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Structure analysis of actinide compounds in solution by X-ray absorption spectroscopy

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Actinides with their large number of oxidation states are susceptible to redox conditions, forming different complexes in aqueous solution which may greatly differ by solubility and mobility. These complexes are often difficult to investigate due to their complex species distribution and thermodynamic metastability. Thermodynamic estimation of species distribution may fail for higher actinide concentrations. In such cases X-ray absorption spectroscopy is able to reveal structural parameters that provide information on the solution species. A spectroelectrochemical cell was developed for the study of structure and speciation of actinide complexes in situ by X-ray absorption spectroscopy, while applying and maintaining a constant potential. This equipment allows the investigation of actinide complexes under different redox conditions. The use of actinides at a synchrotron requires safety precautions. An experimental station for radiochemical experiments, the Rossendorf beam line (ROBL), is operated by the Forschungszentrum Rossendorf/Germany at the ESRF/France. An introduction and overview on typical actinide structures in solution will be presented.

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Short- and long-range structure of crystals as revealed by XAFS spectroscopy

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X-ray absorption fine spectroscopy (XAFS) is widely acknowledged to be one of the most effective methods to determine the local environment around a selected atom (the absorber). Its prize properties are atom selectivity over a wide range of Z (from B to Au), and very low detection levels (ppb) at high resolution ($>10^4$), when the X-ray source is synchrotron radiation. Furthermore, mathematical fitting of the experimentally recorded extended structures (EXAFS) allows determining the probed atom coordination number and bond distances with its ligands to $\pm$20-30% and $\pm$0.02-0.03 Å, respectively. Thus, combined with the determination of the oxidation state and the quantitative evaluation of two or more oxidation states, both of which are obtained from the pre-edge (PE) features, XAFS is able to provide local (short-range) information on essentially any cation in any compound (gas, liquid, and solid). The main structures occurring near the absorption edge (XANES) received less attention so far. Yet they provide semi-quantitative information on the medium- to long-period ordered environment around the probed atom, thus linking EXAFS local data with the long-period structural results best determined by single-crystal X-ray diffraction (SC-XRD). In recent years, the multiple-scattering theory underlying XANES progressed so much that codes such as CONTINUUM [1] and FEFF [2] can satisfactorily compute XANES spectra starting from standard structure data, and other codes such as MXAN [3] can fit better the spectra computed in this way so as to obtain agreement with experimentally-recorded spectra by moving atoms around from their initial structural positions i.e., those determined by SC-XRD on similar, but not necessarily the same materials. Consequently, understanding real structures is made possible that accounts for both atomic substitutions and structural deformations present in most natural materials. Examples of clinopyroxenes [4], olivines [5], and micas [6, 7] are given, with descriptions of the computing steps inherent in the procedure, and with implications on the understanding of the revealed structural and electronic characteristics of the probed atom. Actually, the entire real structure of a solid crystalline material can be determined at both the short and long range, provided most or all essential atoms are investigated.

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