Charge separation and the early stages of dissolution in hydrated salt clusters

C. Johnson, C. Leavitt and M. Johnson

Sterling Chemistry Laboratory, Department of Chemistry, Yale University, 225 Prospect St., New Haven, CT, 06511

E-mail: mark.johnson@yale.edu

We investigate the intermolecular interactions involved in the first steps of salt dissolution by Cryogenic Infrared Vibrational Predissociation spectroscopy of cold (~35 K), tagged, size-selected hydrated salt clusters. These clusters are produced by electrospray ionization of salt solutions and transferred to a 10 K Paul trap where they are cooled so that messenger “tag” molecules (D₂, N₂) condense on them. From the trap they are extracted into a tandem time-of-flight mass spectrometer and interrogated by a tunable infrared laser system. For MOH⁺(H₂O)ₙ (M=Mg, Ca, n=1-6) clusters we follow the evolution of the OH stretching bands with increasing hydration. The spectra show that the once-distinct hydroxide stretch becomes indistinguishable from the water OH stretches, signaling the beginning of dissolution to M^{2+} + OH⁻ as the hydroxide begins to integrate into the water network. Simultaneously, an extremely broad (~500 cm⁻¹ FWHM), red-shifted OH stretching band appears which is attributed to large-scale motion of shared protons in the water network. Calculations show that these phenomena occur at size ranges where hydration in the second water shell becomes energetically competitive with first shell hydration. Additionally, infrared spectra of the cluster [(H₂O)ₙMgSO₄Mg(H₂O)ₘ]^{2+} reveal the striking effect of asymmetric solvation (n ≠ m) of the Mg cations on the splitting of the nominally degenerate SO₄ asymmetric stretching bands. This splitting is tracked to the partial dissolution of the more hydrated Mg cation.