Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information:

Study of the slow water transport in $MgSO_4$ aerosol droplets at gel-forming relative humidities

Chen Cai[1], Seehua Tan[1], Hongnan Chen[1], Jiabi Ma[1],
Yang Wang[1], Jonathan P. Reid[2*] and Yunhong Zhang[1*]

[1]*The Institute of Chemical Physics, School of Chemistry, Beijing Institute of Technology, Beijing 100081, People's Republic of China*

[2]*School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom*

Surface analysis with physisorption analyzer method

The system included an air oven, which was kept at constant temperature (313 K) to avoid vapor condensation during the vapor adsorption and desorption experiments, as well as the influence from external environmental temperature changes. The manifold tube was connected to turbo pump, helium port, vapor generator, pressure sensors, P_0 station, and three further sample stations. The P_0 station was a cell at a saturated water vapor pressure at 298 K, and can provide water vapor with a given pressure for the sample station. In our case, one sample station was used for the measurements; two are shown in Figure S3 for illustration purposes. The vapor generator was a glass bulb in which liquid water (vapor source) was held. For this work, in conducting humidifying and dehumidifying experiments, the temperatures of the sample stations were controlled by using a thermostatic water bath, and temperature was set at 298 K. The samples needed to be pretreated. Herein, the $MgSO_4$ particles in the sample cell were heated for 3 hr at 150 degree centigrade under vacuum before measurement, which ensured formation of the anhydrous state.

An isochoric method was used for instrumental measurement and the system volume was measured precisely to determine the adsorption. As shown in Figure S3(b), the dead volume V_d, the volume in the sample cell, was measured for every experiment because it changed when the sample cell and the amount of sample were changed. After installing the sample cell and evacuating the measurement system, helium was dosed into the reference volume buffer, V_s, and the pressure $P1_i$ was measured using the pressure sensor P1. Notably, the reference volume buffer V_s has been calibrated. Then, the valve C between V_d and V_s was opened to diffuse He gas into the space of V_d, and closed several seconds later. The pressure at the pressure sensor P1 and P2 were recorded as $P1_e$ and $P2_e$, respectively. The V_d can be determined applying the following equation.

$$V_d(1) = \frac{(P_{1i} - P_{1e}) \times V_s}{P_{2e}} \qquad (1)$$

Then, additional helium gas was continually dosed, and the above measurement processes were repeated. $V_d(2)$, $V_d(3)$...... $V_d(n)$ were calculated in the same manner, and average value of V_d determined.

After obtaining V_d, the adsorptive gas (water vapor) was dosed to V_s through the valve-A. Due to adsorption, the adsorptive gas pressure decreased, and the adsorption was calculated from the pressure difference before and after the adsorption. The gas volume V_1 in V_s (cm^3(standard state)/g^{-1}), which changed before and after the adsorption, was expressed as the following equation. W_s and T are the sample weight and the absolute temperature of V_s, respectively.

$$V(1) = \frac{(P_{1i}(n) - P_{1e}(n)) \times V_s \times 273.15}{101.325 \cdot W_s \cdot T} \qquad (2)$$

The gas volume V_2 in V_d, which changed before and after adsorption, can be determined from the (n-1)th point equilibrium pressure $P_{2e}(n\text{-}1)$ in V_d, and the nth point equilibrium pressure P_{2e} (n) in V_d, as follow.

$$V(2) = \frac{(P_{2e}(n-1) - P_{2e}(n)) \times V_d \times 273.15}{101.325 \cdot W_s \cdot T} \qquad (3)$$

The sample's adsorption change ΔV in the n-th point's adsorption process is equal to the gas volume in V_s and V_d that changed before and after adsorption. Therefore, the adsorption $V(n)$ at the adsorption equilibrium pressure $P_2e(n)$ was

$$V(n) = V(n-1) + V1 + V2 \ (4)$$

The adsorption water vapor ($V(n)$, cm^3(STP).g^{-1}) can be converted into WSR by using the equation

$$WSR = \frac{Va\ [cm^3(STP)g^{-1}] \times M\ [g.mol^{-1}]}{22400\ [cm^3.mol^{-1}]} \qquad (5)$$

in which M [g.mol^{-1}] was the molar mass of the inorganic salt. The measurements of desorption were similar to those of adsorption.

Figure S1. Schematic diagram of experimental setup used for single droplet optical tweezing.

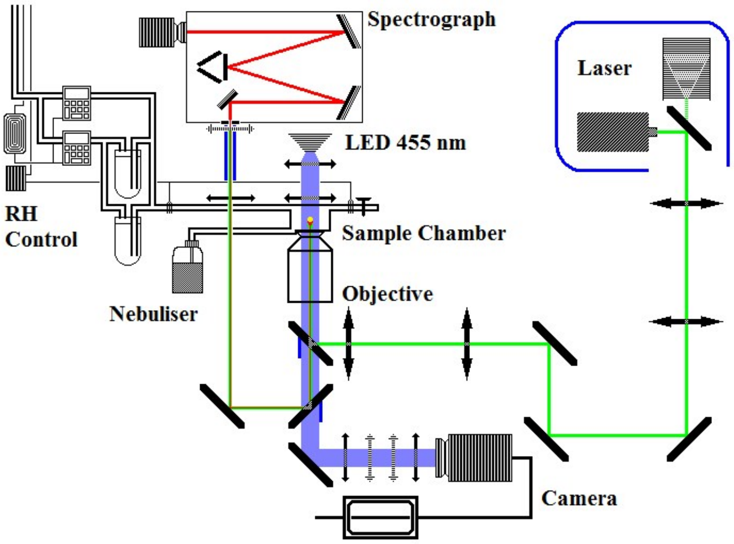

Figure S2. Schematic diagram of the FTIR-ATR experimental setup.

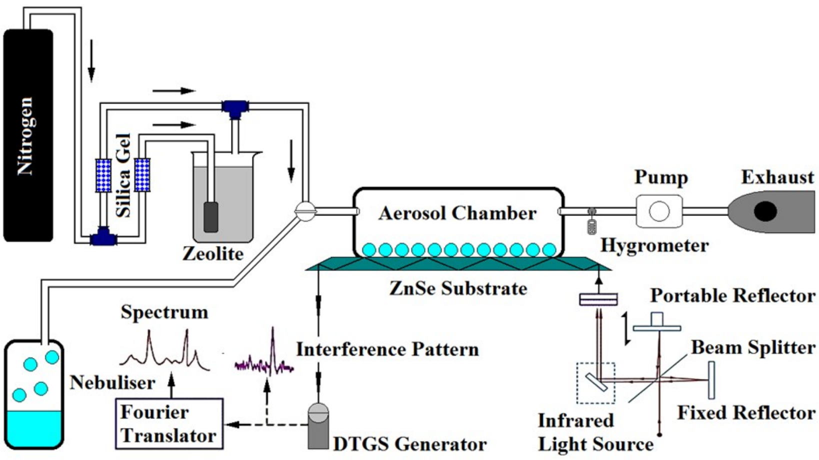

Figure S3. Schematic diagram of physisorption analyzer in which water vapor is used as adsorbate (a) and that of BELSORP-max measured dead volume (b).