

## High resolution X-ray emission spectroscopy: an advanced tool for actinide research

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**Abstract.** High resolution X-ray emission spectroscopy (HRXES) is becoming increasingly important for our understanding of electronic and coordination structures. The combination of such information with development of quantum theoretical tools will advance our capability for predicting reactivity and physical behavior especially of 5f elements. HRXES can be used to remove lifetime broadening by registering the partial fluorescence yield emitted by the sample (i.e., recording a windowed signal from the energy dispersed fluorescence emission while varying incident photon energy), thereby yielding highly resolved X-ray absorption fine structure (XAFS) spectra. Such spectra often display resonant features not observed in conventional XAFS. The spectrometer set-up can also be used for a wide range of other experiments, for example, resonant inelastic X-ray scattering (RIXS), where bulk electron configuration information in solids, liquids and gases is obtained. Valence-selective XAFS studies, where the local structure of a selected element's valence state present in a mixture of valence states can be obtained, as well as site-selective XAFS studies, where the coordination structure of a metal bound to selected elements can be differentiated from that of all the other ligating atoms. A HRXES spectrometer has been constructed and is presently being commissioned for use at the INE-Beamline for actinide research at the synchrotron source ANKA at FZK. We present the spectrometer's compact, modular design, optimized for attaining a wide range of energies, and first test measurement results. Examples from HRXES studies of lanthanides, actinides counter parts, are also shown.

### 1. Introduction

We are tackling the complexity of the interrelated processes determining the fate of radionuclides released into the geo- and hydrosphere and a thermodynamic/kinetic description of these processes via two avenues: 1) investigation of simplified model systems under controlled conditions, in order to ascertain and characterize determinant reactions and processes, and 2) investigation of natural systems to ensure transferability of the knowledge gained. The combined results of this strategy provide information of radionuclide speciation under a broad range of conditions and of processes occurring at mineral/water interfaces prerequisite to successful development of codes for nuclear waste repository performance assessment (PA) and for safe disposal design. We also address questions concerning the

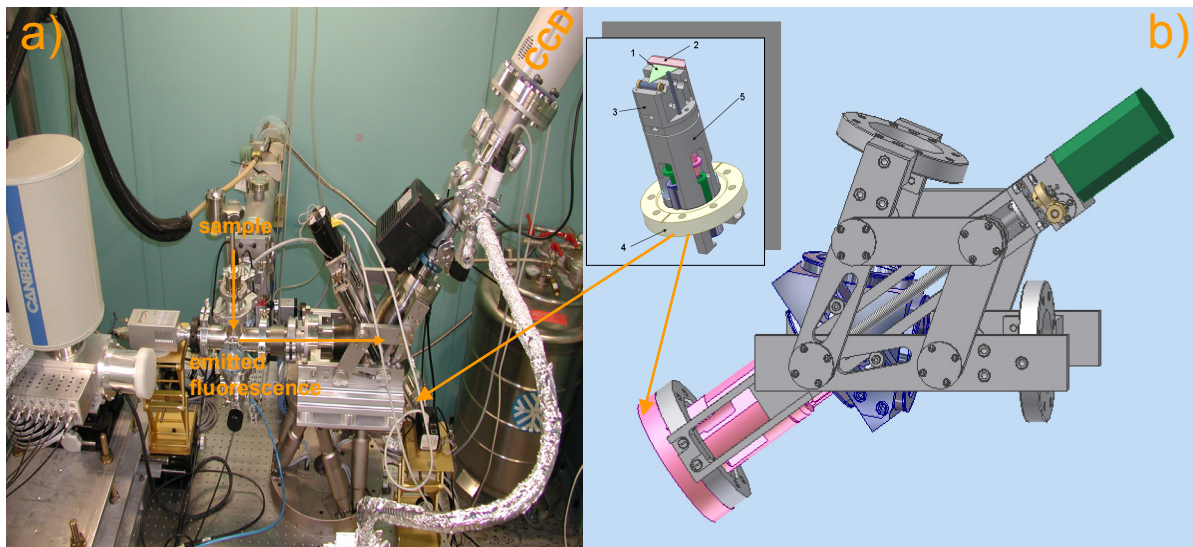
partitioning strategy, which involves separation of 5f elements from their chemically similar 4f counterparts, a major step in the so-called partition and transmutation (P&T) strategy for reducing the long-term radiotoxicity of high-level nuclear waste. A number of aspects of the physical and chemical properties of f elements involved in these processes are not fully understood and are a remaining frontier in present research, sometimes referred to as the “f electron challenge” [1]. High resolution X-ray emission spectroscopy (HRXES) provides site-selective information on electronic structure and local geometric atomic environment of a chemical element of interest and therefore is a suitable tool for tackling this challenge. It is based on observation of secondary optical processes having an intermediate state corresponding to a final state in X-ray absorption fine structure (XAFS) spectroscopy. HRXES includes resonant and non-resonant fluorescence emission measured near or above an absorption edge, respectively. In the region of resonant emission, the electronic structure of the absorbing atom is probed. This can be exploited to provide detailed information on, e.g., lanthanide and actinide (An) electronic properties as a true bulk probe, an obvious advantage over surface sensitive XPS techniques. Results from such studies can enable theorists to refine models and computer codes describing the behaviour of 4,5f electrons and bonding characteristics of f element complexes. Recent work is available on the 4f elements and the results are very promising for understanding and refining theoretical approaches [e.g., 2]. Only a few reports of RIXS investigations on An elements have been reported by researchers from Berkeley and Uppsala [3], based on experiments performed at the American Light Source (ALS) at Lawrence Berkeley National Lab. To our knowledge only one peer-reviewed report of RIXS on transuranium elements has yet been published in a scientific journal [4]. When available, the HRXES spectrometer will be the only existing spectrometer of its type at a dedicated radioactive synchrotron experimental station, the INE-Beamline for actinide research at ANKA. The INE-Beamline itself, with radioactive controlled laboratories in close vicinity, is a unique facility in Europe.

