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EWinS 2016

EUSpec **Win**ter **S**chool on core level spectroscopies

February 1–11, 2016 | Ajdovščina, Slovenia

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COST Action MP1306:
Modern Tools for
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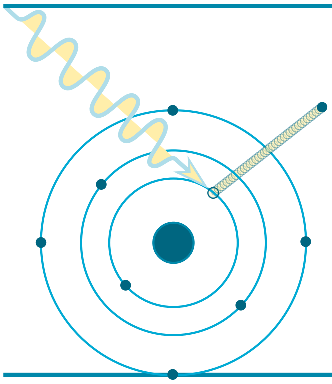
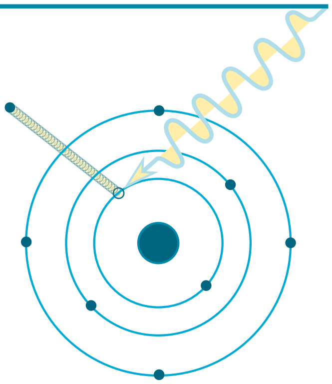


BOOK OF ABSTRACTS



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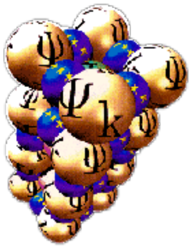

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Scope of the winter school

The two-week winter school *EWinS 2016 – EUSpec Winter School on core level spectroscopies* is an activity of the ***COST Action MP1306 EUSpec – Modern Tools for Spectroscopy on Advanced Materials*** that is closely related to the *ETSF* (European Theoretical Spectroscopy Facility) and will take place in February 2016 at the University of Nova Gorica (Slovenia).

The aim of the school is to introduce theoreticians as well as experimentalists to foundations of modern approaches for studying core level spectroscopies from first-principles modeling to the most advanced experimental spectroscopy techniques. The school will bring together experts and early career investigators working on advanced materials science, with a common interest in high level and up-to-date sophisticated spectroscopy experiments and modeling tools. The school may provide an extraordinary opportunity for students and young researchers to be introduced to core level spectroscopies and to discuss with worldwide recognized scientists in a friendly environment.

Regular lectures and talks will be followed by hands-on courses on the following three program packages: QUANTUM ESPRESSO (http://www.quantum-espresso.org/), WIEN2k (http://www.wien2k.at/), and ORCA (https://orcaforum.cec.mpg.de/). The aim is to make participants familiar with codes based on pseudopotentials, all-electron DFT as well as quantum chemical computational schemes covering a wide range of condensed matter as well as molecular systems.

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Program

1st Week Program

Legend: *plenary (60 min)* *invited (30 min)* *hands-on (4 h)* *Contributed talk (20 min)*

	Monday (01/02/2016)	**Tuesday** (02/02/2016)	**Wednesday** (03/02/2016)	**Thursday** (04/02/2016)	**Friday** (05/02/2016)
9:00 – 9:15	*Welcome and info*				
9:15 – 10:15	**N. M. Piancastelli** Intro to SR & FEL spectroscopy; interaction between radiation & matter (1)	**N. M. Piancastelli** Intro to SR & FEL spectroscopy; interaction between radiation & matter (2)	**C. Hébert** EELS: recent developments and new perspectives (1)	**S. Baroni** DFT approaches for vibrational and optical spectroscopies (1)	**S. Baroni** DFT approaches for vibrational and optical spectroscopies (2)
10:15 – 10:30	Coffee break	Coffee break	Coffee break	Coffee break	Coffee break
10:30 – 11:30	**L. Reining** Theoretical approaches to the many-body electronic problem: an introduction (1)	**L. Reining** Theoretical approaches to the many-body electronic problem: an introduction (2)	**F. de Groot** Introduction to core level spectroscopies (1)	**F. de Groot** Introduction to core level spectroscopies (2)	**I. Arčon**, Operando (micro) XAFS analysis **M. Amati**, Scanning photo-emission imaging and spectro-microscopy: a direct approach to spatially resolved XPS
11:30 – 13:00	Lunch	Lunch	Lunch	Lunch	Lunch
13:00 – 14:00	**P. Blaha & F. Tran** Core-level spectroscopies with all-electron DFT & hands-on: WIEN2k (1)	**P. Blaha & F. Tran** Core-level spectroscopies with all-electron DFT & hands-on: WIEN2k (2)	**K. Hatada** Multi channel multiple scattering theory for X-ray absorption spectroscopy **D. Cvetko** Ultrafast electron transfer at molecular interfaces by core-hole clock spectroscopy	**S. de Gironcoli & P. Giannozzi** Core-level spectroscopies with pseudo-potential DFT & hands on: QUANTUM ESPRESSO (1)	**G. Radtke & N. Mas** Core-level spectroscopies with pseudo-potential DFT & hands on: QUANTUM ESPRESSO (2)
14:00 – 15:00			**C. Hébert** EELS: recent developments and new perspectives (2)		
15:00 – 15:15	Coffee break	Coffee break	Coffee break	Coffee break	Coffee break
15:15 – 17:00			*Contributed talks (1-5)*		
17:30 – 19:30	Dinner & free exercises	Dinner & free exercises	**Poster session** *& wine tasting*	Dinner & free exercises	Dinner & free exercises

Contributed talks

Wednesday 03 Feb, 2016

15:15 – 15:35 **M. Hunault** *et al.*, XAS K pre-edge of low symmetry sites: p-d hybridization in ligand field multiplet model

15:35 – 15:55 **W. Sun** *et al.*, The role of many-body effects on the electronic structure of palladium and nickel oxide

15:55 – 16:15 **D. Kilymis** *et al.*, Raman spectra of binary sodo-silicate glasses from first principles calculations

16:15 – 16:35 **K. Batalović** *et al.*, Noble metal clusters on nitrogen doped TiO_2 – XPS and DFT study

16:35 – 16:55 **J. Radaković** *et al.*, Behavior of interstitial hydrogen in Laves phases – modifications of electronic structure from first principles

2nd Week Program

Legend: *plenary (60 min)* *ECI invited (60 min)* *hands-on (4 h)* *Contributed talk (20 min)*

	Monday (08/02/2016)	**Tuesday** (09/02/2016)	**Wednesday** (10/02/2016)	**Thursday** (11/02/2016)	**Friday** (12/02/2016)
9:15 – 10:15	*Visit to Elettra Sincrotrone*	**D. Manganas** Quantum chemistry approaches to correlations & spectroscopies (1)	**D. Manganas** Quantum chemistry approaches to correlations & spectroscopies (2)	**Y. Kvashnin** L-edge spectra calculations of the 3d metals in strongly correlated systems: an ab initio MLFT approach	*Departure*
10:15 – 10:30		Coffee break	Coffee break	Coffee break	
10:30 – 11:30		**C. Masciovecchio** Frontier research at FERMI	*Contributed talks (6-8)*	*Contributed talks (9-11)*	
11:30 – 13:00		Lunch	Lunch	Lunch	
13:00 – 15:00		**D. Manganas**, **B. Van-Kuiken** & **G. Cutsail** Core-level spectroscopy with quantum chemistry & hands-on: ORCA (1)	**D. Manganas**, **B. Van-Kuiken** & **G. Cutsail** Core-level spectroscopy with quantum chemistry & hands-on: ORCA (2)	*Contributed talks (12-15)* *STSM experiences*	
15:00 – 15:15		Coffee break	Coffee break	Coffee break	
15:15 – 17:00				*ECI meeting & Closing of the school*	
17:30 – 19:30		Dinner & free exercises	Dinner & free exercises		

Contributed talks

Wednesday 10 Feb, 2016

10:30 – 10:50 **F. Iesari** *et al.*, Local symmetry in liquid metals probed by x-ray absorption spectroscopy

10:50 – 11:10 **I. Pankin** *et al.*, In-situ experimental study and DFT modeling of hydrogen storage material using XAS spectroscopy

11:10 – 11:30 **G. S. Michelitsch** *et al.*, Core-Hole constraining approaches in the Density-Functional Theory simulation of Near-Edge X-Ray Absorption Fine-Structure (NEXAFS)

Thursday 11 Feb, 2016

10:30 – 10:50 **N. Yamamura** *et al.*, Angular dependence of plasmon loss in core-level photoemission with Multiple Scattering Theory

10:50 – 11:10 **S. Tripathi** *et al.*, X-ray magnetic circular dichroism study of rare-earth $M_{4,5}$ and transition metal $L_{2,3}$ absorption edges in $Nd_2Fe_{15}B$ permanent magnets

11:10 – 11:30 **R.-P. Wang** *et al.*, Charge transfer multiplet analysis of CoF_2, $CoCl_2$, $CoBr_2$ and CoS_x 2p3d RIXS spectra

13:00 – 13:20 **M. Corva** *et al.*, Carbon dioxide reduction on Ir(111): stable hydrocarbon surface species at near-ambient pressure

13:20 – 13:40 **V. Carnevali** *et al.*, Defects in epitaxial graphene on Ni(111): first-principles atomistic simulations

13:40 – 14:00 **F. Mohamed** *et al.*, Metallic nanoclusters on supported graphene: insights from ab-initio calculations

14:00 – 14:20 **B. Liu** *et al.*, 2p3d RIXS probe of Co^{II} polyoxometalates ground state electronic structure

Plenary lectures

Intro to SR & FEL spectroscopy; interaction between radiation & matter

Maria Novella Piancastelli*[,1,2]

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A general overview will be presented on the use of synchrotron radiation and free-electron laser sources in the field of photoionization, photoexcitation and photofragmentation dynamics of isolated atoms and molecules. The principles of the techniques will be illustrated, and several examples will be provided.

In general, the interaction between electromagnetic radiation (in the spectral region from ultraviolet to X rays) and the matter induces a disturbance on the nuclear geometry and a rearrangement of the electronic cloud surrounding the nuclei. This perturbation can cause chemical processes, such as formation and breaking of chemical bonds. Molecular dynamics investigates energy transfers between the molecular modes, breaking and creation of chemical bonds, transitions between the various electronic states etc. The radiation-matter interaction often causes the emission of a particle such as a photon, an ion or an electron. I will deal with spectroscopies implying photoelectron emission, using a tunable source such as synchrotron radiation.

Traditionally speaking, the method of choice to study of the electronic structure of occupied core and valence levels of isolated species is photoelectron spectroscopy [1-3]. The general principle is to use a monochromatic ultraviolet source (for valence levels) or X-ray source (for both core and valence levels) to induce a photoionization process in a gas of isolated atoms or molecules, then the kinetic energy of the emitted electrons is measured, and on the ground of some approximations it is possible to derive the electron binding energy in the ground state of the neutral species. In the early days of such technique, the only sources used were laboratory sources (X-ray anode or rare gas discharge sources). Successively, synchrotron radiation has began to be used as ionizing source, which has the big advantage to be a tunable source whose wavelength can be selected in a very wide range (typically from infrared to hard X rays). Furthermore, synchrotron radiation is almost 100% linearly polarized in the horizontal plane, which allows one to measure the distribution of photoelectrons with respect to the direction of the polarization vector. Therefore photoionization studies have been performed as a function of photon energy. This new experimental possibility has opened the way to a series of deeper investigations on the electronic structure of isolated species, in particular the possibility to measure the photoionization cross section and the angular distribution of photoelectrons as a function of photon energy [4,5].

A very important development of synchrotron radiation photoemission has been resonant photoemission. With this technique, synchrotron radiation is used to induce a photoexcitation process, e.g. the promotion of a core electron to a virtual state, which can be an empty molecular orbital or a Rydberg state. Afterwards, the deexcitation processes of the intermediate state are studied. A possible deexcitation pathway is the so-called nonradiative decay, where an electron emission takes place which leaves the system in a ionized state [5,6].

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Following the primary excitation, decay processes are investigated of the intermediate states, which are short-lived because of the core hole. In particular, the possibility to perform experiments under resonant Auger Raman conditions [7], i.e. to measure decay spectra at several different photon energies in small steps within the energy range of a resonance has allowed one to study in great detail the variations in the vibrational envelope of a specific final state. Studies "resonant Auger Raman" are also extremely important where the intermediate and/or the final states are dissociative: it has been demonstrated that the effective excitation time, or better, the spectral formation time, called in the literature "duration time", varies as a function of photon energy. In particular, the effective excitation time is shortened if the photon energy is detuned from the resonance maximum in both positive and negative directions [8]. It has been demonstrated that the amount of fragmentation is in turn a function of photon energy, therefore by varying the excitation energy in a narrow range around a resonance maximum it is possible to influence the photofragmentation percentage [9].

While synchrotron radiation is a very versatile source, in the last few years the advent of free-electron lasers (FELs) has added a very powerful tool in the studies of electron and nuclear dynamics of isolated species. In particular, the availability of very intense and very short light pulses opens a new dimension in the field of investigation of fast phenomena, such as photochemical reactions at the atomic scale. Some examples include the study of molecular motion in response to light and other chemical triggers, and the possibility to shot "molecular movies" of these changes. This could help unravel the steps of e.g. photosynthesis, which could help scientists design artificial systems to replicate the process and produce new sources of clean, renewable fuel. Furthermore, it is nowadays possible to explore the earliest steps in chemical reactions at the atomic scale, which could help inform scientists how to better control reactions and make them more efficient [10].

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Theoretical approaches to the many-body electronic problem: an introduction

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Electronic excitations determine the characteristics of materials all over science and technology, from photochemistry to radiation defects, from synchrotron experiments to cancer research. Theory and numerical modelling are valuable tools for the understanding and prediction of many of the important phenomena. During the last decades the field has evolved rapidly, but there are still many challenges. For example, some structures in the excitation spectra of interacting electrons, called quasiparticle peaks, can be directly related to excitations of independent electrons, but others cannot be understood in such a simple way. They are pure consequences of interaction and correlation. Photoemission spectra of solids, for example, show satellite structure that cannot be interpreted in a pure bandstructure picture. First principles calculations are today very efficient in describing bandstructure, especially methods based on many-body perturbation theory such as the so-called GW approximation [1], while they often have difficulties to describe quantitatively, or even qualitatively, everything that goes beyond.

In this introduction we will discuss signatures of correlation in observations, and some important ideas to approach the many-body problem theoretically. We will see where state-of-the art first principles calculations stand today, focussing on the main ideas of the underlying theories, their conceptual and technical limitations, and useful comparisons with, and interpretation of, experiment.

The results used for illustration [2] have been obtained in collaboration with many colleagues in the Theoretical Spectroscopy Group of the Laboratoire des Solides Irradiés and in the European Theoretical Spectroscopy Facility.

References

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Electron Energy Loss Spectroscopy: recent developments and new perspectives

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EELS in the transmission electron microscope is a very powerful technique for the investigation of materials at a nanometric and subnanometric level. With an energy rage from almost 0 to some thousands of eV, it is able to access both the optical and core level spectroscopies.

In this lecture, we will present the basics of the experiments setup, explaining the accessible information, and present recent fascinating developments in the instrumentation, as well as new perspectives. This will be put in context of challenges for the theoretical calculation of EELS both in the optical energy range and in the core level energy range.

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Introduction to core level spectroscopies

Frank de Groot*

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An introduction to core level spectroscopies is given, introducing some theoretical and experimental aspects. The core electron is excited in x-ray absorption spectroscopy (XAS) and x-ray photoemission (XPS) and the decay of the core hole gives rise to x-ray emission spectroscopy (XES) and Auger electron spectroscopy (AES). The XAS spectral shape is calculated with the Fermi golden rule, which contains the transition from the many body ground state to the many body final state. Under the assumption of a single electron excitation, the many body wavefunction can be approximated with single electron states and the XAS spectral identifies with the empty states, as for example calculated with LDA+U within codes such as Wien2K and QuantumEspresso. In case of the L edges of 3d transition metal systems, the local correlations are too strong to approximate the many body wavefunction and so-called multiplet calculations must be performed. It is possible to perform approximated multiplet calculations within a local model on a laptop, using the CTM4XAS software. A brief introduction is given to XAS, XPS, XES, AES and also to resonant spectroscopies such as resonant photoemission and resonant inelastic x-ray scattering.

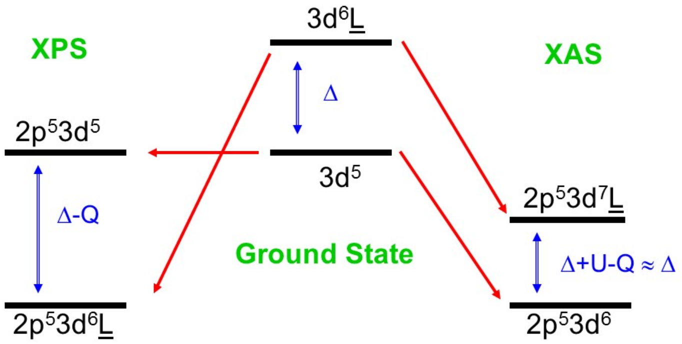

Figure 1. The comparison between XAS and XPS within the charge transfer multiplet model.

