



Experiment title: Photon-in photon-out spectroscopy in the tender X-ray energy range: a systematic study on 4d transition metals.

Experiment number:
HC-3794

Beamline:	Date of experiment: from: 11/04/2018 to: 17/04/2018	Date of report: 18/07/2018
Shifts:	Local contact(s): P. Glatzel	<i>Received at ESRF:</i>

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Report:

The aim of the proposal was a systematic study of the possibilities of L-edge spectroscopy as applied to characterization of chemical and structural state of the 5th row elements.

During the experimental session, 43 high energy resolution fluorescence-detected x-ray absorption near edge structure (HERFD-XANES) spectra were collected at the top $L\alpha_1$ line ($3d_{5/2,3/2} \rightarrow 2p_{3/2}$ transition) in the well-characterized compounds of Mo, Rh, Pd, Ag, Cd, and Sn. Typical examples of these are presented in Figs. 1(a)-(c). The spectra reveal featurefull structure with strong dependence on the symmetry of local environment, type of a ligand and oxidation state. In Fig. 1(d), HERFD-XANES spectra of AgCl and AgBr are presented. These compounds have the same crystal structure, but the spectra reveal distinct changes in the positions and amplitudes of the peaks, originating from different Ag-halogen distances and scattering amplitudes. Also, preliminary analysis shows strong sensitivity of the L-spectra to the small changes in the parameters of crystal field. For example, in Na_2MoO_4 , $CaMoO_4$ and $H-ZrMoO_4$ Mo is in 6+ oxidation state, and the 2p electrons excited resonantly just above the absorption edge probe the unoccupied 4d states directly. In the first 2 compounds, molybdenum is surrounded by ideal oxygen tetrahedrons with slightly different Mo-O bond lengths (1.787 vs 1.757 Å, respectively), whereas the tetrahedron in $H-ZrMoO_4$ has 4 different bond lengths. These differences are clearly revealed by the L-edge HERFD-XANES spectra (see Fig. 1(e)).

Also, 26 resonant inelastic X-ray scattering (RIXS) planes were taken from Mo, Rh, Pd, Ag, and Cd compounds. RIXS is a powerful tool in studying the electronic density of states while offering high spectral resolution. It directly probes the unoccupied and occupied density of states, usually studied by X-ray absorption spectroscopy and X-ray emission spectroscopy, respectively. The intensities are measured as a function of incident and emitted photon energies, in the XANES region, identifying their interdependencies and thereby uncovering additional features. As an example, such RIXS planes taken from several Rh compounds are shown in Fig. 2. The planes reveal some features, missing from regular HERFD-XANES spectra, which evolve with composition. The analysis aimed to relate the observed changes with physical parameters is ongoing.

