from the fitting model in [1]. The pump-probe coincidence time is set to t = 0. The dashed line in the (λ,t) plane is the region accessible to the experiment. The solid line is the transmission curve calculated along the border of the accessible region.

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O5. Evidence of a Two-Step Pressure-Driven Metallization in Transition Metal Dichalcogenides by Far-Infrared Spectroscopy

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Transition Metal Dichalcogenides (TMDs) are graphene-like crystals, serving as interesting platforms for the physics of low-dimensional systems and potential candidates for optoelectronic devices. In TMDs, single layers are held together by covalent bondings stacked through weak inter-layer van der Waals (vdW) interaction. Despite its weakness, the latter plays a key role in determining the electronic and optical properties of the crystals [1]: a better comprehension of its impact can be obtained through the application of pressure via Diamond Anvil Cells (DACs), a clean and direct tool to enhance the vdW interaction between TMD layers. Several studies show that the application of high-pressure on semiconducting TMDs results in a pressure-induced transition toward a metallic state [2-3]. However, in many cases, the estimate of the metallization pressure remains controversial, with a general disagreement between the thresholds estimated through resistivity and near-infrared spectroscopy [4]. To reconcile these results, we investigated the effects of pressure application on different semiconducting TMDs using synchrotron-based far-infrared (FIR) spectroscopy [5], performed at the beamlines AILES and SMIS of the synchrotron SOLEIL, where the small spot size and high brightness of synchrotron radiation allowed us to measure micrometrical single crystals in DACs. The resulting FIR spectra provided us with two spectral descriptors indicative of the onset of metallicity and the origin of the free carriers in the metallic state: the absorbance spectral weight (figure 1a), whose abrupt increase defines the metallization pressure threshold, and the asymmetric line shape of the E_{1u} peak (figure 1b), whose pressure evolution, interpreted within the Fano model, suggests the electrons in the metallic state originate from n-type doping levels. Combining our results with those reported in the literature, we hypothesize that a two-step mechanism is at work in the metallization process, in which the pressure-induced hybridization between doping and conduction band states drives an early metallic behaviour, while the band gap closes at higher pressures.

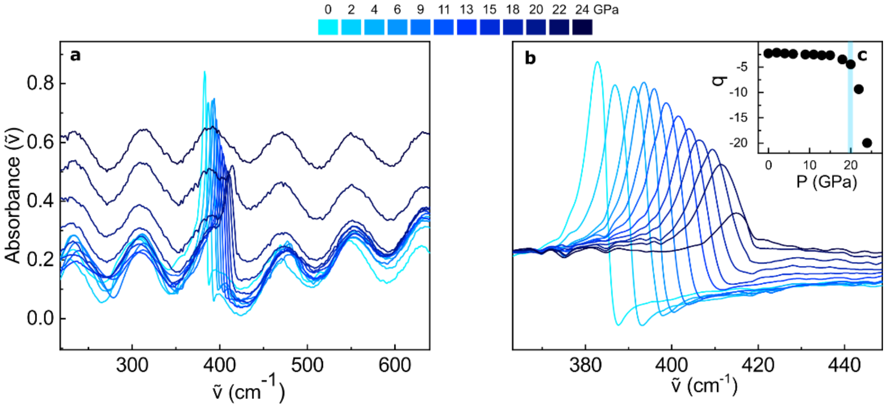

Figure 1: **a)** Bare FIR spectra of MoS_2 showing the pressure-induced abrupt increase of the spectral weight. **b)** Same spectra of **a** after background subtraction. The symmetrization of the E_{1u} phonon peak at increasing pressure is evident and it is described by the dramatic decrease of the Fano parameter q in panel **c**.

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O6. REALSEI: Operando chemical space- and time-resolved quantification of solid electrolyte interphase in hard carbon anode for sustainable sodium ion batteries

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In this seminar the Marie Sklodowska-Curie project entitled REALSEI (Operando chemical space- and time-resolved quantification of solid electrolyte interphase in hard carbon anode for sustainable sodium ion batteries) will be presented. In particular the goal of REALSEI is to visualize for the first time in real-time the Solid Electrolyte Interphase (SEI) formation at the hard-carbon (HC) anode in a Na-ion battery (NIB). Local electrochemical processes occurring at the solid-liquid interface of Na-ion batteries are currently largely unexplored. To keep global warming around 2.7°C by 2100, the installed global grid energy storage capacity needs to be tripled by 2050. A technological breakthrough is required to meet this challenge: we need a low cost and sustainable alternative to Li-ion batteries. Thanks to recent advances, the so-called 'beyond-lithium' batteries such as K+ and Na+ based systems could be an everyday reality. Bio-waste mesoporous HC is one of the most promising anode materials as a universal ion host for beyond lithium batteries. The use of bio-waste HC as a low-cost and recycled solution in beyond lithium batteries might provide the breakthrough required and give rise to the next generation of batteries. However, uncontrolled SEI formation limits the large-scale application of bio-waste HC in NIBs, the most mature and promising among beyond lithium technologies. For NIBs, the SEI is still an unresolved issue that limits its long-term stability. REALSEI wants to establish a comprehensive operando time- and space- resolved characterization methodology to transit from bulk (transmission mode) to surface analytical characterization (grazing incidence mode) based on lab and synchrotron high-resolution X-ray techniques which will results for the first time in a comprehensive visualization and quantification of the species forming the SEI in real-time on HC. REALSEI will apply principles of physics and electrochemistry and its results will have substantial scientific, technological, and societal impact.

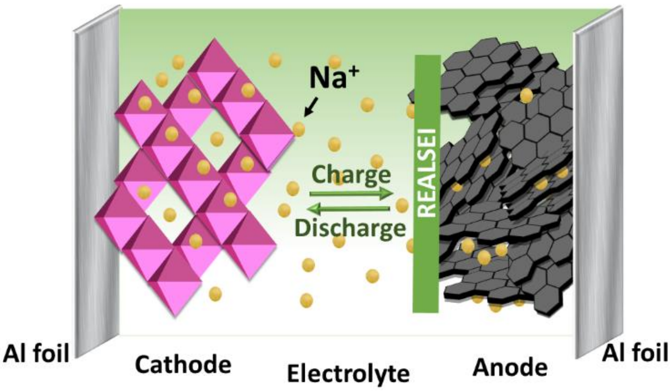

Figure 1. A schematic view of a NIB battery

MS4 - Synchrotron and XFEL radiation for life-science

KN1. Exploring the native cellular environment with soft X-ray microscopy

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Cryo soft X-ray tomography (SXT) of whole hydrated cells in the water window energy range can provide relevant structural information of complex cellular phenomena with chemical sensitivity at spatial resolutions of 30 nm half-pitch [1, 2, 3]. Functional studies can be achieved by correlating this information with visible light fluorescence microscopy to elucidate, for example, the asexual life cycle of Babesia divergens [4], or with super resolution techniques allowing to pinpoint specific therapeutics intracellularly [5]. Cryo-SXT can also be combined with 3D cryo hard X-ray nano-fluorescence to locate and quantify a specific anticancer metallodrug [6]. Examples of 3D correlative cryo X-ray imaging research will be presented.

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O1. Shedding Light on Osteosarcoma Cell Differentiation: Impact on Biomineralization and Mitochondria Morphology

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OBJECTIVE: Osteosarcoma (OS) is the most common primary malignant bone tumor and its etiology has been recently associated to osteogenic differentiation dysfunctions [1,2]. A deeper understanding of the relationship between defects in osteogenic differentiation and malignant bone tissue formation could help the

comprehension of osteosarcoma tumorigenesis and the development of new treatment strategies. In order to characterize the defective biomineralization process that occurs in OS, we studied osteoblast-like SaOS-2 cells during the early stages of differentiation. Cryo-soft X-ray tomography (Cryo-SXT) and cryo-XANES at the $CaL_{2,3}$ edges imaging were combined to investigate the evolution of the Ca-depositions during differentiation allowing to simultaneously track morphological variations in intracellular organelles at nanometric resolution.
MATERIALS and METHODS: Bone mineralization in SaOS-2 cells was investigated by combining cryo-SXT and cryo-XANES imaging. SaOS-2 were grown on electron microscopy grids, treated for 4 and 10 days with a differentiating cocktail, plunge frozen in liquid ethane and were subsequently imaged in a quasi-native state using the soft X-ray transmission microscope installed at the Mistral beamline of the Alba synchrotron.
RESULTS and DISCUSSION: Untreated SaOS-2 produced calcite depositions (Fig. 1) as previously observed in early differentiated bMSCs (bone mesenchymal stem cells) [2]. This confirms that the early phases of osteoblastic differentiation are similar in both bMSCs and SaOS-2 cells, supporting the hypothesis that OS cells arise from MSCs unable to undergo complete differentiation [3, 4]. The evolution of mineral deposits from calcium phosphate to hydroxyapatite (Fig. 1) induced by the differentiating treatment suggests a partial restoration of the physiological biomineralization process in SaOS-2 cells, as previously assessed in differentiating bMSCs [2]. At 4 days after induction (Fig. 1), mitochondria contain small Ca structures and are linked to vesicles containing calcium phosphate depositions highlighting calcium transfer between the two intracellular organelles (Fig. 1). At 10 days after induction, no Ca minerals are detected in the mitochondria, supporting the interplay between mitochondria and vesicles in calcium trafficking (Fig. 1). Interestingly, during differentiation, mitochondria show a change in morphology from elongated to rounded indicating a metabolic reprogramming of OS cells possibly linked to an increase in glycolysis contribution to energy metabolism. These findings add a dowel to the genesis of OS giving new insights on the development of therapeutic strategies able to restore the physiological mineralization in OS cells.

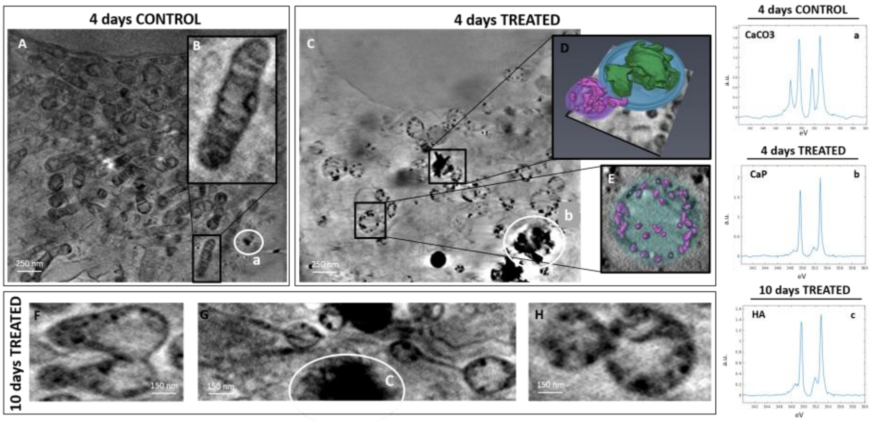

Figure1: A) Tomogram of a 4 days control cell, **B)** zoom on an elongated mitochondrion. White circle indicates CaCO3 deposition and **a)** reports the XANES spectrum. **C)** Tomogram of a 4 days treated cell, **D)** zoom on a mitochondrion containing Ca linked to a vesicle, **E)** 3D reconstruction of a mitochondrion. White circle indicates calcium phosphate deposition and **b)** reports the XANES spectrum, **F)**, **G)** and **H)** zoom on mitochondria from a tomogram of a 10 days treated cell. White circle indicates HA depositions and **c)** reports the corresponding XANES spectrum.

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O2. Structural characterization of flexible proteins by SAXS complemented with advanced computational modelling

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Flexible proteins, for example those constituted by rigid domains connected by flexible linkers, can be hardly crystallized. Thus, their high-resolution structural characterization by X-ray diffraction cannot be achieved. But cryo-EM investigations are also hindered due to the difficulty of reconstructing a three-dimensional image of flexible objects. Small Angle X-ray Scattering (SAXS) can provide a low-resolution (>20 Å) structural characterization of these proteins in solution. SAXS data are not affected by the typical artifacts due to sample preparation for X-ray diffraction and cryo-EM, i.e., crystal packing or vitrification, respectively, however their interpretation is far from being unique and demand for extensive computational modelling to be useful. We have developed a procedure to combine SAXS data with homology modelling and molecular dynamics, where the limited data resolution achievable by SAXS is compensated by available structural knowledge of homologous proteins and by *a priori* knowledge of interatomic interactions and laws of motion. The average structure of flexible proteins is determined by restraining molecular dynamics with SAXS data: in direct space the *ab initio* molecular envelope obtained by SAXS data plays the role of a potential that generates forces restraining the protein model within it [1]; in reciprocal space the agreement with the SAXS profile is used to select the best frames of the trajectory. The final model is then validated by comparison with the results of the ensemble optimization method [2], which specifically addresses flexible scatterers.

Applications of the procedure to three case studies to determine the mutual confomation of interacting domains in solution will be shown.

1) Rituximab, the first monoclonal antibody (mAb) developed as a therapeutic agent to target CD20 protein. We have determined the structure of the full-length antibody (Figure 1), characterized its flexibility and estimated the Fab elbow angle, a crucial determinant for antigen recognition and binding [3].

2) The C-terminal domains of NSD3, a member of six H3K36-specific histone lysine methyltransferases in metazoans, whose overexpression or mutation is implicated in developmental defects and oncogenesis [4].

3) K48-linked diubiquitin alone and in the presence of Copper and Zinc ions [5].

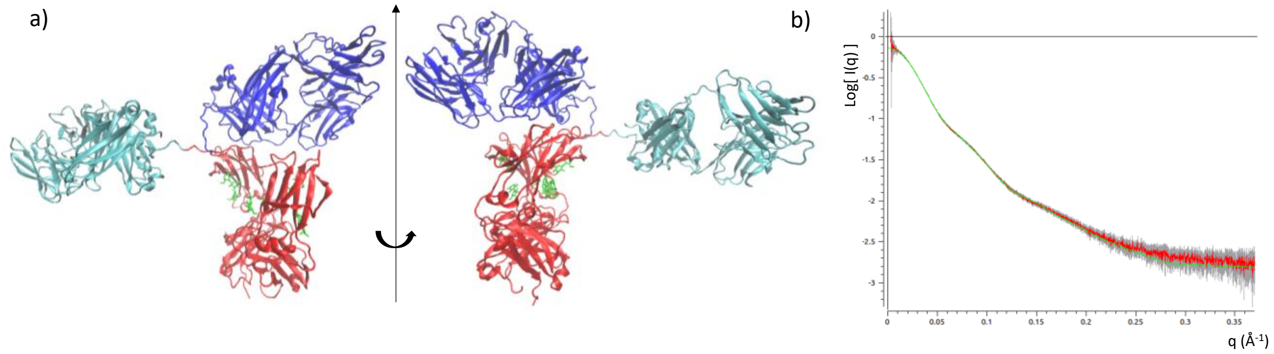

Figure 1. Full-length structural model obtained for rituximab (a) and fit between observed (red line) and calculated (green line) SAXS profiles (b).

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O3. The composition of asbestos bodies in human lungs

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The asbestos bodies (AB) form in the lungs through an *in vivo* biomineralization process started by the alveolar macrophages in the attempt to isolate asbestos and become the actual interface between asbestos and the host organism. The AB are believed to be mainly composed of the Fe-proteins and mucopolyssaccharides. However, the presence of hydroxyapatite and Fe-oxy(hydro)oxides, other than ferrihydrite (the mineral core of ferritin), has also been proposed. We performed synchrotron X-ray diffraction (XRD) and absorption (XAS) measurements to unravel the Fe form in the AB and to check the crystallinity of the inner fiber. XRD revealed the presence of goethite in the Fe-rich coating (Figure 1b), and that the inner fiber (crocidolite) maintained a high degree of crystallinity (Figure 1c) despite the prolonged stay in the lungs (>10y). XAS results, on the other hand, revealed the co-existence of ferrihydrite and goethite in a ~70:30 ratio (Figure 1d). The results are discussed in terms of the increased toxicity of goethite with respect to ferrihydrite [1].

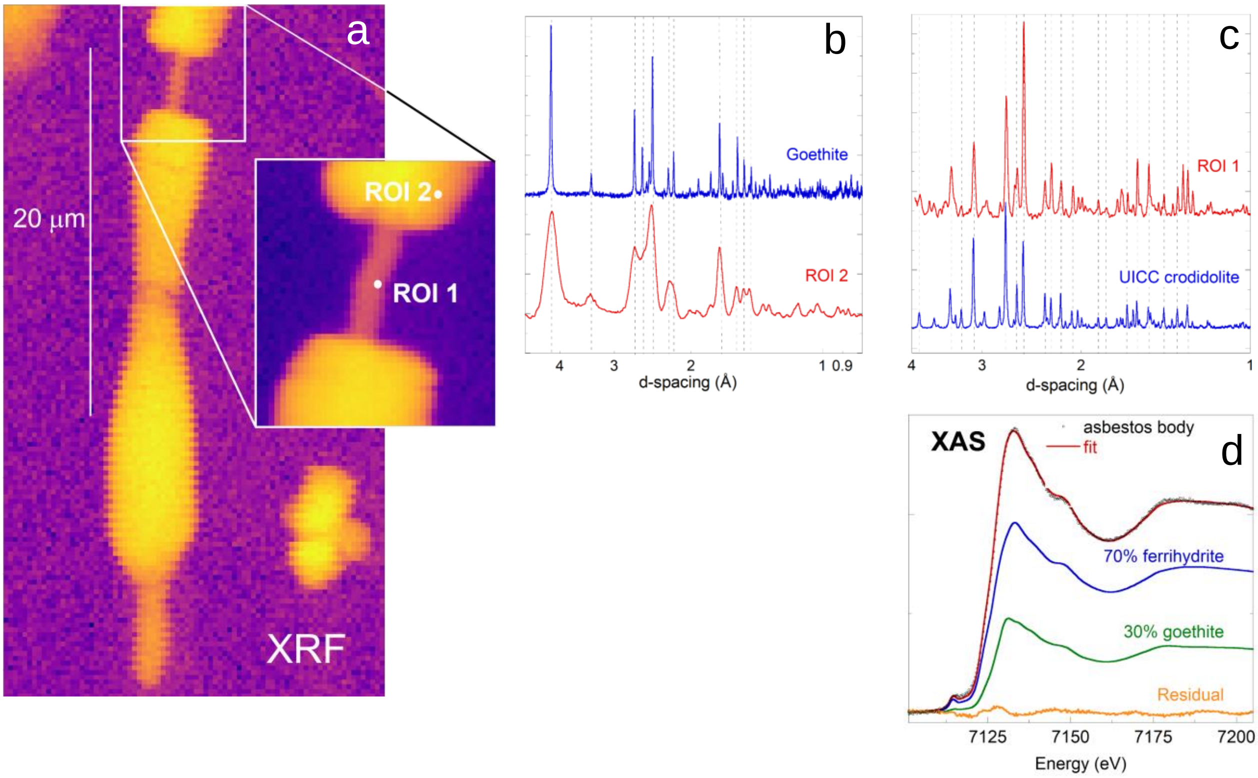

Figure 1. a) X-ray fluorescence (XRF) map of an AB (Fe signal) showing the region of interests (ROI 1 and ROI 2) chosen for point XRD acquisitions, which are shown in b) and c). d) Linear combination fit of the XANES spectrum of an AB using the spectra of ferrihydrite (70 mol%) and goethite (30 mol%).

