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Electronic structure of matter probed under *in-situ* conditions by means of X-ray spectroscopy techniques

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The study of chemical processes at *in situ* conditions is a challenging task due to the often extreme reaction conditions, reaction complexity, reaction time scales and low chemical sensitivity to the element of interest. The available techniques are usually too slow or insensitive to probe reaction intermediates. X-rays based techniques are an ideal tool for the *in-situ* study because of their penetration properties, chemical specificity and sensitivity. The X-ray absorption and emission spectroscopy (XAS/XES) or their combination, resonant emission X-ray spectroscopy (RXES), allows for accurate mapping of local electronic and geometric structures in catalytic and biologically relevant systems [1].

I will present recent advances in *in-situ* RXES techniques, with main focus on application to chemistry and material science. I will also discuss, improvements in chemical sensitivity as well as temporal resolution by means of high energy resolution off-resonant spectroscopy (HEROS) technique [2]. Fixed optical arrangement of HEROS methodology allowed us for sub-second measurements at synchrotron [2] and shot-to-shot spectroscopy at XFEL [3]. Finally I will discuss recent experiments at XFEL where self-amplified spontaneous emission operation of LCLS machine was employed for RXES spectroscopy on 3d metal-complexes to probe the non-linear regimes of X-ray interaction with matter.
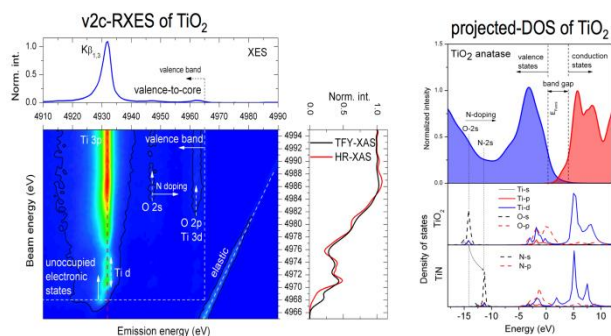
Resonant X-ray emission spectroscopy RXES, relies on second-order interaction of photon with core electrons. By tuning the incidence beam energy around an absorption edge of element, the unoccupied electronic states are probed via dipole-allowed transitions leading to intermediate atomic state. The following decay from intermediate to final state is accompanied by the emission of an X-ray. Thus the RXES technique is based on monitoring, at high energy resolution, the intensity of incoming/emitted X-ray radiation versus incoming/emitted X-ray energies.

Recently at SuperXAS beamline of Swiss Light Source we developed a dispersive-type spectrometer [4] that allowed us to extend the RXES spectroscopy into the real time-resolved domain. We focused our research into the materials characterization, materials at working conditions and interaction of molecules with metal surfaces. For material characterization, we applied valence-to-core (v2c) RXES in order to probe, within the same measurement, lowest unoccupied and highest occupied electronic structure of different photo-catalytic materials. Typical v2c-RXES plane for TiO_2 anatase is plotted in Figure 1 together with main electronic states accessed by the experiment [5]. The measured spectra can be compared with full-mutiple scattering calculations for determination of main electronic states contributions to the measured X-ray signals as demonstrated in Figure 1. We showed that v2c-RXES measured with dispersive-type spectrometer allow to probe very small changes on electronic structure, which indeed have large effects on catalytic properties of the material [6].
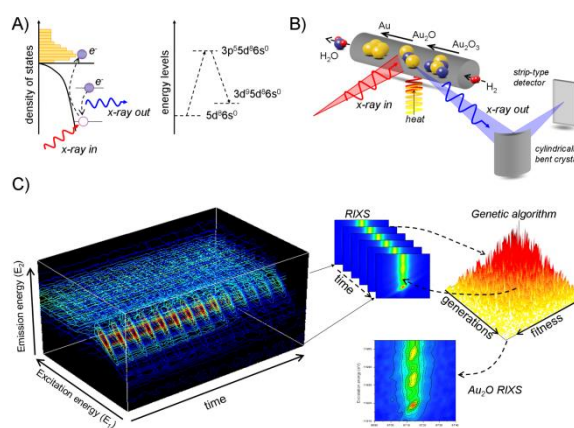

Figure 2. (a) Schematic representation of the RXES process in a Au atom. (b) Experimental setup for time-resolved RXES. The Au_2O_3 powder is enclosed in a reactor cell and heated up in a reducing H_2 environment. (c) Time evolution of the RXES spectra during the experiment (time-resolved RXES) and schematics of the data analysis procedure employing genetic algorithm computations. From [7].

Figure 1. (Left) TiO_2 anatase RXES plane. (top) Non-resonant XES spectrum; (right) TFY- XAS versus HR-XAS extracted at constant emission energy (4931.7 eV). Right) Valence and conduction band electronic states extracted from measured RXES plane (top); calculated Ti, O, and N DOS for TiO_2 and TiN (below). From [5].

