# Capturing the freeze-drying dynamics of NaCl nanoparticles using THz spectroscopy

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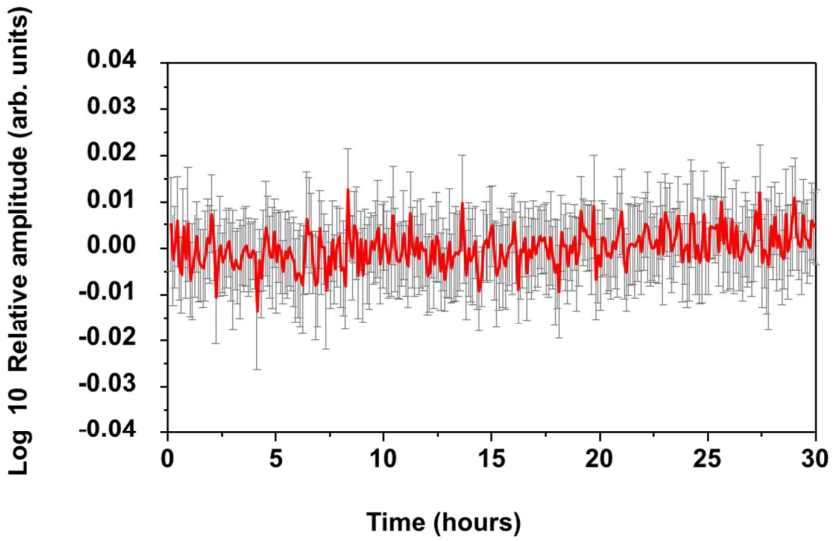



**Figure S1. Measured amplitude variation of detected THz response.** Average amplitude including all frequency components (red) and variation for individual frequency components from 0.3 to 2 THz (gray). Standard variation of all data points is 0.0085 in terms of absorbance, log 10 of relative amplitude, which corresponds to a 1.97% variation in THz signal intensity on a linear scale.

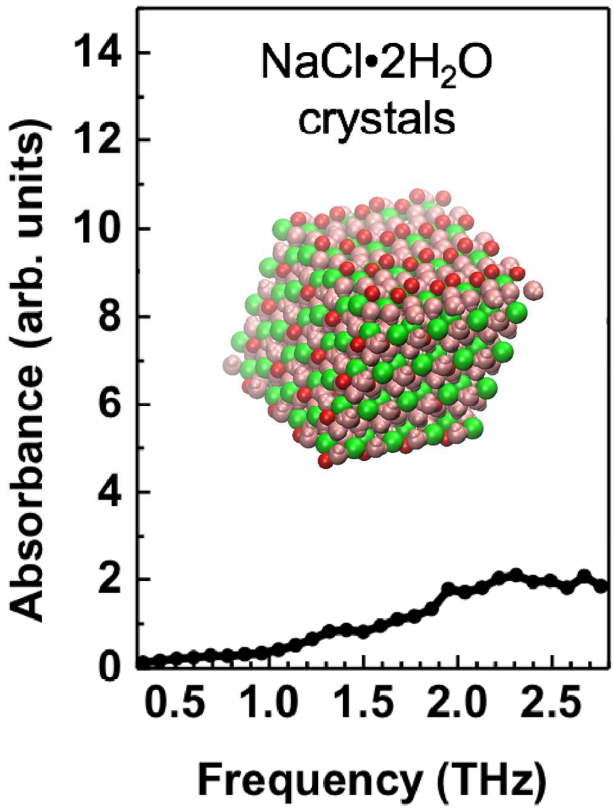



**Figure S2. Calculated THz absorption spectrum of sodium chloride dihydrate crystals.** Illustration: $Na^+$ (red), $Cl^-$ (green) ions, and coordinated $H_2O$ (pink) molecules in sodium chloride dihydrate ($NaCl \cdot 2H_2O$) crystal.

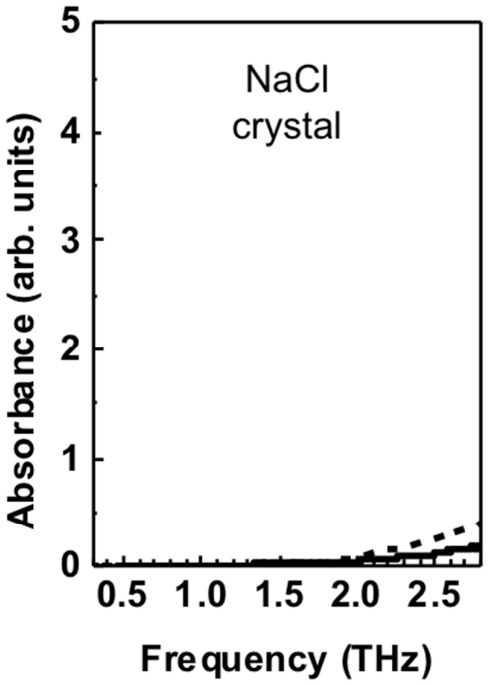



**Figure S3. THz absorption spectra of NaCl crystals.** THz absorption spectra of round polyethylene tablets including 1 mol/L (solid line) and 2 mol/L (dashed line) of NaCl crystal powder measured at 273 K. The THz absorption spectrum of a pure polyethylene tablet was subtracted as a baseline. The tablets were formed with a mechanical compress machine after crushing NaCl crystal powder (Sigma-Aldrich) with polyethylene powder (Sigma-Aldrich) in an agate mortar. The diameter and thickness of the tablets were 10 mm and 1.5 mm ±0.2 mm, respectively.