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DFT approaches for vibrational and optical spectroscopies

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In these lectures I will review the path that has led to the design of several simulation techniques to compute excited-state properties within (time-dependent) density-functional theory, without ever having to compute DFT virtual orbitals. This path started three decades ago with the establishment of density-functional perturbation theory to compute vibrational frequencies and many other lattice-dynamical properties, and has been recently revived by extending it to the dynamical regime, thus permitting to simulate optical and electron energy-loss spectra within time-dependent density-functional theory (TDDFT). The resulting formalism lends itself to a natural and easy extension to many-body perturbation theory. I will conclude by outlining some misconceptions that have obfuscated the scope of applicability of TDDFT to Rydberg and charge-transfer states in molecules and excitons in insulators.

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Quantum chemistry approaches to correlations & spectroscopies

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Quantum chemistry plays a vital role in developing the information content of experimental spectroscopic data. The lectures will go through the quantum chemical principles required to predict spectroscopic properties. Detailed examples will be provided in order to illustrate case-by-case experimental and theoretical correlations. Particular emphasis will be given to core electron spectroscopies.

In the first lecture, the role of particle/hole and configuration interaction techniques for predicting core level spectroscopic data will be explored. More specifically, recent progress in our method development efforts in efficiently treating the multiplet structure of the final states, electron correlation, relativity, as well as, accuracy versus molecular size scaling will be analyzed in detail.

In the second lecture, specific examples in the areas of X-Ray absorption (XAS), X-Ray Emission (XES) and Resonant X-Ray Emission (RXES) spectroscopy will be presented. A wide range of chemical systems ranging from molecular compounds, proteins and extended solid networks will be covered. In all cases, a detailed evaluation of various theoretical approaches in terms of accuracy versus computational cost will be discussed. In addition, practical guidance for successful application of the different theoretical protocols and an understanding of limitations of each protocol will be provided.

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Frontier research at FERMI

Filippo Bencivenga, Claudio Masciovecchio*

Elettra – Sincrotrone Trieste, S.S. 14 km 163,5 in Area Science Park, 34149 Basovizza, Trieste, Italy

The most recent light sources, extreme ultraviolet (EUV) and X-ray free electron lasers (FELs), have extended tabletop laser experiments to shorter wavelengths, adding element and chemical state specificity by exciting and probing electronic transitions from core levels. Through their unique properties, combining femtosecond X-ray pulses with coherence and enormous peak brightness, the FELs have enabled studies of a broad class of dynamic phenomena in matter that crosses many scientific disciplines and have led to major breakthroughs in the last few years. In this seminar, we intend to discuss how the advances in the performance of the FELs, with respect to multi-color pulse production, may push the development of original experimental strategies to study behavior of matter at the femtosecond–nanometer time–length scales. This would have a tremendous impact as an experimental tool to investigate a large array of phenomena ranging from nano dynamics in complex materials to phenomena that are at the heart of conversion of light into other forms of energy [1].

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Invited lectures

Multi channel multiple scattering theory for X-ray absorption spectroscopy

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It is well known that branching ratios of L-II and -III edges of X-ray absorption of transition metal oxides are deferent from the statistical ratio obtained by single particle theory. It is due to the mixing of the final states originated by many body effect under existence of core hole. This is so called multi channel effect.

Multiple scattering approach [1] is a powerful method to treat continuum state for wide energy range above the absorbing edge. The advantage of this approach is that it can be extended without any change of the theory to EXAFS which can be precisely analyzed by scattering theory, so that XANES and EXAFS are described within one theory.

Multichannel multiple scattering method [2,3] is a unified method to gather the multi channel effect in multiple scattering theory, so that the ligand field effect is taken into account correctly without any adjusting parameters.

We will see the basis of this theoretical approach and recent results for L-II,III edge XANES of transition metal oxides.

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Ultrafast electron transfer at molecular interfaces by core-hole clock spectroscopy

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Understanding the interplay between molecular bonding and charge transfer effciency in heterojunctions is a key issue for molecular engineering and design of novel organic nanodevices. Experimentally, different channels for carrier transfer within molecular assemblies can be probed with resonant x-ray photoemission (RPES) by measuring the time of electron and/or hole delocalization from the specific site of creation. The detection of ultrafast charge delocalization may reveal orbital pathways for fast carrier transport and provide unique insight in the origin of the assembly's conductive properties. The basics of core-hole-clock (CHC) experiments [1] and the models used to extract the timescale of the excited charge delocalization and the spatial distribution of molecular valence states will be briefly discussed. CHC measurements of fast electron dynamics in a few organic systems with π–π and donor-acceptor molecular coupling will be presented to demonstrate the essential coupling motifs for efficient transport in non-covalent molecular junctions [2].

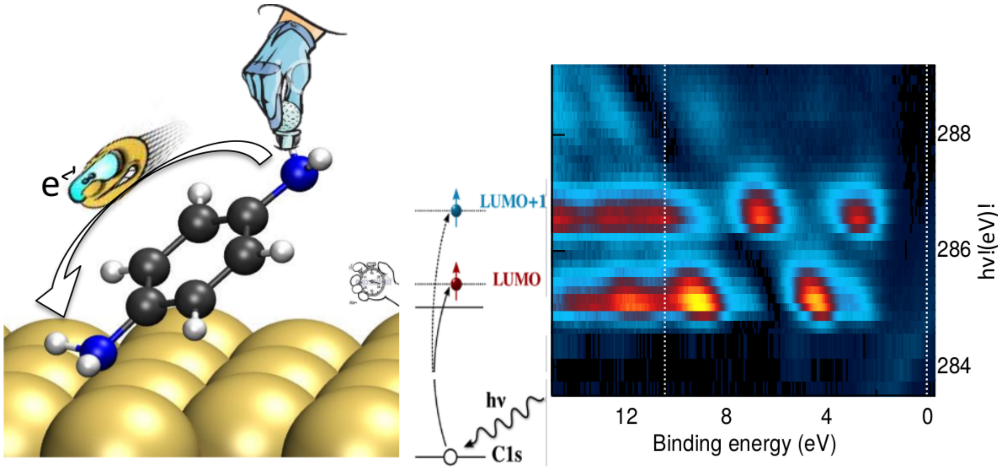

Figure 1. CHC method and the RPES experiment.

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Operando (micro) XAFS analysis

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High resolution X-ray absorption spectroscopy (XAS) with synchrotron radiation is a powerful experimental method for the investigation of atomic and molecular structures of materials which enables identification of the local structure around atoms of a selected type in the sample [1-4]. In XANES (X-Ray Absorption Near Edge Structure) the valence state of the selected type of the atom in the sample and the local symmetry of its unoccupied orbitals can be deduced from the information hidden in the shape and energy shift of the x-ray absorption edge. In EXAFS (Extended X-ray Absorption Fine Structure) number and species of neighbor atoms, their distance from the selected atom and the thermal or structural disorder of their positions can be determined from the oscillatory part of the absorption coefficient above K or L absorption edge. The analysis can be applied to crystalline, nano-structured or amorphous materials, liquids and molecular gases, or complex biological or environmental samples. EXAFS is often the only practical way to study the arrangement of atoms in materials without long range order, where traditional diffraction techniques cannot be used.

On modern synchrotron X-ray sources with high brilliance, fast detection modes have been developed for studying chemical reactions in real time, allowing acquisition of up to 100 XAS spectra per second. Bright synchrotron radiation sources make possible also a powerful combination of microscopy and X-ray absorption spectroscopy. There are several beamlines at different SR laboratories (ESRF, DESY, ELETTRA, BESY, SOLEIL, SLS, DIAMOND, and others) equipped with high energy resolution Bragg monchromator and micro focusing optics (capillary lenses, zone plates, or Kirkpatric–Baez mirrors), with lateral resolution below 1 micron. A 2D or 3D distribution of the elements under investigation can be performed with micro-XRF and complemented with XAS spectra measured at selected spots on the sample. The X-ray micro-spectroscopy combination is very useful for biological samples, since it allows mapping of element distribution and chemical state (valence state and local atomic structure) of selected elements on the sub-cellular level [4].

In the talk the principles of XAS methods will be presented with practical examples which illustrate the possibilities and advanced approaches for their use in structural analysis of different types of materials. The emphasis will be on to the use of XAS spectroscopy in operando mode and in combination with X-ray microscopy.

It will be shown how operando XANES and EXAFS analyses can be used as powerful and indispensable tools for the characterization of the redox chemistry in Li-ion and Li-Sulphur batteries [5-7]. They provide detailed information on the local symmetry and oxidation state as well as short-range order around metal cations during charging and discharging of the Li-ion batteries, or in case of Li-sulfur batteries, they are used to monitor the formation of different sulfur compounds that coexist in the battery (elemental sulfur, polysulfides and sulfur

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contained in the electrolyte). All sulfur forms can be efficiently distinguished, and their relative amount in the cathode can be determined precisely during the battery operation.

In another example we will examine how a combination of micro-XRF imaging and micro-XANES and EXAFS analysis is used for characterization of metal pollutants or essential elements on subcellular level, providing information on elemental spatial distribution and local ligand environment of the metals in different plant tissues [4,8]. The information on the valence states and the local structures around metal cations can provide direct evidence for metal complexation with organic molecules in plant tissues or information about availability of toxic metals in soil or water. In this way insight into tolerance mechanisms in metal (hyper) accumulating species is provided, and important questions about soil-plant interactions and metal accumulation can be resolved. The goal is to efficiently assess metal bioavailability and toxicity, and gain more knowledge on the mechanisms of metal uptake, accumulation and detoxification in living organisms.

The methodological approaches for efficient operando and micro-XAS experiments in transmission and fluorescence detection mode will be presented. The limitations and sources of potential systematic errors in XANES and EXAFS analysis due to the energy dependent penetration depth of the X-ray beam and self-absorption effects in the sample, especially at low energies, will be discussed.

Acknowledgement: XAS experiments, discussed in the talk, were performed at different synchrotron radiation sources. Micro-XRF imaging and micro-XANES measurements were performed at ESRF Grenoble, beamline ID21 (project EC-719 and LS-2225) and beamline BM23 (projects LS-2209 and LS- 2275). The results were complemented by EXAFS analysis on the level of plant organs at XAFS beamline of ELETTRA, Trieste (p. 20110086), and at A1 and C beamline of DESY, Hamburg (p. I-20110511 EC), supported by DESY and the EU FP7/2007–2013, CALIPSO grant agreement, no. 312284. The operando XAS experiments were performed at XAFS beamline of Elettra (project 20120044), supported by the European Union Seventh Framework Programme under grant agreement No. 314515 (EUROLIS) and the Slovenian Research Agency (P1-0112).

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Scanning photoemission imaging and spectro-microscopy: a direct approach to spatially resolved XPS

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The Scanning PhotoEmission Microscope (SPEM), hosted at the ESCAmicroscopy beamline at the Elettra synchrotron light source, uses a direct approach to characterize chemically surfaces and interfaces at the submicron scale i.e. the use of a small focused x-ray photon probe to illuminate the sample (Figure 1). The focusing of the x-ray beam is performed by using a Zone Plate (ZP) which is a Fresnel type lens. The SPEM can operate in two modes: imaging and spectroscopy. In the first mode the sample surface is mapped by synchronized–scanning the sample with respect to the focused photon beam and collecting photoelectrons with a selected energy. The second mode is X-ray Photoelectron Spectroscopy (XPS) from a microspot. The X-ray beam can be downsized to a diameter of 120 nm which allows imaging resolution of less than 50 nm. The overall energy resolution is better than 200 meV [1].

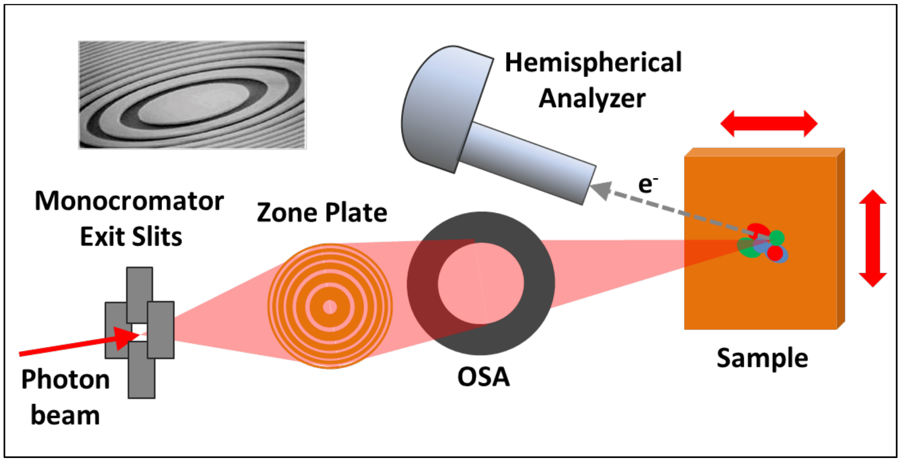

Figure 1. SPEM Layout.

Recent achievements in the chemical and electronic characterization at the micro- and nanoscale as the characterization of single micro- and nanostructure, for example the single nanotube evolution under plasma oxygen exposure [2] reported in Figure 2, will be presented providing an overview of the capabilities of this powerful technique. A full list of work done at Escamicroscopy can be found in reference [1]. A particular focus

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will be on examples where *in-situ* and *in-operando* characterization is of primary importance, as in electrochemistry and catalysis, like the in situ characterization of novel non-noble metal catalysts for the Oxygen Reduction Reaction (ORR) [3] and the characterization of a Self-Driven Single Chamber Solid Oxide Fuel Cell (SOFC) in operando condition [4].

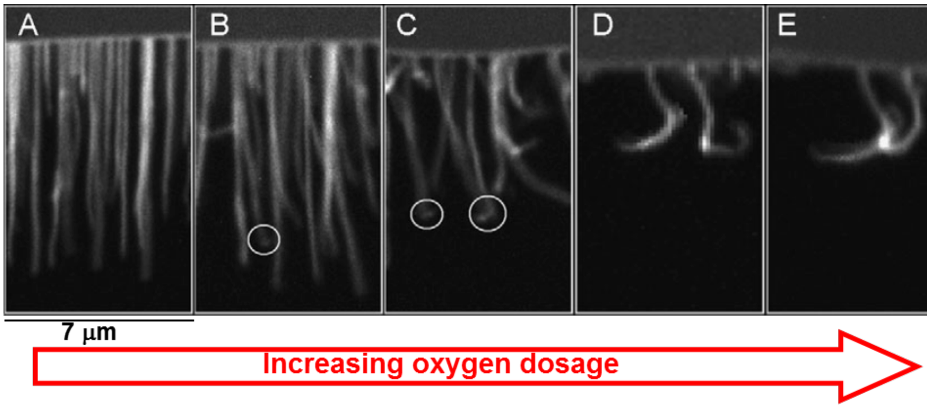

Figure 2. SPEM image of CNTs evolution under plasma oxygen exposure.

The requirement for high-vacuum conditions in photoelectron spectroscopy and microscopy, allowing a maximum pressure of 10-5 mbar for SPEM, is a strong limiting factor for the *in-situ* and *in-operando* characterization of materials in realistic conditions. Only recently the development of electron energy analyzers with differentially pumped lens systems allowed to perform in situ XPS measurements up to few mBar (near ambient pressure). Due to their cost, technical complexity and intrinsically low efficiency it was not possible to export such solution to photoemission spectromicroscopy so far. Results of innovative and cheap solutions developed at Elettra for photoemission microscopes, which can be potentially used to address the "pressure gap" in any XPS system, will be also presented and discussed [5,6].

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L-edge spectra calculations of the *3d* metals in strongly correlated systems: an *ab initio* MLFT approach

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Generally, there are two ways of finding the ground state of an interacting many-electron system. The first approach is inspired by the mean-field theories and consists of simplifying the original problem to a problem of non-interacting particles moving in some effective potential. Another way is to reduce the number of available degrees of freedom (i.e. the dimension of the Hilbert space) and find the eigenstates for an approximated system. These two approaches have been developed independently and were applied to simulate the core-valence excitation spectra of various materials. It is nowadays well-understood which method suits better to each particular problem.

The mean-field treatment is a core of the Density Functional Theory (DFT), which is the most widely used tool for modern electronic structure calculations. The DFT is able to describe from first principles the hybridisation of various orbitals, crystal field effects, charge transfer phenomena, etc. This method is supposed to work well for the systems with weak electronic correlations. There has been many examples, where x-ray spectra produced with this theory were found to be in excellent agreement with the experiment [1,2].

The approach based on the full many-body treatment of an interacting system has to be used when the correlation effects are pronounced. In this case electrons show more atomic-like features and therefore it is more reasonable to describe their states starting from Atomic Multiplet Theory [3]. In order to be more applicable to real materials, the latter theory was extended to the Multiplet Ligand Field Theory (MLFT) [4], where the details of the band structure are added to the atomic Hamiltonian via additional terms containing *ad hoc* parameters.

Until recently the problem was to merge the two approaches, so that both band and many-body effects could be treated on the same footing. A great advancement has been recently done: a computational scheme which utilises the information from the DFT to parametrise the MLFT-based calculations was proposed in Ref. 5. This way one obtains a parameter-free description of the initial and excited state properties of the strongly correlated compounds.