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O4. A fragment- based approach targeting trypanothione reductase for the development of new antileishmanial agents

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Leishmaniasis is a vector-borne neglected disease with high morbidity and mortality rates, considered an emergent global health concern. The disease is endemic in tropical and subtropical areas but also in southern Europe, comprising up to 1.2 million cases each year. Currently used drugs possess several drawbacks, such as limited efficacy, toxic side-effects, and resistance development. All in all, this alarming scenario advocates for the development of new drugs. Trypanothione reductase (TR), a validated antileishmanial target, is a parasite-specific enzyme critical for antioxidant defence. The absence of TR in the host, its vital role for the parasite and the development of numerous TR inhibitors make this enzyme an attractive target for antileishmanial drugs [1-3]. However, among the TR-inhibiting compounds reported so far, only few molecules possess adequate antiparasitic/inhibitory activity, mainly due to two aspects: i) survival of the parasites is affected when TR activity is reduced by more than 90% [4]; ii) a large and featureless TR active site hampers efforts to develop effective inhibitors [5]. However, as TR displays different sub-pockets, it represents an optimal target for fragment based drug discovery (FBDD) aiming at identifying small fragments binding to adjacent sub-pocket in the protein and using them to design larger molecules with optimal binding profile. On this basis, a crystallographic fragment screening, performed at the XCHEM lab (Diamond, UK), allowed us to identify 12 fragments able to bind TR sub-pockets. Among the screened ligands, the five compounds interacting with trypanothione-binding cavity were selected to design TR inhibitors [6]. Supported by docking studies, a small library of compounds was obtained by merging, linking and/or growing the selected fragments. The molecules have been synthetized and have been tested to evaluate TR binding and inhibitory activity, followed by anti-leishmanial phenotypic assays of the most promising TR inhibitors. In conclusion, the FBDD approach will potentially contribute to discovering new lead candidates with the aim to optimize the leishmanicidal profile and to perform a preliminary structure-activity relationship study.

Acknowledgements:
This research was funded by: Ministero dell'Università e della Ricerca, grant number FISR2019_03796 PROLEISH and CNCCS COLLEZIONE DI COMPOSTI CHIMICI ED ATTIVITA' DI SCREENING, Progetti bandiera e di interesse, CUP: B56G15001140005.

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O5. Multilevel X-ray imaging approach to assess the sequential evolution of multi-organ damage in neurodegenerative diseases

F. Palermo[1], A. Sanna[1,2], B. Parodi[3], C. Venturi[3], L. Massimi[1], L. Maugeri[1], E. Longo[6], L. D'Amico[6,7], G. Saccomano[6,7], G. Tromba[6], I. Bukreeva[1], M. Fratini[1,9], G.P. Marra[1], G. Gigli[1], N. Kerlero de Rosbo[1,3] and A. Cedola[1]

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The 3D complexity of biological tissues and intricate structural-functional connections call for state-of-the-art X-ray imaging approaches. Unlike other imaging techniques, X-ray phase-contrast tomography (XPCT) offers a highly sensitive 3D imaging approach to investigate different disease-relevant networks at levels ranging from the single cell through to the whole organ. We present here a concomitant study of the evolution of tissue damage and inflammation in different potential target organs for the disease in the murine model for multiple sclerosis, a demyelination autoimmune disorder of the central nervous system. XPCT identifies and monitors structural and cellular alterations throughout the central nervous system, but also in the gut, and eye, of mice induced to develop multiple sclerosis-like disease and sacrificed at pre-symptomatic and symptomatic time points. This approach rests on a multiscale analysis to detect early appearance of imaging indicators potentially acting as biomarkers that can predict the disease. The longitudinal data obtained permit an original evaluation of the sequential evolution of multi-organ damages in the murine model shedding light on the role of the gut-brain axis in the disease development and progression, of relevance for the human case.

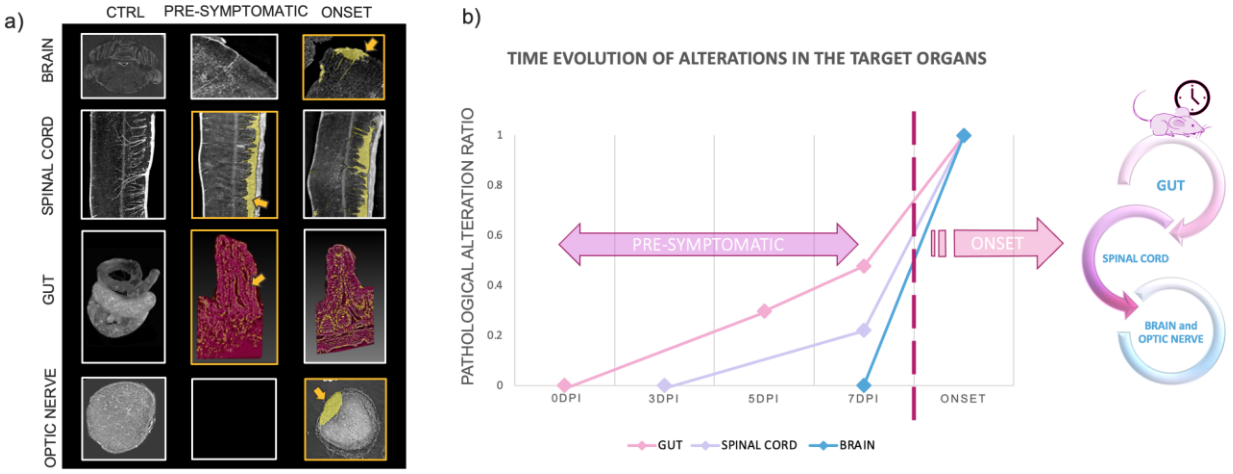

Figure 1. a) Representative XPCT images and/or rendering of the multi-organ investigation and temporal assessment of imaging markers at early stages. b) Graphical representation of alteration spatial distribution over timer.

Acknowledgements: Financial support from the TECNOMED Project (Regione Puglia); PNRR Roma Technopole – Innovation Ecosystem (Next Generation EU); bilateral project CNR/RFBR (2018–2020); Project DARIAH IT (MUR D.D. n. 2595 PON CIR01_00022).

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MS8 - Open Session

O1. Industrial Applications of AichiSR

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Aichi Synchrotron Radiation Center (AichiSR) opened for users in March 2013 as the core facility of Aichi Prefecture's "Knowledge Hub Aichi," which was developed at the Aichi Expo site to enhance high value-added manufacturing technologies. As many people in Japan know, Aichi Prefecture is the center of manufacturing industries in Japan. Therefore, Aichi Prefectural government intends to promote technological innovations and the creation of new industries for continuous growth of society through the activities of this Knowledge Hub. Although AichiSR is a very compact facility, it has the advantage of having sufficient hard X-ray capability. This is because, according to preliminary studies, there are many users of synchrotron radiation in the industry of this region, and many of them have requested the use of hard X-rays. To realize this requirement, superconducting bending magnets (super-bend) with a magnetic field of 5 T were installed at four locations in the electron storage ring shown in Fig. 1. The super-bends enable us to use hard X-rays excess of 20 keV to up to 12 beamline ports, even though the electron energy of the storage ring is 1.2 GeV. Figure 1 also shows the current configuration of the light source of AichiSR as well as the 12 beamlines in operation with super-bends and normal-bends.

115 companies, 43 universities and 16 public research institutes used the facility in FY2022, and it also welcomed users from overseas. Of the industrial users, more than half are from companies in Aichi Prefecture. We believe this is not only because of the geographical advantage, but also because there are many companies in Aichi Prefecture that are willing to use synchrotron radiation. Among them, DENSO Corporation has constructed two their own beamlines in our facility and is promoting the use of synchrotron radiation. The fields of use are not limited to the manufacturing industries, such as automobiles, electronics, ceramics, and chemicals, reflecting the regional characteristics, but also to wide range of fields, including protein, medical materials, agricultural products, cultural assets, and basic physics. AichiSR has put emphasis on industrial use and new applications, and provides well-organized user support system and user-friendly usage system unlike other synchrotron radiation facilities that are mainly for academic research. Coordinators for industrial use are available to optimize actual measurement plans. It is especially useful for new users in companies.

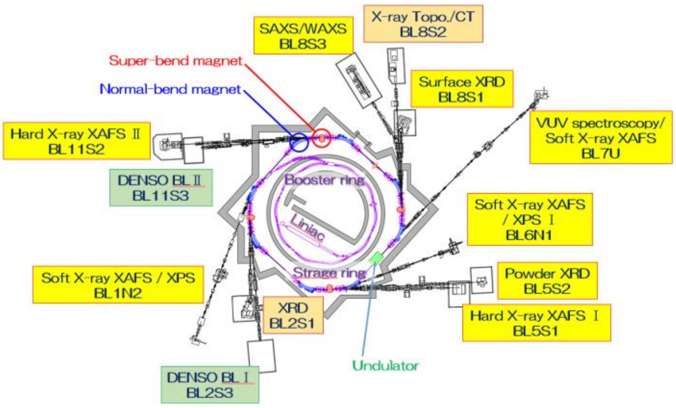

Figure 1. Light Source and beamline map of AichiSR. In the storage ring, 4 super-conducting bending and 8 normal conducting bending magnets are installed together with an Apple-Ⅱ type undulator. A 50-MeV linear accelerator (Linac) and a 1.2-GeV booster ring supply X-rays in top-up operation with constant current of 300 mA. Beamline with “S” is connected to a 5T super-conducting magnet.

O2. Identifying chemical environments and hydrogen-related density of states in metal hydrides

Francesco Offi[1], Curran Kalha[2], Laura E. Ratcliff[3], Giorgio Colombi[4], Christoph Schlueter[5], Bernard Dam[4], Andrei Gloskovskii[5], Tien-Lin Lee[6], Pardeep K. Thakur[6], Prajna Bhatt[2], Yujiang Zhu[2], Jürg Osterwalder[7], Anna Regoutz[2] and Giancarlo Panaccione[8]

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Metal hydrides are potential candidates for efficient hydrogen storage, since their high volumetric hydrogen density and feasible reversibility of the hydrogen adsorption/desorption process. An efficient application of metal hydrides goes through a fine tuning of their thermodynamic properties, which in turn depends on a detailed investigation of their electronic structure, therefore calling for a fundamental understanding of the electron interaction between hydrogen and the metal atoms at a local atomic level. In the present work we investigated the electronic character and the chemical environment of hydrogen in two prototypical metal di-hydrides, $YH_{2-\delta}$ and $TiH_{2-\delta}$, by means of Hard X-ray Photoelectron Spectroscopy (HAXPES) [1]. Exploiting the photon tunability offered by synchrotron radiation the information depth can be varied [2], allowing to obtain a non-destructing depth profile of as grown samples, thus distinguishing the contribution of the true bulk-hydride from the inherently oxidized surface, as show in Fig. 1 for the case of Y 3d core level. Furthermore, the sensitivity to specific orbitals offered by the dependence of the photoionization cross section from the photon energy and the combination of experimental valence band spectra collected at varying photon energies with theoretical insights from density functional theory (DFT) calculations [3], provides a description of the bonding nature and the role of *d* versus *sp* contributions of states near the Fermi energy. Finally, by using the experimental values of the energy position of metal *s* band features close to the Fermi energy in the HAXPES valence band spectra, a reliable determination of the enthalpy of formation is proposed.

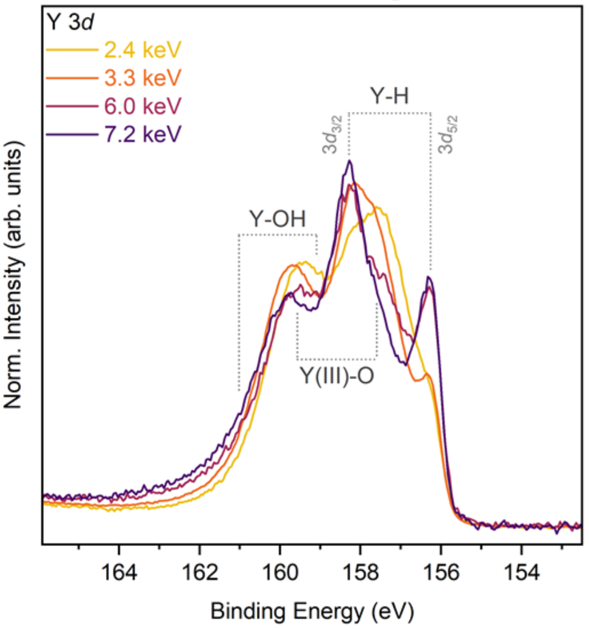

Figure 1. HAXPES spectra around Y 3*d* core level allowing to identify the Y-H and the Y-O components.

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O3. Unveiling the crystal structure of novel hybrid organic-inorganic perovskites by synchrotron X-ray powder/single crystal diffraction data

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In the last decades, perovskites attracted a growing scientific interest and revealed themselves promising and appealing candidates for technological applications (*e.g*., solar cells, LEDs, lasers, photodetector devices). Among them, the hybrid organic-inorganic perovskites (HOIPs), consisting of alternating layers of organic cations and inorganic corner-sharing octahedra, offer a great potential, relying on the large tunability of their optoelectronic properties, greatly influenced by the interaction between the organic and inorganic components: *e.g.*, by changing the type of organic cations and/or the number of layers in the inorganic slabs, strong differences in the emitted wavelength can be observed.

To optimize and tune the optoelectronic properties of new HOIPs Crystallography plays a fundamental guiding role: a successful structure determination process, *i.e.*, the knowledge of the crystal structure, can give precious insights into the structure-property relationships of the investigated compounds.

The success of the *ab-initio* structure solution process can be hampered by the small size of the crystals and/or their low crystallinity and weak diffraction power; for example, in the case of a-few-μm-thick laminar single crystals, a crystallographic study based on conventional laboratory X-ray sources usually fails. The access to non-conventional high-brilliance X-ray sources (*i.e.*, the use of synchrotron radiation) made the difference, enhancing the power of Crystallography by enabling to reduce the size of the single crystals that can be successfully characterized and to increase the complexity of the crystal structures that can be determined by X-ray diffraction data.

Some latest successful crystallographic cases of study and their relevant outcomes regarding the structure characterization of new HOIPs by synchrotron X-ray powder [1] and single crystal [2-4] diffraction data will be outlined.

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O4. Multi-element X-ray Detectors for High Count-Rate Spectroscopy

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We will present our research projects on high count-rate X-ray detectors for synchrotron applications. When dealing with high-brilliance sources, such as synchrotron light, fluorescence detectors must provide outstanding throughput capability while maintaining satisfactory energy resolution.

The ARDESIA project [1], aims at developing a low-noise high resolution X-ray spectrometer for synchrotron applications, including X-ray absorption spectroscopy (XAS), X-ray fluorescence (XRF) spectroscopy, and X-ray nanoprobing imaging, covering an energy range of 0.2-20 keV.

ARDESIA-16 is a multichannel X-ray spectrometer based on a monolithic 16-element Silicon Drift Detector (SDD) matrix coupled with custom 4-channel CUBE preamplifiers. It is specifically optimized to achieve a high-count rate (>1Mcps per channel) and good energy resolution (e.g. below 150 eV at peaking times faster than 200 ns) for X-ray fluorescence detection. Two 16-channel SDD-based spectrometer prototypes have been already installed in synchrotron beamlines in Europe: one at the ID-16A beamline in ESRF (Grenoble, France), and one at the P06 beamline in PETRA (Hamburg, Germany). The detection module and the complete spectrometer will be described at the conference along with experimental results of the 16-channel detector in the beamlines and an outlook towards a 64-channel evolution.

A new project, supported by DESY (Hamburg, Germany), is under development at Politecnico di Milano. Its goal is to make X-ray Fluorescence Microscopy (XFM) experiments more efficient, reducing the dwell time. This innovative spectrometer, called ASCANIO, takes advantage of two main features: a backscattering geometry [2] and a new SDD-tilted configuration that allows a more uniform distribution of the fluorescence light among pixels. The detector is composed of four monolithic arrays, each one consisting of four, 1-mm-thick SDD pixels with 5 mm pitch. ASCANIO is expected to achieve about 1 sr solid angle at 8 mm sample distance, and a potential Output Count Rate higher than 20 Mcps. Advantages regarding solid angles and tilted geometry will be presented at the SILS Conference along with the mechanical design of the spectrometer for installation in the P06 beamline (Petra, Hamburg).

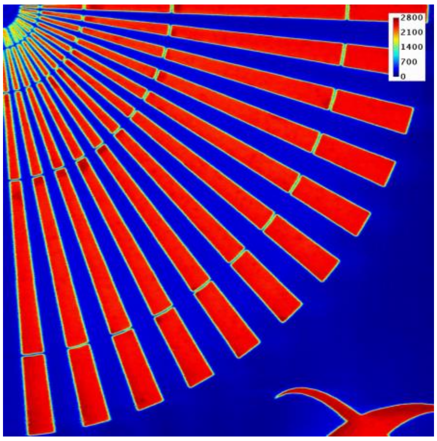

Figure 1. Gold map of a Siemens star taken with ARDESIA-16 at ID-16A beamline.