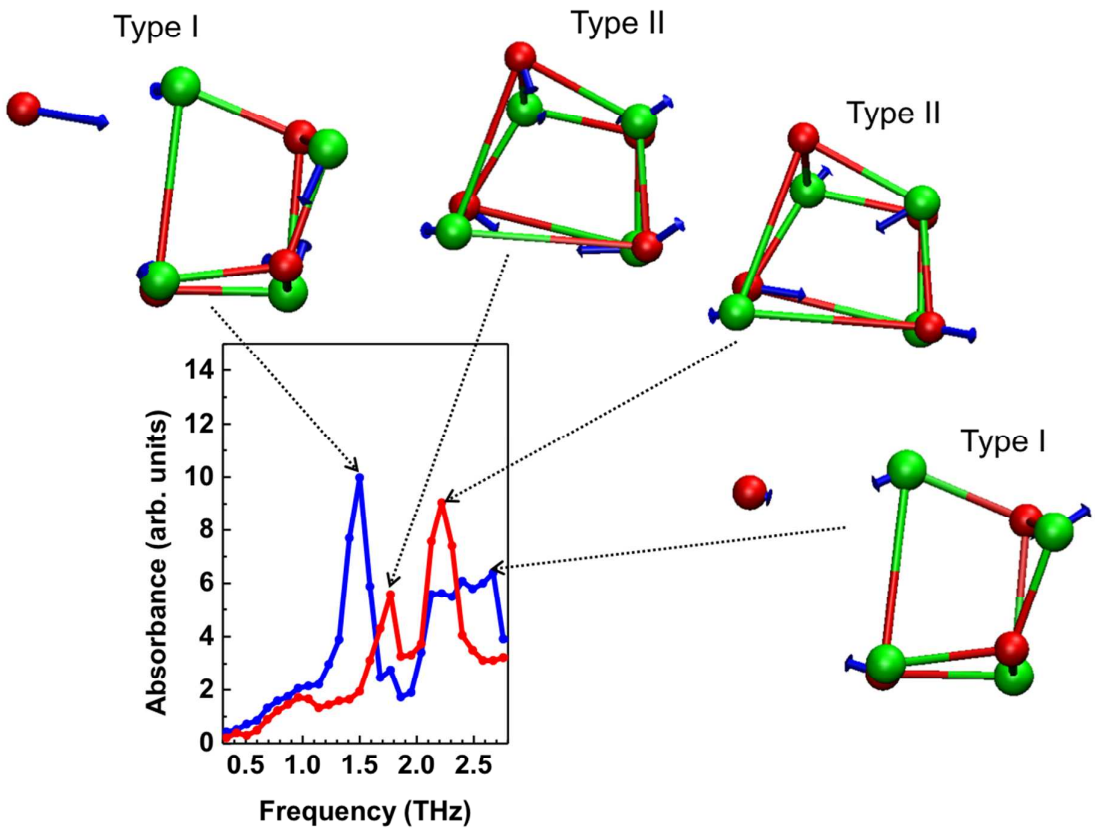
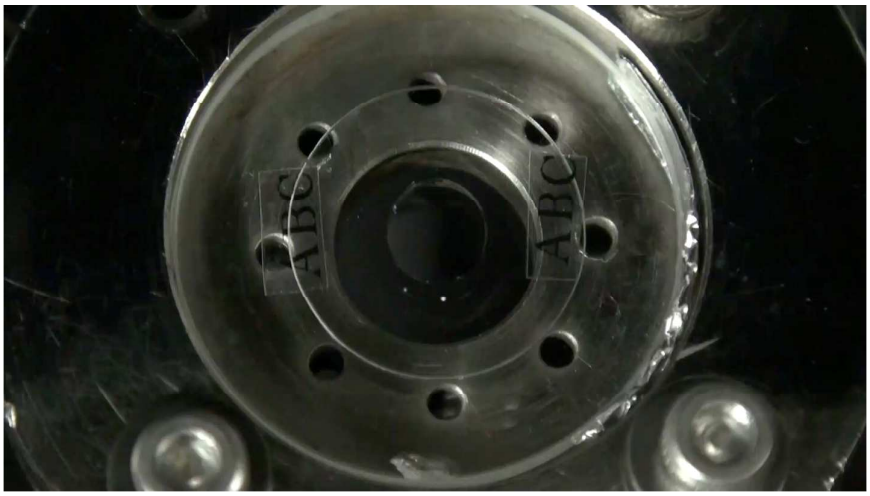
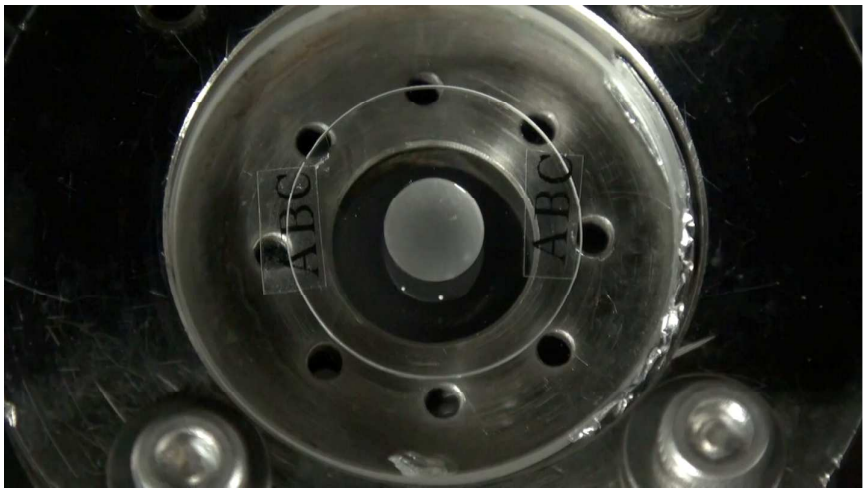


