

Supporting Information for

**Simulating Atmospheric Freezing of Single Aqueous Droplets to Ice in a  
Cryogenically Cooled Ultrasonic Levitator**

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## **S1. Experimental methods**

**S1.1. Ultrasonic levitator apparatus:** In the acoustic levitator apparatus used in the present experiment, ultrasonic sound waves with a frequency of 58 kHz are produced by a piezoelectric transducer and they are reflected from a concave plate mounted vertically upwards thus generating a standing wave. The soundwaves produce acoustic radiation pressure, which allows a liquid droplet or a tiny solid particle to levitate slightly below one of the pressure minima of the standing wave (1-7). The distance between the transducer and reflector is set to 2.5 times the wavelength of the soundwave used in the set up (or 14.8 mm) producing five pressure nodes in total, although only the second and third pressure nodes above the ultrasonic transducer are suitable for levitation. The largest diameter of droplets or particles that can be held steadily while levitated in the present apparatus is approximately 3 mm, whereas the smallest could be as low as 15  $\mu\text{m}$ . Here, the water droplets loaded in the pressure node assume an oblate spheroidal shape due to the acoustic radiation pressure and their volumes are determined accordingly.

**S1.2. Cryogenically cooled process chamber and sampling system:** The levitator assembly is enclosed within a pressure-compatible process chamber with a total volume of about 15 liters made of stainless steel to permit levitation in an inert gas or a highly reactive gas to investigate chemical reactions. The process chamber is also surrounded by spectroscopic (FTIR, Raman and UV-Vis spectrometers) as well as visualization tools (high-speed optical and infrared cameras) to identify any characteristic chemical or physical alterations of the levitated sample(s). A custom-made cylindrical cooling jacket fillable with liquid nitrogen is inserted from the top to be placed in between the wall of the process chamber and levitator unit to cool the environment inside the chamber. To allow all the spectroscopic and camera probes on the levitated samples, the cooling jacket was designed with customized cuts, and it is interfaced with a liquid nitrogen Dewar housed outside. Further, the process chamber is well insulated outside to expedite the cooling process. In the present experiments, the chamber was filled with nitrogen gas (Matheson, Research Purity 99.9999%) at the temperature and total pressure of 293 K and 760 Torr, respectively, instead of (dry) air, since the trace gas impurities within the dry air could not be totally removed and they may chemically interact with the aqueous droplets, influencing freezing process and stability of the ice particle (8, 9). Therefore, in order to prepare a pristine and inert environment surrounding the aqueous droplet, dry nitrogen was used as a benchmark.

Temperature inside the process chamber was monitored by a silicon diode sensor (Lakeshore, DT-670) mounted on a copper block, held by a second wobble stick and read out via a temperature controller (Lakeshore, 331 Temperature Controller). The (inner) surface temperature of the cooling jacket measured by attaching the silicon diode sensor was noted to be  $140 \pm 10$  K, slightly hotter than the liquid nitrogen temperature (77 K) due to thermal conduction across the metal wall and thermal equilibration with the gaseous nitrogen medium inside. By translating the temperature sensor mounted on top of the wobble stick from the atmosphere near the inner wall of the cooling jacket towards the center of the process chamber (the pressure nodes of the acoustic levitator) a slow increasing gradient of temperature was measured. Under thermal equilibrium, the maximum temperature difference between the two mentioned positions were recorded to be about 1.8 K. Along the central vertical axis of the acoustic levitator, the variation in temperature was minimal ( $<0.5$  K). To load water droplets (HPLC grade, degassed, 18.2 M $\Omega$ ), a syringe is attached to an outside port on the chamber which is connected via chemically inert PTFE tubing to a microneedle inside the chamber. The needle is attached to the end of a wobble stick. The PTFE line is wrapped with heating tape to defreeze at lower temperatures below 273K allowing smooth sampling. This droplet deposition system enables the needle tip to be precisely positioned within the second pressure minimum to load a droplet before being withdrawn to a rest position prior to the experiments. During the experiments with levitated aqueous droplet / ice particle in the second pressure node, the temperature sensor was placed at rest about 15 mm from the levitating sample.

