**Experiment title:**

XAS Exploration of the Second Coordination Shell in Aqueous Solutions of Highly-Charged Cations

Experiment**number:**

CH-1192

Beamline:

BM29

Date of experiment:

from: 31.8.2001 to: 4.9.2001

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Shifts:

12

Local contact(s):

Dr. Stuart Ansell

*Received at ESRF:***Names and affiliations of applicants** (* indicates experimentalists):

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Report:

EXAFS and XANES spectra for 0.1 M aqueous solutions of a series of metal cations in acidic aqueous solution were recorded including:

- Co²⁺, Mn²⁺,
- Nd³⁺, Tb³⁺, and Tm³⁺ L₃ edges,
- Rh³⁺ K-, Pd²⁺ and Pt²⁺ L₃-edges,
- and Cu²⁺ tetracoordinated complexes with phtalocyanine, histidine, and amino-ligands.

These spectra form a good basis for theoretical work and a thorough investigation of the structure/spectrum interplay.^{1,2} As an example, the case of the rhodium spectrum has been investigated. A spectrum of aqueous Rh³⁺ was recorded at SRS in Daresbury Lab in 1993 using a Si(111) monochromator. Given the characteristics of this monochromator, no features could be resolved in the rising edge of the XANES spectrum. XAS calculations performed based on structures from a simulation of this system revealed that a splitting of the absorption peak is to be expected. This was one of the reasons for requesting a Si(311) monochromator for this beam time allocation. The spectrum recorded at our stay at ESRF is shown below. It exhibits the expected splitting. This good agreement reinforces the interpretation of the contribution of the different hydration shells to the total spectrum, and especially the clear contribution of the second hydration shell to the second absorption peak.³

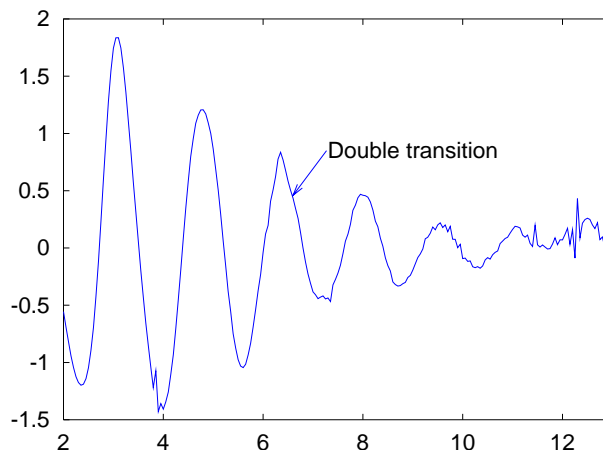
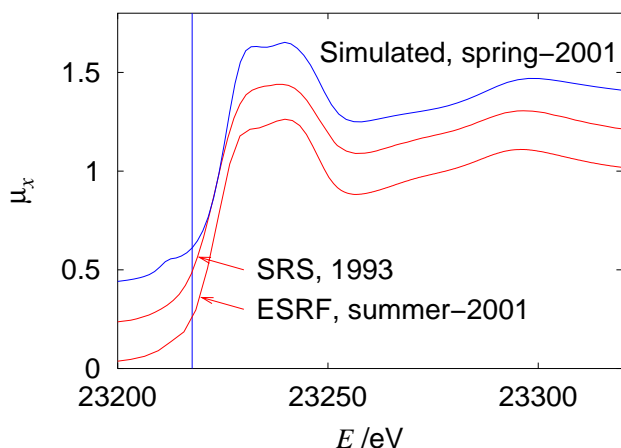


FIG 1: K-edge XANES of Rh^{3+} in water

FIG 2: L3-EXAFS spectrum, Tb^{3+} in water

Another example of a spectrum recorded during our stay is the EXAFS spectrum of Tb^{3+} in water (Figure 2). The cations of the rare earth elements form a systematic series that exhibit a gradual decrease of the ionic radius (lanthanide contraction). The unusually high solvation in water (8 or 9) can be characterized well by XAS spectroscopy. In the EXAFS region, multielectron excitations which are known for rare earths L-edge spectra,⁴ are found. In the recorded spectrum a bump due to double transitions $5d$, $5d \leftarrow 2p$, $4d$ can be observed around 6.6 \AA^{-1} .

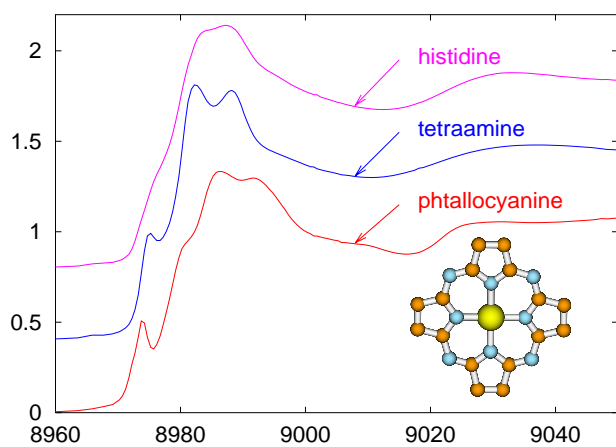


FIG 3: K-edge XANES of Cu^{2+} complexes. The inset shows the phtalocyanine backbone.

Cu^{2+} forms a number of square planar complexes that can be distinguished by their characteristic XANES spectrum. These compounds serve as models for the active sites of copper-containing enzymes, that may be determined in solution. With the methodology and the X-ray sources available, we plan to investigate further the structural characterisation by both EXAFS and XANES of complexes of biological interest.

References

1. Merklings, P. J.; Muñoz-Páez, A.; Martínez, J. M.; Pappalardo, R. R.; Sánchez Marcos, E. *Phys. Rev. B* **2001**, *64*, 012201.
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3. Merklings, P. J.; Muñoz-Páez, A.; Sánchez Marcos, E. *Submitted* **2002**.
4. Chaboy, J.; Tyson, T. A.; Marcelli, A. *Relative Cross Sections for Bound-State Double-Electron $LN_{4,5}$ -Edge Transitions of Rare Earths and Nonradioactive Elements of the Sixth Row*; Prensas Universitarias de Zaragoza: Zaragoza, 1995.