Nitrate Ions and Ion Pairing at the Air-Aqueous Interface
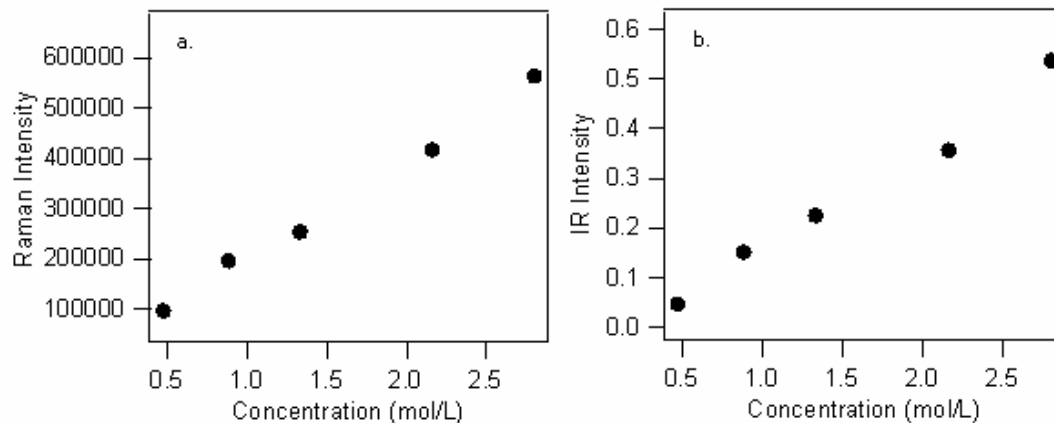Man Xu, Cheng Y. Tang, Aaron M. Jubb, Xiangke Chen, and Heather C. Allen*

Figure S1. Raman (a) and IR (b) intensities of the nitrate symmetric stretch peak as a function of molarity. Molarity units (dividing by volume) allows comparisons of transition moment strengths at different concentrations.

Table S1. Nitrate concentrations in units of m, x, and M.

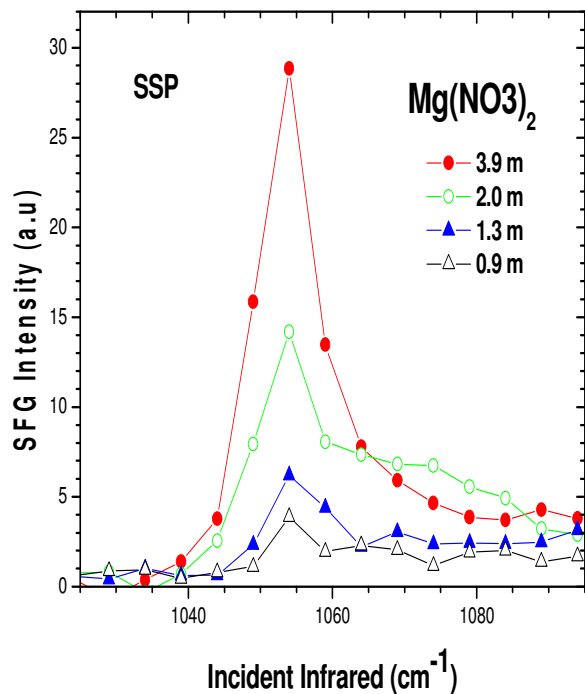|	Molality, m (moles per kg of water)	Salt Mole Fraction, x	Molarity, M (moles per liter)
$Mg(NO_3)_2$	2.6	0.045	1.9
	3.3	0.056	2.2
$Ca(NO_3)_2$	2.6	0.045	2.0
	3.3	0.056	2.3
$Sr(NO_3)_2$	2.6	0.045	2.3
	3.3	0.056	2.7

Figure S2. ssp polarized VSFG spectra (arbitrary intensity units) of aqueous $Mg(NO_3)_2$ revealing a decreasing SFG intensity trend with decreasing concentration. A higher frequency peak is observed for 2.0 m similar to the 2.6 m spectra in the article. For the 1.3 m and 0.9 m, the higher frequency region is below our signal to noise level.

Figure S2 data acquisition details:

1. 30 s exposure time with 5 cm^{-1} step-size (1025 cm^{-1} to 1095 cm^{-1})
2. Applied EM gain on CCD: 150
3. 3.9 m spectrum (average of 2)

   2.0 m spectrum (average of 3)

   1.3 m spectrum (average of 2)

   0.9 m spectrum (average of 2)
4. DFG crystal GaSe (8 μm -16 μm)

   a. Average IR energy at the sample stage ~50 μJ in the range of 1025 cm^{-1} to 1095 cm^{-1}

   b. Visible energy ~300 μJ