

 ROBL-CRG	Experiment title: Investigation of U(VI)/U(V) carbonato complexes in aqueous solution by spectro-electrochemistry	Experiment number: 20-01-639
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The carbonato complex of uranium in aqueous solution is due to its good solubility one of the most important species for the migration study on nuclear waste repositories. Although uranium can change its oxidation state from U(III) to U(VI) in aqueous solution, only U(VI) and U(IV) are dominant species under subsurface conditions. U(V) is in absence of strong ligands metastable, but it may play an important role if the solution undergoes a change in the redox condition. However, reliable information about the structure of uranyl(VI)- and uranyl(V) carbonato complexes is still missing. Hence, we have investigated the structure of these uranyl carbonato complexes in aqueous solution by EXAFS spectroscopy.

The uranyl(V) carbonate species is extremely sensitive to O₂ and reoxidizes promptly. Therefore, the uranyl(V) carbonate sample was placed in a glass cuvette under dry N₂ atmosphere in a glove box (O₂ concentration in the glove box was less than 1 ppm). The cuvette was then sealed up by hot melting. The sealed uranyl(V) sample was confirmed to be stable at least for two weeks by successive UV-visible absorption measurements, indicating that the measured XAFS spectrum for the uranyl(V) sample comprises the information only for the uranyl(V) carbonate species. Fig. 1 shows the Fourier transforms (FTs) of the U L_{III}-edge EXAFS spectra for uranyl(VI)- and uranyl(V) carbonate species. It is obvious that both uranyl(VI)- and uranyl(V) ions form a bidentate-coordinated tricarbonato complex, [UO₂(CO₃)₃]ⁿ⁻ (*n* = 4 for uranyl(VI) and 5 for uranyl(V)), in the present basic Na₂CO₃ solution. As a result of the reduction of U(VI) to U(V), U-O_{ax} and U-O_{eq} distances become 0.10 and 0.06 Å longer, respectively. Because the ligand arrangement is unchanged, the changes of the bond length

is affected only by the charge difference of uranium. Additionally, we succeeded in obtaining the detailed structural information about the outer coordination sphere. Surprisingly, the U-O_{dist} distances show a relative small difference. These structural parameters are in good agreement with the results by DFT quantum calculation, assuring the validity of our EXAFS results.

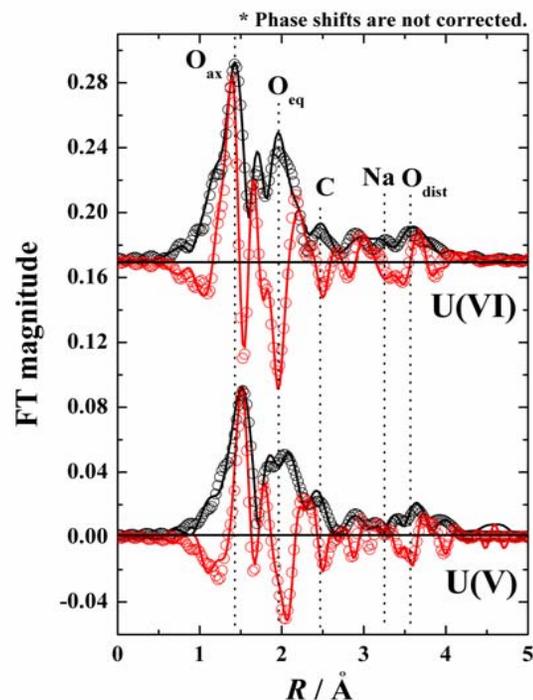


Fig. 1: Fourier transforms of U L_{III}-edge EXAFS for uranyl(VI)- and uranyl(V) carbonate species in 1.4 M Na₂CO₃ solution: -; experimental data, o; theoretical curve fit, black-colored data; FT magnitude, red-colored data; imaginary part

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