## 2. HRXES spectrometer design

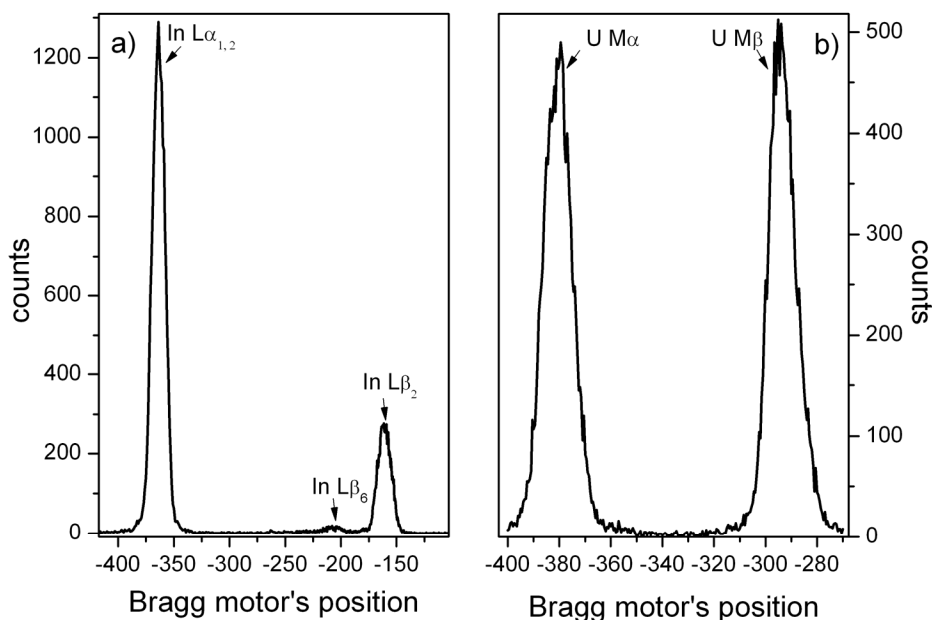
The design of the spectrometer is based on that originally built by the ALS, National Institute of Standards and Technology (NIST) [5]. It consists of a main block, to which three membrane bellows are attached. One bellow is mounted to the sample flange (figure 1 a)), which is orientated by 90 degree with respect to the primary X-ray beam. The analyzer crystal (figure 1 b)), clamped onto the bending mechanism, is inside the second bellow. The crystal itself is changeable. The emitted fluorescence is energetically dispersed by the cylindrically bent triangular crystal and focused onto a position sensitive detector (for example, a CCD camera) mounted onto the third bellow (figure 1 a)). The Bragg angle is changed by a system of movable linkage arms, whose position is determined by a stepping motor and two worm gear pairs. The Bragg angular range covered by the NIST spectrometer is from 30 to 50 degrees. The spectrometer covers both the An M emission lines (3-4 keV) and An L emission lines (13-20 keV) by utilizing, e.g., Si(111); Si(444) or Si(555) crystals. The bending radius of the analyzer crystal can be easily changed by the bending mechanism [6]. A large bending radius (large crystal-detector distance) improves energy resolution, whereas a small bending radius provides an improved signal-to-noise ratio (SNR). The compact assembly of the spectrometer makes it easily movable and thereby perfectly adapted to the modular design concept of the INE-Beamline. The instrument allows measurements in vacuum, necessary for low energy emission lines. This also leads to an improved SNR, partially overcoming one of the challenges of such experiments, the small fluorescence cross section.

