



neptunyl(VI) ion is coordinated by 5.3 water molecules with a shorter interatomic distance of 2.42 Å. Our EXAFS data show therefore a structural rearrangement of Np hydrate species with oxidation state as illustrated in Figure 2: both Np(V) and (VI) ions exist predominately as pentaquo neptunyl complexes,  $[\text{NpO}_2(\text{H}_2\text{O})_5]^{n+}$  with  $n = 1$  for Np(V) and 2 for Np(VI), whereas the Np(IV) ion forms a spherically coordinated decaquo complex,  $[\text{Np}(\text{H}_2\text{O})_{10}]^{4+}$ . It is this drastic change in complex structure between Np(IV) and Np(V), which makes the transition between these two redox states almost irreversible (DE ~0.9 V), while the transition between Np(V) and Np(VI) requires no structural change, hence is quasi-reversible (DE = ~0.2 V). These results support our initial hypothesis that there is a strong relationship between the electrochemical behaviour of Np and its complex structure.

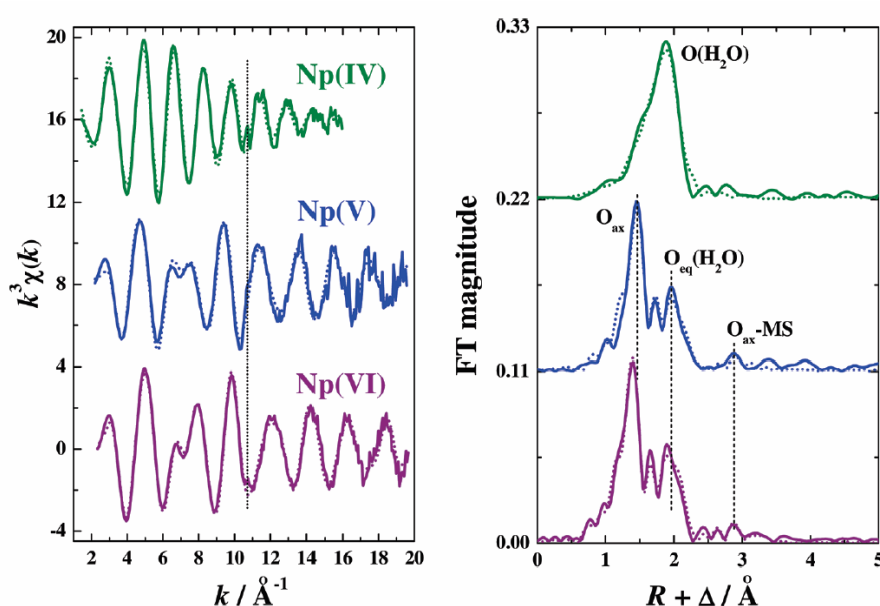


Fig. 1:  $k^3$ -weighted Np- $L_{\text{III}}$  edge EXAFS spectra. Solid lines represent experimental data and dotted lines represent theoretical fit. The line colours reflect the actual colour of sample solutions.

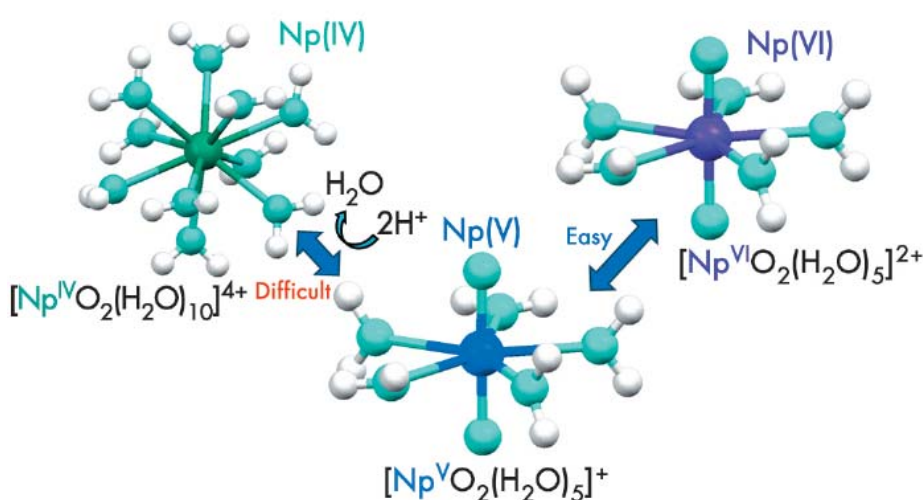


Fig. 2: Structural rearrangement of Np hydrate species through the redox reaction.

Ikeda-Ohno, A., Hennig, C., Rossberg, A., Funke, H., Scheinost, A.C., Bernhard, G., Yaita T. Electrochemical and complexation behavior of neptunium in aqueous perchlorate and nitrate solutions, *Inorg. Chem.* **47** (2008) 8294-8305.