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Supplement of

Measurement report: Water diffusion in single suspended phase-separated aerosols

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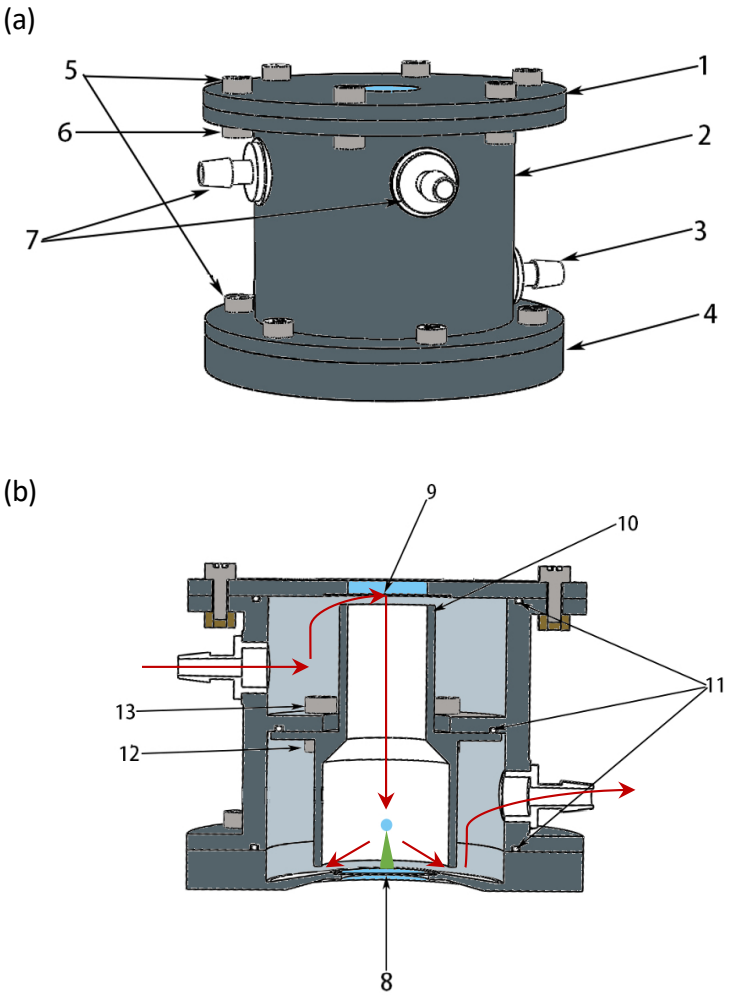
S1 Aerosol trapping chamber

Figure S1 Aerosol trapping chamber - (a) Overview, 1-Top cover with coverslip, 2-Chamber exterior, 3-Exhaust port, 4-Bottom baffle, 5&6-Fixing bolts and nuts, 7-Inlets for aerosols, nitrogen, and other possible substances; (b) Profile, 8-Bottom coverslip, 9-Top coverslip, 10-Inner cylinder baffle, 11-Rubber O-rings, 12&13-Fixing bolts and nuts. The path of incoming aerosol droplets and mixture of dry and wet nitrogen is expressed with red arrowed lines.