**S1.3. Raman spectroscopy:** In the Raman spectrometer, the allowed vibrational transitions were excited by the 532 nm line of a diode-pumped, Q-switched Nd:YAG laser (CrystaLaser, model QL532-1W0) having a beam diameter of 0.35 mm and a divergence angle of 3.8 mR. The average power output from the laser was about 200 mW and its pulse width was 13.5 ns operating at 1 kHz repetition rate. The laser beam was introduced into the chamber through an antireflection coated window from a mirror (Edmund Optics, model NT45-991,  $>99\%$  reflectance) followed by a dichroic beam splitter (Semrock, RazorEdge, model LPD01-532RU-25  $\times$  36  $\times$  2.0). A plano-convex lens with a focal length of 60 mm focused the laser beam onto the sample to form a spot with a diameter ( $1/e^2$ ) of approximately 20  $\mu\text{m}$ . The Raman-shifted photons, backscattered from the droplet are then passed through an ultra-steep long-pass edge filter (Semrock, model LP03-532RE-25) which cuts down the elastically scattered 532 nm laser light. Further the resultant backscattered photons were focused by a 50 mm f/1.8 camera lens (Nikon, Nikkor 2137) into a

HoloSpec f/1.8 holographic imaging spectrograph (Kaiser Optical Systems, model 2004500-501 and Holoplex HPG-532) equipped with a PI-Max 2 ICCD camera (Princeton Instruments) through a slit (width = 100  $\mu\text{m}$ ). The CCD detector is composed of  $1024 \times 256$  pixels each having a spatial resolution of 26  $\mu\text{m}$ . The spectra were collected over the Raman-shift ranges of 200-2450  $\text{cm}^{-1}$  and 2400-4000  $\text{cm}^{-1}$  simultaneously which are obtained by dispersing the total signal by the two overlaid holographic transmission gratings. The resolution of the Raman spectrometer is 9  $\text{cm}^{-1}$ . Both the excitation laser and the detector are operated at 1 kHz repetition rate, and they are externally triggered and synchronized via a pulse generator, Quantum Composer Plus, model-9518. To accumulate only Raman scattering signal, the pulse width for the ICCD detector is kept typically around 50 ns and accumulation time for each spectral trace can be kept in the range of 5-100 seconds. For the experiments presented here a typical gate delay in the range of 480-500 ns was used and gates per exposure was fixed at 1000 shots. The Raman spectrometer was calibrated, i.e. pixel versus wavenumber by recording Raman spectra for levitating droplets of cyclohexane ( $\text{C}_6\text{H}_{12}$ ), toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ) and acetonitrile ( $\text{CH}_3\text{CN}$ ).

**S1.4. Optical and infrared movies and snapshots:** To record the visuals of freezing, a Phantom Miro 3a10 camera operating at repetition rate up to 1 kHz combined with a Navitar Zoom 6000 modular lens system was aligned on the levitated sample via an optical viewport. The temperature measured by the silicon diode sensor represents the temperature of the gaseous atmosphere inside and did not correspond to the accurate temperature of the loaded aqueous droplets. Hence, a high-speed infrared camera (FLIR A6703sc) camera was utilized at a repetition rate in the range of 10 - 250 Hz to determine temperature changes during the freezing of levitated water droplets to ice through an infrared transparent zinc selenide (ZnSe) optical window. The observable levitating samples were selected within the region of interest (ROI) of the camera for precise temperature reading. The mean temperature in the selected ROI was considered, while the error bars designate the deviations from the noted maximum and minimum temperatures. For small aqueous droplets ( $\sim 1\mu\text{l}$ ), the temperature readings from the silicon diode sensor and the IR camera did not differ much ( $< 2\text{ K}$ ) after attaining the thermal equilibration. In the presented freezing event (Figure 2, Movie S1), a typical repetition rate of 40 Hz was used and it was synchronized with the high-speed optical camera via a pulse generator (Quantum Composer Plus, model-9518). Notably, the temperature of the sample at the second pressure node was observed to be the closest to that of the surrounding atmosphere (measured by the silicon diode temperature sensor) than other pressure

nodes. Crystallization of dual aqueous droplets (levitated at second and third nodes) revealed that the timeframe of the freezing processes of individual droplets to be different. This phenomenon can be attributed to the difference in the resulting droplet temperatures arising out of variation in the acoustic radiation pressure acting on the droplets.

