Supporting Information for

Measurements of Immersion Freezing and Heterogeneous Chemistry of Atmospherically Relevant Single Particles with Micro-Raman Spectroscopy

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Additional Experimental Methods. Supporting information contains calibration data for relative humidity and temperature within the environmental cell. This includes: relative humidity (RH) calibration data using different inorganic salts – NaCl, NaNO₃, Na₂SO₄, NH₄NO₃ and (NH₄)₂SO₄; temperature calibration data using NaCl deliquescence across a temperature range from -25 to 25°C; wet-dry air ratios needed to maintain constant RH and; ozonolysis of oleic acid

Relative Humidity Calibration Data. To calibrate the RH control of the environmental cell, the deliquescence relative humidity (DRH) and efflorescence relative humidity (ERH) values of five inorganic salts, NaCl, NaNO₃, Na₂SO₄, NH₄NO₃, and (NH₄)₂SO₄ were studied. These compounds were chosen because they are well characterized in literature and cover a range of DRH and ERH values. The experimental DRH and ERH values fall within the reported literature error, showing good agreement, as seen in Figure S1.

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Figure S1. Plot comparing experimental (circle) and literature (triangle) deliquescence relative humidity (DRH, blue markers) and efflorescence relative humidity values (ERH, red markers) for different of inorganic salts with a wide range of DRH and ERH values.

Temperature Calibrations Data. The temperature within the environmental cell was calibrated to correct for differences between the set temperature and the actual temperature that the particles experience in the environmental cell. Using the DRH of NaCl and equations 1-6 given in the main text, the actual temperature that the particles experienced was back calculated. Spectra were taken throughout the water uptake experiments, monitoring for spectral changes (growth of the OH peak between 3200cm⁻¹ and 3600cm⁻¹) indicating water uptake. Figure S2 shows water uptake spectra from selected temperatures at the DRH. The correlation between set temperature and actual temperature experienced by the particle is shown below in Figure S3. The deviation between set temperature and the actual temperature is largely due to the use of the water/glycol chiller and may potentially be improved by the use of a cryogenic chiller. There is good linearity through the full range of temperatures.



Figure S2. Plots a) through f) show spectra of NaCl before (red) and after (varying colors) DRH at ~75% RH as indicated by the growth of the O–H stretching band between 3200 and 3600 cm⁻¹ seen at the DRH. The temperatures decrease from 25°C through -25°C in spectra a) through f).



Figure S3. Calibration of environmental cell set temperature to actual temperature experienced by the particle. As shown above there is an ca. ten degree offset.

Wet-Dry Air Ratios for Constant RH. One crucial component to conducting immersion freezing ice nucleation measurements is maintaining a constant RH throughout the freezing event. To do this, water uptake experiments were conducted to find the wet to dry ratios of N₂ to maintain constant RHs throughout different temperature and RH ranges. Plotted in Figure S4 are trajectories for several different RHs and the different wet to dry ratios to apply to maintain constant RH at different temperatures.



Figure S4. Trajectories of wet to dry mixing ratios followed to maintain a constant RH as temperature changed. Each different color marker corresponds to a different RH (red: 20%, orange: 40%, green: 85%, blue: 90%, purple: 100%).

Ozonolysis of Oleic Acid. Prior to studying the impact of ozone on ice nucleation, validation of the system was preformed using oleic acid. Following the procedure detailed in the Experimental Methods section, oleic acid was deposited on a substrate and then reacted in the environmental cell at 50% RH and 10 ppm ozone for 1 hour. Figure S5 shows the spectra of oleic acid before and after reaction. Loss of peaks at 1302, 1658, and 3011 cm⁻¹ correspond to the loss of the C=C bond at 1658 cm⁻¹ and the olefinic C-H stretching and bending modes at 3011 and 1302 cm⁻¹ due to the ozonolysis reaction, consistent with literature on this well-known reaction.¹



Figure S5. Spectra of oleic acid particle before (red) and after (blue) reaction with ozone. Most evident in the spectra is the loss of the C=C bond at 1658 cm⁻¹, loss of the olefinic C-H bend and stretching modes at 1302 and 3011 cm⁻¹, respectively, as a result of reaction with ozone.

References

(1) Zahardis, J.; Petrucci, G. A. *The Oleic Acid-Ozone Heterogeneous Reaction System: Products, Kinetics, Secondary Chemistry, and Atmospheric Implications of a Model System-a Review*; 2007; Vol. 7.