Structures of solvated metal ion clusters by infrared multiphoton dissociation (IRMPD) spectroscopy and ab initio calculations

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Molecular complexation and microsolvation processes play a key role in the transport of metals in aqueous fluids. Understanding the structure of molecular metal ions in aqueous media has therefore become a topic of intense research, with important implications for the transport of metals by vapor and isotopic fractionation processes at gas/liquid interfaces. In order to probe metal speciation and, in particular, the solvation environment around larger ion clusters, we have begun a systematic survey of representative metal-perchlorate clusters $[M_n(ClO4)_{2n-1}]^+(H_2O)_m$, M=Mn, Ni, Cu, Co, Zn) using a combination of electrospray ionization (ESI), ion resonance mass spectrometry and tunable IR spectroscopy. Briefly, ion cluster experiments were conducted on a modified ESI FT-ICR mass spectrometer mated to a Nd:YAG pumped table-top OPO/POA laser system. The OPO/OPA produces 10-15 mJ/pulse IR radiation over the 2500-4500 cm^{-1} range and is coupled to a CW-CO$_2$ IR laser that is employed to preheat more strongly bound ion clusters. Metal perchlorate clusters were generated by ESI of dilute (0.1-1mM) solutions of metal perchlorate salts, and IR spectra, in the OH-stretching range (3400-3750 cm^{-1}), were recorded on mass-selected ion clusters of the type $[M_n(ClO4)_{2n-1}]^+(H_2O)_m$. For example, in ESI mass spectra of aqueous $Mn(ClO_4)_2$ we identified clusters of the general form $[Mn_n(ClO_4)_{2n-1}]^+(H_2O)_m$ with $n \leq 3$ and $m \leq 5$. Upon mass isolation of $Mn_2(ClO_4)_3]^+(H_2O)_3$, we observed slow dissociation to more stable $[Mn_2(ClO_4)_3]^+(H_2O)_2$, primarily due to background black-body radiation, and a shift in the IR spectra of the dihydrate to vibrations of O-H bonds not involved in hydrogen bonding. Measured IRMPD spectra of $[Mn_2(ClO_4)_3]^+(H_2O)_m$ have also been compared against those predicted using MP2 theory using cc-pVTZ basis sets for Mn, cc-pVTZ for O and H and cc-pV(T + d)Z for Cl. Trends in the measured OH-stretching bands in $[Mn_2(ClO_4)_3]^+(H_2O)_2$ are qualitatively consistent with theory, which predicts a global minimum in which each H_2O molecule attaches to one Mn site in $[Mn_2(ClO_4)_3]^+$ and, a higher energy (20.5 kJ/mol) isomer in which both water molecules are bound to one Mn site of $[Mn_2(ClO_4)_3]^+$ and H-bond with perchlorate oxygens giving rise to red-shifted OH stretching vibrations.