**S1.5. FTIR spectroscopy:** The minimal presence of moisture (or other trace gases) in the simulated atmosphere inside the process chamber was spectroscopically identified by collecting FTIR absorbance spectra (acquisition time = 50 s; spectral resolution = 1 cm<sup>-1</sup>) through the full width of the process chamber with an effective path length of 53.35 cm. The FTIR spectrometer system operates in vacuum and combines a VERTEX 70v spectrometer (Bruker) with two stages of copper mirror optics and a liquid nitrogen cooled MCT-B (mercury cadmium telluride, wide band, D315/B) detector. During the experiment, first a background spectrum was recorded of the evacuated process chamber, which was then subtracted from the recorded spectra after filling with nitrogen gas or loading aqueous droplet to check the moisture content.

**S1.6. Relative humidity:** The concentration of the water vapor present in the simulated chamber was measured from the absorption intensity of the mid-infrared band at 1652.92 cm<sup>-1</sup>. The absorption cross-section value for this band (8.12×10<sup>-19</sup> cm<sup>2</sup>·molecule<sup>-1</sup>) was adopted from PNNL database (10). The typical absorbance of the above-mentioned vibrational band for the dry nitrogen filled (760 Torr, 293 K) process chamber was 0.0002 and the concentration of the water vapor evaluated was 4.63×10<sup>12</sup> molecules·cm<sup>-3</sup>. Using this measured water vapor concentration, the relative humidity (RH) of the surrounding atmosphere was calculated. RH is the percentage of the ratio of water vapor pressure (P<sub>w</sub>) to the saturation water vapor pressure (P<sub>ws</sub>) as given in eq. S1

$$RH = (P_w/P_{ws}) \times 100 \quad (\text{eq. S1})$$

Here, the P<sub>w</sub> is the corresponding pressure of the measured water vapor concentration (~ 2.4×10<sup>-4</sup> hPa or 1.76×10<sup>-4</sup> Torr) and P<sub>ws</sub> (in hPa) for the region of temperature between -20°C to + 50°C can be calculated using the standard simple equation provided by the International Association for the Properties of Water and Steam (IAPWS)(11) as eq. S2

$$P_{ws} = 6.116441 \times 10^{((T \times 7.591386)/(T+240.7263))} \quad (\text{eq. S2})$$

Where, T is the temperature in °C.

By using our measured concentration of water vapor within the simulation chamber, the RH of the simulated atmosphere filled with dry nitrogen at 760 Torr and 293 K was found to be only 0.001 %.

We also noted a slight increase in the RH value to 0.004% when a water droplet was levitated at 293 K for substantial duration (60 min) allowing evaporation to vapor phase (with a typical 30% loss in volume of the droplet). However, no significant increase in RH due to the mass loss from the droplet was recorded for usual experimental duration (up to 15 min). The negligible mass loss for the aqueous droplets could be attributed to comparatively lower vapor pressure of water (17.5 Torr at 293 K)(12) and the acoustic radiation pressure acting on the levitated droplet.

Approaching the lower temperature (0°C or 273 K),  $P_w$  and  $P_{ws}$  are also lowered to  $2.15 \times 10^{-4}$  hPa ( $1.60 \times 10^{-4}$  Torr) and 6.116 hPa (4.587 Torr), respectively. The resultant RH is measured to be 0.005%. This negligible magnitude of RH cannot affect the condensation process of the aqueous droplet (13) and does not essentially influence the reported freezing process of the levitated aqueous droplet.

### Other supporting files:

**Movie S1:** Video depicting the stages of freezing process of singly levitated water droplet to ice.

**Dataset:** Raman spectroscopy data

### Supplementary References:

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