Influence of adsorbed water on energetics of cassiterite nanoparticles

N.L. ROSS[1]*, E.C. SPENCER[1], S.F. PARKER[2],
A.I. KOLESNIKOV[3], J. BOERIO-GOATES[4],
B.F. WOODFIELD[4] AND A. NAVROTSKY[5]

[1]VirginiaTech, Blacksburg, VA 24061, USA
(*correspondence: nross@vt.edu)
[2]ISIS, Rutherford Appleton Laboratory, Didcot, OX11 0QX, U.K.
[3]Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[4]Brigham Young University, Provo, UT 84602, USA
[5]University of California at Davis, Davis, CA 95616, USA

Water is ubiquitous on the surface of oxide nanoparticles, displaying varying degrees of deviation from bulk water structure and dynamics, and can exert a profound influence on the thermodynamic properties of the oxide [1]. We have used inelastic neutron scattering (INS) to investigate the structure and vibrational density of states (VDOS) of the surface water of SnO_2 (cassiterite) nanoparticles with differing size distributions and differing levels of hydration. The INS spectra of the water adsorbed on the surface of 1-2 nm, 6-7 nm and 40-50 nm SnO_2 nanoparticles were measured at 4 K over the 0-500 meV range using TOSCA, an INS time-of-flight spectrometer at ISIS. The results from this study show that surface confinement on the surfaces of cassiterite nanoparticles of different sizes strongly influences water vibrations. The VDOS derived from the INS spectra have been used to compute the heat capacity and entropy of the surface water. We will present a comparison of INS measurements with calorimetric data that will provide additional insight into the structure and dynamics of water confined on the surface of SnO_2 nanoparticles. These results will also be compared with our previous results of the influence of adsorbed water on the energetics of TiO_2 (rutile and anatase) nanoparticles [2-3].

[1] Boerio-Goates *et al.* (2006) *Nano Lett.*, **6**, 750-754. [2] A. A. Levchenko *et al.* (2007), *J. Phys. Chem. A*, **111**, 12584-12588. [3] E. C. Spencer *et al.* (2009) *J. Phys. Chem. A*, **113**, 2796-2800.

Landweber-EXAFS structural analysis of aqueous polynuclear U(VI) complexes with tartaric acid

A. ROSSBERG[1,2], C. LUCKS[1], S. TSUSHIMA[1]
AND A.C. SCHEINOST[1,2]

[1]Forschungszentrum Dresden-Rossendorf, P.O. Box 510119, 01314, Dresden, Germany
(*correspondence: rossberg@esrf.fr)
[2]Rossendorf Beamline at ESRF, B.P. 220, 38043 Grenoble Cedex, France

In coordination chemistry, an open question is if the structure of an aqueous metal complex is equal to the structure of its solid form. While the structure of the solid can usually be determined with great reliability and precision by XRD, determination of the structure in solution by EXAFS may be much more biased. An intrinsic problem of EXAFS shell fitting is that the radial pair distribution function (RPDF) is approximated by Gaussians functions imitating the coordination shells. Different combinations of shells can yield different structures with similar fit quality, thereby making the structural solution non-unique. Even the so-called F-test often does not yield a unique solution.

Therefore, we developed two methods which enable the direct calculation of the RPDF and the spatial structure of metal complexes in solution. Solely based on the FEFF scattering theory, the Landweber inverse method [1] yields the RPDF for the aqueous bi- and tri-nuclear U (VI)-tartaric acid complexes without predefined assumptions about the form of the RPDF. With this information and density functional theory (DFT) calculations, the spatial structures of the complexes are refined by Monte Carlo Target Transformation Factor Analysis [2], which also include the calculation of higher order scattering events. Using this combinatorial structural analysis, we were able to show that in the $(UO_2)_3$ $(H_{-1}Tar)_3$ $(OH)_2^{5-}$ complex a central equatorial oxygen atom at a radial U-O distance of 2.22 Å connects the three uranium atoms symmetrically. Consequently, the formula of the aqueous complex corresponds to its stoichiometric equivalent $(UO_2)_3$ $(\mu_3\text{-O})(H_{-1}Tar)_3^{5-}$.

[1] Rossberg & Funke (2010), *J. Synchr. Rad.* **17**, 280-288. [2] Rossberg *et al.* (2005), *Anal. Bioanal. Chem.* **383**, 56-66.