BISULFATE (HSO_4^-) DEHYDRATION AT THE VAPOR/SOLUTION INTERFACE PROBED BY VIBRATIONAL SUM FREQUENCY GENERATION SPECTROSCOPY

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With perspective towards atmospheric chemistry, ion behavior at vapor/solution interfaces has important implications for understanding aqueous aerosols as reactions at this interface control the growth and uptake of the aerosol. Sulfate species are a major ionic component of aqueous acidic tropospheric aerosols with bisulfate (HSO_4^-) being the major sulfate species at pH values lower than 2. The application of inherently interface specific spectroscopic methods such as vibrational sum frequency generation (VSFG) allows for resolution of interfacial chemical species versus the bulk species facilitating a clearer understanding of chemical phenomena taking place at vapor/solution interfaces. Here we present VSFG results on the effects that cation identity have toward the molecular environment experienced by bisulfate anions residing within the vapor/solution interface for aqueous H_2SO_4, Na_2SO_4, and $MgSO_4$ solutions. By probing the ν_{SS}-SO_3 vibrational mode of interfacial bisulfate anions directly we are able to elucidate the influence that Na^+ and Mg^{2+} ions have toward bisulfate hydration within the interface. Our results indicate that Na^+ and Mg^{2+} perturb the hydration of interfacial bisulfate anions but do not form ion-pair complexes. Mg^{2+} is found to exhibit a larger net influence on bisulfate hydration relative to Na^+.