Metals in Nanodroplets

KONO H. LEMKE[1]

[1]Department of Earth Sciences, University of Hong Kong, Pokfulam Road, Hong Kong, SAR (kono@hku.hk)

We have investigated the solvation of metal ions, in particular gold, together with anionic ligands and protons in droplets of 50-2000 water molecules using DFT-based molecular simulations techniques. Hydrated metals ions, such as Au^+, show a strong propensity for the air/water interface comparable to H_3O^+, resulting in a metal-enriched acidic water droplet surface. Anions such as Cl^-, Br^- and I^- reside at the droplet surface, whereas F^- and OH^- exhibit a propensity for deeper regions of water droplets with a strong dependence on droplet size. Our DFT results also show that AuCl readily dissociates at the air/water interface into a linear H_2O-Au^+-H_2O complex, consistent with results from IR spectroscopic experiments and *ab initio* calculations (Li *et al*, 2012), and surface solvated chloride. Both ions Au^+ and Cl^- retain a propensity for the interfacial region in all droplet sizes with a stabilization energy of 4-6 kcal/mol relative to surface-solvated AuCl; larger clusters such as $(AuCl)_n$ on the other hand concentrate into the interior regions of water droplets and are stabilized by ~25 (n=2) and ~33 (n=3) kcal/mol relative to surface-solvated forms. These results reproduce some of the surface solvation effects observed in ESI-MS/IRMPD experiments and theoretical calculations of mass-selected gold water clusters (Reveles 2007; Li *et al*, 2012; Lemke 2014), and suggest that metal complexes, such as AuCl, dissociate at the air/water interface, whereas larger clusters migrate across the interfacial region into the droplet interior. The propensity of Au^+ to partition to the water droplet surface has important consequences for our understanding of metal speciation at the air/water interface of ore vapor droplets; results from ongoing experimental studies and molecular simulations of metal water droplet systems will be presented.

References: Li *et al* (2012) *J. Phys. Chem. A*, **116**, 10793; Reveles (2014) *J. Am. Chem. Soc.*, **129**, 15565; Lemke (2014) *Phys. Chem. Chem. Phys.*, **17**, 7813.