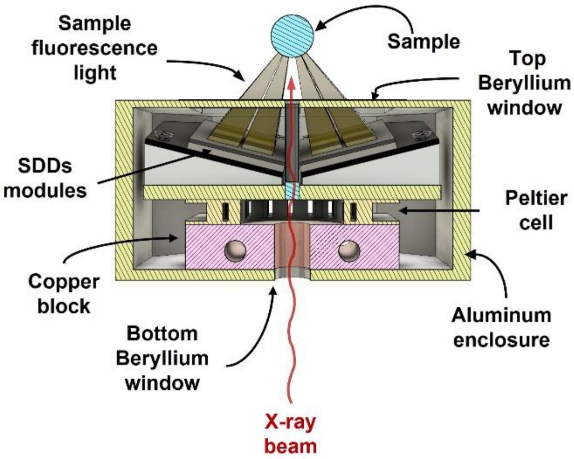

Figure 2. ASCANIO working principle.

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O5. EuPRAXIA@SPARC_LAB FELs for soft x-ray spectroscopy and imaging

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Soft X-ray free electron laser (FEL) sources are unique tools that thanks to high-flux, brilliance and short pulses are suitable to perform experiments looking at electrical and structural dynamics of almost any material through linear and non-linear interactions. Recent advancements in the accelerator technology have also resulted in more efficient, high-quality, and compact FEL sources.

The EuPRAXIA@SPARC LAB project is an interdisciplinary user facility, under construction at the Laboratori Nazionali di Frascati of the INFN, as part of the leading EuPRAXIA project. The aim of this project is to build the first cost-effective, high-gradient plasma-accelerated fifth-generation FEL source facility. The electron beam will be accelerated using a X-band normal conducting Linac, followed by a Plasma WakeField Acceleration (PWFA) stage [1]. The facility is planning the construction of two beamlines that will deliver ultra-bright photon pulses for different experiments. The first beamline, ARIA, will be a seeded FEL operational in the range 50-180 nm [2], while the second, AQUA, will be a SASE operational in the XUV-soft X-ray, i.e. in the wavelength range 4-10 nm [3].

This contribution presents the design of the user facility, as well as an overview of the foreseen applications: imaging and spectroscopy techniques suitable to investigate various samples, such as biological specimens, soft matter, and inorganic materials. These techniques are fundamental to collect information on both structural properties and dynamical behaviors [4], such as the electronic state of excited molecules near conical intersections [5].

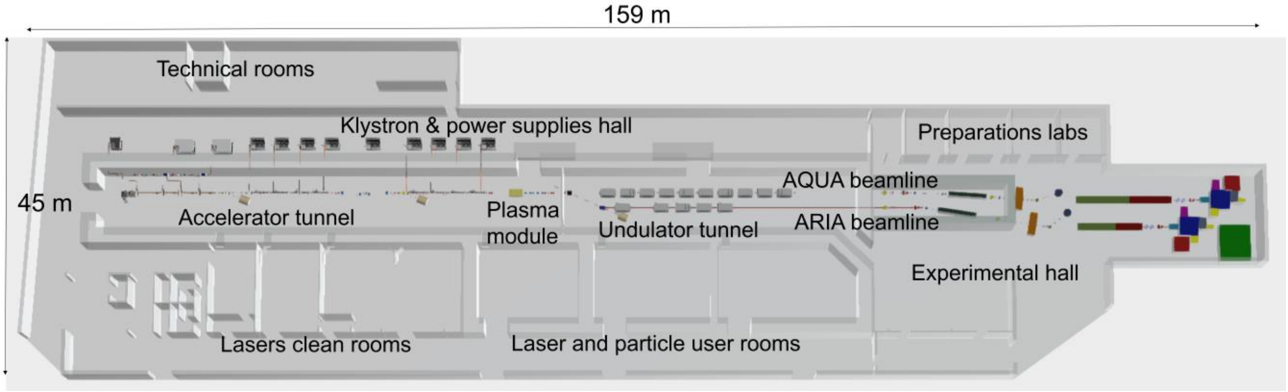

Figure 1. EuPRAXIA@SPARC LAB layout.

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O6. The XRF beamline at Elettra: far beyond microscopy

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The XRF beamline is a multi-purpose instrument that is mainly devoted to the X-ray Fluorescence (XRF) technique [1]. Nonetheless, the beamline offers much more than standard XRF and XRF microscopy. The monochromator has been designed to make the beamline well suited for X-ray Absorption Spectroscopy (XAS) experiments from 2 to 14 keV. Furthermore, the high-vacuum chamber equipped with a high-precision manipulator [2] allows fine movements in the range of 1 µm, while the fluorescence detector equipped with a thin polymeric window guarantees a reliable fluorescence detection even at low energies.

Given the broad range of applications of XRF and XAS, the XRF beamline hosts users from a wide variety of backgrounds including biology, geology, climatology, cultural heritage, fundamental science, environmental science, medicine, and materials science. Henceforth, depending on the system to be studied, a plethora of issues might come up during data acquisition, including but not limited to: ultra-diluted analyte, extremely low thickness, buried interfaces, etc. All these issues (and more) can hinder the signal detection but can be overcome by using non-standard geometries.

The fine sample movements and the broad energy range can be used to adjust the geometry so to fulfil the experimental needs, exploiting grazing incidence (GI) and exit (GE) geometries or even X-ray Standing Wave (XSW) excitation. When XANES or XRF are coupled with such geometries, not only can one obtain chemical selective information on a sample, but the surface sensitivity and the depth selectivity are also obtained.

In this talk, several case studies will be described, portraying the potentialities offered by the XRF beamline in different scientific fields. Examples from fundamental physics, materials science, and environmental science will be discussed, highlighting how the added value of depth selectivity can improve data collected through chemical sensitive techniques [3-5].

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Plenary Lecture 3. New challenges in structural biology: Catching the complexity of dynamic nanomachines

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Structural Biology turned 60 last year if we start counting from the two mythical Nobel prizes awarded to Watson, Crick, and Wilkins, and Perutz and Kendrew in 1962. More than sixty years and several ten thousand structures later, we can now look back and trace the developments of the structural field and consider the new challenges which await us ahead [1]. We are also in the position to look at the future and reflect on the challenges which await us.

A particularly fascinating challenge is to understand the dynamical functioning of entire molecular machines moving beyond the description of static complexes. Machines are typically composed of complex networks of competing interactions which form and disassemble in a time-resolved way. The study of machines recalls other related challenges: can we account in our studies for the complexity of the living cell? Traditionally, Structural Biology has been by election in vitro and relying on the use of highly purified proteins because this is the only way to ensure that what we observe is caused directly by the protein we want to study rather than by impurities or by mediated effects. While this concept cannot be overcome, it has become important to fill the gap between biophysical studies and cellular biology: With this aim, an increasing interest is being paid to studies of molecular crowding in the attempt of designing new ways to approach structural biology in millieux as close as possible to the cellular environment [2]. As a corollary, we also need to develop methodologies that may allow us to look at protein structure directly in cell.

Another remarkable aspect that requires increasing attention is how post-translational modifications affect protein structure and modulate interactions. We have for instance seen the importance of modifications for the histone code where a few chemical groups account for the combinatorial complexity which modulates gene expression [3].

Finally, for too many years we have focused on proteins and nucleic acids, neglecting other important cellular components such as carbohydrates, lipids and small metabolites. These studies have often been hampered by the complexity of these other systems and the difficulties of producing these molecules in high quantities and purity. It is about time to reconsider these questions and extend our structural studies to include these molecules.

In my seminar, I will analyze these important aspects and revise how new emerging techniques may allow us to reach new frontiers of Structural Biology.

[1] H. M. Berman, B. Coimbatore Narayanan, L. Di Costanzo, S. Dutta, S. Ghosh, B. P. Hudson, C. L. Lawson, E. Peisach, A. Prlić, P. W. Rose, C. Shao, H. Yang, J. Young and C. Zardecki, *Biochem. J.*, 2009, **417**, 621–637.
[2] M. Cammarata, F. Piazza, G. Rivas, G. Schirò, P. A.Temussi, A. Pastore, *Front Mol Biosci.*, 2023, **10**, 1153996.
[3] J. Füllgrabe, N. Heldring, O. Hermanson, B. Joseph, *Autophagy*, 2014, **10**.

Large scale facility updates

Operation and Upgrades of Elettra and FERMI

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In 2022 the operation of the third generation synchrotron radiation facility Elettra and of the free-electron laser (FEL) facility FERMI was back to normal after the COVID crisis. All key performance indicators of the two user facilities exceeded the pre-COVID 2019 values. The Elettra source operated with 96% efficiency with 28 beamlines and experimental stations open to international users. Of the 1142 proposals received from 51 different countries, 596 were assigned beamtime. More than 540 scientific publications stemming from experiments performed using the Elettra source appeared in international peer-reviewed journals in 2022.

The FERMI FEL-1 and FEL-2 lasers continued to exploit external seeding to achieve unparalleled pulse-to-pulse wavelength, linewidth and intensity stability, together with the possibility of performing two-color and four-wave mixing experiments. All this makes the FERMI source currently unique in the international panorama. The six operating beamlines DiProI, EIS-TIMER, EIS-TIMEX, LDM, MagneDyn and TeraFERMI were available for 96% of the programmed experimental time, allowing 53 different experiments to be completed. A total of 30 scientific publications stemming from experiments performed using the FERMI FEL source appeared in international peer-reviewed journals in 2022.

In the last quarter of 2022 the dramatic increase in the cost of electric energy and natural gas, together with the absence of any fixed-priced contract in Italy for the supply of energy, lead to energy costs exceeding by 40% our programmed energy budget. We elected to maintain the normal beamtime schedule not to disrupt user operations, hoping the the situation would go back to normal by the beginning of 2023. Unfortunately, this was not the case, and we had to face predictions of a dramatic energy cost increase in 2023 relative to 2022. The only option left to us, in the absence of any governmental intervention, was to curtail accelerator operations in the winter and summer months, leading to a 40% overall reduction in user beamtime at both Elettra and FERMI. We hope that the situation will change in 2024.

The forced reduction in user operations allowed us to speed up some of the upgrade programs of the Elettra and FERMI facilities. The development of the new Elettra 2.0 storage ring continued, with upgrade programs ongoing for the SuperESCA, BaDElPh, Spectromicroscopy, XAFS, Nanospectroscopy, HF-SAXS and TwinMic beamlines, and the construction of new beamlines for Coherent Diffraction Imaging (CDI), hard-x-ray medical imaging (SYRMEP-LS), μ-XRD, μ-XAFS and μ-XRF.

The conversion of the FERMI FEL-1 laser from the high-gain harmonic generation (HGHG) operating mode to the Echo-Enabled harmonic generation (EEHG) mode was completed and commissioning of the new facility is starting as we speak. The change will greatly increase the photon energy range available, further increase the reliability of the source, and serve as an important test case for a similar conversion of the first stage of FEL-2. Theoretical studies to date indicate that an EEHG first stage coupled with a HGHG second stage appears to be the most promising route to extend the FEL-2 photon energy range across the water window.

On May 7-12, 2023 Elettra Sincrotrone Trieste, together with the Istituto Nazionale di Fisica Nucleare (INFN), had the honor to host the 14th International Particle Accelerator Conference in Venice. With 1660 participants from 37 countries, 89 talks, 1709 poster presentations and the presence of 121 industrial partners IPAC'23 exceeded all expectations and set a new record. We hope this bodes well for the future of all accelerator-based photon sources worldwide.

EBS: New scientific opportunities

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The ESRF is the first high-energy, fourth-generation synchrotron, which constitutes a landmark for fundamental and innovation-driven research. With the support of the ESRF's 21 international partner countries, a brand-new generation of high-energy synchrotron, the ESRF's Extremely Brilliant Source (EBS) was launched in 2020 with superior X-ray performances (up to a factor 100) in terms of brilliance, coherence and emittance. This talk will present the EBS benefits, its exploitation and the new experimental capabilities available to academic and industrial users. The first scientific highlights from the main flagship and refurbished beamlines will be briefly described. The presentation will illustrate how the enhanced performance of the X-rays, combined with new stations and state-of-the-art instruments, will improve biomedical phase-contrast imaging, and will make the study the structure of condensed matter possible at the nanometre scale under operando or extreme thermodynamical conditions with higher resolution, greater image quality and faster framerate. Finally, this presentation will give a summary of the status of the beamlines under construction, their design choices and strategic research, a snapshot of its present status and some considerations of their future perspectives.

New scientific opportunities at the European X-ray Free Electron Laser

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In the past decade we have seen very important developments in the field of accelerator-based X-ray user facilities, with the advent of 4th generation synchrotron sources and hard X-ray free electron lasers (XFEL). Among the latter, the European XFEL is the first hard XFEL powered by a superconducting linear accelerator, which enables MHz rate pulse generation, leading to an increase of more than 2 orders of magnitude in the number of delivered photon pulses per second to the sample.

A unique feature of X-ray FELs is the combination of the extremely short (fs) photon pulses with the short (Ȧ) wavelengths of the produced x-rays. These new user facilities are opening novel avenues in the investigation of fundamental processes in many areas of science, from physics to chemistry, biology and materials science, because they allow investigation of matter at the time scales of electron and nuclear dynamics (down to fs), with chemical selectivity and bulk sensitivity.

The aim of this presentation is to provide to the SILS community a glimpse of the new research opportunities that are opening up at EuXFEL. I would also like to take this opportunity to establish a closer communication channel with groups who are interested in learning more about our present and future capabilities and how they match their expectations. In the talk, I will briefly introduce the European XFEL facility and then report on a selection of scientific highlights in different areas of research. Applications address fundamental processes of light-matter interaction, ultra-fast dynamic processes in liquids and solids, investigation of electronic and structural properties and their dynamics in biomolecules, nanostructures, disordered materials and high energy density states of matter. Finally, I will comment on some important challenges ahead.

MS9 - Young scientist session (room: Aula La Ginestra)

O1. Using SAXS to explore novel extraction pathways for plant-sourced proteins suitable for sustainable food

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[2]Department of Physics, Institute for Applied Physics, University of Tübingen, 72074, Germany

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Among all the alternative protein sources, pea seeds are the most competitively priced and sustainable. Plant seeds have been eaten for centuries and are a suitable protein source for vegans and vegetarians. However, pea seeds contain a mixture of high molecular weight and structurally complex proteins whose selective extraction represents a challenge in food science [1].

In this study, we focused on the development and validation of a novel extraction protocol that involves the use of Deep Eutectic Solvents (DESs) to obtain globulins, the most abundant proteins in peas. DESs represent a strong potential substitute for common organic solvents in extraction and purification protocols. In this work, DES is used for the first time to extract proteins from pea seeds.

We used size exclusion chromatography (SEC) and gel electrophoresis to validate an overall comparable protein profile with established protocols in the scientific literature. Importantly, globulins extracted by the novel protocol differ in the legumin/vicilin ratio from conventional protein extracts, which is expected to have consequences for subsequent processing potentials. To further explore these consequences, we characterized a systematic set of solutions and hydrogels of globular proteins from DES and other extractions by means of rheology and SAXS. The abundance of vicilin, among the extracted proteins, affects the structure and the mechanical properties of the food hydrocolloids [2]. The dependence of resulting macroscopic properties is promising for a better rational design of a plant-based food matrix as input for more advanced tuning of texture and mouthfeel in later food processing steps.

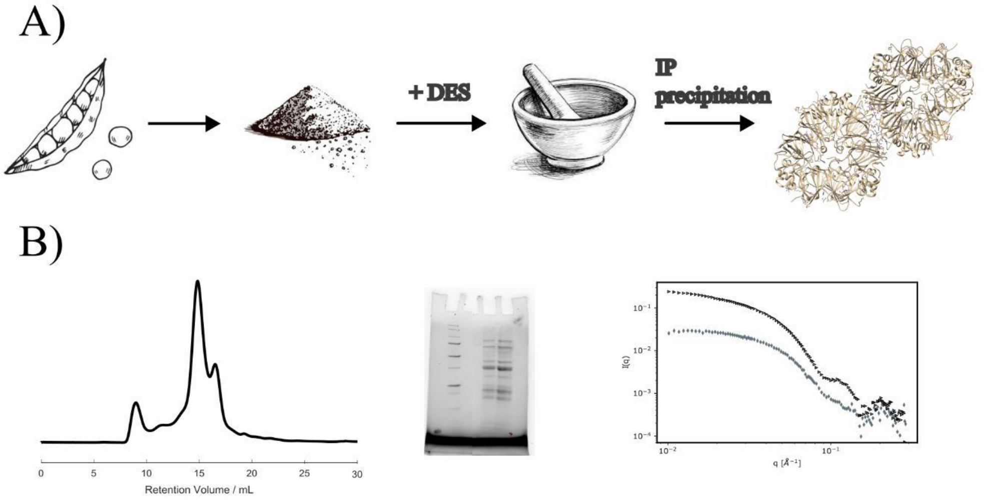

Figure 1. A) Scheme of the DES-based extraction protocol. B) Summary of the different techniques used to characterize extracted globulins.

[1] L. Day, *Trends Food Sci. Technol.*, 2013, **32**, 25–42.
[2] Y. Cao and R. Mezzenga, *Nat. Food*, 2020, **1**, 106–118.

O2. Investigating magneto-acoustic resonances via time-resolved optical polarimetry

P. Carrara[1,2], M. Brioschi[1,2], G. Gubbiotti[3], A. Adeyeye[4], R. Silvani[3], E. Longo[5], D. Dagur[6,2], V. Polewczyk[2], G. Vinai[2], R. Mantovan[5], M. Fanciulli[7], G. Rossi[1,2], G. Panaccione[2] and R. Cucini[2]

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[3]IOM-CNR, c/o Dipartimento di Fisica e Geologia, Via A. Pascoli, 06123 Perugia, IT
[4]Department of Physics, Durham University, South Rd, Durham, DH1 3LE, UK
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[6]Dipartimento di Fisica, Università degli Studi di Trieste, Via Valerio 2, 34127 Trieste, IT
[7]Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, 20125 Milano, IT

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Hybrid quasi-particles in condensed matter systems are observed at the degeneracy points between different degrees of freedom exhibiting non-zero coupling. These solid-state chimeras could be exploited in a wealth of applications, ranging from transducers to sensors, to memory and logic units [1]. In particular, when the dispersion relation of acoustic waves and of spin waves are degenerate, magnetostriction can allow for efficient cross-talk between lattice and spin reservoirs in the few gigahertz and inverse micron range [2].