In my talk I will present the newly developed method based on Ref. 5, which was combined with a highly accurate full-potential electronic structure code "RSPt" [6]. I will show in detail which parameters can be deduced from the DFT and the practical ways of doing it. In contrast to the original scheme, where the Wannier functions are constructed, we have used different basis set and utilised hybridisation function to describe the covalent bonding between the metal and the ligand orbitals. I will discuss the projection techniques for obtaining the localized basis sets and the influence of the projection on the final results. I will show the simulated *L*-edge

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spectra for several *3d* metal monoxides and *3d* metal-containing molecules. The limitations of the present theory will be addressed as well.

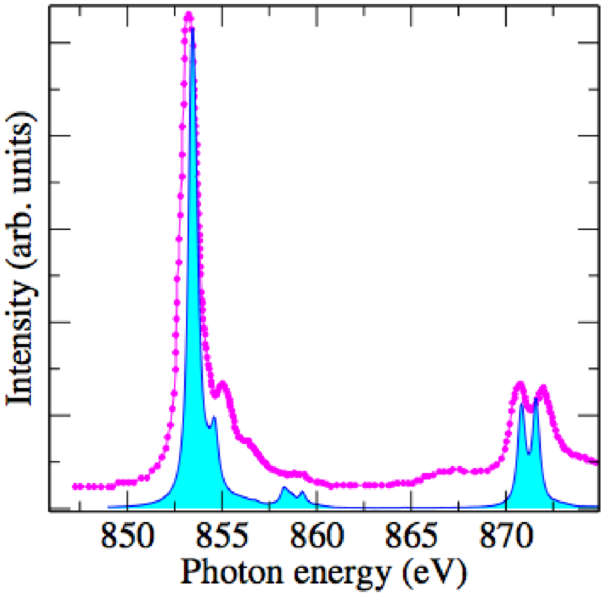

Figure 1. Ni *2p* core level x-ray absorption spectrum for NiO. Purple line corresponds to experimental data taken from Ref. 7. Blue line reads the simulated spectrum obtained with DFT+MLFT approach.

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Hands-on tutorials

WIEN2k – An all-electron full-potential augmented-plane-wave program for the simulation of solids, surfaces and nanostructures

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The program package WIEN2k allows to perform electronic structure calculations of solids and surfaces using density functional theory (DFT) and has been licensed by about 3000 user groups. It is based on the full-potential (linearized) augmented plane-wave ((L)APW) + local orbitals (lo) method, one among the most accurate schemes for band structure calculations. WIEN2k is an all-electron scheme including relativistic effects and can use a large number of different functionals including LDA, various GGAs and meta-GGAs, DFT+U or hybrid-DFT. It can even serve as basis for many-body perturbation theory methods like GW and BSE. WIEN2k is not just a code to simulate certain spectroscopies, but a general band structure program featuring periodic boundary conditions. Novice users are guided by a user-friendly web-based interface "W2web". A short list of features include:

- Atomic structure by means of total energy and forces
  - accurate determination of equilibrium lattice constants
  - optimizing atomic (equilibrium) positions (simultaneously within the scf-cycle)
  - creating and optimizing models (tools for creation of super cells or surface slabs) for novel nanomaterials
  - determine phase stabilities under pressure
  - calculate phonons and compare with IR, Raman or neutron scattering, and perform free energy calculations
- Electronic structure
  - band structure with band character, density of states (DOS) and Fermi surfaces
  - band gaps using the accurate modified Becke-Johnson potential
  - analysis of chemical bonding, electron densities, Bader charges, X-ray structure factors
- Magnetic properties
  - determination of the magnetic structure (FM, AFM), non collinear magnetism
  - magnetization density, spin-orbit coupling and magnetic anisotropy
- Spectroscopies and other properties
  - Core-level spectroscopy: XPS, XAS, XES, EELS
  - Optical spectroscopy: UV-Vis, UPS
  - IR, Raman

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- NMR: chemical shift and Knight shift, electric field gradient (EFG)
- Mössbauer spectroscopy: isomer shifts, hyperfine fields, EFG
- Scanning tunneling microscopy (STM) in constant height and constant current mode
- Berry phases: polarizability, Born effective charges

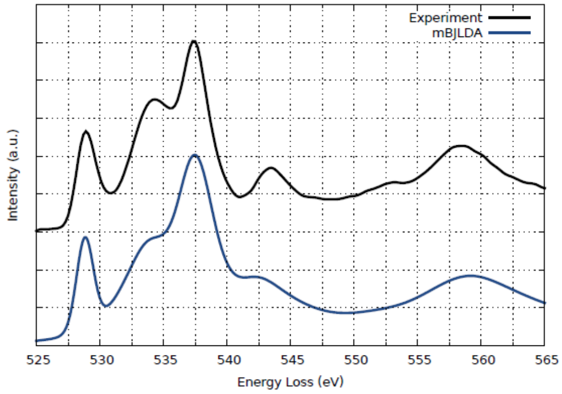

Figure 1. Oxygen K-edge of NiO calculated using the modied Becke-Johnson potential.

First steps with Quantum ESPRESSO

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Quantum ESPRESSO [1,2] is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.

In this hands-on session we will review and demostrate the basic concepts needed to study the structural and electronic properties of a material with the Quantum ESPRESSO package. Simple examples of self-consistent minimization to the electronic ground state for insulators, metal and magnetic systems will be given. Basic convergence parameters will be discussed. Examples of structural relaxation will be shown and the procedure to obtain the Khon-Sham electronic band structure, the atomic-Projected Densities of States (pDOS), and electronic charge density plots will be detailed.

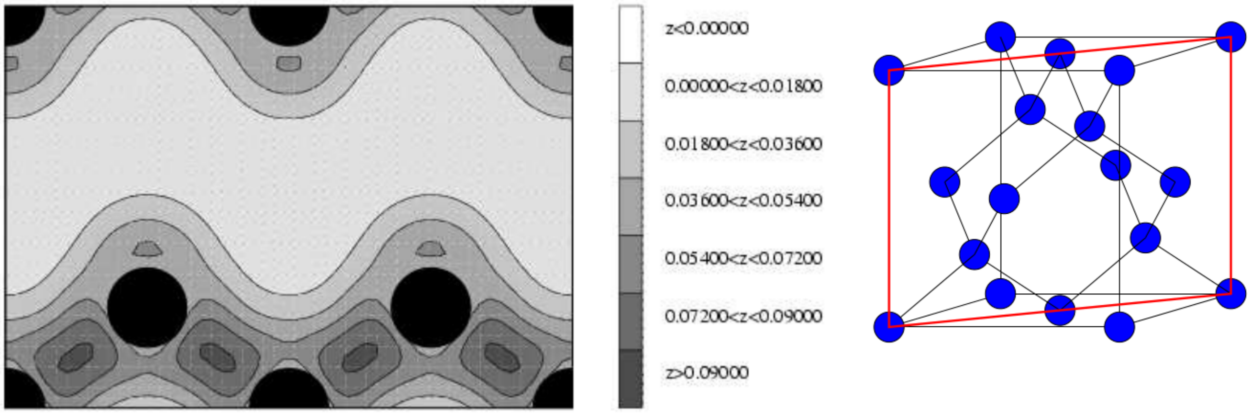

Figure 1. (Right) Charge density of Silicon in the (110) plane; the bonding charge along the chain of bonds in the [110] direction is clearly visible . (Left) Silicon in the Diamond crystal structure; the (110) plane is highlighted in red.

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XSpectra: A tool for X-ray absorption spectra (XAS) calculations

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In this tutorial, we give a hands-on introduction to XSpectra [1], a module for calculating X-ray absorption spectra distributed in the DFT based Quantum ESPRESSO [2] package. XSpectra calculates X-ray absorption dipolar and quadrupolar cross-sections in the pre-edge to near-edge region of K- and L-edges, within the single particle approximation and based on a continued fraction approach [3].

The basic theoretical concepts required for a comprehensive use of the code will be reviewed and systematically illustrated through a series of examples. In particular, the effect of the core-hole on the fine structure, the use of supercells and the calculation of dichroic signal will be illustrated in the case of the Si-K edge in SiO_2 whereas the calculation of quadrupolar contributions will be demonstrated through the example of the Ni-K edge in NiO. School attendees will participate to practical exercises including (i) the generation of GIPAW pseudopotentials including a core-hole; (ii) the construction and self-consistent calculation of supercells containing an excited absorbing atom and (iii) the XAS calculation with XSpectra with a special emphasis on the description of input parameters related to the Lanczos method and continued fraction calculation.

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ORCA – Hands-on tutorial on core-level spectroscopy

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The ORCA quantum chemistry program package

ORCA is a fully parallelized, general-purpose quantum chemistry code that runs on all platforms (unix, windows, mac OS). It is based on atom centered Gaussian basis functions and can perform calculations on all elements of the periodic table (optionally with all-electron, scalar relativistic Hamiltonians or pseudopotentials). ORCA features extensive DFT capabilities (LDA, GGA, meta-GGA, hybrid, double-hybrid, range separated functionals) but is particularly powerful in the domain of wavefunction based ab initio methods (coupled-pair/coupled-cluster methods, multireference methods CASSCF/ NEVPT2/MRCI, MBPT). ORCA is an efficient code that, in conjunction with well-tested approximations (density fitting, chain-of-spheres), can be applied to systems with hundreds of atoms. Pair natural orbital (PNO) based local correlation treatments allow for correlated wavefunction calculations on large systems. Extended systems can be treated with QM/MM methods; solids and surfaces can be approached using cluster models with electrostatic embedding and capping ECPs. Geometry optimization/transition state searches using analytic gradient techniques are available and for Hartree-Fock and DFT methods analytic second derivatives are also available.

ORCA specializes on transition metals and the calculation of spectroscopic properties with an emphasis on many particle wavefunctions and wavefunction based ab initio methods. A broad range of spectroscopic parameters can be calculated with ORCA including all EPR parameters (g-tensor, hyperfine couplings, zero-field splittings, quadrupole couplings), some NMR properties (chemical shielding), Mössbauer parameters (isomer shift, quadrupole splitting), UV absorption spectra, absorption and fluorescence bandshapes using the independent mode displaced harmonic oscillator model, IR-, Raman- and resonance Raman spectra, magnetic circular dichroism spectra, X-ray absorption, X-ray emission spectra as well as RIXS spectra.

Relativistic effects can be treated with a number of approximation including the Douglas-Kroll-Hess (DKH) and 0th order regular approximation (ZORA) Hamiltonians. Picture change effects and finite nuclei can be taken into account. The treatment of spin-orbit coupling features and accurate spin-orbit meanfield approach that includes all two-electron terms and includes the important contributions form the spin-other-orbit interaction.

Valence or core excited states can be approached with a number of methods including configuration interaction singles (CIS, with doubles correction CIS(D)), time-dependent DFT with or without the Tamm-Dancoff approximation, MR-CI, CASSCF/NEVPT2 and EOM-CCSD. A method specific to ORCA is the restricted open shell CI (ROCIS) approach. It is designed to provide a good balance between physical rigor and computational efficiency. It provides many particle wavefunctions that have the correct multiplet structure (unlike TD-DFT or other particle/hole based approaches) and hence is a good basis for the treatment of spin-orbit effects using quasi-degenerate perturbation theory. It can be applied to systems with a few-hundred atoms and readily delivers a few hundred states. Hence, it is particularly useful for the calculation of core level spectra including L-

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edge XAS spectra. In order to account for dynamic electron correlation in a simple, average way, there is a parameterized version of the method (ROCIS/DFT) that introduces three universal scaling parameters that greatly improve the accuracy of the method in actual applications.

ORCA is widely used among various communities in chemistry with an estimate of >10000 academic users. The program is free of charge and can be obtained from the website of the Max Planck institute for chemical energy conversion that also hosts a users forum (https://orcaforum.cec.mpg.de).

The 8 hours Orca hands-on tutorial is expected to familiarize the students with exercises material that involves:

1) Ground state calculations:
    - Structure design
    - Geometry Optimizations

2) Excited state – Property calculations:
    - Metal and Ligand K-edge XAS spectra (TD-DFT)
    - Metal L-edge XAS spectra (ROCIS/DFT)
    - Valence to Core XES spectra (DFT, RASCI)

Contributed talks

XAS K pre-edge of low symmetry sites: *p-d* hybridization in ligand field multiplet model

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The computation of the exact absorption cross-section of electronic transitions is a major challenge for spectroscopists. In particular, transitions arising from parity-forbidden electric dipole are strongly influenced by the local geometry of the absorbing site. Therefore X-ray absorption spectroscopy and in particular, the K pre-edge features have widely been used as powerful tools to determine the local structure of transition metal ions. Point group symmetry of TM ions is a crucial characteristic, which drives their properties and related applications, from solid-state physics to coordination chemistry. In particular, exotic geometries like 5-fold coordinated species are often predicted in coordination complexes, surfaces and interfaces, glasses and amorphous compounds. However their presence is difficult to assess because the spectral features are largely unknown.

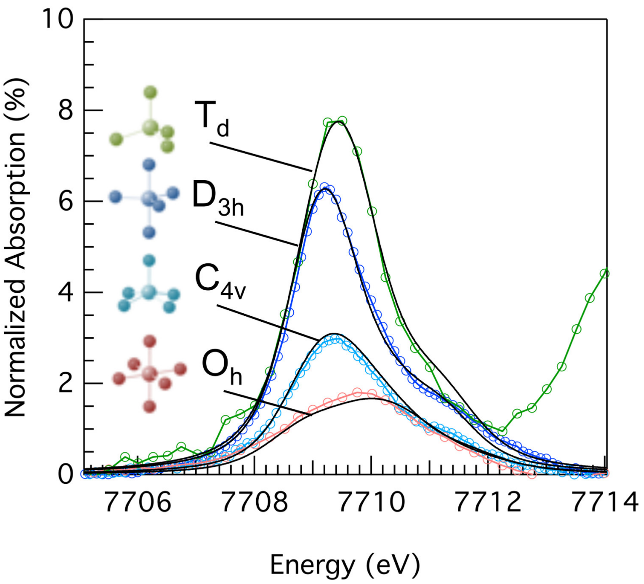

Figure 1. Normalized Co K pre-edge spectra for each of the four symmetries of this study: experimental (colored line and markers) and respective calculation (plain black line) (green: $CoCr_2O_4$ (T_d), dark blue: $LiCoBO_3$ (D_{3h}), light blue: $BaCoP_2O_7$ (C_{4v}) and pink: Co_2GeO_4 (O_h)).

In the particular case of Cobalt(II), a widely used coloring agent, its coordination plays a major role in the coloration of minerals and glasses. Co^{2+} can be found in sites of various symmetries from 4 to 5 to 6-fold

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coordination. The pre-edge spectroscopic signature of these symmetries can be distinguished according the intensity and the shape of the pre-edge [1]. This is illustrated by Figure 1 which compare the K pre-edge spectra of a benchmark set of four crystalline samples bearing Co^{2+} in various symmetries. The variation of the intensity In the particular case of Cobalt(II), a widely used coloring agent, its coordination plays a major role in the coloration of minerals and glasses. Co^{2+} can be found in sites of various symmetries from 4 to 5 to 6-fold coordination. The pre-edge spectroscopic signature of these symmetries can be distinguished according the intensity and the shape of the pre-edge [1]. This is illustrated by Figure 1 which compare the K pre-edge spectra of the pre-edge depends on the *3d-4p* hybridization that, when it is allowed by symmetry in absence of inversion center, enables an electric dipole contribution in addition to the quadrupole transitions. This effect is well-known for the cases of O_h (quadrupole) and T_d (quadrupole + dipole) local geometries and has been reproduced for iron ions by calculations in the ligand field multiplet model [2].

In this work, we present the application of the ligand field multiplet model accounting for 4p-3d on-site hybridization to Co^{2+} in low symmetries. It offers the possibility to interpret quantitatively the pre-edge features of Co^{2+} or other TM ions in terms of spectra characteristics and degree of admixture between *4p* and *3d* levels in the ground state. This information can be further used to interpret the optical absorption spectra, and thus the color, of Co-bearing materials, which strongly rely on the *p-d* hybridization.

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The role of many-body effects on the electronic structure of palladium and nickel oxide

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The local density approximation + dynamical mean-field theory (LDA+DMFT) using fluctuation exchange approximation was employed to optimize the lattice parameters and bulk modulus. It is also found that the matsubara frequency dependent correlation effects or even the sole electronic temperature can modify the Fermi surface at the L-point. Due to the feature of broad 4*d* bandwidth, another many-body perturbation method GW was used to study the electronic structure.

We have revisited the valence band electronic structure of NiO. LDA+DMFT has produced an excellent agreement on the Ni-3*d* spectra with the experiment, but the evident deviation of the peaks far below the Fermi level is present. It is found that GW corrections applied for the *s* and *p* states can adjust their positions to the lower binding energies, which further approaches to the hard x-ray photoemission spectroscopy (HAXPES).

