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XAFS spectroscopic study of uranyl coordination in solids and aqueous solution

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ABSTRACT

To evaluate the ability of X-ray absorption fine structure (XAFS) spectroscopy to elucidate the coordination environment of U^{6+} at the solid-water interface, we conducted an in-depth analysis of experimental XAFS data from U^{6+} solid and solution model compounds. Using the ab initio XAFS code FEFF6, we calculated phase-shift and amplitude functions for fitting experimental data. The code FEFF6 does a good job of reproducing experimental data and is particularly valuable for providing phase-shift and amplitude functions for neighboring atoms whose spectral contributions are difficult to isolate from experimental data because of overlap of Fourier transform features. In solid-phase model compounds at ambient temperature, we were able to fit spectral contributions from axial O (1.8 Å), equatorial O (2.2–2.5 Å), N (2.9 Å), C (2.9 Å), Si (3.2 Å), P (3.6 Å), distant O (4.3 Å), and U (4.0, 4.3, 4.9, and 5.2 Å) atoms. Contributions from N, C, Si, P, distant O, and distant U (4.9 and 5.2 Å) are weak and therefore might go undetected in a sample of unknown composition. Lowering the temperature to 10 K extends detection of U neighbors to 7.0 Å. The ability to detect these atoms suggests that XAFS might be capable of discerning inner-sphere U sorption at solid aluminosilicate-water interfaces. XAFS should definitely detect multinuclear U complexes and precipitates. Multiple-scattering paths are minor contributors to uranyl XAFS beyond $k = 3$ Å^{-1}. Allowing shell-dependent disorder parameters (σ^2) to vary, we observed narrow ranges of σ^2 values for similar shells of neighboring atoms. Knowledge of these ranges is necessary to constrain the fit of XAFS spectra for unknowns. Finally, we found that structures reported in the literature for uranyl diacetate and rutherfordine are not completely correct.