We report on the hybrid magneto-mechanical properties of a 1D magnonic crystal composed of Fe(10 nm)/Py(10 nm) bilayered nanowires. An infrared laser pump triggers both acoustic and spin waves, and the two modes can be driven into resonance by proper tuning of an external magnetic field. The system then behaves as a magneto-mechanical cavity, and the coupling between magnon and phonon is investigated by analysis of time-resolved reflectivity and MOKE. The observed magnetic modes are in agreement with BLS and micromagnetic simulations. We compare the results to acoustic-wave-driven ferromagnetic resonance in Ni thin films [3-4]: here the pump pulse, in Transient Grating configuration, only triggers the acoustic dynamics, and the magnetization precession is completely acoustically-driven, giving neat difference in the spectral phase dependence of the resonance.

These laser-grounded experiments can be fruitfully extended down to the mesoscopic scale, *e.g.* by FEL-based Transient-Grating spectroscopy, a technique that is getting growing attention from the scientific community [5-6].

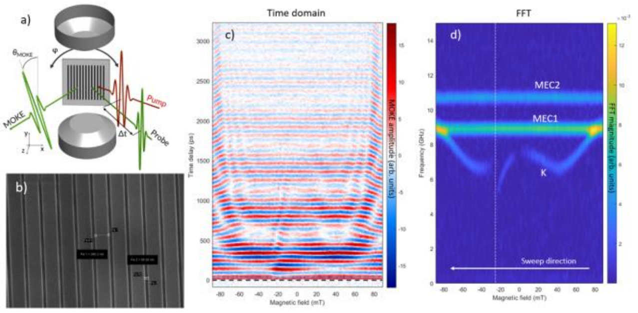

Figure 1. a) Sketch of the tr-MOKE setup. b) SEM micrograph of the 1D magnonic crystal. c-d) Time domain and FFT maps of the MOKE signal for different applied magnetic field strength.

Acknowledgements: Research at IOM-CNR has been funded by the European Union - NextGenerationEU under the Italian Ministry of University and Research (MUR) National Innovation Ecosystem grant ECS00000041 - VITALITY. G. Gubbiotti and G. Panaccione acknowledge Università degli Studi di Perugia, CNR and MUR for support within the project Vitality.

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[6] C. Svetina et al., *Opt. Lett.*, 2019, **44**, 574-57.

O3. EXAFS Analysis of MBE-grown GeSn heteroepitaxial layers

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GeSn epitaxial layer have attracted significant attention in recent years due to their potential use in innovative optoelectronic devices [1, 2]. The unique optical and electronic properties of this material system can be widely tuned through varying Sn concentration, degree of relaxation and other growth parameters, such as substrate temperature and deposition rate. Specifically, the distribution of Sn within the Ge lattice is crucial in determining their structural properties. To investigate the atomic short-range order of Sn in GeSn thin films, the chemical selectivity and local structure sensitivity of XAFS are particularly well-suited [3]. In this work, we investigate the short-range order of a series of $Ge_{1-x}Sn_x$ heteroepitaxial layers deposited on Ge/Si(001) virtual substrates by MBE, with varying Sn content (x = 5%-26%), and thickness (in the 30-100 nm range). The analysis of high-quality Sn K-edge XAFS spectra measured in fluorescence geometry at the Lisa-BM08 beamline (ESRF, Grenoble, Fr) provides valuable Sn local structure details that can be related to changes in the macroscopic, optical and electronic properties of these films and useful to tune optimal synthesis route for specific applications, e.g. thermoelectric or optoelectronics. Representative results of EXAFS analysis are shown in the figures below: **Fig. 1a** presents a spectrum of GeSn thin film with low Sn content of 5%, while **Fig. 1b** shows the spectrum when the Sn content is increased to 13%. While the first shell is always fitted by Sn-Ge neighbors, a clear difference can be observed in the next neighbor region in which Sn-Sn contribution are related to the deposition process conditions and composition of the thin films.

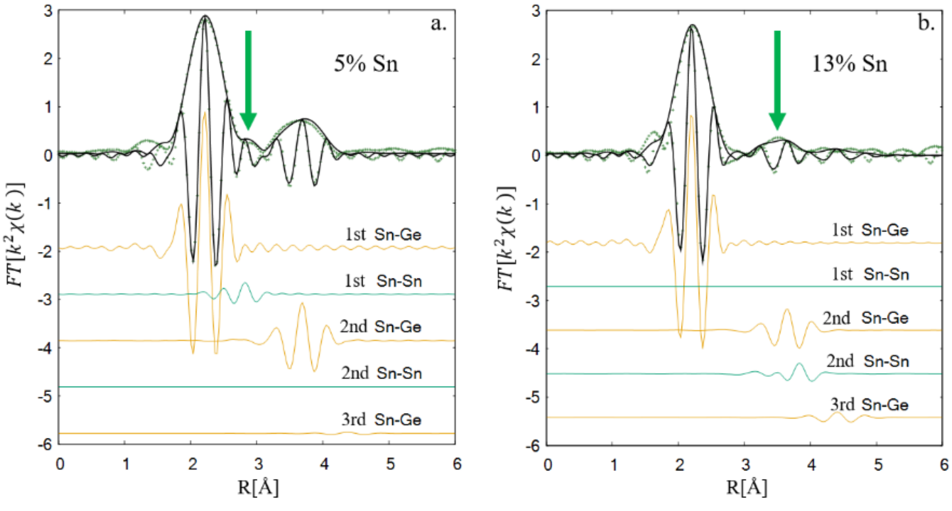

Figure 1. Representative EXAFS data fitting on MBE deposited $Ge_{1-x}Sn_x$, thin films, x=5% (a) and x=13% (b). Moduli and imaginary part of the Fourier transform of $k^2\chi(k)$ experimental data (green dots) and best fit (black lines), along with the partial contributions from different shells numbers used in the fitting.

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O4. Electronic structure of predicted topological superconductor $PbTaS_2$

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$PbTaS_2$ is a metal intercalated layered transition metal dichalcogenide compound which has recently been found to be a potential topological superconductor (TSC), with a superconducting transition temperature of 2.6 K. Besides the strong interest on this class of materials, because of their high potential in quantum computing applications, many aspects of their phenomenology are still undisclosed. Combining angle-resolved photemission spectroscopy (ARPES) measurements and density functional theory (DFT) calculations, we have studied the electronic properties of the centrosymmetric type-II superconductor $PbTaS_2$. In Fig.1, we show the comparison between the calculated and measured Fermi surface characterizing its electronic structure in the first Brillouin Zone. We have investigated the existence of topological nodal lines (NLs), formed by the crossing of Ta $d_{xy}/d_{x^2-y^2}$ and Pb p_x/p_y orbitals, and the presence of drumhead surface states originated by Pb terminations. The presence of surface states connecting the nodes on $PbTaS_2$, as already discovered on structurally similar materials to be typical characteristics in nodal-line semimetals [1,2], makes $PbTaS_2$ a good candidate for exploring the topological nodal-line superconductivity.

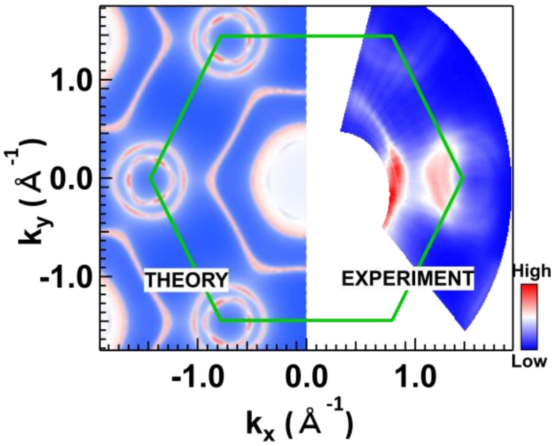

Figure 1. Left: The DFT calculated Fermi surface including spin orbital coupling. Right: Fermi surface measured by ARPES mapping with 31eV photon energy and p-pol at 80K.

[1] W. Chen et al., *Phys. Rev. B*, 2021, **103**, 035133.
[2] G. Bian et al., *Nat. Comm.*, 2016, **7**, 1-8.

O5. Application of X-ray computed microtomography to optical fibres

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X-ray computed microtomography (μCT) is a technique that exploits the contrast of the X-ray absorption of different elements of a given specimen to provide a 3D map of its internal structure or material density. Such a technique has applications in disparate fields, from material science to cultural heritage.

Among the several applications, in photonics μCT has the potential to characterize the materials composing optical fibres. In our work we demonstrate that, besides the structural characteristics of optical fibres, the analysis of μCT images also allows for retrieving the profile of their refractive index (n) [1]. When dealing with fibre optics, the latter is the most important parameter to determine for the characterization of optical fibres. Indeed, the value of n determines the waveguiding properties of fibres, i.e., their capability of transmitting light over long distances.

The novelty of our approach is based on the fact that both the absorption coefficient (μ) at X-ray frequencies and the refractive index n at optical frequencies can be shaped by the doping the fibre core. Consequently, by tracking the intensity of the tomographic image (which is proportional to μ, as long as one is far from the interface between the fibre core and the cladding), one may retrieve a 3D map of n at telecom wavelengths. Remarkably, at variance with common optical techniques for the characterization of optical fibres, μCT is insensitive to the presence of a plastic coating: hence, it can be easily applied to characterize long fibre spans.

Our μCT system at the μTomo beamline of the STAR Lab consists of a microfocus X-ray source (Hamamatsu L12161-07), which emits a conical beam with an aperture angle of 43° and a flat panel detector (Hamamatsu C7942SK-05). The source parameters were chosen so that 10 W of the X-ray beam is emitted with an X-ray tube voltage of 60 kV. Although with our setup we could reach a relatively poor spatial resolution (i.e., of about 5μm) when compared to that achievable in synchrotron facilities, we have retrieved the refractive index profile of several types of optical fibres. At first, we focused our efforts on multimode fibres, i.e., optical fibres with a core diameter of several tens of microns, that support multiple propagation modes at telecom wavelengths. In particular, our μCT setup permitted us to distinguish between the refractive index profile of step-index and graded-index fibres, i.e., fibres having an abrupt and gradual variation of n at the interface between core and cladding, respectively. Besides, we were also able to detect properties of the so-called photonic crystal fibres, which have a complex net-like transverse refractive index profile. We tested the effectiveness of μCT by analysing samples of standard fibres, damaged by high-intensity femtosecond laser pulses [2]. The latter produce a variation of the material internal structure on the micron-scale, which manifests as a local change of n. Remarkably, our μCT setup was capable of detecting even such small features. Finally, we applied μCT to the so-called specialty optical fibres, i.e., novel optical fibres made of non-silica materials, such as soft-glasses. The latter are made of high atomic number elements, which provide a higher X-ray absorption, thus enhancing the potentiality of μCT for profiling the refractive index of optical fibres. Moreover, we extended the study of damaged glass optical fibres to plastic fibres made of polymethyl methacrylate. The investigation of non-silica glass fibres and damaged plastic fibres are still ongoing, and the results are not published yet. Details about these two topics will be given during the presentation.

Acknowledgements: Ministero dell'Istruzione, dell'Università e della Ricerca grant STAR-2 (PIR01-00008).

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O6. Enhanced graphene metallicity via alkali metal deposition: a spectro-microscopy study

Dario Marchiani[1], Riccardo Frisenda[1], Carlo Mariani[1], José Avila[2], Pavel Dudin[2], Samuel Jeong[3], Yoshikazu Ito[3] and Maria Grazia Betti[1]

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Alkali metal (AM) doping is a suitable way to induce charge transfer in graphitic systems, as a way to tune the electronic properties and to increase the metallicity of the system without disturbing its planar sp^2 configuration. Thanks to its linear band dispersion which gives rise to a high carrier velocity and to its ultra-thin nature, graphene (Gr), it is particularly apt to a tuning of its electronic properties via alkali metal doping [1]. A fine tuning can also affect its transport properties also mediating ground states driven by an increased electron-phonon coupling [2].

Herewith, we present a detailed electron spectro-microscopy study, carried out at the ANTARES beamline (SOLEIL Synchrotron radiation facility), of potassium (K) doped graphene by exploiting fully free-standing Gr, namely a nano-porous graphene (NPG) architecture. NPG presents the electronic and vibrational hallmarks of an ideal suspended graphene [3], thus overcoming any substrate-induced effect. The core levels (C 1s and K 2p) and spectral density of states close to the Fermi level are measured by photoelectron microscopy (Figure 1), following their evolution upon K deposition. In the low-doping regime, K acts as an electron donor to the carbon atoms yielding to a rigid shift of the Gr π band and of the Dirac cone apex (Fig. 1c-d) with no significant band defomations [4]. Higher doping induces the neat appearance of a Dirac π^* plasmon correlated with the increased π electronic charge (Fig. 1a-b). The potassium uptake on NPG and the partial π^* band occupation in the valence band measured by micro-spectroscopy maps of the K:C percentage and Dirac cone shift show a rather homogeneous distribution (Fig. 1a). Moreover, we correlate the increased K uptake with the neat appearance of a π^* Dirac plasmon, given by the enriched electron charge density (Fig. 1b). K-NPG data are contrasted with preliminary observations on Cs and Na-doped NPG, bringing to light a different π^* occupation and Dirac plasmon evolution.

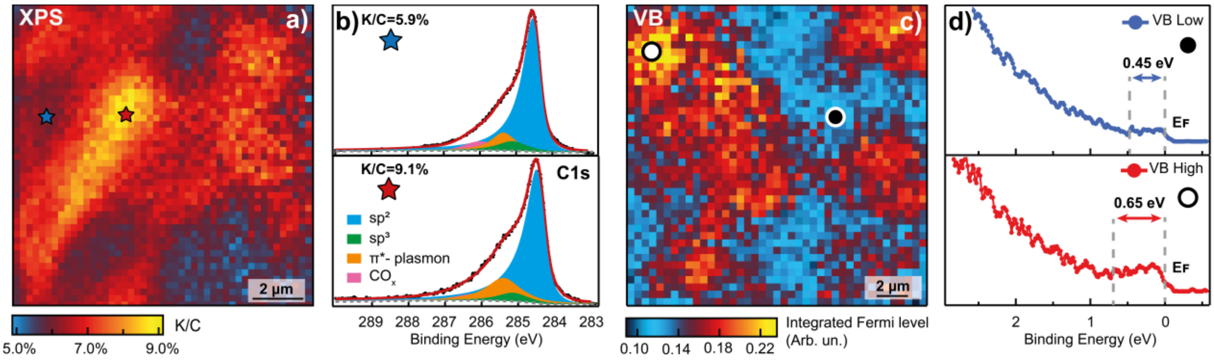

Figure 1: a) Spectro-microscopy map of the K-2p/C-1s core levels intensity ratio in a 12.5x12.5 μm^2 region; b) C 1s core level fitting of selected spectra from panel a) from lower (blue star) and higher (red star) coverage regions; higher K/C ratio is associated with a more pronounced π^*-plasmon due to increased electron charge; c) spectro-microscopy map (20x20 μm^2) of the spectral density close to the Fermi level (1.5-0 eV); d) selected spectra from panel c) of a lower (top) and higher (bottom) doping region.

[1] Struzzi et al., *Phys. Rev. B*, 2016, **94**, 085427.
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[3] Di Bernardo et al., *ACS Omega*, 2017, **2**, **7**, 3691–3697.
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MS9 - Young scientist session (room: Aula A)

O1. Enhancing elastic x-ray scattering by control of transient electronic populations

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The advent of X-ray Free Electron Lasers (XFELs) opened the way for exploring and controlling non-linear and collective emission phenomena. That is possible because XFELs can drive solids into electronically highly excited states at femtoseconds time scales, outcompeting inner-shells relaxation dynamics. The resulting transient state is electronically far out of equilibrium while the crystal structure remains intact. In a recent experiment at the SCS beamline of EuXFEL, we studied the scattering properties of Cu atoms irradiated by intense XFEL pulses. Controlling the electronic occupations, we could enhance the elastic scattering response of individual atoms.

X-ray pulses of 15 fs duration are tuned to the Cu-L_α transition (929.7 eV) and focused down to 20 µm onto a 150 nm thick multilayer ([B4C/Cu/SiC]$_n$) target. Photoionization followed by rapid Auger decay produces hot unbound electrons in the sample. A subsequent cascade of electron-electron collisions generates highly charged ions with severe depletion of the Cu 3d shell. In a previous transient x-ray absorption experiment of Cu [1], with identical pulse parameters, the authors identified an absorption peak below the natural Cu-L_3 edge (932.7 eV). This peak results from the resonant 2p-3d excitation (Cu-L_α transition) of the created 3d vacancies. Correspondingly to resonant absorption, the transient 2p-3d resonances reflect in additional resonant elastic x-ray scattering channels. This results in enhanced scattering strength of individual atoms (see Fig. 1). We demonstrated that the enhancement strongly depends on the intensity of the incoming pulse and can grow to one order of magnitude. Our findings encourage the application of the effect in innovative crystallographic methods where 3d metals may act as heavy scatterers in analogy with single-wavelength anomalous dispersion.