First successful measurements of In  $L\alpha$ ,  $L\beta$  and U  $M\alpha$ ,  $M\beta$  emission lines are shown in figure 2 a) and b), respectively. A Si(111) analyzer crystal is employed in the experiment. The distances between sample and crystal, crystal and detector are both about 0.5 m. The spectrometer successfully separates the In  $L\alpha_{1,2}$ ,  $L\beta_6$ ,  $L\beta_2$  and U  $M\alpha$ ,  $M\beta$  emission lines. The energy resolution achieved is one order of magnitude better compared to that of a conventional solid state fluorescence detector, which makes applications where the analyser crystal is used to filter out or separate fluorescence emission lines

possible (fifth and sixth applications listed in the next section below). Further tests aimed at energy resolution improvement are in progress.



**Figure 1.** a) A picture of the HRXE spectrometer at the INE-Beamline; b) A 3D drawing of the spectrometer and the crystal bender with analyzer crystal 1) clamped 2) in the axis flexure 3), which is mounted to the main body 5) ending with a flange 4).



**Figure 2.** a) In  $L_{\alpha_{1,2}}$ ,  $L_{\beta_6}$  and  $L_{\beta_2}$  and b) U  $M_{\alpha}$  and  $M_{\beta}$  emission lines.

### 3. General description of possible HRXES spectrometer use

- Resonant X-ray emission spectroscopy (RXES)/resonant inelastic X-ray scattering (RIXS): in the region of resonant emission, the electronic structure of the absorbing atom is probed [2, 4]. This can be exploited to provide detailed information on, e.g., lanthanide and actinide electronic properties as a true bulk probe, an obvious advantage over surface sensitive XPS techniques.

Results from such studies can enable theorists to refine models and computer codes describing the behavior of 4,5f electrons and bonding characteristics of f element complexes.

