Sum Frequency Generation of O-H Vibrations on the Surface of H_2O/HNO_3 Solutions and Liquid HNO_3

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The surfaces of aqueous HNO_3 are examined using sum frequency generation (SFG). A molecular-level picture of these atmospherically relevant systems is developed. Consistent with previous interpretations, an electric double layer comprised of subsurface anions and cations develops in 0.005x and 0.01x HNO_3 solutions, where x = mole fraction. Compared to pure water, these solutions generate more SFG signal in the hydrogen-bonded region as water molecules respond to the subsurface electric field by aligning with the surface normal. At higher concentrations, 0.05x and 0.4x HNO_3, ionic complexes or molecules sufficiently approach the surface to disrupt the hydrogen-bonding network and perturb the first water layer. Neither liquid nitric acid nor its solutions show a clear O-H.