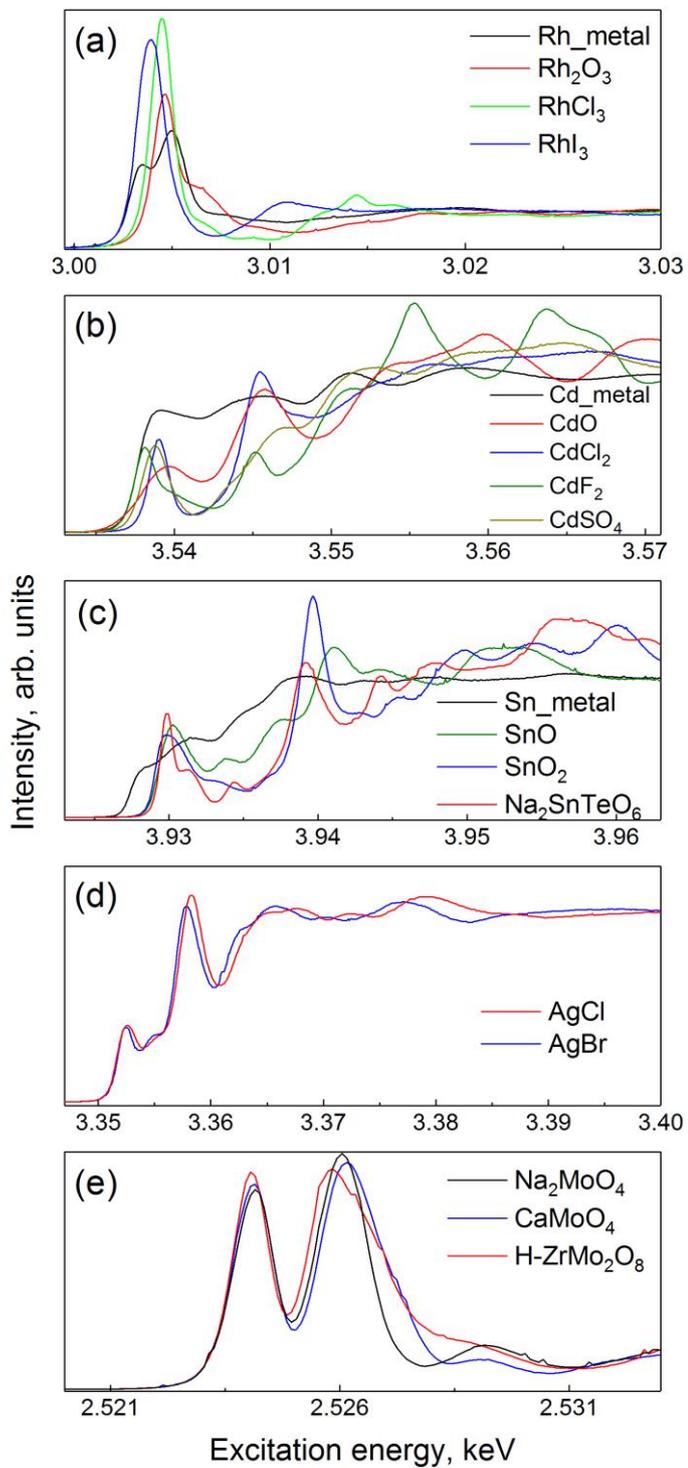


Figure 1.

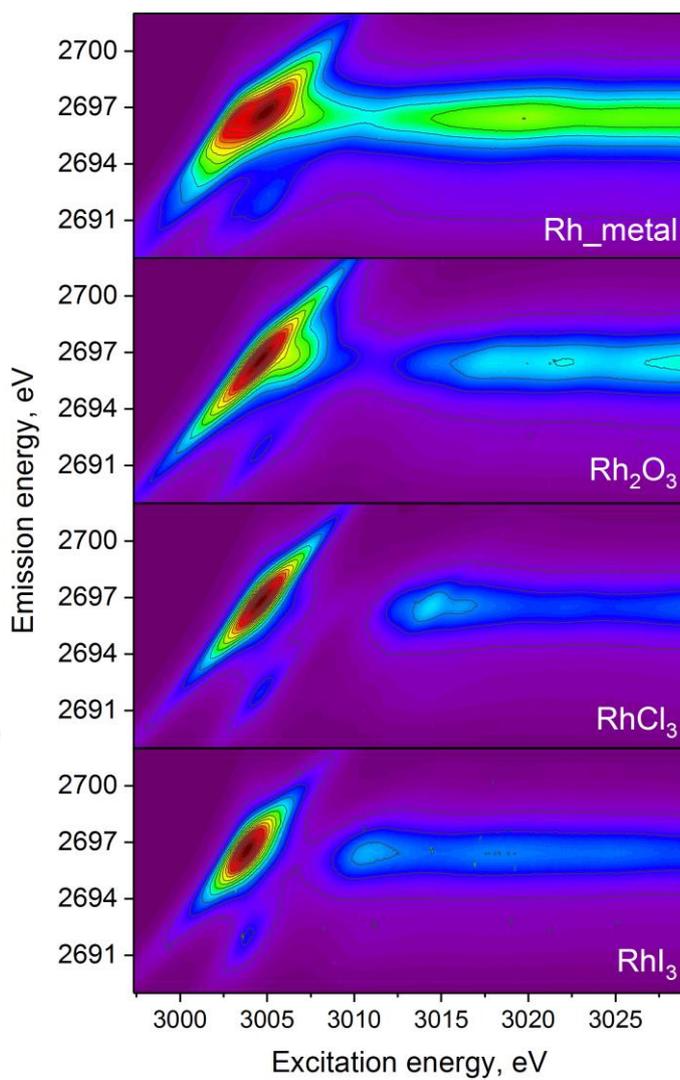


Figure 2.