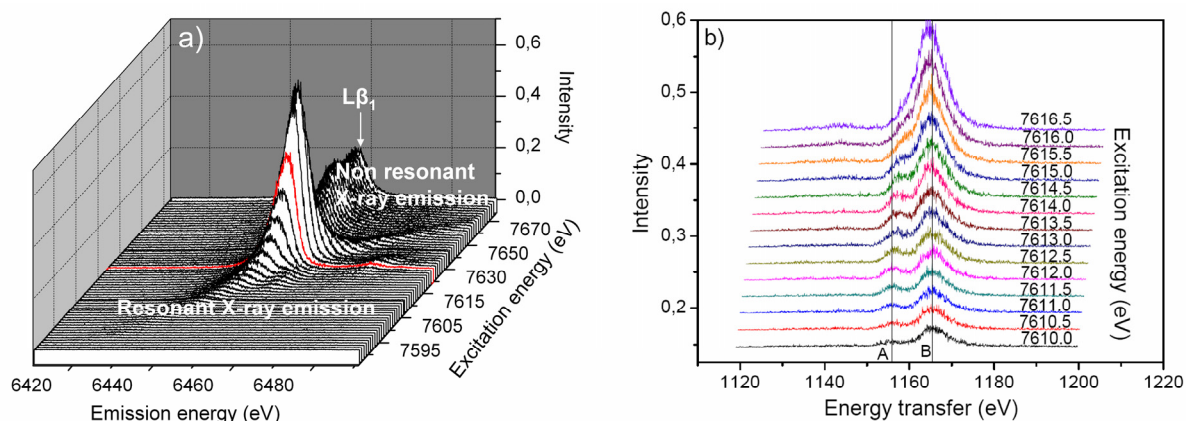
- High resolution fluorescence emission spectra (HRXES): utilizing the line sharpening effect in actinide and lanthanide L3 X-ray absorption near edge structure (XANES) by removal of spectral broadening caused by the short corehole lifetime for deeply bound initial states of actinides. Conventional An L3 XANES are dominated by an intense white line, but otherwise generally featureless. Using an analyzer crystal to register intensity variations in fluorescence with a sub eV resolution in a HRXES experiment can reveal otherwise unresolved spectral features [7, 8].
- X-ray Raman scattering (XRS): measuring the energy transfer in XRS allows investigations of low energetic radiation emission but using highly penetrating X-rays, suitable to penetrate radioactive sample containments or specialized sample cells (e.g., high pressure cells), i.e., it retains the experimental advantages of hard X-ray measurements, while revealing the information contained in the soft(er) X-ray absorption spectra. This has been used to measure, for example, C and O K spectra with an incident energy of near 7 keV; likewise, registering An M edges [9].
- Background suppressed X-ray spectroscopy: achieving suppression of the background radiation in speciation studies of a minority species embedded in a majority element substrate (improving the SNR in dilute systems) for better investigating, e.g., An cations sorbed onto mineral substrates in trace amounts. Such investigations mimic far-field scenarios for radionuclide release from a repository into the environment [10].
- X-ray spectroscopy with increased energy range: the L3 and L2 absorption edges of 4f elements lie energetically close and limit the energy range available for EXAFS. The analyser crystal of the HRXES spectrometer filters out fluorescence emission due to transitions to L1 and L2 electronic states, which extends the usable EXAFS k-range. This increases the resolution in EXAFS analysis and leads to interatomic distance determinations which are more precise [11].
- Site-selective X-ray spectroscopy investigations of valence mixtures: by recording chemically (valence) sensitive X-ray emission spectra to select appropriate energies for registering XAFS spectra, we can unequivocally discriminate between different valence state species in a mixture [12,13,14].

#### 4. Application examples

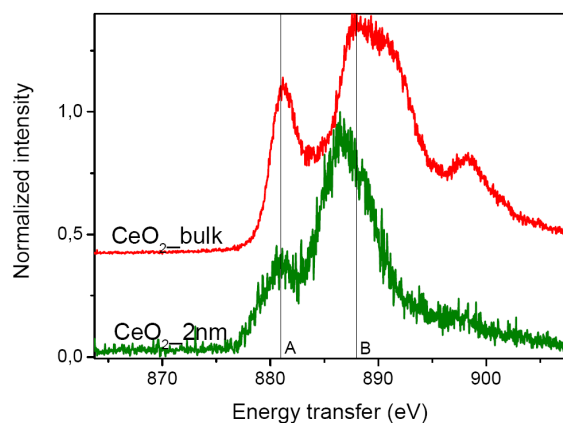
As the spectrometer is not yet available, we presently limit measurements on non-radioactive samples at other synchrotron facilities. We investigate La, Eu, Pr, Sm, Gd, Ho and Dy complexed with ligands exhibiting extraction behavior relevant to potential partitioning technology applications. The aim of the experiment is to study the electronic and local geometric structural properties of 4f and to compare them to homologous 5f complexes (to be measured with our spectrometer). The RXES/RIXS measurements on a number of 4f (non-radioactive) complexes are performed using the spectrometer available at the W1 beamline at HASYLAB. For example, the Eu  $L\beta_1$  emission line of the Eu complex, measured as a function of the excitation energy, is plotted in figure 3 a). The resonant region of the spectrum on the energy transfer scale (difference between excitation and emission energies) is shown in figure 3 b). The energy positions of peaks A and B are a measure of the energy difference between the Eu 4f and  $3d_{3/2}$ , and 5d and  $3d_{3/2}$  states, respectively. The highest probability for excitation of a 2p electron to 4f states is at 7614 eV excitation energy, where peak A has maximum intensity. Comparison of 5f and 4f results may help us to understand why certain N donor ligands selectively separate actinides from lanthanides and thereby enable us to specifically design more efficient ligands and optimize the separation process.