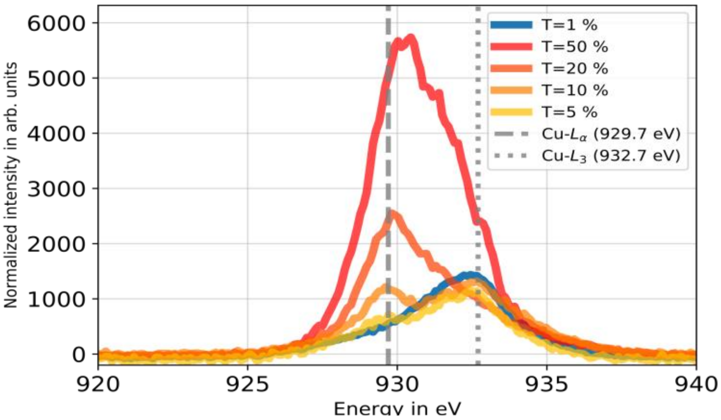

Figure 4. Spectrally resolved scattered intensity from a ([B4C/Cu/SiC]$_n$) multilayer. The incoming SASE XFEL pulse has 15 fs duration, 929 eV central wavelength (5 eV FWHM bandwidth), 100 uJ nominal energy (at 100% transmission) and is focused to 20 µm. Different colors correspond to different level of transmission according to the legend.

[1] L. Mercadier et al., *Preprint*, 2023, 10.21203/rs.3.rs-2396961/v1.

O2. Study of structural changes in different Pd catalysts during the direct synthesis of hydrogen peroxide

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Currently, the process used for the industrial synthesis of hydrogen peroxide (H_2O_2) is affordable only for large-scale production, limiting the application of H_2O_2 in small scale due to the cost and dangerousness of its transport [1]. Catalytic systems for the direct selective synthesis of H_2O_2 (aka direct synthesis, DS) are specifically suited for efficient and cost-effective applications at small/local scale. Pd is specifically suited for these reactions [2], and its catalytic efficiency and selectivity can be aided by ion-exchange supports [3] and the presence of chemical species able to generate stable complexes with Pd(II) ions [4]. This work is aimed at understanding the role of Pd-ligand interactions on the catalytic performance of Pd catalysts in the DS by exploiting the Pd-K edge XAFS. Pd catalyst synthesized on different supports have been studied at the LISA-BM08 (ESRF-Grenoble, FR) in pristine form and after DS tests under different conditions (i. e. both DS tests were carried out in a semi-batch glass reactor with 300mL of solvent, 100mg of catalyst and fed with a gas mixture H_2:O_2 4:96% for 48 hours, with one DS carried out in pure methanol as solvent, and the other in a mixture of 90% methanol and 10% acetonitrile, a known Pd ligand). Data were analysed in the near edge (XANES) and extended (EXAFS) region in order to identify the Pd-containing phases and their evolution after catalytic test.

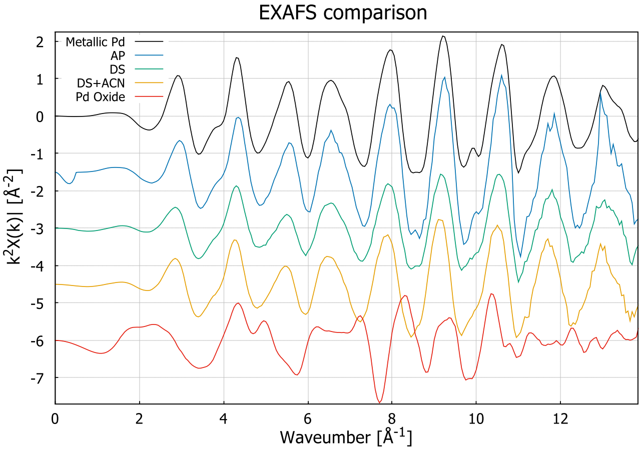

Figure 1. Representative k^2-weighted EXAFS signals of Pd 1% w./w. catalysts loaded on SSZ-13 zeolite by ion-exchange method, as prepared (AP), after the 48 hours DS activity (DS) and 48 hours DS activity in presence of ACN (DS+ACN). The Pd metal and PdO reference compound spectra are shown for sake of comparison.

Acknowledgements: This work was supported by University of Padova, BIRD project PDiSC#03BIRD2020-UNIPD.

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[2] P. Centomo, C. Meneghini, S. Sterchele, A. Trapananti, G. Aquilanti and M. Zecca, *ChemCatChem.*, 2015, **7**, 3712.
[3] Z. Jin, Y. Liu, L. Wang, C. Wang, Z. Wu, Q. Zhu, L. Wang and F. Xiao, *ACS Catal.*, 2021, **11**, 1946.
[4] F. Sandri, F. De Boni, M. Marelli, F. Sedona, V. Causin, P. Centomo and M. Zecca, *Catal. Commun.*, 2023, **174**, 106585.

O3. Complex phase behaviour of amorphous selenium under pressure

Emin Mijit[1,2,*], Joao Elias F. S. Rodrigues[2], Marco Perri[1], Laura Silenzi[1], Angelika Dorothea Rosa[2], Tetsuo Irifune[3], Francesco Capitani[4], Angela Trapananti[1] and Andrea Di Cicco[1,†]

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Studies on the pressure induced structural and electronic transition in amorphous Se have provided controversial results, making it difficult to clearly understand the high-pressure properties of this simple elemental amorphous substance. The possible differences in the initial amorphous samples were considered to be one of main reasons for the controversial findings from different experimental studies. In this work, pressure behavior of same amorphous Selenium (a-Se) samples has been systematically investigated under different hydrostatic conditions using complementary x-ray absorption spectroscopy (XAS) and x-ray diffraction (XRD) techniques. Results have shown that the nucleation processes in a-Se samples and the subsequent transitions in the crystalline phase can be significantly different depending on the experimental conditions, providing a different prospective for explaining the controversies on the subject in the existing literature. In addition, detailed quantitative information concerning the pressure induced evolution of local structural parameters in the amorphous phase have been achieved through standard EXAFS refinement procedures. Complementary information concerning the evaluations of the vibrational modes and changes in the intermediate range ordering were also obtained through the analysis of XANES and far infrared (IR) spectroscopy data. Precise local structural information that can be used for more accurate refinements of the crystalline phases have been also obtained by analyzing the EXAFS at higher pressures.

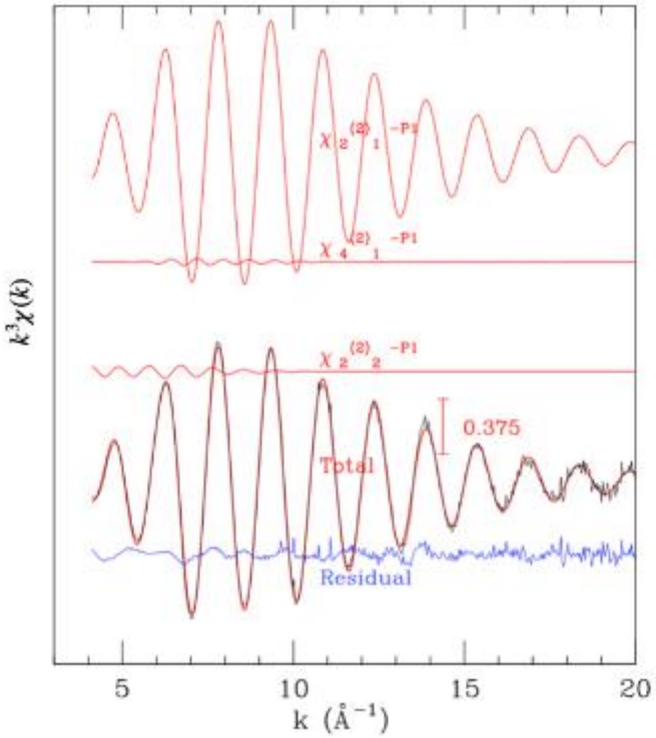

Figure 1. An exemplary EXAFS refinement for the structure a-Se.

O4. Enhancement of the structural stability in Li-ion batteries active material through oxide coating - a XAS study

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In lithium manganates, such as $LiMn_2O_4$, it has been shown that the redox process form an unstable cathode electrolyte interface (CEI) that induces higher Jahn-Teller distortion orders, resulting in the acceleration of the capacity fading of the battery [1]. A thin alumina coating of the $LiMn_2O_4$ active material has been suggested to improve the cycling performances of the battery device via formation of a more stable CEI [2]. However, the key to understand the overall structural dynamics of the active material and hence the battery performance lies within the expansion of the structural evolution to the bulk. In this presentation, we confront the propagation mechanism of the structural evolution of uncoated and alumina coated $LiMn_2O_4$ active materials from surface to the bulk using X-ray absorption spectroscopy (XAS).

XAS is a powerful, non-destructive technique that can be exploited to obtain information on the local environment and the oxidation state of a photo-absorbing element. The intense, collimated and tunable X-ray beams available at synchrotron facilities are ideal for this technique and give the possibility to probe even low concentration elements. XAS has been widely utilized in the field of electrochemistry, and proved to be a valuable tool for the investigation of the structural and electronic properties of Li-ion cathode materials [3], in which a critical role is played by the electrode/electrolyte interface. Surface-sensitive measurements can be carried out in the soft X-ray regime, with penetration depth from ~5 nm in total electron yield mode (TEY) to ~100 nm in fluorescence mode. The propagation of the structural changes to the bulk structure can be investigated in the hard X-ray regime, probing the whole sample in transmission mode. O K-edge and Mn L edges in TEY mode confirm that the coating strongly hinder of the Mn^{3+} disproportion and Mn dissolution at the electrode/electrolyte interface, while hard X-ray results at the Mn K-edge in transmission mode show that in the pristine sample the side products formation occurring at the electrode/electrolyte interface partially propagates into the bulk. Our EXAFS analysis suggest that the Jahn-Teller distortion favour a cubic-to-tetragonal transition, resulting in a nonuniform Li concentration. On the other hand, the alumina coating suppresses the superficial Jahn-Teller active Mn^{3+} species. This results in a more stable CEI as well as in the hindering of bulk distortion and side products formation [4].

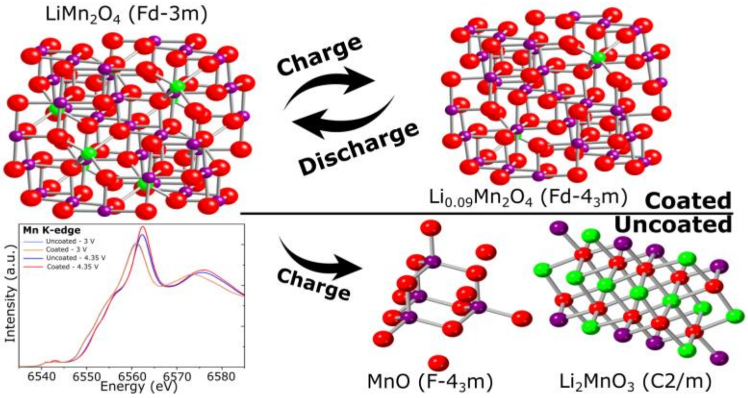

Figure 1. Proper structural dynamics upon cycling (top) and side products formation occurring in uncoated $LiMn_2O_4$ samples. At the bottom left, Mn K edge spectra of coated (red) and uncoated (blue) at two galvanostatic points (3 and 4.35 V).

[1] S. J. Rezvani et al., *J. Phys. Chem. C*, 2020, **124**, 26670-26677.
[2] R. Parmar et al., ACS Appl. Energy Mater., 2020, **3**, 8356-8365.
[3] S. J. Rezvani et al., *Journal of physics and chemistry of solids*, 2020, **136**, 109172.
[4] F. Paparoni et al., *J. Phys. Chem. C*, 2023.

O6. Characterization of Metal Based Deep Eutectic solvents

Giorgia Mannucci[1], Matteo Busato[1], Alessandro Tofoni[1], Francesco Tavani[1], Alessandra Del Giudice[1], Andrea Colella[1], Mauro Giustini[1] and Paola D'Angelo[1]

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Deep eutectic solvents (DESs) are formed by two or more compounds that melt upon contact at a precise molar ratio and produce a mixture with a melting point (MP) lower than those of the pure constituents. DESs show interesting properties such as negligible volatility, non-flammability, high solvating capability and low toxicity [1]. Common components of DESs are biocompatible and for this reason they have been proposed as sustainable solvents media in different applications including extraction processes, purification, and catalysis. In the recent years, interest was directed towards the study of the so-called "metal-based deep eutectic solvents" (MDES). This class of DESs exhibit important chemical-physical properties such as high polarity and conductivity, making these mixtures ideal candidates as new electrolytes and media for electrodepositions and catalytic processes. Common MDESs are composed by chlorides of Ni^{2+}, Co^{2+}, Zn^{2+} and Cu^{2+} and frequently their formation is impossible using the anhydrous form of the salts. Some examples are the $NiCl_2 \cdot 6H_2O$:Urea 1:3.5, $CoCl_2 \bullet 6H_2O$:Urea 1:3.5 and $CoCl_2 \bullet 6H_2O$:ChCl 1:3.5 MDESs (some representative samples are shown in Figure 1 [2]).

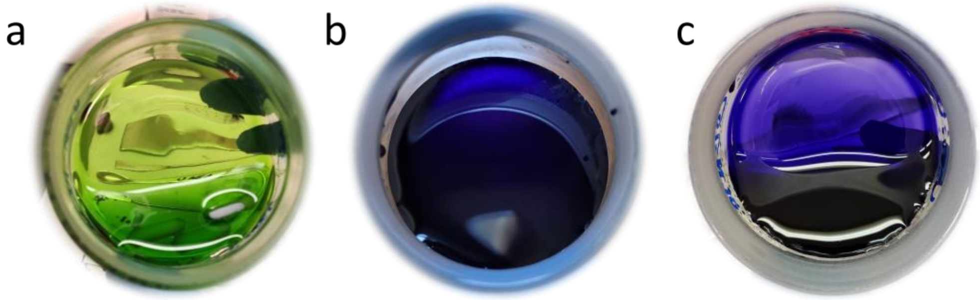

Figure 5. Photographs of the a) $NiCl_2 \cdot 6H_2O$:Urea 1:3.5, b) $CoCl_2 \bullet 6H_2O$:Urea 1:3.5 and c) $CoCl_2 \bullet 6H_2O$:ChCl 1:3.5 MDESs.

Here, we present a structural characterization of different MDESs using X-Ray absorption spectroscopy (XAS), small- and wide- angle X-Ray scattering (SWAXS) and UV-visible absorption spectroscopy, integrated with molecular dynamics simulations (MD). Moreover, with this work we aim at understanding the role of water in eutectic formation, being water often a component of DESs as a consequence of the high hygroscopic nature of many common constituents. Thanks to this combined approach, we were able to reconstruct the structural arrangement of the MDESs and their aqueous mixtures on both short- and intermediate-scale levels respectively with the analysis of XAS and SWAXS spectra. Finally, MD simulations were performed in order to have a more atomistic description of the systems.

[1] M. Francisco et al., *Angew. Chem.*, 2013, 52, 3074–3085.
[2] M. Busato et al., *Inorg. Chem.*, 2022, **61**, 23, 8843-8853.

P1. Inner shell ionization of highly charged ions with synchrotron radiation

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Information on energy, cross-sections, and natural width (Γ) of electronic transitions of neutral and ionized atoms is crucial to properly characterize the physics, kinematics, and chemistry of gaseous astrophysical environments. The soft (0.1-2 keV) X-ray band contains thousands of inner shell electron absorption of elements heavier than He (metals, in astrophysical jargon) in highly charged ionization states. But the vast majority of these transitions are poorly known, and they are mainly derived from theoretical modeling. The advent in the near future of high-throughput and high-resolution X-ray spectrometers, onboard space missions like XRISM (JAXA/NASA) [1], ATHENA (ESA) [2], and Arcus (NASA) [3] calls for experimental efforts to fill this deficiency planning dedicated campaigns of measurements of X-ray spectrometry. To contribute to this important astrophysical problem, a collaboration has been established between CNR, INAF, Elettra-ST and Max Planck Institute for Nuclear Physics (MPI-K, Heidelberg, D) at the Elettra synchrotron laboratory (Trieste, I). The collaboration is funded by the AHEAD2020 UE project, in order to exploit a compact electron beam ion trap (EBIT) from MPI-K for the production and trapping of highly charged ions (HCI) [5]. HCI stored in the EBIT are directly exposed to monochromatized XUV synchrotron radiation available at the GasPhase beamline [6], so that energy and cross-section of their inner-shell electronic transitions can be precisely determined [9]. Two different modes are available to detect absorption of HCI: fluorescence and photoionization. In the fluorescence mode, emission of XUV light induced by the initial photoexcitation is collected by 2 silicon drift detectors placed perpendicularly to the synchrotron light propagation axis [8]. In the photoionization mode pulsed extraction of ions followed by time-of-flight mass spectrometric detection is exploited to observe changes in the charge state distribution of stored ions due to the photo ionization processes induced by primary absorption.Here we present our first measurements of K_α transition lines of Be-like O, for both species O_{16}^{4+} and O_{18}^{4+}: $1s^22s^2(0)\rightarrow 1s2s^22p(1)$ at 553.468 eV and 553.4726 eV respectively. To calibrate the energy, several theoretically well-known transition lines of He-like O, He-like N, and Li-like O were measured.

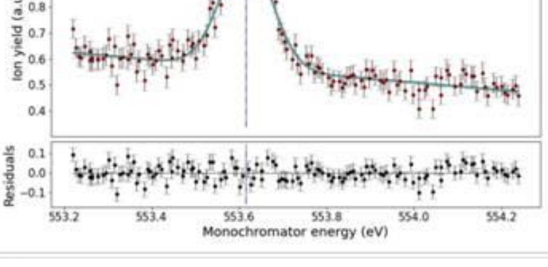

Figure 1. show photoionization of Be-like O from ion yield

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P2. Multiple scattering description of multicentre coherent emission in photoionization: the Cohen-Fano interference term in diatomic molecules revisited

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In the light of a multiple scattering (MS) description of molecular photo-diffraction and photoabsorption processes, we present an investigation of the interplay between initial state coherence and intramolecular scattering, leading to a reinterpretation of the molecular interference in diatomic molecules and in particular of the Cohen-Fano (CF) interference term in the *K*-edge photoabsorption of the N_2 molecule [1]. Working in the framework of MS theory, we show that when the initial state in a photoemission process is extended over many atomic sites, like in a valence molecular state, new MS processes are generated compared to the case of emission from a single localized site, due to the fact that emission from different sites is coherent. In photoabsorption, these processes are characterized by the fact that the emitter does not coincide with the detector, as is the case of a localized emitter (where EXAFS type of oscillations are generated in the cross section), but any two atoms at sites *i* and *j* share this role, giving rise to a propagation of the photoelectron wave between them with a period given by $\Delta k = 2\pi / R_{ij}$. This case encompasses the emission from delocalized occupied core states of diatomic molecules, like the $1\sigma_{g/u}$ state of the N_2 molecule treated by Cohen-Fano, and characterizes their interference term as the lowest order of such new processes, rather than the realization of a microscopic Young's experiment [2].