In order to apply RXES technique for *in-situ* time resolved studies and to probe materials under working conditions, the core-to-core (c2c) transitions are used that allow for more efficient detection in combination with dispersive spectrometer for quick spectral acquisition [7]. The typical *in-situ* experimental scheme is drawn in

Figure 2b, used for study temperature-programmed reduction of Au_2O_3. From the experiment a short-lived Au_2O compound has been detected for the first time under *in situ* conditions. On the basis of time-resolved RXES data analysis combined with genetic algorithm methodology (Figure 2c), we could determined the electronic structure of the metastable Au_2O intermediate species. The result was confirmed with support of DFT calculations and we found that such a structure may indeed be formed and that the expanded lattice constant is due to the termination of Au_2O on the Au_2O_3 structure.

The *in-situ* c2c RXES also proofed to be ideal tool to probe electronic structure changes of surface metals interacting with molecules. We showed, that based on electronic structure changes detected by RXES with support of theoretical calculations, and it is possible to determine not only the metal density of states, but also the geometry at which a molecule bounds to the metal structure [8]. Finally, I will describe on how the high chemical sensitivity c2c-RXES allow to track at *in-situ* conditions interaction of Pt-based drugs with DNA structure [9]. Further prospects on technical developments for simultaneous c2c and v2c RXES spectroscopy will be described as applied to anti-cancer drug studies and binding mechanisms to DNA.
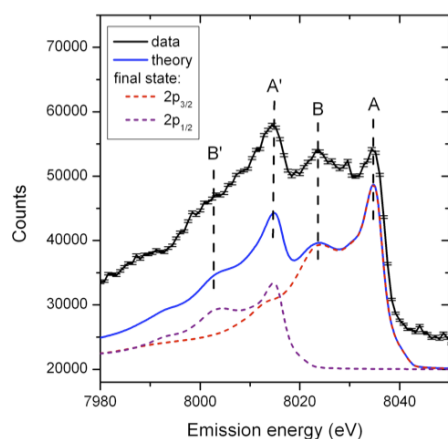

Figure 3. HEROS spectra of Cu recorded for 2000 self-seeded pulses at LCLS (black curve). For comparison, we plot the calculated spectrum using the Kramers-Heisenberg relation with a Cu K-edge X-ray absorption spectrum as input for calculations.

In the second part of the presentation I will focus on development of high energy resolution off-resonant spectroscopy (HEROS) in application to time-resolved *in-situ* spectroscopy and shot-to-shot spectroscopy at XFELs. The off-resonant excitation relates to the second-order photon-atom interaction, in which the energy of the incidence X-ray is smaller than the binding energy of core-electron. Nonetheless, due to the photon-electron interaction, a core electron may be excited into an unoccupied state above the Fermi level. This intermediate ''virtual'' state of the neutral atom decays then radiatively, with the initial core hole being filled by another inner-shell electron. Because the total energy of this scattering process has to be preserved, the energy of the emitted X-ray is lower by the amount of energy needed to promote the core-electron above the Fermi level. Most importantly, in the off-resonant excitation regime, the shape of the X-ray emission spectrum is dominated by the shape of the unoccupied density of states; i.e. proportional to X-ray absorption spectrum [10]. By combination of off-resonant excitation regime and high energy resolution dispersive-type detection, HEROS methodology was applied to monitoring the kinetics of chemical reactions [11]. Thanks to applied scanning-free approach, tracking of chemical reactions in gas-switching or temperature programed reduction/oxidation experiments at sub-second time resolution was possible and allowed to determine intermediate species involved in reactions. Recently we demonstrated that HEROS approach is free of self-absorption effects which very often affects the spectra measured by fluorescence X-ray absorption [12].

The fixed optical geometry of the von Hamos spectrometer has allowed us to probe the unoccupied electronic states of a solid sample using HEROS on a shot-to-shot basis at an XFEL source. The experiment was performed at the CXI experiment station at the Linac Coherent Light Source, USA, and was focused on studying the X-ray interaction with solid matter under off-resonant conditions [3].

In Figure 3 we plot experimental XFEL data for Cu metal at an incidence X-ray energy tuned to -12eV below the K-shell X-ray absorption edge. The measured HEROS spectrum is compared to the result of theoretical calculations employing Kramers-Heisenberg relation [10]. In the calculations we used an X-ray absorption spectrum measured at a synchrotron facility. As shown in figure 3, a good agreement is obtained indicating that the same electronic states are probed with HEROS at an XFEL and X-ray absorption at a synchrotron source. Finally, I will present the preliminary results from XFEL experiments where the nonlinear two-photon absorption (TPA) process in condensed matter was observed. In application at hard X-ray energies, the TPA in condensed matter was observed for the first time only recently [13]. Comparing to one photon absorption which is determined by dipole-allowed transitions, the TPA process requests changing the electron quantum number by +/-2 or 0, allowing thus to access a quadrupole or forbidden excitations. Therefore, the TPA process may allow, for example, to study quadrupole-allowed transitions in K-edge spectroscopy in 3d- or 4d-type metal compounds. However, at this point, a number of fundamental experiments have to be performed first before a real approach to applied TPA spectroscopy.

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