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Raman spectra of binary sodo-silicate glasses from first principles calculations

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Silicate glasses possess a central role in glass technology due to their multiple applications ranging from optical devices to the immobilization of nuclear waste. Raman spectroscopy is a key method for the investigation of their structure and the study of their properties. However, the inherent structural disorder found in glasses results in very broad and overlapping peaks in their spectra. In this context, an accurate theoretical modeling of the spectra can be proven to be invaluable in order to optimize their performance and tailor their fabrication method to match requirements for future applications.

In this work, we present results on binary sodo-silicate glasses [xNa_2O- $(1-x)SiO_2$], which have been prepared by combining classical and ab-initio Molecular Dynamics. The Raman spectra (polarized and unpolarized), as well as the IR spectra, have been obtained using the Quantum Espresso package [1] in the GGA framework by employing norm-conserving pseudopotentials. Calibration runs have been carried out on the crystalline α-quartz and Na_2SiO_3 systems in order to optimize the choice of pseudopotentials. Concerning the glasses under study, we focused on the effect of local structural units, such as Q-species (Figure 1) and their interconnection, alongside the role of sodium atom content in order to assign the corresponding bands. The initial results show very good agreement with previous theoretical and experimental spectra [2-5], while the ongoing decomposition relative to the exact contributions from each of the structural units of the glasses is expected to provide insight to the interpretation of the experimental spectra.

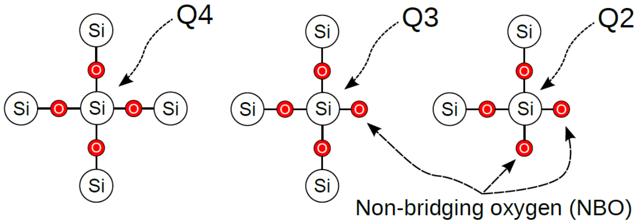

Figure 1. Q-species in a silicate glass.

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Noble metal clusters on nitrogen doped TiO_2 - XPS and DFT study

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Numerous researches are dedicated to the investigation and modification of TiO_2, since it was shown to be promising, cheap and easily accessible photocatalysts for environmental-friendly energy solutions [1]. Main drawbacks of TiO_2 are its poor visible light absorption and fast recombination of photo-generated electron/hole pars [1,2]. Doping bulk TiO_2 with nitrogen, boron, transition metals was shown to improve visible light activity [2]; however, downside of such modifications is the fact that defects and metal dopant sites act as recombination centers for photo-generated electrons and holes [1,2].

In this work we study the influence of nitrogen doping combined with surface modification using Pd and Pt on the properties of anatase TiO_2. Nanosized N-doped TiO_2 is synthetized via hydrothermal process, and 0.1 wt% Pt and 0.05 wt% Pd are subsequently reduced at the surface of the particles using UV light. Pt,N-TiO_2 and Pd,N-TiO_2 are characterized using XRD and UV/VIS spectroscopy. XPS is used to gain information on surface composition and nature of noble metals at the surface. To study electronic structure and address the location of nitrogen atom in the anatase cell, we performed electronic structure calculations using full potential APW+lo method as implemented in WIEN2k program package [3]. Using Slater's transition state method, energy of the N 1s electronic level is calculated in two cases, i.e. for interstitial and substitutional nitrogen in anatase TiO_2 and results are compared to XPS results.

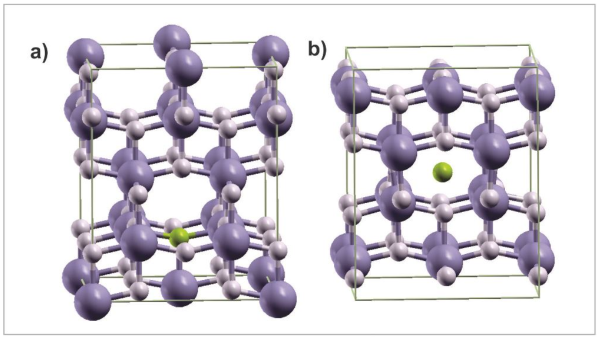

Figure 1. Model cells of N-doped anatase TiO_2; a) nitrogen substitutional doping at O site; b) nitrogen interstitial doping

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Behavior of interstitial hydrogen in Laves phases – modifications of electronic structure from first principles

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Laves phases are a large class of intermetallic compounds that exhibit reasonably high hydrogen storage capacity and favorable absorption/desorption kinetics around room temperature and ambient pressures [1]. Consequently, they are being extensively investigated as potential hydrogen storage materials, or electrodes for Ni/MH batteries; however, optimization of their performance and practical properties is still necessary for such applications. Formation enthalpies and binding energies of hydrides, and changes in the ground state structure that occur after hydrogenation are constantly being reported for various types of compounds [2], but linking the practical features of the material to its microscopic structure still remains a challenging issue. For example, subtle modifications in the electronic structure of hydrogen storage materials, induced by the absorbed hydrogen, can stabilize or destabilize initial compounds. Evaluating the cause of such behavior contributes to better understanding of the hydride formation process and experimentally observed properties of hydrides. Consequently, it is of paramount importance to thoroughly investigate the effect that hydrogen has on the electronic structure of prospective hydrogen storage materials, and this study represents a contribution in that regard. It deals with the local electronic structure modifications that occur in cubic Laves phase compounds $ZrCr_2$, $ZrMn_2$, and $ZrNi_2$, due to the formation of corresponding monohydrides $ZrCr_2H$, $ZrMn_2H$, and $ZrNi_2H$.

Understanding the microscopic aspect of the hydride formation process provides an insight into the experimentally observed properties of prospective hydrogen storage materials. We have studied the local structural and electronic modifications induced by hydrogen absorption in cubic C15 Laves phases AB_2 (A = Zr; B = Cr, Mn, Ni), as well as the stability of the formed hydrides, by means of density functional theory (DFT). To address the effect of hydrogen absorbed in one of three tetrahedral sites (96g, 32e, and 8b) on the electronic structure of its surrounding atoms, we have calculated the electric field gradient (EFG) on the position of Cr, Mn, and Ni in pure and hydrogenated compounds. EFG is associated with the hydrogen site-preference, and formation enthalpies of ZrB_2H hydrides are used to examine their formation feasibility. Obtained enthalpies reveal that $ZrMn_2H$ and $ZrNi_2H$ are both unstable regardless of the occupied site, and the only attainable hydride is $ZrCr_2H$, with comparable occupational probability of sites 96g and 32e. EFG results indicate that a hydrogen distribution within the crystal depends on the level of induced electronic structure modifications; *i.e.*, the hydrogen site-preference is governed by the condition of minimal divergence of the electronic charge from its initial distribution.

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Local symmetry in liquid metals probed by x-ray absorption spectroscopy

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In recent decades, several computational studies were devoted to investigating locally preferred structures in simple atomic liquids (see, for example, Refs. [1,2]), and most of these works support the existence and importance of icosahedral short range ordering (ISRO). Besides computer simulations, only few experimental results on the local symmetry in undercooled and stable liquids exist, due to the the difficulties in accessing the supercooled state and also in the interpretation of collected data. In fact, usual scattering experiments provide information limited to the structure factor S(q) and the pair distribution function g(r) while a complete picture of the local short-range order requires a better knowledge of local point symmetry.

On the other hand, XAS is particularly suitable to investigate liquid and amorphous matter because of its high sensitivity to higher order distribution functions and local geometry, tough being almost blind to long-range order. We present here an extensive investigation on exemplary liquid and undercooled liquid metals such as Cu, Ni and Cd using a Reverse Monte Carlo (RMC) approach [3,4], incorporating GNXAS [5] XAS calculations, we are able to obtain structure models compatibles with experiments. From these realistic models we calculate interesting physical quantities, such as pair distribution functions (Fig. 1) and bond-angle distributions. We also assess the nature of local geometries using common-neighbors and spherical invariants analysis.

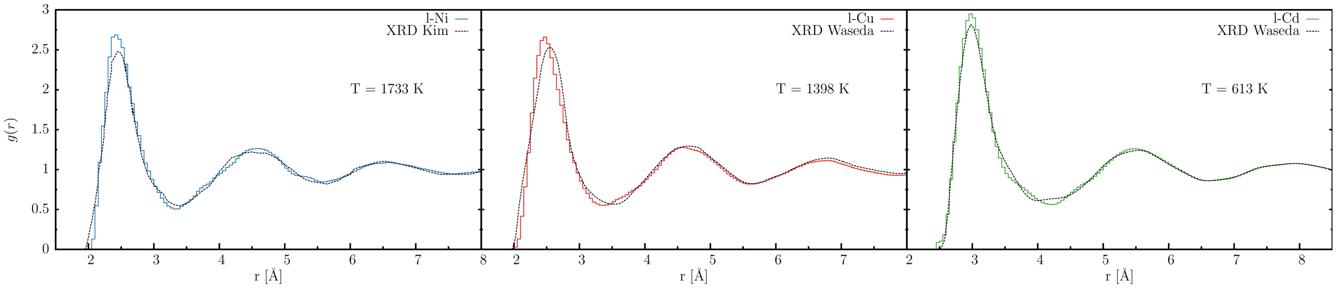

Figure 1. Pair distribution functions of Ni, Cu and Cd obtained from averaging 100 different Reverse Monte Carlo configurations compared with x-ray diffraction determinations.

The emerging picture for close-packing metals is that of a mixture of nearly icosahedral structures embedded in a disordered network mainly composed of fragments of highly distorted icosahedra, structures reminiscent of the crystalline phase, and other configurations. RMC refinements allowed us a quantitative analysis of the local

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symmetry, and in particular of the amount of icosahedral ordering in those liquid metals. Clear changes are observed for non-close-packing metals for which the weight of icosahedral structures is reduced.

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In-situ experimental study and DFT modeling of hydrogen storage material using XAS spectroscopy

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The material under study is borohydride of manganese $Mn(BH_4)_2$. The unique thermodynamics and kinetic properties in combination with high volumetric and gravimetric hydrogen densities make this compound a very promising candidate to solid state hydrogen storage. Gravimetric capacity, temperature of desorption and cycling ability are the main requirements for hydrogen storage material [1]. $Mn(BH_4)_2$ among all other transition complex borohydrides is stable at room temperature [2]. The hydrogen release process is observed at low temperature and pressure and up to 10 mass % of hydrogen can be released at the temperature range from 120 °C to 160 °C [3,4]. $Mn(BH_4)_2$ have unique porous atomic structure which makes it similar to MOFs and provides enhanced absorption ability. Porous channels located along ***c*** crystallographic axes and have a size up to 6.5 Å at cross section - thus powder material is able to absorb external gas molecules [5]. But so far has not been shown to exhibit reversible hydrogenation for $Mn(BH_4)_2$. Degradation of initial material and irreversible decomposition $Mn(BH_4)_2$ is observed for temperatures above 120 °C.

The process of hydrogen desorption from manganese borohydride upon heating was monitored *in-situ* by X-ray absorption spectroscopy and X-ray powder diffraction. X-ray absorption spectra and diffraction patterns were obtained for different temperatures of the sample. XRD patterns indicate significant structural changes in the material when temperature exceeds 120 °C. The amorphisation process makes XRD patterns useless, so our further analysis is based on ab-initio DFT simulations and Mn K-edge XANES (X-ray Absorption Near Edge Structure) analysis. XANES spectra also undergo significant changes at temperature range from 120 °C to 160 °C [6]. TGA analysis reveals drastic weight reduction (up to 10 mas %) of $Mn(BH_4)_2$ upon heating at the same temperature range [3,4]. It was concluded that we have observed temperature induced phase transition which is accompanied by sample amorphisation process as well as abundant hydrogen release.

Table 1. Results of ab-initio calculations for structural models with different contents of hydrogen per unit cell $Mn(BH_4)_2$.

	Average Mn–B distance (Å)	Average Mn–Mn distance (Å)	Volume of unit cell (Å^3)
XRD data	**2,44** ± 0,02	**4,80** ± 0,01	**1021.8**
DFT. Model 1	**2,41** ± 0,01	**4,77** ± 0,01	**998.7**
DFT. Model 2	**2,11** ± 0,04	**3,64** ± 0,21	**474.9**
DFT. Model 3	**2,17** ± 0,05	**2,72** ± 0,18	**216.3**

The process of hydrogen desorption was studied by means of DFT simulations using VASP simulation package. We started from the crystalline structure described by Cerny et. al. [3], and allowed to relax the atomic positions and cell parameters for the structure with totally occupied hydrogen sites (model 1), totally unoccupied hydrogen sites (model 3) and structural model which was obtained by removing of 50 % hydrogen atoms from the unit cell (model 2) which are corresponds different state of the material: before and after hydrogen desorption process as well intermediate model respectively. The result of optimization for model 1 (Table 1) reproduce well the volume of unit cell and interatomic distance for the structure described at literature [3]. A significant reduced of Mn-B and especially Mn-Mn

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distance in result of optimization can be explained by dramatically reducing of cell volume from 998,8 Å^3 to 216,9 Å^3 after removal of hydrogen atoms from the structure of $Mn(BH_4)_2$. Results of DFT modeling reveals that the process of collapse of initial porous structure is accompanied by significant disorder in longe-range atomic structure (Figure 1).

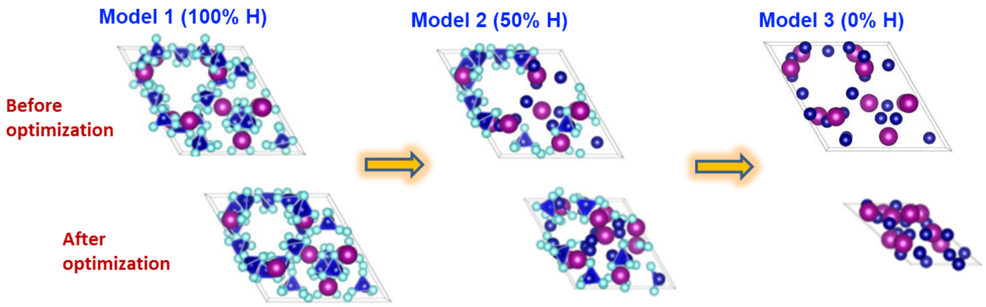

Figure 1. Visualization of results of geometry optimization for structural models with different contents of hydrogen atoms.

An accuracy of geometry optimization is approved by XANES Mn K-edge spectra calculated for relaxed structural models using optimized Finite Difference Method [7] and full potential approximation implemented in FDMNES package. Both a difference in the energy localization and ratio of intensity of main maximum (white line) for experimental spectra obtained at 30 °C and 140 °C are in a good agreement with XANES spectra calculated for models with totally occupied and totally unoccupied hydrogen positions. It is a good reason to confirm the correctness of the geometry optimization calculations. The associative between energy locations of peaks at absorption spectra (A-B, A*-B* at Figure 2) suggests that interatomic distance determined in result of geometry optimization is correct. It was claimed that the most probable of decomposition reactions products of $Mn(BH_4)_2$ are dense amorphous manganese borides (Mn_2B, MnB and MnB_4) with interatomic distance 2,17±0.05 Å and 2,72±0.18 Å for Mn-B and Mn-Mn respectively.

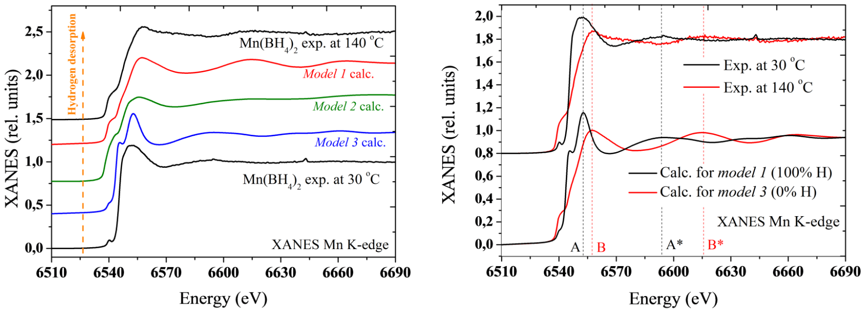

Figure 2. Evolution of theoretical Mn K-edge XANES spectra calculated for relaxed structural models (with different contents of hydrogen atom per cell) in comparison with experimental curves obtained at 30 °C and 140 °C.

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Core-Hole constraining approaches in the Density-Functional Theory simulation of Near-Edge X-Ray Absorption Fine-Structure (NEXAFS)

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NEXAFS allows to directly probe the electronic structure of a surface-adsorbate system by excitation of core electrons to unoccupied states. The simulation of experimental spectra is currently available on different levels of theory ranging from empirical fitting procedures (multiplett-calculations) over approximate ground-state Density-Functional Theory (DFT) based approaches up to the explicit treatment of excited states (either density-based (TD-DFT) or post-HF). Depending on the computational resources available and the size of the system studied, different approaches are employed. We are currently working on an ab-initio based methodology which permits to simulate NEXAFS for large systems using the all-electron DFT code FHI-aims [1]. In the current work we assess different core-level constraining strategies using a small library of organic gas-phase molecules in ground-state DFT by comparing the resulting excitation energies and intensities of the final spectra to experimental data in the K-edge region of light elements. The approximations employed encompass the Transition Potential (TP) [2], Excited Core-Hole (XCH) [3], Full Core-Hole (FCH), Transition State (TS) [4], Delta Self-Consistent-Field (DSCF), and calculations based on the ground state (GS).