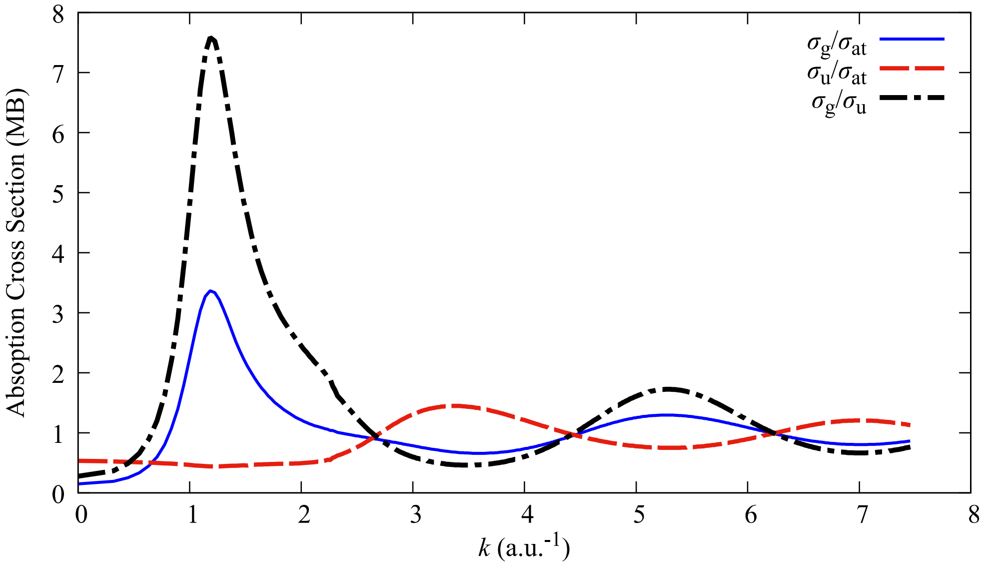

Figure 1. Total absorption cross for the gerade σ_g (full line) and ungerade σ_u (dashed line) initial state and their ratio (dot-dashed line) in N_2 molecule. Photon polarization along the molecular axis. The oscillations have a period of $\Delta k = 2\pi/R$, where R is the molecular bond length. See Ref. [2].

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P3. Investigation of the spectra reconstruction requirements of high-resolution inelastic x-ray scattering spectra using SASE radiation

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In general, the fine structure of inelastic scattering measurements is often obtained with seeded or monochromatized X-ray Free Electron Laser (XFEL) pulses [1-3], instead of self-amplified spontaneous emission (SASE) pulses since SASE pulses are generated through a stochastic process, resulting in a broadened energy width due to the presence of numerous narrow spikes.

However, inelastic experiments may be considerably simplified if the full range of SASE pulses could be used without compromising the energy resolution. This has been suggested to be possible using suitable data-analysis strategies[4-6] where a series of SASE pulses are considered in the construction of the response matrix $\mathbf{R}_{\mathrm{mn}} = \mathbf{J}^{+}_{\mathrm{km}} \cdot \mathbf{S}_{\mathrm{kn}}$, where $\mathbf{J}^{+}_{\mathrm{km}} = (\mathbf{J}^{\mathrm{T}}_{\mathrm{km}}\mathbf{J}_{\mathrm{km}})^{-1}\mathbf{J}^{\mathrm{T}}_{\mathrm{km}}$, is obtained by $\mathbf{J}_{\mathrm{km}}$ incident SASE spectra (k is the pulse number and m is energy point), and $\mathbf{S}_{\mathrm{kn}}$ the XES spectra (n is the energy point). This approach would allow for the observation of the fine XES structure using SASE pulses.

In this work, we have applied the above mentioned reconstruction strategy using a synthetic data-set, in a realistic simulation of a real XFEL experiment. In particular, we have shown that a successful reconstruction of the inelastic fine structure using trains of SASE pulses can be achieved by a suitable choice of relevant parameters, like the noise intensity, number of photons, energy grid, number of pulses.

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[6] W. Błachucki et al., *Applied Sciences*, 2021, **11**, 8775.

P4. Structural investigation of Deep Eutectic Solvents: far and medium infrared synchrotron characterization

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In the last years many systems were proposed as alternative to traditional solvents. The idea behind this compelling research field is to improve the eco-compatibility of traditional solvents and their solvents properties. Many systems were proposed: Deep Eutectic Solvents (DESs) are among the most recent[1]. These eutectic mixtures are in general composed by two or more natural and low-toxic organic and inorganic compounds. The primary concept behind these systems is to achieve a stable liquid phase by starting with two or more solid molecules. The significant decrease in melting point observed in DESs can primarily attributed to the formation of strong secondary interactions among the components, particularly hydrogen bonding[2]. To accurately predict and model the macroscopic behavior of these systems such as the possible technological application, it is essential to have a deep understanding of the microscopic coordination among their components.

With the aim to investigate the molecular mechanisms regulating the formation of DESs we studied several binary mixtures composed by Choline Acetate (ChAc) and three different natural acids, namely Ascorbic (AA), Citric (CA) and Maleic (MA). All acids act as hydrogen bond donors (HBD), with varying degrees of acidity depending on their substituents. The three studied molecules differ not only in their chemical structure but also in the number and type of acidic groups, which play a critical role in determining the strength of the hydrogen bonds formed in the liquid phase.

The starting materials and their mixtures were studied by infrared spectroscopy at AILES beamtime of SOLEIL Synchrotron in Paris as a function of temperature in a wide frequency range covering both the far and mid-infrared range (FIR and MIR, respectively). The obtained spectra were interpreted performing density functional theory calculations and classic molecular dynamics simulations. All techniques show the presence of an intense H-bond network between the components of the mixtures. In the FIR spectra (30-600 cm^{-1}), especially at low temperatures, we observed the bending and stretching of H-bonds and we obtained information about the different conformers distribution. In the MIR spectra we observed the coordination between the components: the bands of $\nu_{C=O}$ and ν_{OH} are progressively shifted when the ratio of acids changes, sign that the interactions occur between OH and C=O groups. As expected the acids predominantly exploit their more acidic hydrogens; this result was confirmed by the analysis of MD trajectories.

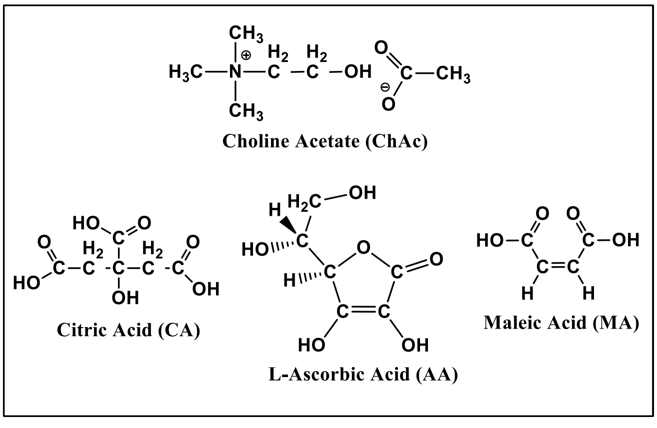

Figure 1. Chemical structure of the components

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P5. Complex phase behaviour of amorphous selenium under pressure

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Studies on the pressure induced structural and electronic transition in amorphous Se have provided controversial results, making it difficult to clearly understand the high-pressure properties of this simple elemental amorphous substance. The possible differences in the initial amorphous samples were considered to be one of main reasons for the controversial findings from different experimental studies. In this work, pressure behavior of same amorphous Selenium (a-Se) samples has been systematically investigated under different hydrostatic conditions using complementary x-ray absorption spectroscopy (XAS) and x-ray diffraction (XRD) techniques. Results have shown that the nucleation processes in a-Se samples and the subsequent transitions in the crystalline phase can be significantly different depending on the experimental conditions, providing a different prospective for explaining the controversies on the subject in the existing literature. In addition, detailed quantitative information concerning the pressure induced evolution of local structural parameters in the amorphous phase have been achieved through standard EXAFS refinement procedures. Complementary information concerning the evaluations of the vibrational modes and changes in the intermediate range ordering were also obtained through the analysis of XANES and far infrared (IR) spectroscopy data. Precise local structural information that can be used for more accurate refinements of the crystalline phases have been also obtained by analyzing the EXAFS at higher pressures.

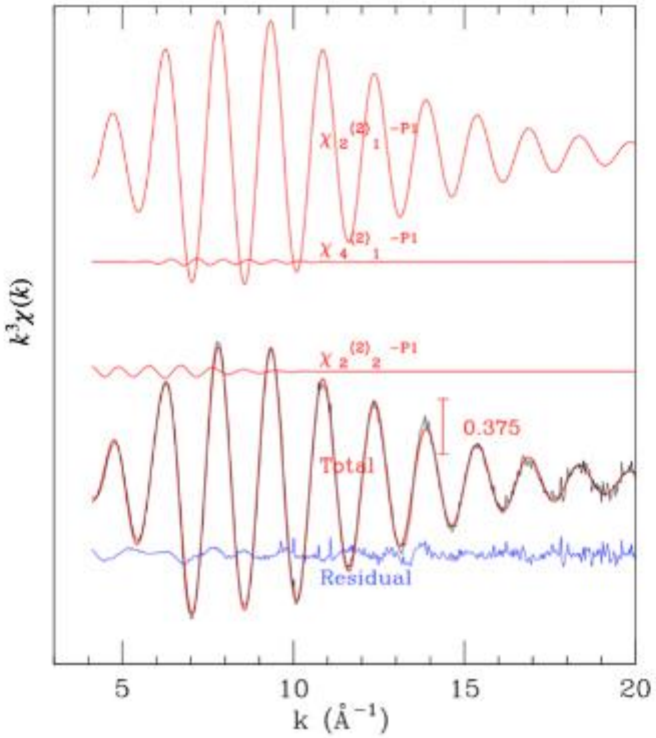

Figure 1. An exemplary EXAFS refinement for the structure a-Se.

P6. Bifunctionalized silver nanoparticles for detection of Fe(III) ions in water

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In the recent years, nano-systems such as silver nanoparticles (AgNPs) have attracted attention due to their unique physical and chemical properties and therefore they are widely studied in many fields of research. In particular, AgNPs, thanks to their high surface reactivity, tunable size, and high degree of functionalization [1], have received increasing interest in the areas of sensing nano-systems and water remediation treatments[2]. In this framework, with the aim of producing nanoparticles potentially applicable as Fe(III) detection system, we synthetized AgNPs functionalized with L-glutathione and citrate, and analyzed their electronic and molecular structure, as well as their morphology, in the presence of iron ions (Fig. 1-2). The characteristic structure at the interface between ligands and AgNPs was probed by Synchrotron Radiation-induced X-ray Photoelectron Spectroscopy (SR-XPS) and the sensitivity to the presence of iron (III) ions was assessed in water by UV-visible absorption spectroscopy.

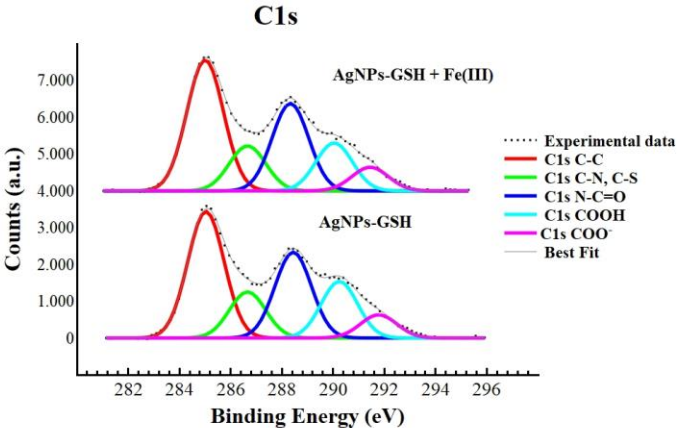

Figure 1: XPS spectra collected on AgNPs-GSH and AgNPs-GSH + Fe(III) at C1s core level.

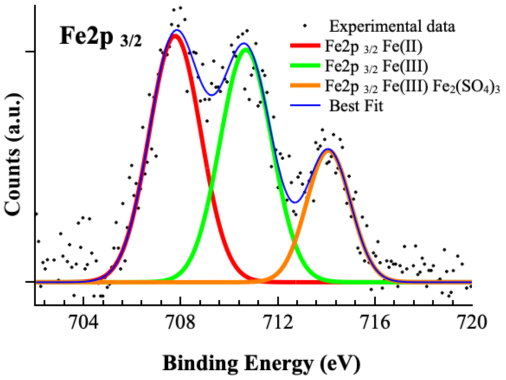

Figure 2: SR-XPS spectrum collected on AgNPs-GSH + Fe(III) at Fe2p core level (high-resolution acquisition of the Fe2p 3/2 spin-orbit component).

[1] B. Jamil Ahmed, S. Amin, I. H. Syed, I. B. Muhammad and R. S. Amber, *Environ. Sci. Pollut. Res. Int.*, 2021, **28,** 58994–59002.

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P7. Time-resolved Raman spectroscopy on bulk and monolayer MoS_2

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MoS_2 belongs to the class of graphene-like, layered materials called transition metal dichalcogenides (TMDs). Semiconducting TMDs, like MoS_2, show an indirect to direct band gap transition when the system is exfoliated down to the monolayer structure. This characteristic makes them promising materials for future applications in optoelectronics and related fields [1]. For this reason, unravelling the relaxation pathways of photoexcited electrons in such systems is of great applicative interest. Remarkably, the structural and dimensional tunability of their electronic properties makes TMDs benchmark systems to study the interplay between electronic and vibrational degrees of freedom.

Time-resolved Raman spectroscopy (TRRS) can provide direct access to the incoherent phonon relaxation, as well as the electron-phonon coupling dynamics [2]. The aim of our experiment is to study the deexcitation dynamics of MoS_2 after the impulsive optical excitation in resonance with its excitonic bandgap. To do so, at the SPRINT-NFFA facility, we have carried out a time resolved Raman spectroscopy study on the system. We monitored the temporal evolution of two specific Raman active features, namely the out-of-plane A_{1g} mode and the in-plane E^1_{2g} mode, after the photoexcitation. Indeed, equilibrium spectroscopy studies have linked the modification of such phonon lineshapes to doping effects, suggesting the possibility to study the optically induced, transient doping of the system [3,4,5].

In detail, the red, short (< 300 fs) pulses produced by an OPA system at 633 nm (~1.96 eV) were used to pump the system in resonance with the excitonic bandgap at the K point of the Brillouin zone. At variable delay, green (513 nm) laser pulses of ~1 ps duration were used as a probe to collect the transient Raman spectra with sufficient spectral resolution (~15 cm^{-1}) to monitor not only the evolution of the phonon population, extracted by the antiStokes/Stokes intensity ratio, but also the transient modifications induced on the phonon lineshapes. To explore the effect of the indirect to direct bandgap transition on the system relaxation dynamics, the experiment was performed on both bulk and monolayer MoS_2.

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P8. Time-resolved optical and Raman spectroscopy under UHV conditions: a novel apparatus for pump-probe multi-messenger investigations

A. M. Finardi[1,2], C. Fasolato[3,4], A. Giugni[1,2], R. Cucini[2], A. Fondacaro[2], G. Panaccione[2], F. Sacchetti[4], P. Postorino[5], C. Petrillo[4] and G. Rossi[1,2]

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Over the last decades, the possibility to generate and manipulate ultrashort light pulses allowed photon and electron spectroscopies to access the time domain in the consolidated pump-probe scheme. Measuring the dynamic response of materials after impulsive photoexcitation, these techniques have been proven effective in disentangling phenomena with different time-scale evolution in various systems and have opened new perspectives for light-induced phase transformations. In this framework, the adoption of a “multimessenger” spectroscopic approach, characterized by the detection of scattered photons, photoemitted electrons and electron-spins as messengers of energy, momentum, and spin of the out-of-equilibrium states of a selected material can set more stringent limits of interpretation than a single technique [1].

At the SPRINT-NFFA facility, we developed a time-resolved Raman and optical spectrometer for pump-probe experiments with sub-ps time resolution on samples spanning the 8-350 K range under UHV conditions. The laser system, comprising multiple-OPA and a table-top HHG source, can deliver, in a two/three-pulse scheme, ultrashort (200 fs for the OPA, 100-150 fs for the HHG) IR-to-XUV pump pulses and visible sub-ps probe pulses for Raman and optical measurements [2]. The reflected/scattered signal is collected at variable angles. Two CW lasers at 532 nm and 785 nm allow to perform equilibrium measurements for reference. The UHV chamber is coupled, via UHV-suitcase, with the angle- and spin-resolved photoelectron spectroscopy setups already operative at the facility [3].

We will present the experimental setup layout and the first time-resolved Raman measurements performed on Si and on MoS2, a prototypical member of the layered family of transition metal dichalcogenides (TMDs) and an ideal platform to fully exploit the multimessenger approach to investigate the complex interplay between electronic, phononic and spin degrees of freedom.

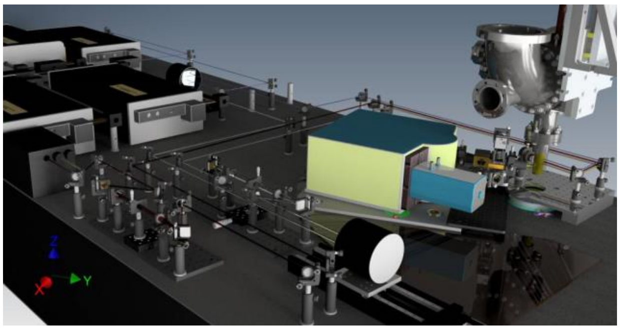

Figure 1. CAD representation of the current experimental setup for time-resolved optical and Raman spectroscopy.