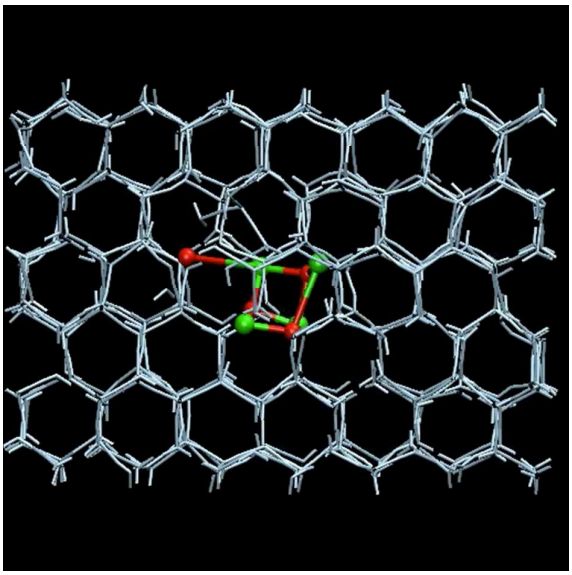

**Figure S4. Normal modes of vibration in Type-I and Type-II unit-cell-sized NaCl-cluster particles in ice.** The blue arrows indicate the vectors of the normal mode of the vibration. The colors of the ions and ionic bonds in the cluster are the same as those in Fig. 4.



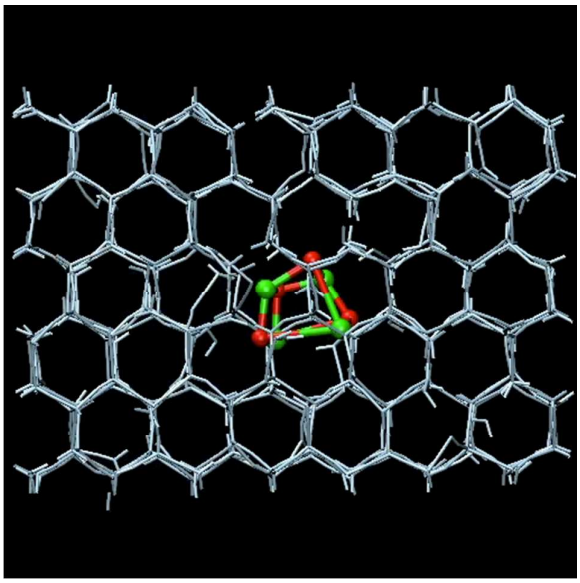

**Movie S1. Movie of freezing NaCl solution.** The 1-mol/L NaCl aqueous solution in a container with polymer sides and a THz-transparent glass plate bottom was cooled down to 250 K. The movie shows that the NaCl solution froze just after the supercooling and hexagonal (Ih) ice appeared (gray in color and corresponding to what is depicted in Fig. 2A and Fig. 2B). The movie is in real time.




**Movie S2. Movie of NaCl solution freezing after the end of Movie S1.** The frozen NaCl aqueous solution was cooled down to 248 K. The movie shows that the frozen NaCl solution transformed into sodium chloride dihydrate (white in color and corresponding what is depicted in Fig. 2B and Fig. 2C).



**Movie S3. Three-dimensional representation of Type-I unit-cell-sized NaCl-cluster particle obtained by molecular dynamics simulations.** The structure in Movie S3 corresponds to that in Fig. 3A. The OH bonds of water molecules composing the honeycomb structure of ice Ih are depicted as white lines. The ionic bonds between the $Na^+$ (red) and $Cl^-$ (green) ions are shown coupled to the centers of ions of the same color. One $Na^+$ ion is at a distance of one ice lattice from the main cluster.



**Movie S4. Three-dimensional representation of Type-II unit-cell-sized NaCl-cluster particle.** The structure depicted in Movie S4 corresponds to Fig. 3B. The colors of the ions are the same as in Movie S3. The cluster is distorted from a cubic lattice configuration.