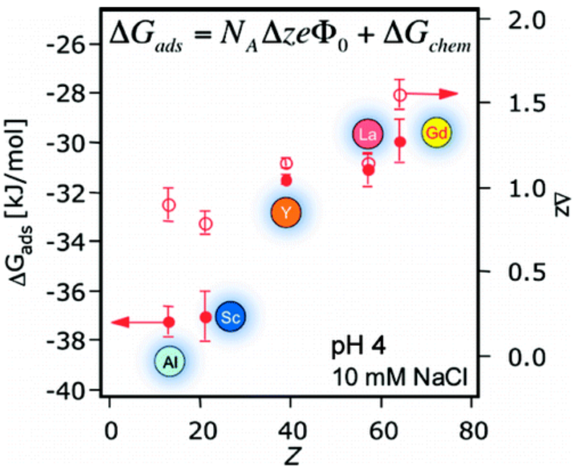
As part of the above-mentioned grant project, a total of two papers were published. The abstracts are given below.

Two graduate students who worked on the grant received their PhDs and are now gainfully employed at Nalco (Dr. David Jordan) and at Dupont (Dr. Jessica Malin). A third PhD student involved in the project is completing her PhD this summer and will likely move on to a postdoctoral position following graduation.

U(VI) Adsorption and Speciation at the Acidic Silica/Water Interface Studied by Resonant and Nonresonant Second Harmonic Generation (Cited 7 times)

Jessica N. Malin, Joseph G. Holland, Sarah A. Saslow, and Franz M. Geiger

J. Phys. Chem. C, **2011**, *115* (27), pp 13353–13360

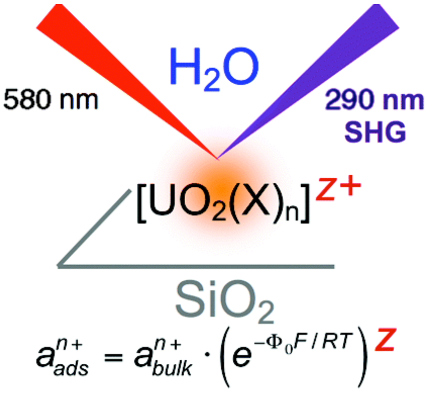


Second harmonic generation (SHG) was used to study U(VI) interactions with a buried mineral oxide/water interface using pH 4 uranyl solutions that contained carbonate and environmentally relevant electrolyte concentrations. SHG resonance enhancement at 290 nm was observed at a NaCl concentration of 10 mM, whereas it was necessary to collect the adsorption isotherm using the nonresonant $\chi^{(3)}$ technique at 1 mM NaCl concentration. Both methods resulted in the same (within one kT) adsorption free energy of −33 kJ/mol. This value is 10 kJ/mol less favorable than the free energy that was previously reported for the same system at pH 7, indicating that uranyl–surface interactions depend on pH. The charge density due to adsorbed uranyl species was also determined via the $\chi^{(3)}$ technique to be +0.0031(5) C/m^2, which is half the magnitude previously measured at pH 7. On the basis of the resonant and nonresonant SHG data, it is concluded that the surface-active uranyl species at pH 4 are neutral or univalent, cationic species, which, based on thermodynamic speciation calculations, can consist of the following aquated species present in bulk solution at pH 4: $UO_2(OH)_2$, UO_2OH^+, and UO_2CO_3. The results of this work are of value as benchmarks for geochemical transport models of uranium pollution resulting from acid mine drainage and nuclear waste storage.

Exponential Sensitivity and Speciation of Al(III), Sc(III), Y(III), La(III), and Gd(III) at Fused Silica/Water Interfaces (Cited 6 times)

David S. Jordan, Sarah A. Saslow, and Franz M. Geiger

J. Phys. Chem. A, **2011**, *115* (50), pp 14438–14445



The binding contants, adsorption free energies, absolute adsorbate number densities, and interfacial charge densities of Al(III), Sc(III), Y(III), La(III), and Gd(III) interacting with fused silica/water interfaces held at pH 4 were determined using second harmonic generation and the Eisenthal $\chi^{(3)}$ technique. By examining the relationship between the measured adsorption free energies and the electric double layer interfacial potential at multiple electrolyte concentrations, we elucidate the charge state and possible binding pathways for each ion at the fused silica surface. Al(III) and Sc(III) ions are

found to bind to the fused silica surface as fully hydrated trivalent species in a bidentate geometry. In contrast, the Y(III), La(III), and Gd(III) ions are each shown to adsorb to the silica surface in a decreased charge state, but the extent and mode of binding varies with each ion. By quantifying the exponential sensitivity of the surface coverage of the adsorbed ions to their charge state directly at the fused silica/water interface, we provide benchmarks for theory calculations describing the interactions of metal ions with oxide interfaces in geochemistry and hope to improve the prediction of trivalent metal ion transport through groundwater environments.