[1] JA. Yang, S. Parham, D. Dessau et al., *Sci. Rep.*, 2017, **7**, 40876
[2] R. Cucini, T. Pincelli, G. Panaccione et al., *Struct. Dyn.*, 2020, **7**, 1, 014303
[3] https://www.trieste.nffa.eu/techniques/spectroscopy/

P9. Photoexcited carriers at $MAPbBr_3$-$SrTiO_3$ interface studied by grazing angle Infrared spectroscopy

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In the past years Hybrid Perovskites (HP) have been considered as one of the most promising photoactive materials for the realization of low-cost, high-performance photovoltaic devices [1]. The interest in these compounds lies in their extraordinary optoelectronic properties, deriving primarily from their organic-inorganic nature. The slow thermalization time of charge carriers of HP allowed us to perform an experimental investigation exploiting joint IR and visible continuous wave radiation to study a photoexcited carrier gas at the interface of thin films of $MAPbBr_3$ deposited on $SrTiO_3$ (STO) substrates. In this experiment, carried out at the AILES beamline of SOLEIL synchrotron, we propose an all-optical method based on grazing angle IR spectroscopy to infer accurate information on the electrodynamics of the photogenerated carrier population at the HP-STO interface as a function of film thickness and temperature. As expected from Berreman theory [2], the presence of a thin layer of carriers induces a blueshift of the LO phonon of STO that can be detected by collecting the IR spectra in both p and s polarization. We analysed our results in terms of the ellipsometric angle $\Psi = \tan^{-1}\sqrt{R_p/R_s}$ (being R_p and R_s the STO reflectivity in p and s polarization respectively) and observed the variation of this quantity when the charge density at the HP-STO interface is generated. The temperature evolution of the dip-like feature in the $\Delta\Psi$ profile provided by the blueshift of the LO phonons (see Fig.1), shows that both dip depth and position slightly change during the temperature route, with the most noticeable changes between 150 and 250 K, possibly ascribed to the low temperature phase transitions of $MAPbBr_3$ from tetragonal to orthorhombic. Additionally, the $\Delta\Psi$ profile was fitted to obtain the electrodynamic parameters of the 2-dimentional charge population (carrier density and mobility). The outcome of this work provided us with a precise, non-invasive measurement of the charge carriers electrodynamic properties at the HP-STO interface, giving us interesting results to be used as a basis to improve of HP-based photovoltaic devices performances.

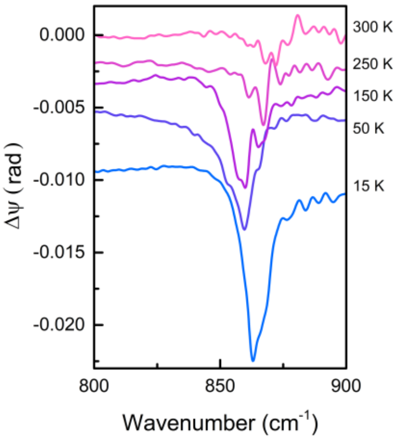

Figure 1. Difference in the ellipsometric angle between the photoexcited and unperturbed states ($\Delta\Psi = \Psi_{Phex} - \Psi_0$) on a 100 nm thick $MAPbBr_3$ film deposited on $SrTiO_3$ at different temperatures.

[1] J. Y. Kim et al., Chem. Rev. 2020, **120**, 7867-7918.
[2] D.W. Berreman, Phys. Rev., 1963, **130**, 2193.

P10. Charge Dynamics properties of Tripyrenboroxine on metal surfaces

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I present the synthesis of trimers of Pyrene-1-Boronic Acid (PBA) on top of the Au (111) surface, and their characterization by means of XPS, UPS, NEXAFS and RESPES spectroscopy and STM microscopy.
The creation of organic-based electronic devices is an important and extensively studied application for organic molecules, with a particular interest in their interaction with metal and inorganic semiconductors. Specifically, molecules based on extended aromatic structures are interesting in a range of optoelectronic applications because of the capability of their π core to absorb Near-UV and visible light.
In my research, I studied trimers of pyrene-1-boronic acid, a pyrene that presents a $B(OH)_2$ substituent. These trimers result from a self-condensation reaction where three boronic acid groups react to form a six-member ring structure constituted of alternating B and O atoms. This trimeric derivative was chosen because presents higher stability on the Au(111) and other metal surfaces compared to the monomer. Furthermore, previous studies have demonstrated that the central B_3O_3 ring, known as boroxine ring, presents ultra-fast delocalization channels towards the Au(111) surface [1], resulting in possible applications of these molecules in the creation of electron transporting films. The molecule was treated thermically in a quartz crucible, up until 290 °C, to allow the condensation reaction directly in the crucible, and the so-created try-pyrenboroxine (TPyB) were evaporated on top of the Au(111) surface in UHV conditions. The resulting material was then analyzed using XPS, UPS and NEXAFS, and RESPES spectroscopy, pump-probe spectroscopy and STM microscopy. The XPS demonstrated that B, O and Carbon where present on the surface, and showed a B:O ratio of around 1:1, compatible with the formation of boroxine rings. The B1s NEXAFS analysis revealed three main π components, that is in agreement with the DFT calculation for boron involved in boroxine rings. The STM imaging showed that the trimers are organized into a ordered, platelet-like structure, on top of the Au(111) structure. The Pump-Probe measurements showed a laser-induced shift of the C1s Peak [Fig 1], attributable to space charge effects. Given the established p-type semiconductor behavior of pyrene [2], we suggest that this effect is attributable to hole-transport capabilities of the film.
The RESPES measurements allowed for a chemical assignment of the electronic states of the valence band. Interestingly, the analysis of the resonant Auger signal reveals the presence of super-Participator decay process, which is related to an electronic coupling with the substrate, in terms of dynamic charge transfer from it [Fig 1].

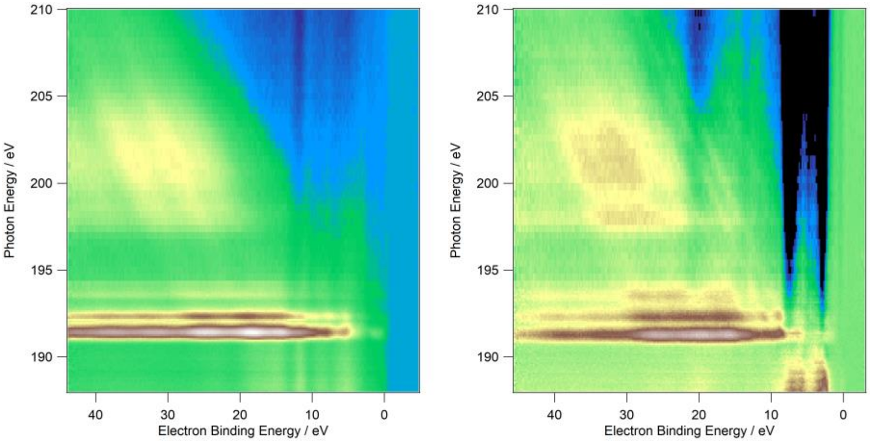

Figure 1. Comparison between the Resonant photoemission Plot at the B1s edge of a Monolayer (left) and a multilayer(right) of Tripyreneboroxine. The striped states evidenced in the multilayer show indications of a

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P11. Effects of the confined space on the synthesis of non-doped and Eu^{3+}-doped calcium molybdate nanophosphors

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In recent years, many efforts have been devoted to pursue inorganic nanomaterials with controlled size, shape and crystalline phase, features which all play a relevant role in determining the final functional properties [1]. In this regard, the synthesis of inorganic nanostructures within the constrained environment of *nanoreactors* [2,3] has been demonstrated to be a challenging and effective route to control these features [1], as it is known that confined space (*i.e.*, enclosed nanoscaled volume with limited accessibility) might allow non-conventional crystallisation pathways and finely control on reaction outcomes [2].

In this work, the restricted environment of independent water-in-oil nanodroplets (size range of 50-300 nm) in inverse miniemulsion was employed as a *nanoreactor* to synthesise inorganic nanostructures with controlled size and shape [3]. To investigate how the confined space affects the final features of the synthesised nanoparticles, the synthesis of a functional model system, calcium molybdate, both non-doped and Eu^{3+}-doped, was addressed. In particular, Eu^{3+}-doped calcium molybdate $CaMoO_4$ [4,5] is an interesting promising material for the development of new phosphors for optics and solid-state lighting [6] due to its intrinsic photoluminescence properties, its chemical and thermal stability.

The target inorganic system, both non-doped and Eu^{3+}-doped with different Eu amount (Eu:Mo = 1, 3, 5, 7 at%), was synthesised via inverse miniemulsion and, for comparison, via a simple precipitation bulk synthesis (without spatial confinement). By a systematic comparison of the results obtained from the inverse miniemulsion method with the bulk synthesis, it was possible to demonstrate the remarkable effect of the spatial confinement of the reaction environments on the final features of the inorganic material. In particular, significant effects ascribable to the confined space were found *i*) in a successful control of the size and shape of the nanoparticles, leading to a narrow size distribution and regular spherical shape of the nanoparticles (via XRD and TEM), *ii*) in the doping effectiveness (via XRD, XAS at Eu L3-edge and Mo K-edge), and *iii*) in the photoluminescence properties (via photoluminescence studies). Indeed, a homogeneous distribution of the Eu^{3+} ions into the host matrix was evidenced for the miniemulsion samples, leading to more promising photoluminescence properties. Therefore, these results enabled us to highlight how the space confinement provided by inverse miniemulsion nanodroplets allows a step forward towards the excellent control of the outcome of the synthesis of inorganic materials.

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P12. High pressure intrusion of ternary aqueous solution in pure silica chabazite: structural investigation)

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Nowadays, an efficient energy transformation and storage is one of the main technological challenges of the world. Heterogeneous lyophobic systems (HLS), *i.e.* systems composed by a nanoporous solid and a nonwetting liquid, have attracted much attention as promising candidates for innovative mechanical energy storage and dissipation devices [1,2]. In these systems, mechanical energy (*i.e.* an external pressure) is required to force the intrusion of a non-wetting liquid into the pores of material. The penetration of the liquid inside the pores strongly increases the liquid-solid interface area leading to a conversion of mechanical energy into the breaking of intermolecular bonds of the liquid and the interactions at liquid-solid interface. In the case of microporous materials, during the intrusion, the bulk liquid is transformed to molecular chains and clusters inside the pores. When the external pressure is released, the liquid can be extruded, completely or partially, or can remain trapped into the solid. Therefore, the whole or a part of the initial energy is restored, or it is entirely absorbed. Consequently, the system can display a *spring* or *shock absorber* or *bumper* behaviour or a combination of them. Heterogeneous lyophobic systems with shock-absorber and bumper behavior can be used or integrated in devices aiming to dissipate mechanical energy, for example, for new types of dampers for automotive and aerospace industry [2-5] while those with spring behavior are promising for applications in mechanical energy storage.

In this work a new Heterogenous Lyophobic System based on a pure silica chabazite and a double salt electrolyte solution ($KCl+CaCl_2$) is studied from porosimetric and crystallographic point of view. The combined approach of this study is fundamental to unravel the properties of the system, in fact thanks to porosimetric experiments it has been possible to determine the energetic behavior, while crystallographic analyses will help in the understanding of the mechanism of intrusion involved and ruling the phenomenon. To gain information on the system, *in situ* high pressure synchrotron radiation Diffraction experiments (HP-XRPD) were performed in diamond anvil cell (DAC) at XPRESS beamline at Elettra Sincrotrone Trieste using as pressure transmission media the solution of interest.

The results are compared with those obtained for the systems involving the same zeolite but intruded with solution containing only single salts ($CaCl_2$ or KCl). Porosimetric results of the three Si-CHA systems intruded by simple and complex electrolyte solutions (KCl 2M, $CaCl_2$ 2M and the mixture KCl 1M + $CaCl_2$ 1M) suggest that the intrusion pressure is mainly influenced by the nature of the cations. Indeed, $CaCl_2$ 2M shows the highest intrusion pressure, KCl 2M the lowest one whereas the mixture KCl 1M + $CaCl_2$ 1M is almost in the middle. These differences are probably related to the higher hydration enthalpy and Gibbs energy of Ca^{2+} compared to the one of K^+ ($\Delta H = -1515$ kJ mol^{-1}, $\Delta G = -1505$ kJ mol^{-1} and $\Delta H = -305$ kJ mol^{-1}, $\Delta G = -295$ kJ mol^{-1}, respectively). In fact it has been demonstrated that a partial ion desolvation is needed to promote the penetration of the species and a higher solvation energy requires higher pressure. The "intermediate value" of the intrusion pressure, shown by the complex electrolyte solution, arises from the fact that, statistically, the second/third solvation cation shells can be assumed to be partially shared between K^+ and Ca^{2+}. The stronger interaction of Ca^{2+} with H_2O molecules influences thus also the desolvation of K^+ increasing the pressure needed to activate the process compared to the one of the pure KCl 2M solution. This is confirmed by structural investigation, which shows that at the beginning of intrusion only K^+, Cl^- and H_2O penetrates the pores, whereas the intrusion of also Ca^{2+} required higher pressure in agreement with the hydration enthalpies of the two cations.

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P13. The LISA beamline at ESRF: present status

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The LISA beamline is operative on a bending magnet source of the new ESRF-EBS storage ring. It is presently open to users through the open access programs provided by ESRF and CERIC.
In this poster we will present the latest user statistics, updates and technical developments of the beamline. In particular, we will show the LISA capability of dealing with small sized samples with an example on rare earth dopants in the core of optic fibres. Moreover, the new data collection and storage policy that follows the FAIR prescriptions will be presented as well as the new software for the collection of data in pump-and-probe mode [1]. The new data pre-treatment code and a renewed version of the beamline user manual will also be shown. As a perspective, we will introduce the new BLISS beamline control environment that has become the new standard for ESRF and that will be soon implemented at the beamline.

Acknowledgements: The experiment on the optic fibres was carried out in collaboration with W. Blanc from Nice University.

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P14. X-ray absorption spectroscopy allows the detection of general Bromine oscillatory behaviour in the Belousov-Zhabotinskii reaction

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The Belousov-Zhabotinskii (BZ) reaction [1,2] involving the cerium ion catalyzed oxidation and bromination of malonic acid (MA) by bromate is the most extensively studied oscillating chemical reaction and continues to fascinate chemists to this day. A wide variety of chemical processes proceed in fact in a cyclic fashion exhibiting concentration periodic changes. Since the elucidation of the main mechanistic features of the BZ reaction by Field, Körös and Noyes (FKN) in 1972 [3] whose work laid the foundation to understand the temporal and spatial phenomena present in numerous BZ reagents, experimental and theoretical efforts have been devoted to investigate the BZ reaction mechanistic details, e.g. those regarding the reaction destabilizing, negative feedback processes. A revised semiquantitative model of the BZ reaction based on 80 elementary reactions and 20 concentration variables was proposed by György, Turányi and Field [4], and reaction pathways are still being added upon collection of additional experimental evidence.

Nonetheless, it appears clear that when tackling a chemical mechanism of this size with many variable parameters the availability of experimental techniques that may accurately track the oscillating concentration time evolution of the key reaction intermediate species is of paramount importance. Herein, we tackle the previously unaddressed issue of gaining comprehensive real time spectroscopic insights into the speciation of the Br reactants during the BZ oscillatory reaction by resorting to X-ray absorption spectroscopy (XAS). XAS is advanced spectroscopic tool that stands out among the laboratory-based techniques routinely used to investigate reaction mechanisms. XAS may be in fact employed to investigate all periodic table elements, it is an element-specific probe due to core electron excitation and is frequently used to determine oxidation states since the energy shifts of the K (1s) edge often correlate well with the ionization energy of the core orbital. Notably, a multivariate statistical analysis of the XAS data may further complement the information acquired on the chemistry of the given reactive system.

In this presentation, we will provide new insights into the behaviour of the Br–related species of the cerium ion catalyzed BZ reaction and show that periodic oscillations not only occur in the concentrations of Br^-, $HBrO_2$, HOBr and Br_2, but also in those of the main reactants BrO_3^- and bromomalonate. Specifically, we measure detectable oscillations in the concentrations of BrO_3^- and bromomalonate by monitoring the BZ reaction through Br K-edge XAS. Further, by coupling XAS with UV-Vis spectroscopy, we simultaneously track the oscillatory time evolution of the Ce and main Br reactants. Multivariate Curve Resolution (MCR) and kinetic analyses are used to interpret the observed oscillatory patterns. Our work evidences collective oscillations in the BZ system and extends the use of X-ray spectroscopy to investigate the mechanisms of oscillatory chemical systems whose key species are often silent to conventional methods of detection.

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P15. X-ray absorption spectroscopy probes Ca^{2+} electrochemical intercalation in anatase nanotubes

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The need for a rapid development of energy storage devices with excellent performance, eco-compatibility, safety, and scalability, has become in recent years a key point for reaching eco-sustainability and preserving the environment's health [1]. The main storage devices used nowadays are lead-acid and lithium ion-based intercalation batteries (LIBs), which, until now, have played a pivotal role in devices powered by electricity but also for long-term energy storage. However, the low crustal abundance of lithium (and of cobalt, a secondary ingredient of LIBs) made it necessary to study the development of new batteries based on the intercalation of other ions. In this way, interest in new elements and chemistries has grown rapidly in both academia and industry and is now a major player in the transition to new environmentally friendly and sustainable energy sources.

Calcium, due to its physical-chemical characteristics and crustal abundance, is an optimal solution for the formation of these alternative devices, offering a more economic, safer, and environmentally sustainable alternative to the lithium technology [1]. However, even though the working principles are very similar, the know-how gained during the many years of employment of the LIBs technology is not always transferable to these new batteries. The current research in Ca-ion batteries (CIBs) must therefore deal with the identification of reliable and efficient electrode materials and electrolyte formulations. In this context, titanium oxide (TiO_2) is a fascinating material with a variety of practical applications ranging from dyes to advanced technologies. Large part of this success is due to the possible fine tuning of the morphology of TiO_2 nanostructures using mild chemical routes. In this way, a large variety of materials can be obtained with different shapes, and TiO_2 has been also demonstrated as a promising negative electrode material due to this structural and morphological flexibility.