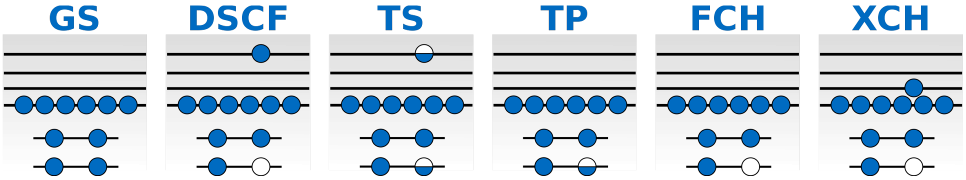

Figure 1. Pictorial representation of evaluated core-hole constraining approximations

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Angular Dependence of Plasmon Loss in core-level photoemission with Multiple Scattering Theory

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We have theoretically studied the polar and azimuthal angular dependence of surface and bulk plasmon losses in Al 2s photoemission spectra. Plasmon losses observed in XPS spectra are classified into two types: intrinsic loss (shake-up in the excitation process) and extrinsic loss (inelastic scatterings during the photoelectron propagation). These two losses can interfere each other and total plasmon loss appears as the sum of Intrinsic, extrinsic and interference. These plasmon losses have angular dependence; azimuthal scan reflect the crystal structure [1] and polar angle of the detector have an influence on surface and bulk plasmon loss intensities [2].

To elucidate the polar and azimuthal dependence, we use the quantum Landau formula for 1st plasmon loss intensity [3]. Here, full multiple scatterings of photoelectrons are taken into account before and after plasmon losses. In this formula, the geometrical effects of crystal can be taken into account.

Figure 1 (a) shows the schematic view of the set up. The incident X-rays are linearly polarized, whose electron vector is normal to the surface. Photon energy is 307 eV. Figure 1 (b) shows the azimuthal scan of plasmon loss detected at polar angle θ = 45° and (b) shows the polar scan of plasmon loss at azimuthal angle ϕ =0°. The diffraction patterns appeared with elastic scattering, which doesn't appear without elastic scattering. Diffraction pattern reflects local geometry of the models. Moreover, the features of intrinsic and extrinsic are similar in azimuthal scan on the other hand are different in polar scan. We will show more detailed discussion for angular dependence of each plasmon losses with depth analysis in the presentation.

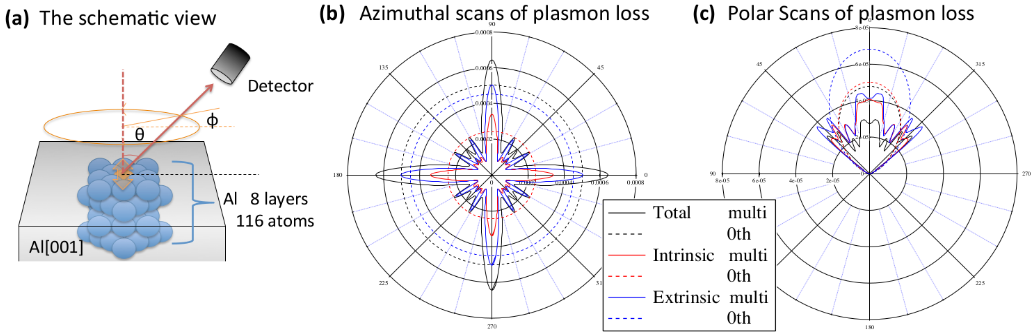
(a) The schematic view **(b)** Azimuthal scans of plasmon loss **(c)** Polar Scans of plasmon loss

Figure 1. (a) The schematic view of the calculation setup. **(b-c)** Azimuthal scans at theta = 45 (b) and polar scans at phi = 0 (c) of Al 2s photoemission from Al (001) single crystal calculated by quantum Landau formula with and without multiple scatterings (mult and 0th). The incident photon energy is 307 eV.

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X-ray magnetic circular dichroism study of rare-earth $M_{4,5}$ and transition metal $L_{2,3}$ absorption edges in $Nd_2Fe_{15}B$ permanent magnets

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Rare earth permanent magnets (REPM) provide the highest energy product 50MGOe at room temperature, but recently dramatic increase in prices for RE metals has occurred. In the process of development of rare earth lean REPM, we investigated a highly textured $Nd_2Fe_{15}B$ (350nm) reference sample grown on Cr (1100 nm) [1] buffer layer. We used the element specific X-ray magnetic circular dichroism (XMCD), in order to investigate quantitatively the sub lattice magnetization of every single element, their interplay and influence on the magnetic properties.

We performed angular dependent XMCD measurements at the Fe $L_{2,3}$ and for the first time at the Nd $M_{4,5}$ edges (Figure 1a and b) to investigate the role of Fe and Nd in the hard magnetic system. Furthermore, we determined element specific magnetic hysteresis loops for in-plane (Figure 1d) and out-of-plane (Figure 1c) geometry, measuring the field dependent scaling of the XMCD effect at the Nd M_4 and the Fe L_3 edge respectively. The respective magnetization curves qualitatively reproduce the corresponding SQUID measurement results, showing that the magnetization reversal is the same for both elements and related to irreversible single grain switching. Using sum rule analysis we determined the spin (m_s) and orbital (m_l) magnetic moments of Fe and Nd. The XMCD related Fe and Nd spin magnetic moments are reduced by a factor of two compared to theoretical calculations and neutron diffraction data [2,3].

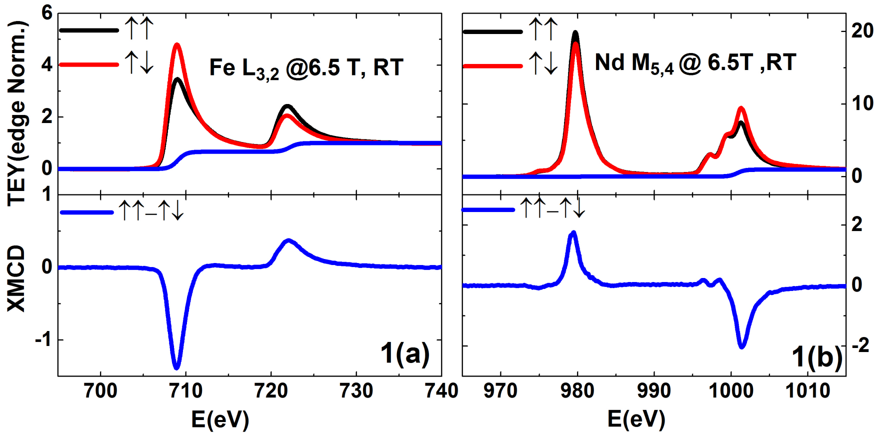

Figure 1. (a) XAS and XMCD spectra of Fe $L_{3,2}$ edge at 300 K (out of plane), (b) Nd $M_{4,5}$ edge at 300 K (out of plane).

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The most remarkable observation is related to a nearly vanishing orbital moment at the Nd site, which is about one order of magnitude less than expected from Hund's rules. As XMCD only sees rotatable magnetic moments, our results suggest strong pinning of RE orbital moments, even under magnetization reversal conditions.

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Charge transfer multiplet analysis of CoF_2, $CoCl_2$, $CoBr_2$ and CoS_x 2p3d RIXS spectra

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Charge transfer is an important effect in 3d transition metal oxides, related to Mott-insulator systems [1]. The electrons are redistributed from their atomic states to hybridization states. This implies that the system can be switched from an insulator to a metal by the combination of the Hubbard energy (U) and charge transfer energy (Δ). The charge transfer scheme gives rise to two specific set of features: First, ligand hybridization between metal t_{2g} and e_g are influenced differently. More generally, all dd-excitation energies in the Tanabe-Sugano diagram are shifted differently, depending on their specific couplings. The second feature are the bonding and anti-bonding states between original ground state $|d^n>$ and ligand hole states $|d^{n+1}L>$, $Id^{n+2}L^2>$[2, 3].

In the poster, we provide high resolution resonant inelastic X-ray scattering (RIXS) results of CoF_2, $CoCl_2$, $CoBr_2$ and CoS_x. 2p3d RIXS is a good candidate to investigate the charge transfer effect. Because it is a state-sensitive measurement, it can distinguish excitation states with variable exciting energy and separate the anti-bonding charge transfer excitations from dd excitations [2,3]. We compare the RIXS data with charge transfer multiplet (CTM) calculations of Co^{2+} with different charge transfer energies (Δ). The experimental results show that $^4T_2$ excitation energy is increasing in energy with increasing Δ. We correct the ionic crystal field energy (10Dq) with respect to Δ by calculating a linear relation function. The anti-bonding states of the charge transfer hybridization present a big hump in the experiment result that are reproduced well by the CTM calculations. Fig. 1 shows L edge absorption of the charge transfer multiplet calculation results and total electron yield measurement results. The RIXS experiments are measured at the incident photon energy from A to G, as indicated in Fig. 1. In CoS_x, the states are much closer to each other. So we find that peak B and C are merged together in the experimental spectra. We calculate the RIXS spectrum with the same parameters as the X-ray absorption calculation and compare them in the Figure 2. The excitation energy of $^4T_2$ state should be pretty accurate. However, the relative intensity are not reproduce at different excitation energies. In Fig 2(b), we also observe a big hump with low intensity shifting with Δ. In first approximation, in the spectra in CoF_2, the anti-bonding state is almost out of the scheme and weak, implying that in CoF_2 we can consider Co^{2+} without CT effect. In contrast, the anti-bonding states strong mix with the bonding states in the CoS_x compound.

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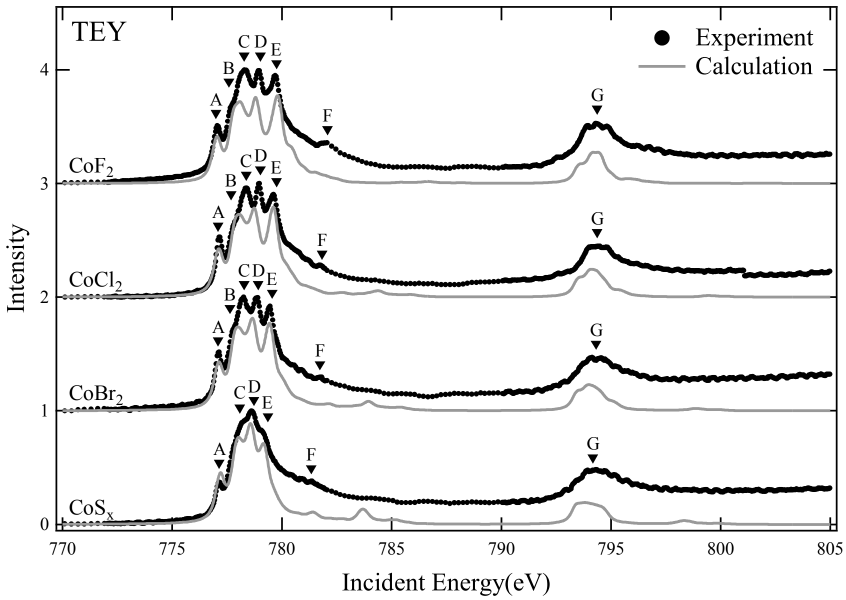

Figure 1. Total electron yield (TEY) 2p XAS spectra (black dot) and the charge transfer multiplet calculations (gray line) of CoF_2, $CoCl_2$, $CoBr_2$, and CoS_x (from top to bottom).

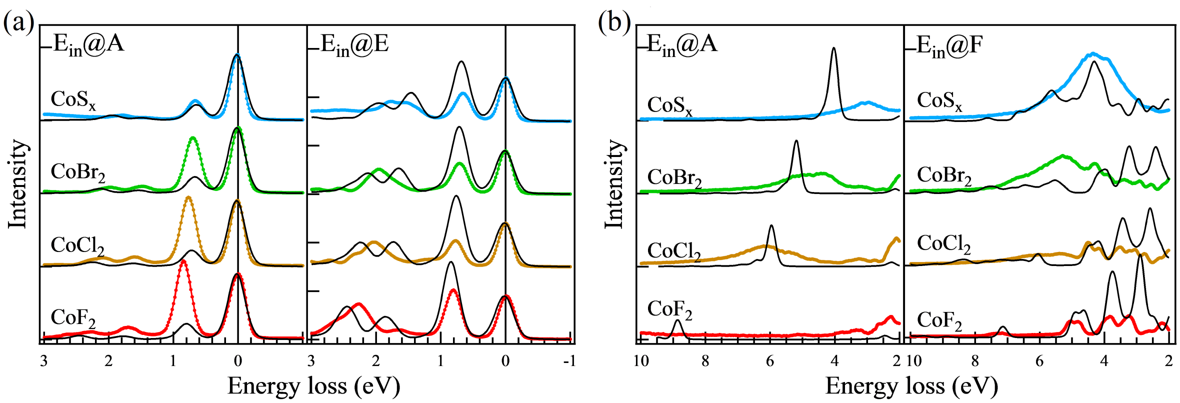

Figure 2. The comparison between different compounds. (a) RIXS spectrum in the region $E_{loss} < 3eV$ with exciting energy at A and E. (b) RIXS spectrum in the region $E_{loss} > 2eV$ with exciting energy at A and F. Note here, we times a factor 3 on the spectrum in (b) with E_{in}=A.

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Carbon dioxide reduction on Ir(111): stable hydrocarbon surface species at near-ambient pressure

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The catalytic reduction of carbon dioxide to generate useful chemicals, as methanol and formic acid, represents an interesting route to recycle this waste gas [1-3]. Many approaches have been investigated, involving electro-catalytic systems, solar energy harvesting devices, and homo- and hetero-geneous catalysis [2,4].

In particular, Ir demonstrated interesting properties in homogeneous catalysis [3]. However, detailed, atomic-level knowledge about the interaction of CO_2 with Ir is almost not available due to the low interaction energy of the molecule with the metal [5], and insight at reactions conditions close to ambient pressure are still lacking due to the well-known instrumental pressure gap.

In this work, a joint Near Ambient Pressure (NAP)-XPS and Infrared-Visible Sum Frequency Generation non linear optical spectroscopy (IR-VIS SFG) investigation was performed in order to shed light on the catalytic behavior of iridium towards CO_2 reduction at NAP conditions. An Ir(111) surface was exposed to 0.1 mbar of CO, CO_2 and H_2 mixtures, varying the partial pressures and the surface temperature (from 300 K to 600 K).

The acquisition of photoelectronic and vibrational spectra allowed the characterization of stable adsorbed intermediates: as in the thermal decomposition of ethylene, $CHCH_3$, CCH_3, and CCH species were identified, appearing in specific temperature ranges and favored by higher partial pressures of CO_2. Both photoelectronic and vibrational information suggest the presence on the surface of aromatic rings and strongly interacting graphenic domains up to 600 K, as pointed out by characteristic frequencies and binding energies.

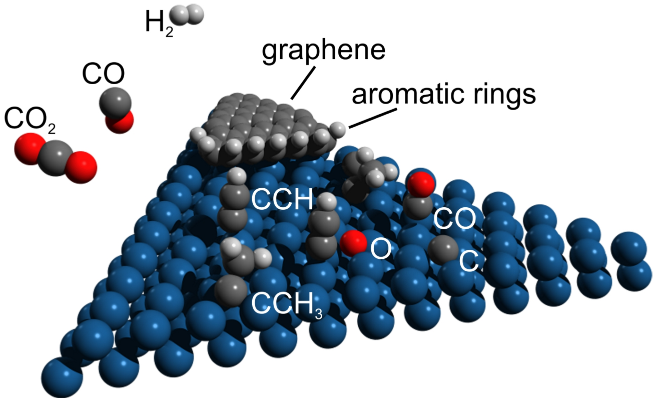

Figure 1. Cartoon summary of the stable adsorbed species identified at the Ir(111) surface upon hydrogenation of CO and CO_2 at NAP conditions.

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Similarities between the UHV thermal decomposition of C_2H_4 and the CO_2 reduction in the NAP regime have been found and will be discussed.

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Defects in epitaxial graphene on Ni(111): first-principles atomistic simulations

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The analysis of unprecedented high-resolution scanning tunneling microscopy (STM) images of graphene/Ni(111) obtained at the TASC laboratory of CNR-IOM [1] shows the occurrence of different domains [2] with several types of defects [3,4], manly due to carbon vacancies and partially filled with trapped Ni adatoms. We have proposed some structural models and verified their reliability on the basis of the energetics and the comparison between observed and simulated STM images, obtained from ab-initio density functional theory calculations. In particular, we have studied in details a triple-vacancy defect with one Ni atom trapped inside, that shows a peculiar dynamical behavior in the interaction with carbon monoxide. We have investigated and characterized also other defects, even more extended, extracting some general trend to predict their stability and their abundance. Preliminary results concerning their activity under the exposure of small molecules of environmental importance have been also obtained [3,4].

