

# Actinet workshop 2007

## How can we improve coupling theoretical chemistry with X-ray absorption spectroscopy?

11 - 12 October 2007

Petit-Louvre, Avignon

Several spectroscopic tools are well adapted to actinide investigations such as infra red spectroscopy and spectrophotometry. X-ray absorption spectroscopy (XAS) is also an ideal structural and electronic probe of the cation coordination sphere; one the reasons being that it is virtually independent of the physical state of the sample under study. XAS actinide  $L_3$  edge is presently most frequently used because the energy range involved of the corresponding dipolar  $2p_{3/2}$ -6d transition can penetrate radiological barriers or sample containments. Both the high and low energy XAS regions (EXAFS and XANES, respectively) yield structural information on the actinide coordination polyhedron. However, due to short core-hole lifetimes, leading to deleterious broadening of the near edge signal, and lack of sufficient theoretical treatment, especially for the heavy actinide elements, the extractable molecular and electronic structure information from the XANES regime is limited. Systematic, combined theoretical and experimental efforts to improve or introduce sophisticated quantitatively correct *ab initio* calculations of core  $\rightarrow$  localized final state transitions for actinide materials and for simulating coordination structures are needed in order to make molecular and electronic information accessible from XANES studies. XANES investigations in the soft X-ray range provide better resolution due to associated longer core-hole lifetimes and a direct electronic probe of 5f and 6d orbital electron states. Such investigations include  $M_{4,5}$  edges,  $N_{4,5}$ , and  $N_3$ . Tuning of the photon probe from soft X-rays to hard X-rays allows to selectively investigate both structural and electronic properties of the actinide with its coordination sphere, taking advantage of the variation in electronic transitions, thereby allowing decomposition into s-, p-, d-, and f-type contributions. These experimental endeavors, combined with theoretical quantum chemical calculations will ultimately render XANES a quantitative -not only qualitative- method for molecular and electronic structure investigations of actinide elements.

This workshop's major goal was to bring together members of the European theoretical actinide community and X-ray spectroscopists, in order to instigate a concerted effort in combining X-ray spectroscopic data with simulation and quantum chemical calculation codes and to ultimately effect accurate interpretation/prediction of actinide-ligand bond properties.

The program of the workshop reflects the variety of interests from this community.

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## Thursday the 11<sup>th</sup>

- 09 h 00      Welcome and presentation of the Theoretical User Lab.
- 09 h 30      **K. Meyer** (Friedrich Alexander Universität, Nuremberg)  
*Synthesis, molecular and electronic structure of a series of isostructural uranium complexes with oxidation states III, IV, V, and VI*
- 10 h 15      Break
- 10 h 45      **E. Sanchez Marcos** (Universidad de Sevilla, Sevilla)  
*Coupling X-Ray Absorption Spectroscopy and MD Simulations to Study Ions in Solutions: Looking at the Synergy of the Procedure*
- 11 h 30      **Ricardo Spezia** (Université Evry Val d'Essonne)  
*Structure and dynamics of metallic complexes by first-principles molecular dynamics simulations.*
- 12 h 15      lunch
- 13 h 45      **S. Tsushima** (FZR, Dresden)  
*Combining DFT calculations, EXAFS, IR and UV-Vis spectroscopy.*
- 14 h 30      **L. Maron** (INSA Toulouse)  
*A combined theoretical and experimental study of the reactivity of organouranium complexes*
- 15 h 15      break
- 15 h 45      **R. Denning** (Inorganic Chemistry Laboratory, Oxford)  
*The X-ray Spectroscopy and Electronic Structure of Actinyl Ions*
- 16 h 30      **C. Fillaux** (CEA Cadarache, Saint Paul Lez Durance)  
*Investigation of actinide compounds by coupling XAS at various energies and quantum chemistry*
- 17 h 00      Poster session and aperitif

## Friday the 12<sup>th</sup>

- 09 h 00      **S. D. Conradson** (Los Alamos National Laboratory, Los Alamos)  
*Structure and Bonding in Actinide Oxides: The Ultimate Challenge*
- 09 h 45      **K. Hermann** (Fritz Haber Institut, Berlin)  
*XAS at catalytic metal oxide surfaces : ab initio cluster models help to interpret experimental results*
- 10 h 30      break
- 11 h 00      **M. Pernpointner** (Insitut für Physikalische Chemie, Heidelberg)  
*The four-component ADC method : a tool for investigating slectronic structure in heavy element compounds. Current status and perspectives*
- 11 h 45      Lunch
- 13 h 15      **V. Vallet** (Université Sciences et Technologie de Lille, Lille)  
*Ab initio structures and scattering EXAFS Debye-Waller factors*
- 14 h 00      **R. Ayala** (Universidad de Sevilla, Sevilla)  
*Po(IV) hydration by QM and MD calculations*
- 14 h 45      break
- 15 h 15      **D. Duflot** (Université Sciences et Technologie de Lille, Lille)  
*Ab initio simulation of K-shell spectra of small molecules*
- 16 h 00      **S. Butorin** (Uppsala University, Uppsala)  
*RIXS spectra of actinides*
- 16 h 30      **Conclusions**