Metal speciation and solvation in vapor-like ore fluids by FT mass spectrometry and quantum chemistry

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Metal clustering and solvation in hydrothermal ore vapors

Solvation takes place on mineral and bacterial surfaces, around ions in solution and on the surface of biomolecules, and is intimately linked to metal transport and deposition in the Earth's upper crust; e.g., upon boiling, there is extensive vapor partitioning of metals (e.g. Cu, Au) in minerals or on mineral surfaces as H and OH, or as free water; As this water buoyantly rises through the crust to shallower depths, boiling takes place leading to a low-density water phase (vapor) and a coexisting bulk fluid, both with different physico-chemical properties. This vapor phase stands out due to its high mobility, but more importantly, it has a polarity similar to that of an organic solvent. In other words, boiling in the upper crust produces large quantities of water vapor with methanol-like solvent characteristics. This low polarity vapor is intimately linked to metal transport and deposition in the Earth's upper crust; e.g., upon boiling, there is extensive vapor partitioning of metals (e.g. Cu, Au), complexity and aggregation of metals toward larger cluster is enhanced, and the solubility of minerals is affected by this low dielectric constant aqueous medium. There are, however, still large knowledge gaps in our understanding of the molecular-scale solvation and stability of metal species in water vapor, in particular, with respect to metal ion clusters.

Clusters: intermediate states between gas phase and bulk

![Fig. 1. Ion mass spectra of polynuclear sodium chloride clusters with magic number structures at 1,13 and 1,22](image)

Metal clusters are receiving increasing interest because they have physicochemical properties characteristic of both gases and solids, but also because they exhibit size-dependent properties. At present, there are only a handful of experimental and theoretical studies, which have probed interactions between water molecules and metal clusters in simulated water vapor. The majority of these studies have focused on the composition of a given solvated metal cluster, rather than examining the structure of the solvation shell itself. The key interest of our group at HKU is the ion resonance mass spectrometric (ESI FT-ICR MS), infrared multiphoton dissociation (IRMPD) spectroscopic and theoretical investigation of metal clusters, and participation to probe the water solvation shell surrounding mass-selected molecular ions by IRMPD.

Ion resonance mass spectrometry and IRMPD spectroscopy

The IRMPD laser system (a, b, d) is housed in a nitrogen-purged DH chamber and is located around 2 m from the mass spectrometer’s ZnSe viewport. Tunable IR (2400-4500 cm⁻¹) is directed from the OPO/OPA laser system at 10Hz into the FT-MS ICR cell pumped by a Surelite Nd:YAG surelite laser at 1064 nm; IR photofragmentation experiments in more strongly bound systems are conducted using a combination of OPO/OPA and cw CO₂ lasers.

Metal speciation in water vapor: a case study of [Au₂Cl₅₋₉OH₊(H₂O)ₙ]⁺

![Fig. 2. Photocyclotron excitation, detection, CID, ejection (schematic below), FT-MS (a–e) and IRMPD (lower panel)](image)

The FT mass spectrometer and IRMPD systems are located in the Department of Earth Sciences at HKU. The mass spectrometer uses a shielded 7 Tesla superconducting magnet (e, below) and rests in a 4 K liquid helium bath (400 L), which is housed in a liquid nitrogen bath surrounding the He reservoir.

Cluster structures and energies: basin-hopping and ab initio results

Correlations between ESI-MS and vapor speciation data can be obtained provided that solutions are electrosprayed over a broad concentration range with minimal pH change (here pH 1.98-2.98). So, if the distribution of clusters were merely an artifact of the ESI process, then changes made to ESI stock (concentration, pH and solution age) would have little or no effect on the species distribution and abundance in the ion mass spectra. This is quite the opposite of what we have observed in our ESI-MS experiments here, and, in fact, by systematically modifying the composition of the ESI solution, we have observed a direct response in the ESI mass spectra, a feature rooted in Au-ligand complexation and solvation equilibria occurring in the vapor.

![Fig. 3. Positive ion-mode ESI mass spectra of aqueous AuCl₄⁻ (50mM) showing four major families of microsolvated gold clusters](image)

![Fig. 4. Theoretical MP2/aVTZ equilibrium structures of dinuclear ion-molecule clusters with Au(I) and Au(III)](image)

![Fig. 5. Normalized ion abundances of solvated mono- and dinuclear gold clusters obtained from electrosprayed aqueous solutions of AuCl₄⁻ in the concentration range 5–50 mM](image)

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