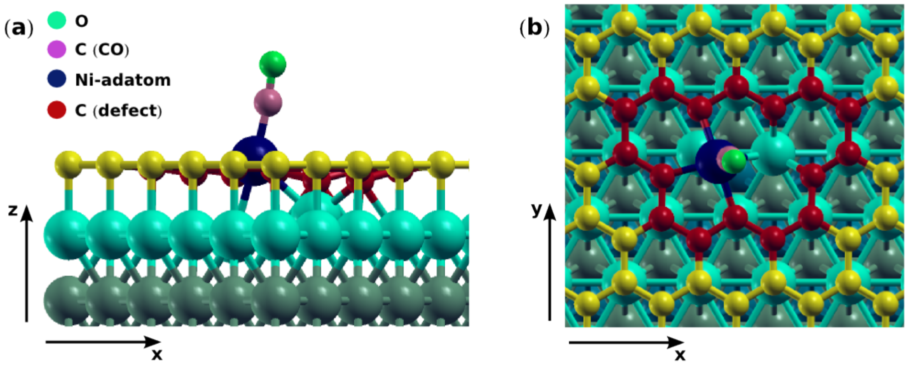

Figure 1. (a) Top and **(b)** side view of triple vacancy with CO adsorbed on nickel adatom trapped inside the defect. Only the carbon atoms of the defect, CO, nickel adatom and the nickel atoms just below the defect are relaxed.

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Metallic nanoclusters on supported graphene: insights from ab-initio calculations

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For most practical applications, metal nanoparticles (NPs) need to be supported on a substrate that can act as a deposition template for growing them in regular arrays. This prevents sintering at high temperatures, a process that would deactivate the catalytic devices. The Moire' pattern due to the small lattice mismatch between graphene and Ir(111) support works as an efficient template for the ordered growth of some transition metal NPs [1,2]. With the help of ab-initio calculations performed for adsorption of monomers and small clusters of Cu, Pt, and Ir, we explain the behavior of different metals, predicting results in agreement with the available experimental findings and identifying the criteria for the suitability of a metal to form ordered nanocluster arrays. Moreover, preliminary results indicate that even materials that do not form cluster superlattices can be grown through the application of cluster seeding using properly chosen metals (see Figure 1) [3].

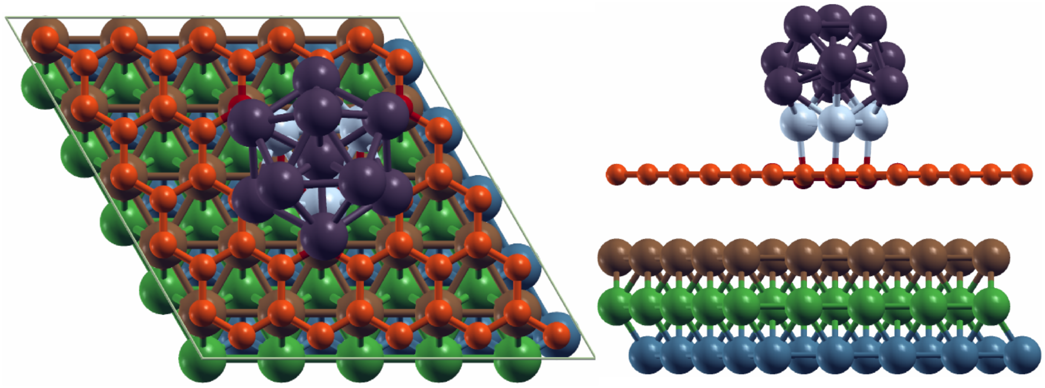

Figure 1. Stick-and-ball model for $Cu_{10}Ir_3$ nanocluster adsorbed in the hcp region on graphene/Ir(111).

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2p3d RIXS probe of Co^{II} Polyoxometalates ground state electronic structure

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Cobalt ions, in Co-based polyoxometalates (POMs), have been demonstrated to be the catalytic active center for water oxidation, however, this only limits to POMs with multiple Co sites within a single molecule structure. Prior x-ray studies , like L edge x-ray absorption spectra (XAS), of homogeneous Co POMs system only showed limited ground state information of Co which could be hardly used for understanding the difference of catalytic activities. In this work, high energy resolution (< 100 meV) 2p3d resonant inelastic x-ray scattering results allows the visit of ground state electronic structure of Co^{II} tetrahedral (Td) site in $K_5H[Co^{II}W_{12}O_{40}]\cdot 15H_2O$ POM.

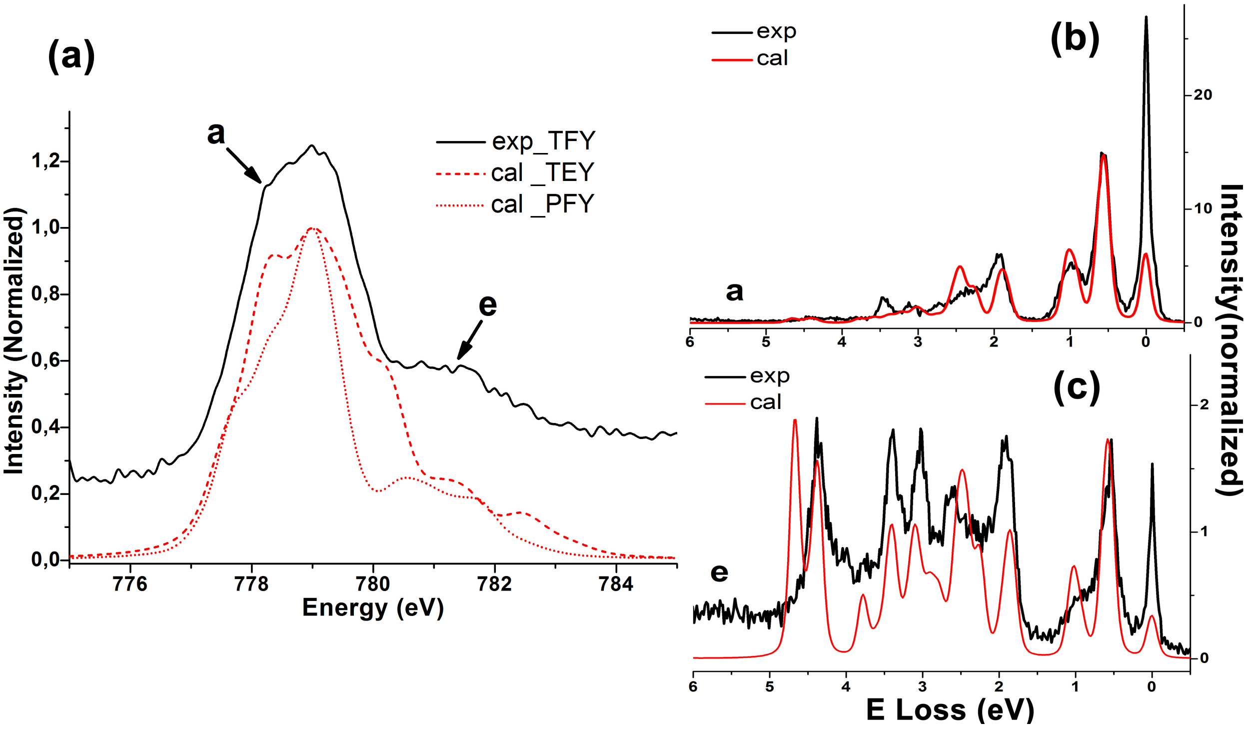

Figure 1. (a) Experiment (exp) and the multiplet calculation simulated (cal) Co^{II} Td L_3 edge XAS; (b) 2p3d RIXS at excitation energy a in XAS result; (c) 2p3d RIXS at excitation energy e.

The experimental L_3 edge XAS and selected 2p3d RIXS results excited at energy a and e in XAS are shown in Figure 1. Simulation by multiplet calculation using Cowan's code are also shown as a comparison of

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experimental data. For XAS simulation, both total electron yield (TEY) and 2p3d partial fluorescence yield results were simulated to compare the measured total fluorescence yield (TFY) results. From the simulation of 2p3d RIXS results, the crystal field parameters, electron-electron interaction, electron-core hole interaction strength, and structure distortions are obtained with relatively high accuracy. By the projection calculation, the electron configuration of each states are also obtained, which could be used to better understand the ground state information of this Td Co^{II} sites. More 2p3d RIXS results on similar POMs samples with detailed calculation results will be shown on the poster presentation during the winter school.

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Posters

The calculation of plasmon losses in core-level photoemission spectra from hcp metal

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In core-level photoemission spectra for metals, plasmon loss peaks appear in addition to main peak. The plasmon loss occurs in two processes, intrinsic loss (shake-up) and extrinsic loss (inelastic scatterings during photoelectron travel in the solids). It’s not possible to separate these two processes. These two losses can interfere with each other. Therefore, total intensity of the plasmon loss peak is sum of intrinsic, extrinsic and interference terms. Additionally, the plasmon loss in photoemission is influenced by the elastic scattering, and it is necessary to take into account the effect to analyze the experimental data in detail [1].

A practical formula of plasmon loss peaks is the quantum Landau formula originally derived by Hedin *et al.* [2]. Fujikawa *et al.* added the multiple scattering effect before and after the plasmon loss to this formula [3]. In previous studies, fcc and bcc metals single plasmon loss spectra were calculated by this formula [4,5]. In this work, we applied this formula to hcp metal, and calculated its plasmon loss spectra.

This paper shows the plasmon loss of photoemission from Be 1s core level. Figure 1 shows the schematic view of the calculation setup. The incident light is linearly polarized, and the electric vector tilts 10° from the surface normal. Photon energy is 260eV, and the direction of detector is the surface normal. We use the cylinder model including 52 atoms (eight layers).

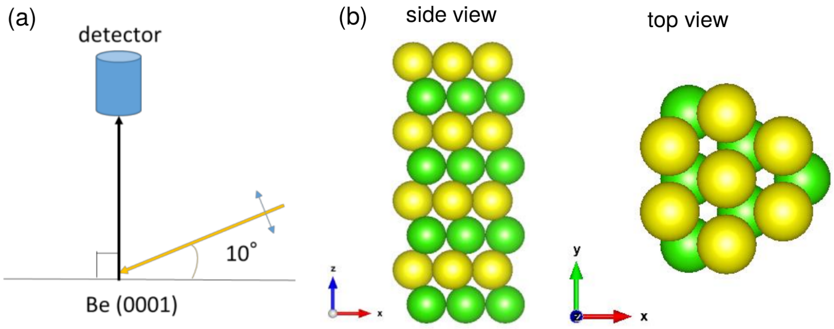

Figure 1. (a,b) The schematic view of the calculation setup.

In Figure 2, we show the calculated beryllium (Be) 1s single plasmon loss spectra with and without full multiple scatterings. The bulk and surface plasmon energy are 19eV and 15eV respectively. Figure 2 shows elastic scattering reduces the plasmon loss intensity, and the bulk plasmon loss intensity decreases more than the surface plasmon loss intensity.

Figure 3 shows the depth profiles of the Be 1s single plasmon loss intensity with and without elastic scattering. Without elastic scattering, the total intensity smoothly reduces with increasing $|Z_A|$ (Z_A is depth from the surface).

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On the other hand, 'Total' in Figure 3(a) shows the elastic scattering causes two features. First, compared to the result without elastic scattering, the intensity increases at Z_A=-4.725Å (third layer). That's because photoelectrons emitted from third layer atom are strongly scattered in the forward direction (forward focusing effect). Second, multiple scattering causes the intensities decay in deep region, and this behavior can be due to defocusing effect. That's why the intensities from deep layers decrease.

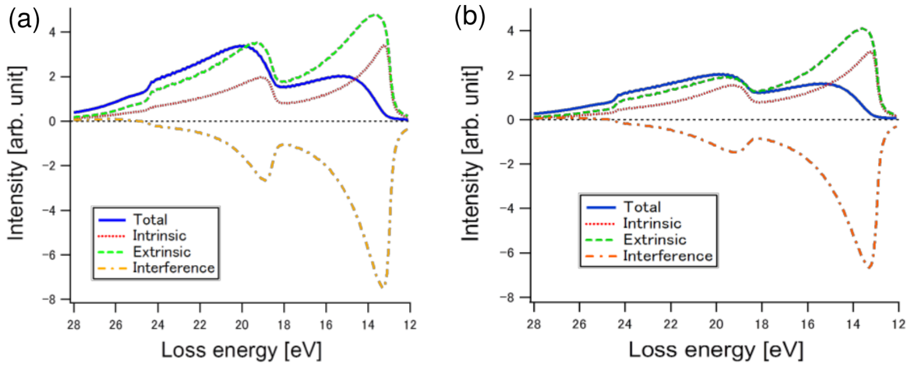

Figure 2. The calculated Be 1s single plasmon loss spectra (a) without and (b) with multiple scattering. The kinetic energy of photoelectron is from 115eV to 131eV.

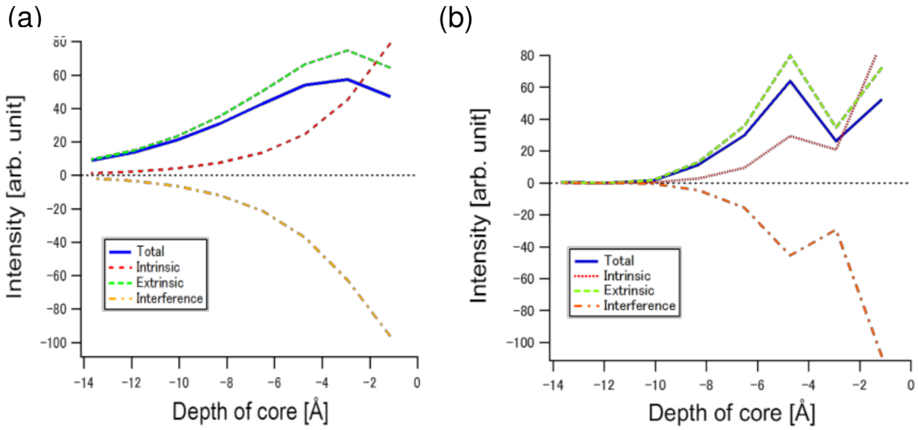

Figure 3. The depth profile of integrated surface and bulk single plasmon loss intensities of Be 1s (a) without and (b) with multiple scattering.

In this work, we have calculated the Be 1s single plasmon loss spectra by using the quantum Landau formula including multiple scattering. We got similar results to the cases of bcc and fcc metals. Compared to the case without elastic scattering, the multiple scattering reduces the plasmon loss intensity. On the other hand, when the multiple scattering is considered, the depth profiles show the contribution of photoelectron emitted from near surface increases because of the focusing effect, and from deeper region decreases because of the defocusing effect. Therefore, elastic scattering is the important effect on the loss spectra.

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STM simulation for COonCO layer/Cu(111)

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CO adsorption on Cu(111) surface has been observed using STM and studied within first principle density functional theory (DFT). In Chiba Univ., the same system has been observed using STM at low temperature, and high density (1.5×1.5) STM image has been obtained. Then, 2nd CO layer is build on 1st CO layer and the spot that seems to be 2nd layer CO molecule's one appeared in the STM image. The purpose of this research is to define the cause of the spot and to examine that CO-CO interaction.

The calculation is done with Vienna Ab-initio Simulation Package (VASP). In VASP, STM simulation is based on Tersoff-Hamann method [1].

According to the structural optimization with 1st and 2nd CO layer, the hollow site is stable at 2nd CO layer with lying CO molecule (Figure 1). However the energy barrier between each site is not enough in the calculation and the reaction time is too short to obtain the STM image of 2nd CO layer. The STM simulation with in 1st CO layer on Cu(111) shows periodic isosurface (Figure 2). Then, within 2nd layer, we will calculate the local DOS and compare with the STS result.

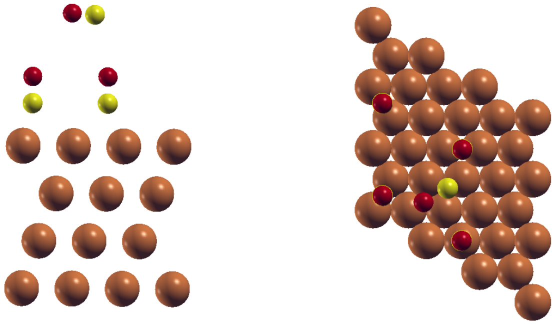

Figure 1: simulation image: 2nd CO layer on 1st CO layer / Cu(111).

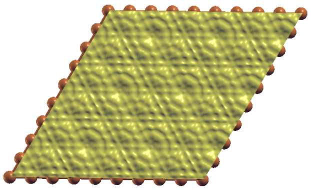

Figure 2: STM simulation of (1.5×1.5) monolayer CO/Cu(111). The position of CO molecules appear as hollows in the picture.