In this contribution, we tackle the study of the Ca^{2+} intercalation in a negative electrode based on TiO_2. X-ray absorption spectroscopy (XAS) measurements have been performed on anatase nanotubes after full electrochemical intercalation of Ca^{2+} ions to probe the intercalation process and the structural modifications induced in the anodic material. To this purpose, the capability of the XAS technique to simultaneously obtain information on different absorbing elements has been exploited by performing measurements at both the Ca and Ti K-edge energies. As a result, the intercalation process is observed to induce a serious loss of crystallinity around the titanium centers in the TiO_2 lattice with respect to the pristine material. A quantitative determination of the local structure around the photoabsorber has been obtained with the analysis of the extended X-ray absorption fine structure (EXAFS) spectra and testifies that a highly disordered environment is found also around the intercalated Ca^{2+} centers [2]. The data analysis performed on the fully discharged state provided similar structural results, strongly suggesting that the Ca^{2+} ions preserve a similar environment in the TiO_2 matrix even after the attempted de-intercalation process.

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P16. Qualitative and quantitative assessment of Cu-MOFs redox properties through in situ XAS analysis

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The possibility to convert light hydrocarbons into value-added chemicals (e.g. direct methane to methanol, DMTM) by means of direct C-H activation would have an enormous industrial and environmental impact[1]. Nature masters the DMTM conversion at ambient conditions, using methane monooxygenases (MMO) enzymes; among them, pMMO relies on a Cu active site[2]. Recently, extensive research efforts were dedicated to the investigation of pMMO-inspired Cu-based catalysts to enable DMTM conversion under industrially viable conditions. Although a number of materials and techniques have been explored for these purposes, Cu-MOFs represent promising candidates because of their stability compared to enzymatic systems, together with the possibility to tunable the active center[3].

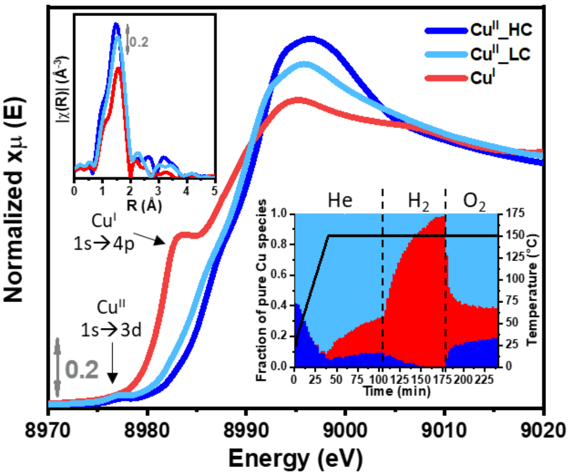

Figure 6. summary of Cu-UiO-67-bipy MCR reconstruction, including XANES and EXAFS spectra and concentration profile of pure Cu species.

Cu-MOF samples potentially active towards DMTM were synthetized, tested and characterized at beamline BM23 of the ESRF synchrotron by in situ X-ray absorption spectroscopy (XAS). The experimental protocol consisted of an activation step in He until 150°C, followed by an isothermal reduction in H_2 and re-oxidation in O_2. The investigated samples belong to UiO-67 family, in which the diphenyl ligands are partially (10%) replaced by thoughtfully modified bipyridine ones (i.e. having methyl moieties in 6-6' positions), as anchoring sites for Cu ions[4]. Besides basic XAS data treatment, Multivariate Curve Resolution and Wavelet Transform EXAFS advanced analysis methods are applied, allowing a deeper interpretation of the experimental data in complex multi-component cases. The Cu-UiO-67 sample showed interesting redox properties passing from inert to reducing/oxidizing environment. The MCR analysis allowed the for the distinction of three pure Cu species, identified by the typical XANES fingerprints (**Figure 6**). Cu^{II} species differ in the white-line intensity, suggesting differences in the Cu-site coordination number. In inert conditions, these species are present simultaneously with different fractions in the as-prepared material. Modifying the gas feed from inert to H_2 at 150°C, a virtually complete $Cu^{II} \rightarrow Cu^{I}$ reduction is verified, while the initial Cu^{II} species are restored in O_2.

Acknowledgments: this work is financially supported by the European Research Council, under the Horizon 2020 research and innovation program: CuBE ERC-Synergy project (G.A. n° 856446).

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P17. Exploring the potential of theoretical XANES calculations in the analysis of phosphorus speciation

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Phosphorus K-edge X-ray absorption spectroscopy (XANES) is a routine tool for the analysis of phosphorus speciation in an increasing number of scientific fields, including solution chemistry [1], catalysis, wastewater treatment, the characterization of exhaust particulates [2], and environmental sciences. In particular, the technique has been employed widely in the latter discipline, due to the technique's structural sensitivity and its capability of identifying different phosphorus minerals in a mixture while preserving the analyzed sample [3]. However, most reported studies rely on simple linear combination fitting (LCF) or principal component analysis (PCA) approaches for the quantitative analysis of P K-edge XANES data. These protocols are however highly prone to systematic errors and require extensive validation to be carried out properly [4]. Moreover, the detection and quantification of compounds not included in the reference database is cumbersome. Conversely, theoretical P K-edge calculations only require a structural model of the investigated compound to be carried out. However, even though the necessary theoretical background and software resources for the rigorous calculation of XANES spectra are currently available, these have been seldom applied to the analysis of phosphorus speciation and an extremely number of theoretical P K-edge spectra has been reported [5].

Here, we present an in-depth theoretical analysis of the P K-edge XANES spectra of four phosphorus minerals including some that are commonly employed as standards in the analysis of soils, namely $NaH_2PO_4{\cdot}H_2O$, $AlPO_4$, α-$Ti(HPO_4){\cdot}_2H_2O$ and $FePO_4{\cdot}2H_2O$. We identify and separate the structural and electronic contributions that shape the X-ray absorption signal, providing an interpretation of the spectral features in the higher energy region of the spectra, which are associated with different coordination shells of the photoabsorber phosphorus atom. In addition, we provide an interpretation of the observed pre-edge transitions by means of density of states (DOS) calculations. Finally, we show how the exceptional structural sensitivity of P K-edge XANES allows this technique to even distinguish between isostructural phases of the same compound that present the same chemical connectivity but crystallize in different space groups (see Figure 1).

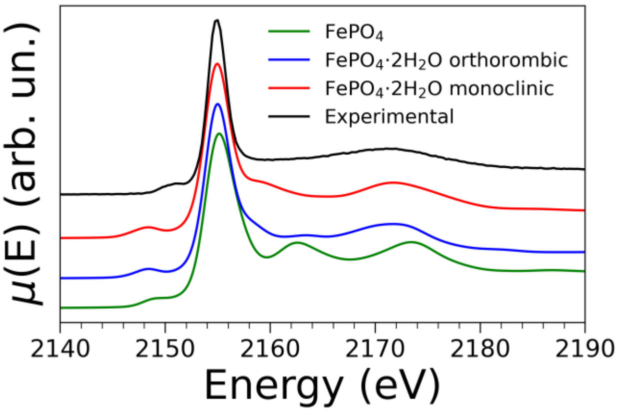

Figure 1. Comparison between the experimental P K-edge XANES spectrum of $FePO_4{\cdot}2H_2O$ and the theoretical spectra of orthorhombic $FePO_4{\cdot}2H_2O$, monoclinic $FePO_4{\cdot}2H_2O$ and $FePO_4$.

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P18. Nanoscopic Segregation in Deep Eutectic Solvents with Different Hydrophobicity upon Cosolvent Addition

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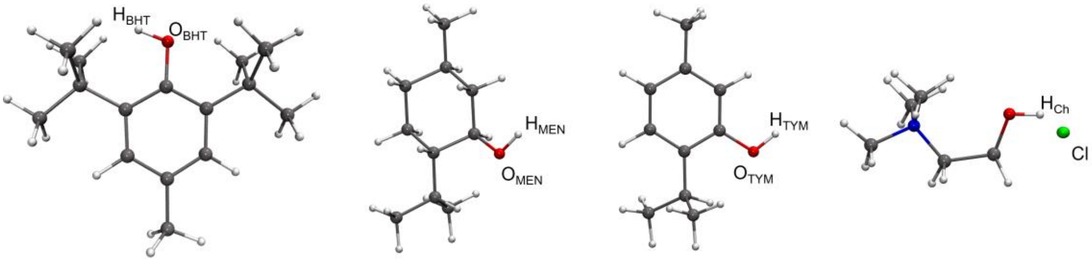
Deep eutectic solvents (DESs) are a class of solvents usually composed by a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). DESs components melt upon contact at a precise molar ratio and produce a mixture with a melting point (MP) that is lower than those of the pure constituents. In the recent years they gained a lot of interest as a consequence of their physical chemical properties such as negligible volatility, high conductivity, non-flammability, high solvating capability and low toxicity and for this reason are ideally suited for different applications including the extraction of pesticides, fat-soluble micro-nutrients and metal species [1]. DESs are also known to be designer solvents and therefore it is possible to obtain a solvent with specific chemical-physical requirements by tailoring the components or by adding the right cosolvent. Moreover, cosolvents are frequently used in extraction processes to act as dispersing agents and for this reason it is essential to understand how they affects DESs structure [2].
Here, we present a study on the changes upon the addition of an apolar solvent on systems with different hydrophobicity using small- and wide-angle X-ray scattering (SWAXS) integrated with molecular dynamics (MD) simulations. Mixtures of butylated hydroxytoluene (BHT) and L-menthol (MEN), thymol (TYM) and MEN, and choline chloride (ChCl) and TYM with n-hexane at 1:3:H, 1:2:H and 1:7:H molar ratios, with H between 1 and 26, were studied in order to detect the formation of segregations. The structure of the studied systems and the used nomenclature are reported in Figure 1.



Butylated hydroxytoluene (**BHT**) L-Menthol (**MEN**) Thymol (**TYM**) Choline Chloride (**ChCl**)

Figure 7. Butylated hydroxytoluene (BHT), L-menthol (MEN), thymol (TYM) and choline chloride (ChCl) molecular structures showing the employed nomenclature for the studied atoms.

No inhomogeneities were found in the BHT:MEN:HEX 1:3:H and TYM:MEN:HEX 1:2:H systems, even at high HEX concentration. On the contrary, from the SWAXS spectra analysis was observed that the addition of HEX led to the formation of inhomogeneities in the ChCl:TYM:HEX 1:7:12 and 1:7:26 systems. MD simulations confirm this result and demonstrate how these segregations are the consequence of the interaction between Ch molecules, which preferably interact with themselves forming increasingly larger segregations when cosolvent is added.

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P19. NOTOS and CLAESS beamlines: complementarities and synergies

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NOTOS and CLAESS are two beamlines in the portfolio of Alba dedicated to Hard X rays spectroscopy. NOTOS beamline at the ALBA synchrotron light source is a beamline devoted to X-ray Absorption Spectroscopy (XAS), X-Ray Diffraction (XRD), and metrology applications. Its energy range is 5-30keV and uses a Bending magnet as photon source. In addition to the capability to perform XAS and XRD investigations separately, the beamline will allow quasi simultaneous XAS-XRD experiments. NOTOS has been designed to study the electronic structure, short- and long-range order by XAS and XRD for wide range of scientific disciplines: chemistry, catalysis, energy science, nanomaterials and condensed matter, environmental science. In addition to typical applications mentioned above, it will be focused on in situ and *operando* measurements on heterogeneous catalysis and electrochemistry.

On the other side CLÆSS provides a simultaneous and unified access to two complementary techniques: XAS and emission (XES) spectroscopes. It is equipped with a fast monochromator and uses a wiggler as photon source. The incoming energy range is 2.4 – 63.2 keV. The outcoming energy range selectable by CLEAR spectrometer is 6.4 - 12.5 keV. CLÆSS is a general-purpose beamline, which aims to cover specific needs of several scientific disciplines such as chemistry, catalysis, energy science, nanomaterials, condensed matter and environmental science for the study of the electronic structure (both occupied and not occupied) and local environment of a specific absorber/emitter.

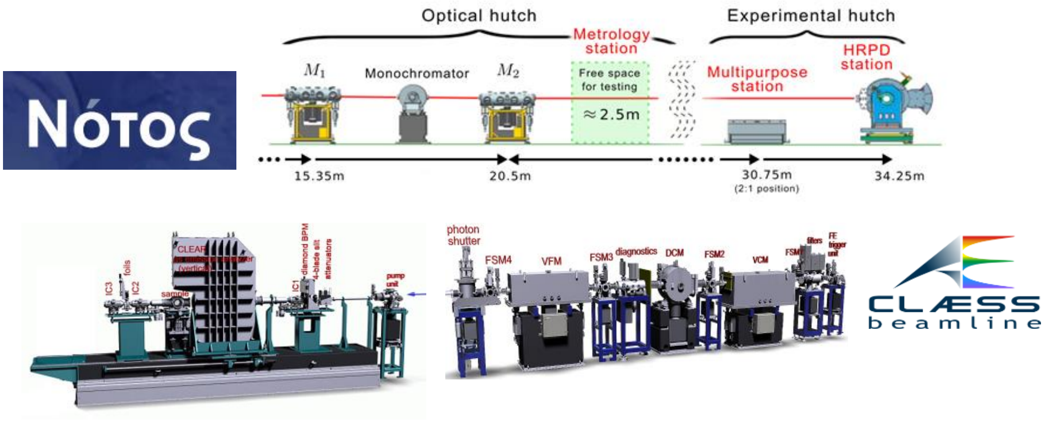

Figure 1. Optical scheme of the two beamlines.

P20. Realtime analysis of electrochemical reactions in batteries: the OpMetBat project

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The development of new battery materials is key to improving the performance, lifetime, safety and cost of energy storage technologies like Li-ion batteries for electric vehicles. However, innovation is hampered by the inability of industry to reliably characterize their structure and chemistry in an operating environment. The OpMetBat project will build a metrological framework supporting traceable operando characterization of state-of-the-art battery materials under dynamic charge / discharge conditions. This includes advancement and validation of ex situ methods, establishing new protocols, cells and a best practice guide for operando approaches and developing new instrumentation enabling hybrid, multiparameter measurement to inform new materials development.

The project aims to develop operando techniques and hybrid (multi-modal) instrumentation, supported by quantitative and validated ex situ analysis and electrochemical measurements methods, to enable beyond state-of-the-art materials characterization for high-capacity energy storage technologies.

The good practice guide developed within this project will benefit the scientific community by improving reliability, repeatability/reproducibility and fidelity of operando measurements. The project will pioneer operando metrology for battery research at several European synchrotron radiation facilities and the transfer into laboratories to support industry and researchers.

Acknowledgements: The 21GRD01 OpMetBat project has received funding from the European Partmership on Metrology Participating States and from the European Union's Horizon 2020 research and innovation programme.

P21. Tracking the ionic exchange mechanism in Cu-exchanged Hydroxyapatites by in situ XAS: potential towards selective redox catalysis

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Hydroxyapatites (**HA**, $Ca_{10}(PO_4)_6(OH)_2$), commonly known as calcium phosphate, are versatile materials that can maintain their structural entity upon substituting any of their basic units by ionic species possessing similar characteristics [1,2]. There has been considerable scientific interest to investigate their unique properties for the potential applications in multiple fields beyond medical applications such as environment remediation, agricultural science and heterogeneous catalysis [1,3,4]. The substitution of the Ca^{2+} by Cu^{2+} ions is particularly interesting due to the versatility of Cu in many applied fields, including heterogeneous catalysis. The substitution mechanism also depends on the HA intrinsic characteristics. Consequently, the great versatility of the **HA** poses challenges in the elucidation of the molecular mechanisms that govern the ionic substitution and the routes leading to M^{2+} ions incorporation into the HA matrix.

In this regard, the ion exchange mechanism and nature of Cu-substituents in **HA** at the molecular level need to be fully understood. Therefore, element specific in-situ XAS was employed to investigate the Cu-exchanged Hydroxyapatite (**Cu-HA**) with a Cu loading of 2-7 wt. % and high surface area. The experimental Cu K-edge XAS spectra combined with theoretical tools (XANES-MCR, EXAFS Wavelet Transform analysis) provided a full characterization of Cu-HA in terms of Cu oxidation state and coordination environment, under model conditions designed to explore the potential of these materials towards selective oxidation catalysis (Figure 1 outlines the IR results [5] and preliminary K-edge X-ray spectroscopic measurements modeling the reaction). This study is an important step towards novel applications of Cu-exchanged HA in the tailored design of green and cheap catalysts.

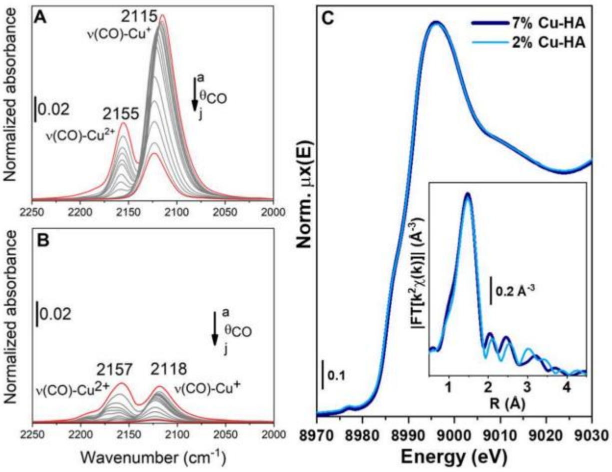

Figure 1. IR spectra at decreasing coverages of adsorbed CO collected at ca. 100 K for HA_Cu_7% (maximum uptake of Cu^{2+}), A) after heating the sample at 150 °C under vacuum for 2 h and, B) performing an oxidation step (30 mbar of O_2) at 150 °C and subsequently outgassing the sample [5]. C) Preliminary XAS spectra of as-prepared HA_Cu_7% and HA_Cu2% collected on the BM23 (ESRF).

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