We also utilize RXES/RIXS to study CeO<sub>2</sub> nanoparticles with varying size [8]. The Ce  $L\alpha_1$  emission line as function of the excitation energy scanned over the Ce L3 edge is detected. The RXES/RIXS spectra resolve three peaks at excitation energies below the Ce L3 edge (see figure 4). Similar to the Eu example above, these peaks represent transitions to 4f (A) and 5d (B) states. Changes in energy and population of these orbitals are detected in the spectra of the nanosized material

compared to bulk  $\text{CeO}_2$ . Especially the large intensity decrease in the A peak indicates that this 4f final state has a higher electron population due to, e.g., increased surface contribution.



**Figure 3.** a) Eu  $L\beta_1$  X-ray emission spectrum (RXES and NXES) of the  $\{[\text{PS}(\text{N}^{\text{Me}}\text{Py})_3]\text{Eu}(\text{OTf})_3\}$  complex. Red marks the  $L_3$  ionization energy; b) The RXES/RIXS part of the spectrum in a) on the energy transfer scale (excitation - emission energy).



**Figure 4.** The RXES/RIXS spectra of  $\text{CeO}_2$  bulk and nano particles with 2nm average size measured at 5720 eV excitation energy.

## 5. Conclusion

The HRXES spectrometer at the INE-Beamline for actinide research at ANKA is a valuable, advanced speciation tool. The close proximity of this instrument to the active laboratories and additional speciation techniques at INE is unique and is expected to help lend momentum to the link between experiment and theory. When the commissioning phase of this spectrometer is complete, it will be available for use by the actinide community at the INE-Beamline at ANKA through the ANKA proposal system.

## References

- [1] Proceedings to the Department of Energy Basic Energy Science Workshop on Advanced Nuclear Energy Systems Report 2006 *Basic Research Needs for Advanced Nuclear Energy Systems*
- [2] Rueff J-P, Itié J-P, Taguchi M, Hague C F, Mariot J-M, Delaunay R, Kappler J-P and Jaouen N 2006 *Phys. Rev. Lett.* **96** 237403
- [3] Zatsepin D A, Butorin S M, Mancini D C, Ma Y, Miyano K E, Shuh D K and Nordgren J 2002 *J. Phys.: Condens. Matter* **14** 2541-2546

- [4] Kvashnina K O, Butorin S M, Shuh D K, Guo J-H, Werme L and Nordgren J 2007 *Phys. Rev. B* **75** 115107
- [5] Brennan S, Cowan P L, Deslattes R D, Henins A and Linde D W 1989 *Rev. Sci. Instrum.* **60** 2243
- [6] Henins A 1987 *Rev. Sci. Instrum.* **58** 1173
- [7] Rueff J-P, Raymond S, Yaresko A, Braithwaite D, Leininger P, Vankó G, Huxley A, Rebizant J and Sato N 2007 *Phys. Rev. B* **76** 085113
- [8] Batuk O N, Szabó D V, Denecke M A, Vitova T and Kalmykov S N *Inorg. Chem.* (submitted)
- [9] Bergmann U, Di Cicco A, Wernet P, Principi E, Glatzel P and Nilsson A 2007 *Journal of Chem. Phys.* **127** 174504
- [10] Vitova T, Lebid A, Liu D, Dardenne K, Brendebach B, Rothe J, Hormes J and Denecke M A *Proceedings of the 5th Workshop on Speciation, Techniques and Facilities for Radioactive Materials at Synchrotron Light Source, special issue of the "Nuclear Energy Agency (OECD-NEA) News"* (accepted)
- [11] Glatzel P, de Groot F M F, Manoilova O, Grandjean D, Weckhuysen B M, Bergmann U and Barrea R 2005 *Phys. Rev. B* **72** 014117
- [12] De Groot F M F 2000 *Topics Cat.* **10** 179-186
- [13] Glatzel P, Jacquamet L, Bergmann U, de Groot F M F and Cramer S P 2002 *Inorg. Chem.* **41** 3121-3127
- [14] Vitova T, Hormes J, Falk M and Buse K 2009 *Journal of Appl. Phys.* **105** 013524