



## Anion-catalyzed Disproportionation of Nitrogen Dioxide on Microdroplets Surfaces

M. R. Hoffmann, S. Enami, and A. J. Colussi

California Institute of Technology, Environmental Science & Engineering, Pasadena, CA, United States (mrh@caltech.edu)

The reactive dissolution of  $\text{NO}_2(\text{g})$  on cloud and fog droplets and the conversion to  $\text{HONO}(\text{g})$  :  $2 \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) = \text{HONO}(\text{g}) + \text{NO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$ , is a viable transformation process. Recently, unexpectedly large HONO concentrations were observed that may account for  $\sim 50\%$  of OH radical production at noon and entail a diurnal source  $\sim 64$  times stronger than the reaction above at night (Kleffmann, *Chem. Phys. Chem.* **2007**, 8, 1137). Reported  $\text{NO}_2(\text{g})$  uptake coefficients in water are at odds in the range from  $\gamma_{\text{g}} 10^{-7}$  up to  $10^{-3}$ . Here we show that the probability of  $\text{NO}_2$  uptake on aqueous microdroplets depends on their ionic composition at the air/water interface, reaching peak values at ion concentrations in the low mM range, using a novel application of electrospray mass spectrometry. We found that the uptake rates under these conditions are three orders of magnitude larger than in pure water. Uptake appears to be controlled by the capture of  $\text{NO}_2$  into radical anion intermediates on droplet surfaces, and is modulated by overall anion concentration. These results would resolve the outstanding discrepancies between previous  $\text{NO}_2$  uptake measurements in water vs. NaCl-seeded clouds, and lead to half-lives for the reactive dissolution of  $\text{NO}_2$  in typical clouds and fogs that are sufficiently short to impact diurnal  $\cdot\text{OH}/\text{HO}_2\cdot$  budgets.