Temperature and electric field dependence of asymmetric stretching of nitrate ion, KONNOR K. JONES\* and MATTHEW J. NEE, Department of Chemistry, Western Kentucky University, 1906 College Heights Blvd., Bowling Green KY, 42101.

Photolysis of nitrate ion in the natural environment produces NO, NO2, and O3, releasing these toxic gases into the atmosphere. Work done by other groups has shown ionic strength dependence of product ratio of aqueous nitrate ion. To better understand the kinetic mechanisms of nitrate photolysis, the effects that ionic strength in solution have on nitrate ion symmetry breaking are needed. Different solvation environments induce nitrate bonding motifs that may be correlated to the product ratio. Fourier-transform infrared spectra of aqueous nitrate–ion solutions were obtained at different temperatures for several total electrolyte concentrations. The electric fields (arising from water molecules and ions in solution) in aqueous potassium nitrate solution distort the trigonal planar shape of the nitrate ion, which may favor a specific initial path of the decomposition of nitrate during photolysis. Van’t Hoff plots of the relative peak areas corresponding to the formally-degenerate asymmetric stretching mode reveals the relative energies of the two solvation geometries. The difference in energy between the two geometries is linearly proportional to the ionic strength of the solution. Electronic structure calculations suggest that the more symmetric geometry has an increased stability relative to the less-symmetric geometry in high ionic strength solutions. Thus, the relative amounts of the nitrate ion solvation geometries can be correlated to the amount of products produced during photolysis to help explain the ionic-strength dependence of the product yields. Nitrate geometries at the water—CCl4 interface and aqueous carbonate ion bonding motifs are being investigated to identify pure-water effects.