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Explicit Solvent Effect as a Parameter influencing the Electronic Transitions of the Novel Molecular Switches

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Molecular switches present a novel group of machines that can be controlled at the molecular level by light, pH or electric current. This type of materials has been extensively studied for the past two decades [1]. To be considered as a possible molecular switch, molecule has to exist in at least two isomers that can be reversely isomerised by the parameters mentioned above. Light-responsive materials have a leading role among the molecular switches because the control by light does not require any direct contact with material and it is based only on the quick change during the interaction of light with material. *N*'-[1-(2-hydroxyphenil) ethyliden]isonicotiloylhydrazide (HAPI) is a molecule previously investigated as a possible molecular switch that can be controlled by the metal ions present in the solution [1,2]. It exists in two stable forms, *E*- and *Z*- isomer that undergo the isomerization upon the UVA radiation. In this contribution, the theoretical analysis of the explicit solvent effect of water molecules on the electronic transitions of HAPI is explored, with the special emphasis on the reproduction of experimental UV-VIS spectra.

In order to investigate the explicit solvent effect five molecules of water (5W) and 1 molecule of water (four 1W) were added around the *E*-isomer of HAPI. The deprotonated form of E-isomer was taken in consideration because HAPI was deprotonated at the experimental pH. All of the structures were optimized at cam-B3LYP/cc-PVTZ level [3,4] using the Gaussian 09 program package [5]. Energy of electronic transitions was calculated by the TD-DFT method. Based on the NBO analysis [6] atoms that are the most affected by solvent were identified. These include phenolate O, carboxyl O and N-N groups. In the starting structure the molecules of water were placed close to the selected groups. Figure 1 shows the optimized structure with five molecules of water.

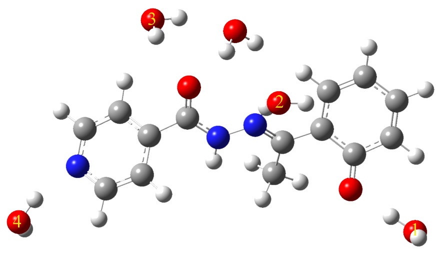

Figure 1. HAPI with five molecules of water

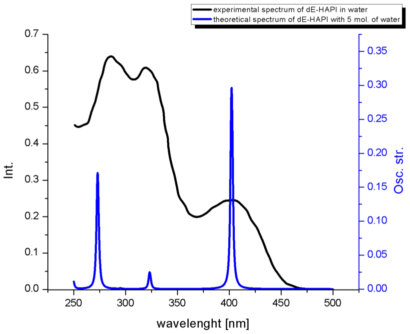

Figure 2. Comparison of experimental and theoretical spectra

When the electronic transitions were calculated for this structure, very good agreement with theoretical values was obtained. Model with five molecules of water proves the significance of the hydrogen bonds between HAPI and solvent. These spectra are shown in Figure 2. Because of this good reproduction, the theoretical spectrum

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was taken for the future comparisons. Four structures with one molecule of water were prepared based on the optimized structure from Figure 1 by removing the rest of molecules. These water molecules are marked with numbers 1-4, except the one without number because that structure lead to the same structure as 3. Figure 3 shows the calculated electronic spectra for the structures with one molecule of water.

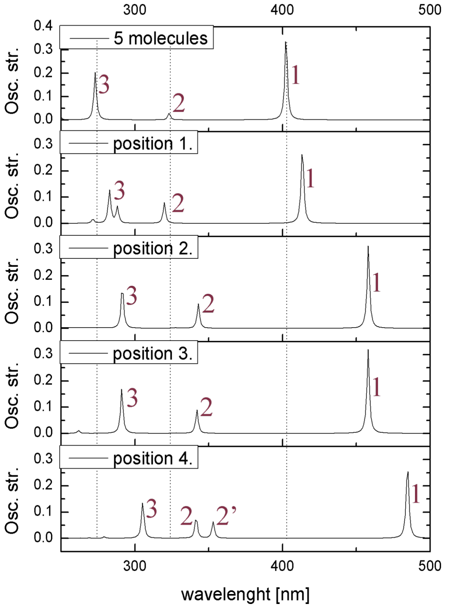

Figure 3. Electronic spectra for structures with positions of water molecules 1-4.

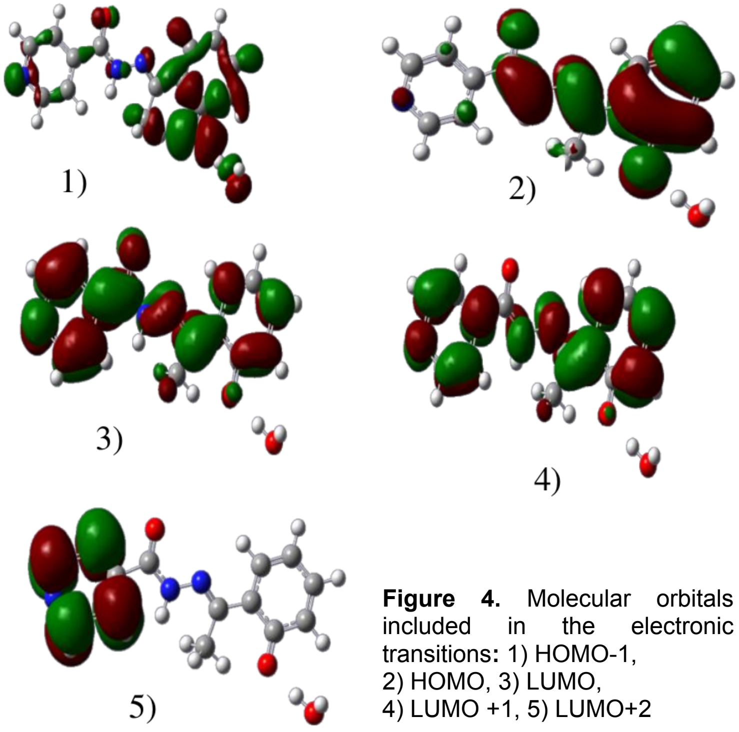

Figure 4. Molecular orbitals included in the electronic transitions**:** 1) HOMO-1, 2) HOMO, 3) LUMO, 4) LUMO +1, 5) LUMO+2

The following transitions are responsible for the peaks marked in Figure 3: **1** HOMO→LUMO, **2** HOMO→LUMO+2, **2'** HOMO-2→LUMO and **3** HOMO→LUMO+1. The best agreement with the first spectrum is for the geometry where the water molecule is placed close to the phenolate O. The reproduction lowers in the order: 2≈3<4. The analysis of electronic density gives possible explanation for these results. The electronic density in HOMO orbital is localized on phenolate ring and hydrogen bond additionally stabilizes this part of molecule, so the distance between water molecule and phenolate ring influences the energy of transition. The localized electronic density is important for the possible bond formation with solvent molecules. The explicit solvent effect for the reproduction of experimental spectra is clearly shown in this comparison and gives the possible route for the theoretical description of the solvent effect for the molecular switches of interest.

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Atomic and electronic structure of colloidal quantum dots: XANES investigation and computer modeling

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X-ray absorption near-edge structure (XANES) spectroscopy is a modern powerful tool allowing investigation of local atomic and electronic structure of materials without long-range distribution in atomic arraignment. In the present study XANES spectroscopy coupled with computer modeling based on density functional theory (DFT) was used to investigate colloidal quantum dots (QDs) of CdS, CdTe, CdSe and ZnS families.

QDs are among promising materials of modern nanotechnologies. They can be used as sensor elements for environment protection, in new generation LED displays, as elements of bio-medical diagnostics [1]. The colloidal QDs based on CdS, CdTe, CdSe, ZnS and those doped by atoms of transition (Co, Mn) and rare-earth (Eu, Gd) elements have been studied. QDs based on CdS, ZnS, ZnS:Mn nanoparticles have been synthesized by microwave method and characterized by the set of techniques such as X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy.

Ab initio computer modeling of QDs of CdS, CdTe, CdSe, ZnS families has been done within DFT using ADF and VASP5.3 codes. The parameters of atomic structure of QD of different sizes have been analyzed. The influence of doping atoms (Mn, Co, Eu, Gd) on structure of QDs has been estimated.

For verification of structural parameters obtained by computer simulations it is desirable to attract experimental techniques. XANES spectroscopy is an appropriate method which allows extracting 3D atomic structure around absorbing type of atoms of nanomaterials. The Cd *K*-XANES in CdS, CdTe, CdSe, Zn *K*-XANES in ZnS, Co *K*-XANES in CdS:Co, CdTe:Co, CdSe:Co, ZnS:Co, Mn *K*-XANES in CdTe:Mn, CdSe:Mn, ZnS:Mn, Eu *K*-, L_1-, L_3-XANES in CdTe:Eu, Gd *K*-, L_1-, L_3-XANES in CdTe:Gd were calculated for initial and optimized structures of nanoparticles. The XANES spectra were calculated on the basis of full multiple scattering theory implemented in FEFF9.6.4 code and full-potential finite difference method realized in FDMNES program. It was shown that XANES spectroscopy is sensitive to small changes in atomic structure of QDs (Figures 1, 2). So, XANES spectroscopy can be used as nondestructive technique for verification of parameters of nanoscale atomic structure of QDs of CdS, CdSe, CdTe, ZnS families [2-4]. It has been shown that measurements of HERFD XANES are preferable to extract structural parameters of investigated QDs [5].

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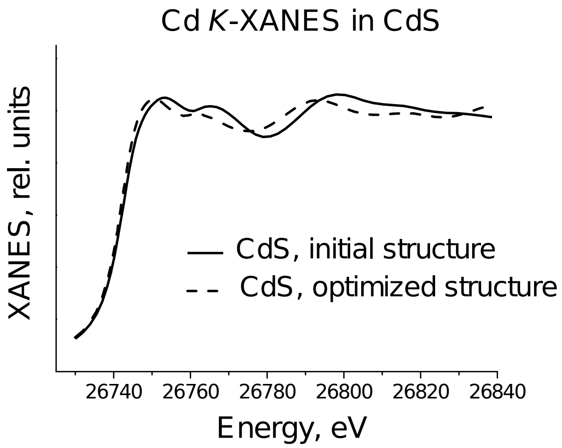

Figure 1. Theoretical Cd *K*-XANES of CdS nanoparticle (174 atoms) [2]. Solid line corresponds to initial structure of the nanoparticle, dashed line – to the structure optimized using VASP5.3 code.

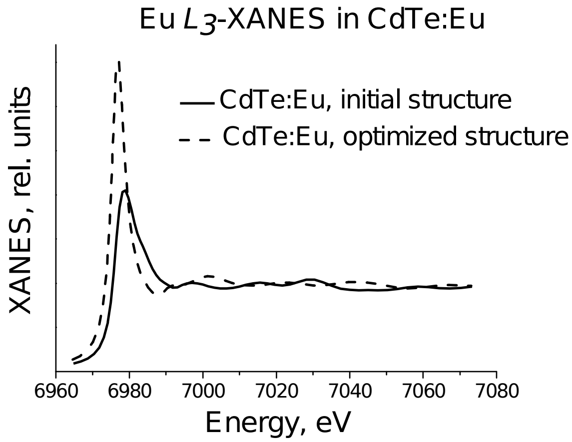

Figure 2. Theoretical Cd *K*-XANES of CdS nanoparticle (123 atoms) [4]. Solid line corresponds to initial structure of the nanoparticle, dashed line – to the structure optimized using ADF code.

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Ab-initio modeling of peroxy bridge defect in amorphous silica

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A major motivation for study of point defects in silica is their role in the degradation of SiO_2 based optoelectronic devices. One of the primary steps for understanding and controlling degradation processes is the one-to-one assignment between defect structure at the atomic scale and experimental signature (optical absorption bands, Electron Paramagnetic Resonance - EPR, Fermi contact/g-tensor, Photoluminescence bands, etc). Experimentally, bi-univocal assignments are not straightforward. Indeed, correlations have to be found between the results of different complementary spectroscopic techniques, such as Optical Absorption (OA), Photo-Luminescence spectra (PL) or (EPR combined with various treatments like irradiation, temperature, etc. Moreover, the sample itself contains always many different defects and impurities that make hard to detect and identify “single signals” against the background of other signals. In this context, ab-initio modelling plays a crucial role for calculating basic properties of defects [1].

Among other defects, the identification of the optical signature of Peroxy Linkage (POL) is still under debate. Experiments report values between 3.8 eV [3] and 7 eV [4,5], while modelling, through mean-field theories, suggest absorption around 6 eV [2]. In this work, electronic and optical properties have been modelled through what is nowadays considered the state-of-the-art approach, i.e. Density functional theory, GW approximation and solution of the Bethe-Salpeter equation. The DFT method provides good ground state configuration, GW approximation provides the quasi-particle band structure (N+1 and N-1 electronic excitations of the N electron gas), by properly including exchange and correlation effects. The Bethe-Salpeter Equation (BSE) takes into account electron-hole interactions through the diagonalization of an effective two-particle Hamiltonian (neutral excitations of the N electron gas) that contains parameter-free exchange and screening effects between holes and electrons. This study shows presence of three bands assigned to POL. Very low calculated values of oscillator strengths indicates very low probability to experimentally detect POL induced transitions.

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DFT study of adsorption of azoles on oxidized copper surfaces

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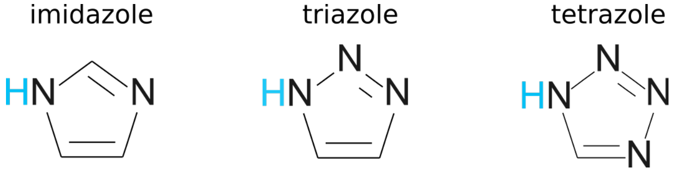
Azoles and their derivatives are among efficient organic corrosion inhibitors for copper [1]. In order to explain the adsorption of azoles on oxidized copper surfaces, we have studied by means of density functional theory (DFT) modeling the interaction of imidazole, triazole, and tetrazole with Cu_2O surfaces.



Scheme 1. Skeletal formulae of imidazole, triazole, and tetrazole.

Surfaces were modeled by periodic slab model composed of several atomic layers. Calculations were performed with the PWscf code from the Quantum ESPRESSO distribution [2], using plane-wave basis set with ultra soft pseudopotentials and PBE functional [3]. The most stable Cu_2O surfaces are $Cu_2O(111)$-w/o-CUS and $Cu_2O(110)$:CuO, both of which are non-stoichiometric, while stoichiometric $Cu_2O(111)$ surface is less stable [4]. The latter surface contains two distinct copper sites, coordinatively saturated (CSA) and unsaturated (CUS) (see the Fig. 1a), whereas $Cu_2O(111)$-w/o-CUS lacks the CUS sites.

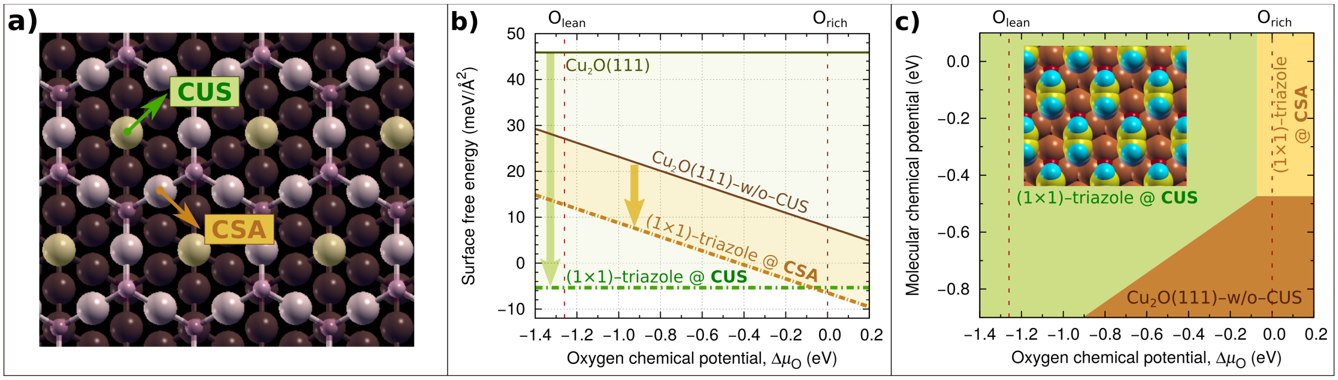


Figure 1. a) Structure of $Cu_2O(111)$ surface with indicated coordinatively saturated (CSA) and unsaturated (CUS) sites. b) Surface free energy as a function of oxygen chemical potential and its stabilization due to molecular adsorption at CSA and CUS sites. c) Phase diagram for adsorption of triazole on considered Cu_2O surfaces.

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Results show that all three azoles bind weakly to CSA sites of Cu_2O(111)-w/o-CUS with the adsorption energy of about −0.5 eV, whereas they adsorb considerably stronger to CUS sites of Cu_2O(111) with the adsorption energy of about −1.7 eV. Calculated values imply that bonding to CUS sites is so strong that it compensates the thermodynamic deficiency of stoichiometric Cu_2O(111) thus making it more stable than non-stoichiometric Cu_2O(111)-w/o-CUS (see the Fig. 1b,c). Phase diagram for triazole (Fig. 1c) on considered Cu_2O surfaces reveals that adsorption at CUS sites (green region) prevails over the adsorption at CSA sites (yellow region). From current results it can be suggested that the corrosion inhibition capability of azoles stems from their ability to passivate the reactive surface sites [5].

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CITIUS: A novel instrument for time-resolved photoemission experiments

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CITIUS (Interregional Centre of Ultrafast Photonic Technology for Spectroscopies) is an innovative facility for time resolved spectroscopies in the femtosecond time domain, founded by the “Italian-Slovenian Cross-border Cooperation Program 2007-2013”.

The light source generates photons in the spectral range from 15 to 70 eV, starting from a high power ultrafast Ti:Sapphire laser system, at 5 kHz repetition rate, via an HHG (High order Harmonic Generation) process in a cell filled with noble gas.

Such harmonics are monochromatized by a novel kind of monochromator, which can work in two different configurations: “time preserving” and “energy preserving”. The first exploits a set of 3 conical gratings to cover the operating spectral range optimizing flux and preserving pulse duration. The second configuration is based on a set of 3 classical gratings. The flexibility of the monochromator makes the CITIUS light source suitable for a wide class of pump-probe experiments [1,2].

The light source also offers the possibility of spanning the spectral region from 200 nm to 2600 nm with an OPA (Optical Parametric Amplifier).

The experimental endstation for time resolved photoemission experiments consists of 2 experimental chambers of which one is equipped with a state of the art angle resolved time of flight electron analyzer from VG-Scienta and a closed circuit liquid He cryogenic manipulator from Prevac. The other is a conventional system for X ray photoemission spectroscopy (XPS) based on a monochromatized Al K alpha source and a hemispherical electrons’ spectrometer.

Time resolved experiments are performed in order to investigate events occurring at a very short temporal scale of femto and picoseconds. In this temporal scale one can observe processes such as electronic transitions, chemical reactions etc. In order to measure such dynamic events use is made of the “pump probe” technique. This technique requires two ultra short pulses with a tunable delay. The “pump” pulse is used to trigger the desired transition, reaction, etc., by exciting the system into an out of equilibrium state. The second pulse “probes” the properties of the system after a certain delay. By performing a sequence of measurements at

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different delays one can obtain the dynamics of the relaxation process of the investigated system. The ongoing studies are focused on the interface between octaethyl (Cu) porphyrin and Au (111) surface.

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Optical and electronic structure properties of Eu^{2+} doped CaO and SrO phosphors

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Eu^{2+} ion is an especially important activator for red phosphors which has been extensively studied for years [1,2], because the visible emission of Eu^{2+} ion in 4f shell is insensitive to the influence of the surroundings due to the shielding effect of 5s, 5p electrons [3]. Recently, J. Fu et al. [4] examine the suitability of CaO:Eu^{2+} and SrO:Eu^{2+} as red luminescent materials.

Using density functional theory (DFT) within the using the GGA+U form we investigated the structural, electronic and optical properties of CaO:Eu^{2+} and SrO:Eu^{2+}. The total energy has been optimized as a function of the unit cell volume. All other parameters like the density of state (DOS), the band structure and the linear optical susceptibility are calculated for the relaxed structure applying the optimized lattice constant. It will be shown that for the calculation of optical properties, which are closely related to the corresponding electronic structure our results are an essential precondition.

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A detailed view on the effect of the spin-orbit coupling on the magnetocrystalline anisotropy: case study of FePt

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To obtain magnetocrystalline anisotropy (MCA) energy via ab-initio calculations, the spinorbit coupling (SOC) has to be accounted for. This can be done either fully by solving the relativistic Dirac equation or pertubatively via the second variation approach. To assess whether employing one or the other method has got a significant impact on the calculated magnetocrystalline anisotropy is not trivial: different ways of dealing with the SOC are implemented in different codes which rely on different methods and as the MCA energy is very sensitive to various technical parameters, a very careful examination of various convergence parameters has to be performed to get a meaningful comparison. Our study of the MCA of bulk FePt focuses on comparison of results of the Wien2k FLAPW code, where the SOC is implemented via the second variation approach, and of the SPRKKR code, where the Dirac equation is solved using a full-potential KKR Green's function method. Additionally, the effect of scaling the SOC either overall or for Fe and Pt atoms separately is investigated.

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Theoretical study on optical and thermoelectrical properties of the direct band gap α/β-Ca_2CdAs_2 pnictide semiconductors

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This article reports the utilization of the density functional theory within the Perdew–Burke–Ernzerhof generalized gradient functional for the electronic structure, optical and thermoelectric properties of the α-Ca_2CdAs_2 and β-Ca_2CdAs_2 single crystals. The theoretical calculations show that both compounds are direct band gap semiconductors with optical band gap of 0.96 eV and 0.79 eV at the point for α- and β-phases respectively, which show that these compounds are optically active. The total and projected density of states, electronic charge density and optical properties like complex dielectric function, energy loss function, absorption coefficient, reflectivity, refractive index, and extension coefficient of α/β-Ca_2CdAs_2 were studied using the above technique. The calculated results for the energy band structures are compared with experimental and other simulated data. Temperature dependent thermoelectric properties such as electrical and thermal conductivity, Seebeck coefficient, power factor and figure of merit were calculated. Our results show that α- and β-Ca_2CdAs_2 compounds are suitable materials for non-linear optical properties and for thermoelectric devices.

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Co-doping with Cr and N as a promising method of TiO_2 modification for hydrogen generation

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Significant effort over last few years has been made to identify alternative semiconductor materials for light energy conversion other than silicon. TiO_2 is being considered as one of the best candidates for semiconducting photoanodes in hydrogen photoelectrochemical reactors. However, due to its large band gap as well as high recombination rate of the photoinduced electron-hole pairs TiO_2 has to be modified. Over the last few years, numerous attempts have been undertaken in order to modify properties of TiO_2. Recently, modification of both anionic and cationic sublattices of TiO_2 by co-doping has been proposed. It is believed that co-doping can promote a separation of the photogenerated electrons and holes which limits recombination process, improves material quality and enhances light absorption. Cr-N has been proposed as a preferred pair of co-dopants for TiO_2 [1].

In this work, studies of stoichiometric $Ti(Cr)O_2$:N as well as non-stochiometric $Ti(Cr)O_{2-x}$:N thin films have been presented. Thin films have been deposited by dc/rf reactive magnetron co-sputtering under predefined conditions of the total gas pressure, constant gas flow, constant input power and current as well as the controlled substrate temperature. Film properties have been compared with those of undoped and singly doped by chromium or nitrogen TiO_2 and TiO_{2-x} thin films. The study of crystallographic structure, phase content (XRD, Raman spectroscopy), surface morphology (SEM, AFM), chemical composition (XPS, EDX) of obtained materials has been investigated. Moreover, electronic band structure has been probed by means of X-ray spectroscopy techniques (RIXS, XANES, XES). Finally, optical (UV-Vis spectrophotometry), electrical and photoelectrochemical measurements have been carried out in order to determine the key factors for improving efficiency of the solar energy conversion into chemical energy of the investigated thin films.

A significant shift of the fundamental absorption edge towards longer wavelengths has been observed. The spectrophotometric data clearly indicated that the overall effect of the substitutional co-doping of both Cr and N species resulted in a shift of the fundamental absorption edge toward longer wavelengths. Incorporation of nitrogen increased the transmittance coefficient due to the reduction of free carrier absorption induced by ionized oxygen vacancies created in Cr doping process. This fact was corroborated by the results of the impedance spectroscopy [2].

Kβ detected Ti K-edge HERFD-XAFS spectra provide information on the influence of Cr, N dopants on charge

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distribution in the TiO_2 structure. Quantitative analysis of the RXES $K\beta_{2,5}$ and its satellites reveals information about N dopants distribution and oxygen stoichiometry, enabling a more accurate determination of local structure evolution of co-doped TiO_2. Band gap energies derived from the RXES analysis are compared to the values obtained from optical measurements.

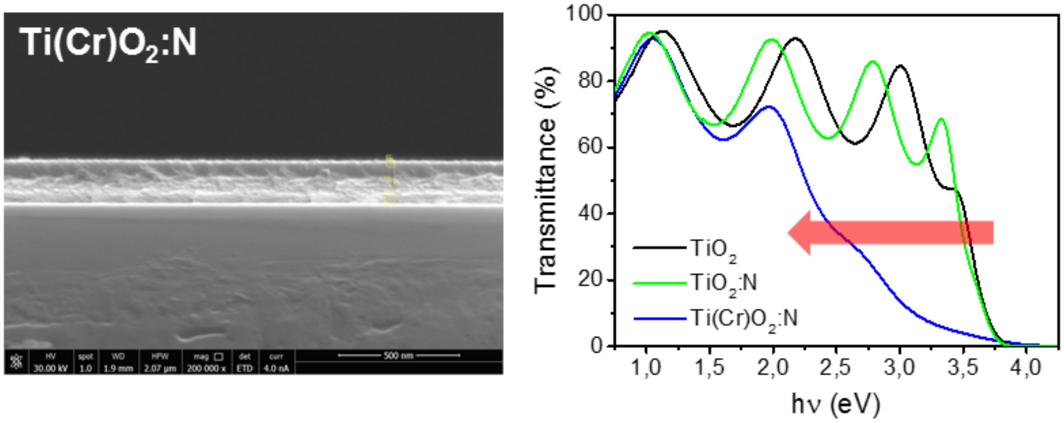

Figure 1. Cross-section view SEM image of $Ti(Cr)O_2$:N thin film deposited onto Si (100) substrate (left) and transmittance spectra of TiO_2, TiO_2:N, $Ti(Cr)O_2$:N thin films deposited onto amorphous silica SiO_2 (right); hν – photon energy.

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Application of Surface Characterization Techniques: On different Material Systems

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The aim of this work is to investigate the metallurgical systems by using the surface characterization techniques: X-ray Photo Electron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Scanning Photoemission Microscopy (SPEM) at ELETTRA synchrotron (Trieste). By using this type of surface-sensitive techniques on metallurgical systems, it is possible to obtain the information on the materials elemental composition, stoichiometry, chemical states of constituent elements, electronic configuration, surface chemical maps, etc. This work can be subdivided into three topics that are linked by the use of the same experimental techniques. These topics are the following: (i) study of the S-phase of 316L kolsterized & plasma treated steels [1] e.g. Fig. 1.

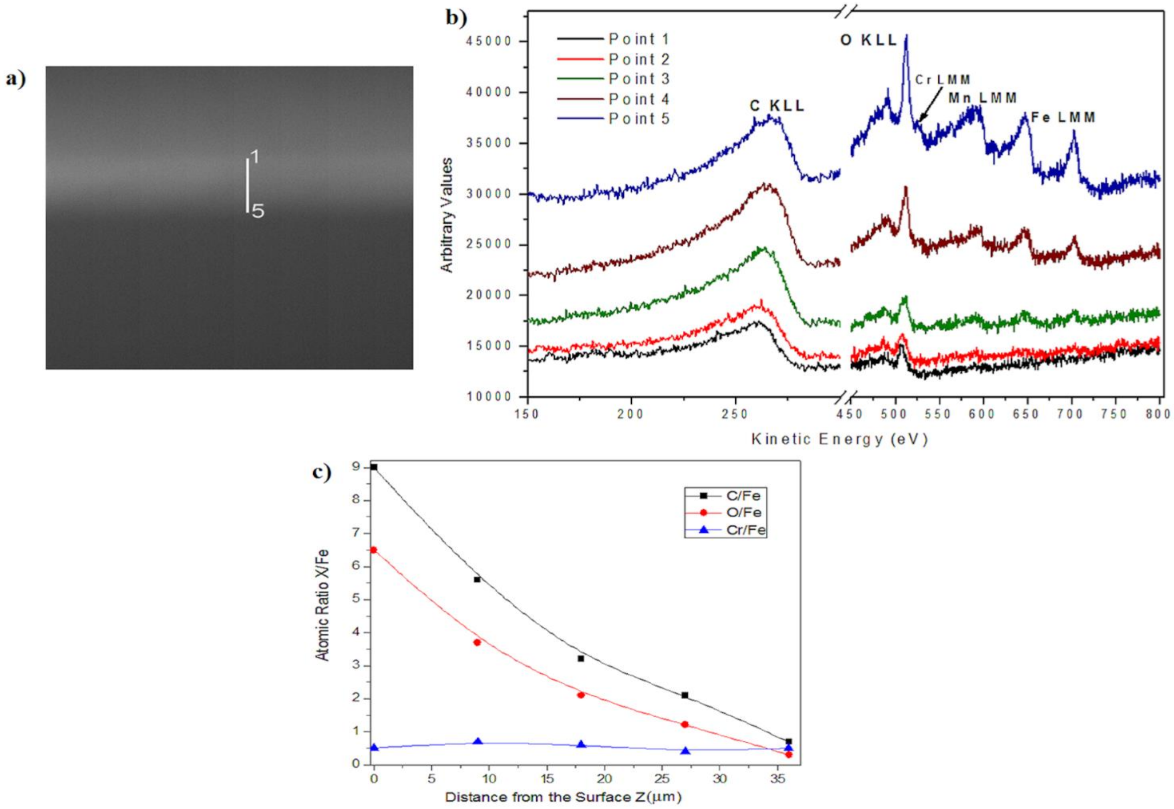

Figure 1. a) SEM image (0.2 x 0.2 mm^2) of the cross-section of industrially treated sample; b) AES line scan; c) C/Fe, O/Fe and Cr/Fe atomic ratios vs depth z determined from AES signals on the cross-section of the industrially treated sample.

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(ii) characterization of thick tungsten coatings on stainless steel for nuclear fusion technology [2], e.g. Fig. 2, (iii) SPEM investigation of eutectic Pb-Bi alloys quenched at different temperatures [3], e.g. Fig. 3.

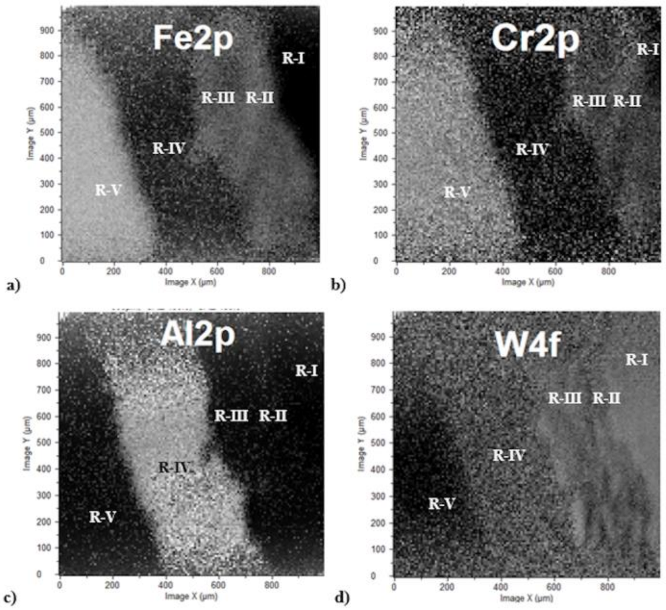

Figure 2. XPS chemical maps acquired by using Escalab 250Xi with standard electrostatic lens (1 x 1 mm^2): a) Fe 2p; b) Cr 2p; c) Al 2p; d) W 4f after topographic correction.

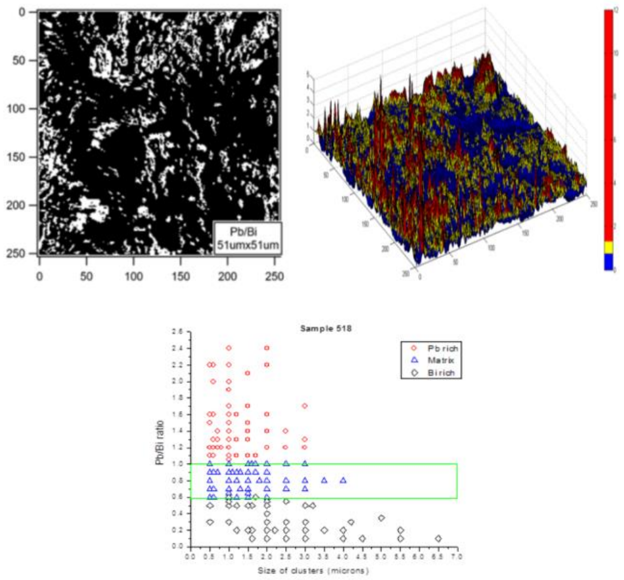

Figure 3. Analysis of PbBi alloy quenched at 518 °C: a) chemical maps of Pb/Bi intensity ratio; b) 3D maps of Pb/Bi intensity ratio (51μm x 51 μm); c) cluster size distribution obtained from the chemical maps a) & b).

Thanks to the wide range of variety and flexibility of applications of XPS, AES & SPEM, these techniques can be used for the investigation of various systems, such as metallurgical, composite materials, ceramics, etc. In future, the potential of surface analysis techniques will be explored for application in different metallurgical systems.

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