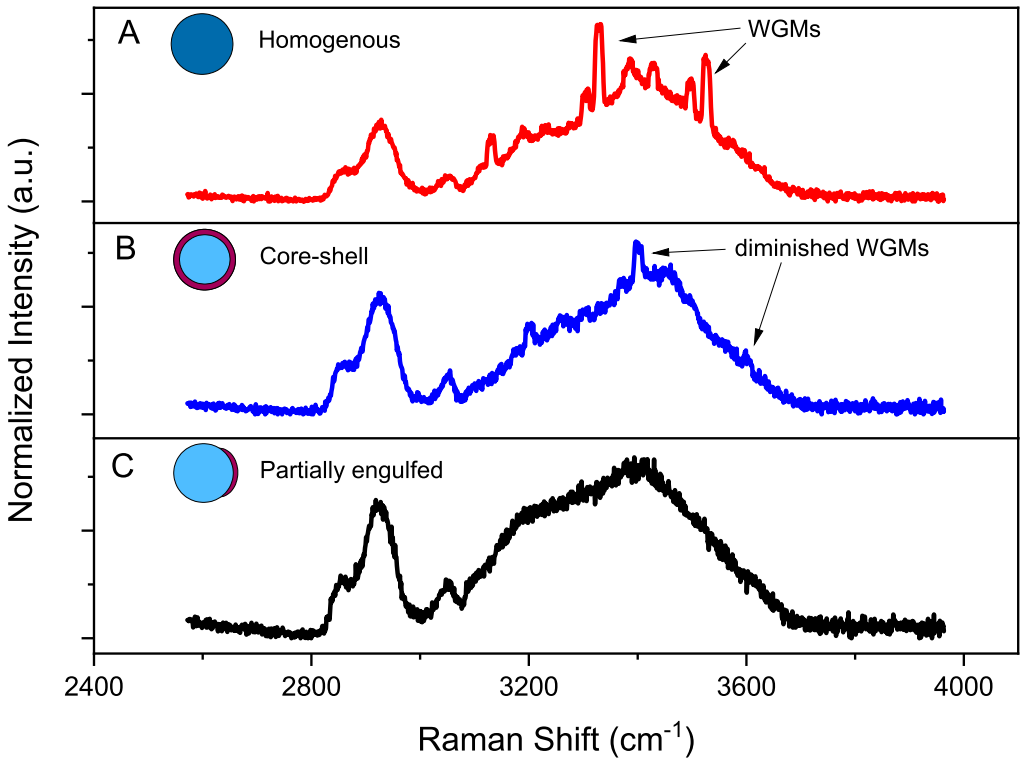


The aerosols were generated from desired mother solutions by a medical ultrasonic nebulizer (Mint PN100). The radii of the generated droplets were 4∼10 μm with a median of

5 μm. The height, inner diameter, and outer diameter of the chamber are 3.5 cm, 3 cm, and 5 cm, respectively, yielding a volume of < 24.74 cm^3. The RH in the chamber was first modulated to maintain at a specified value (60% in this work). After nebulizing desired mother solution and capturing one aerosol droplet, the nebulization process was stopped, and the aerosol inlet was sealed immediately to maintain a relatively isolated environment in the chamber. The trapped droplet was allowed to rest in the chamber vapor for 10$\sim$15 min. In this period, the droplet can achieve an equilibrium with the surrounding gas and the surplus deposited material. Then, the isotope exchange experiment was launched. After one experiment finished, the chamber was disassembled and cleaned using an ultrasonic cleaner.

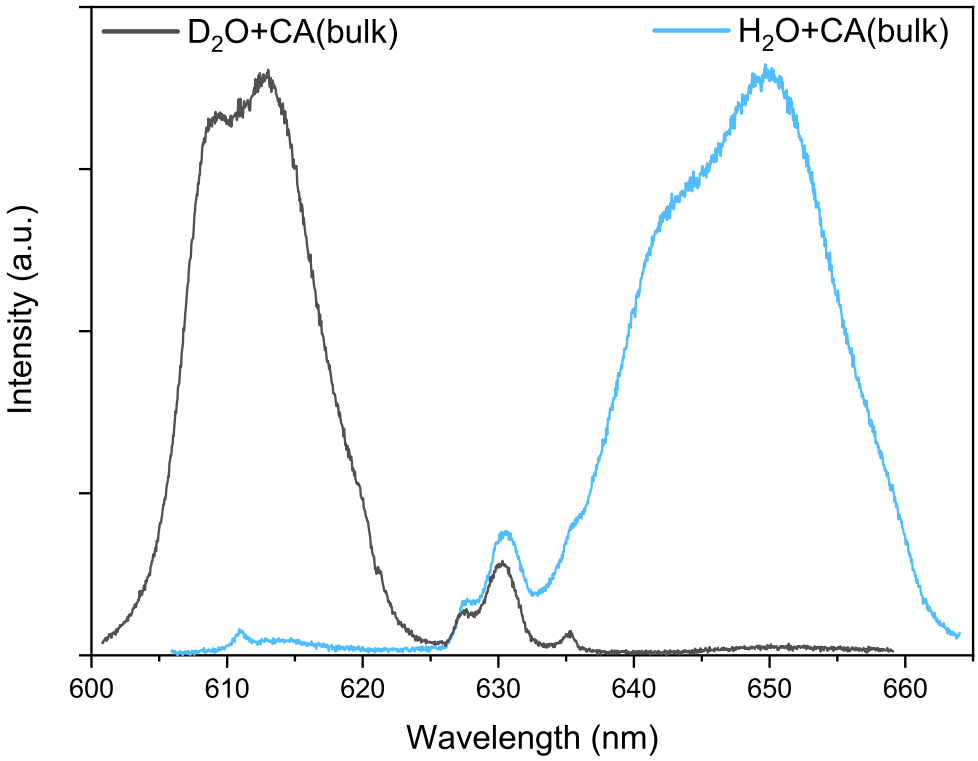
S2 Raman spectra of phase-separated aerosols

Figure S2 Raman spectra of aerosols with various morphologies - (A) Spectrum of homogenous aerosol. The high-quality WGMs indicates a spheric shape and the internal isotropy. (B) Spectrum of core-shell aerosol. The weak but noticeable WGMs indicates the symmetry of the particle remains, albeit the destruction of internal isotropy. (C) Spectrum of partly engulfed aerosol. No WGMs indicates the destruction of both isotropy and symmetry in the particle.



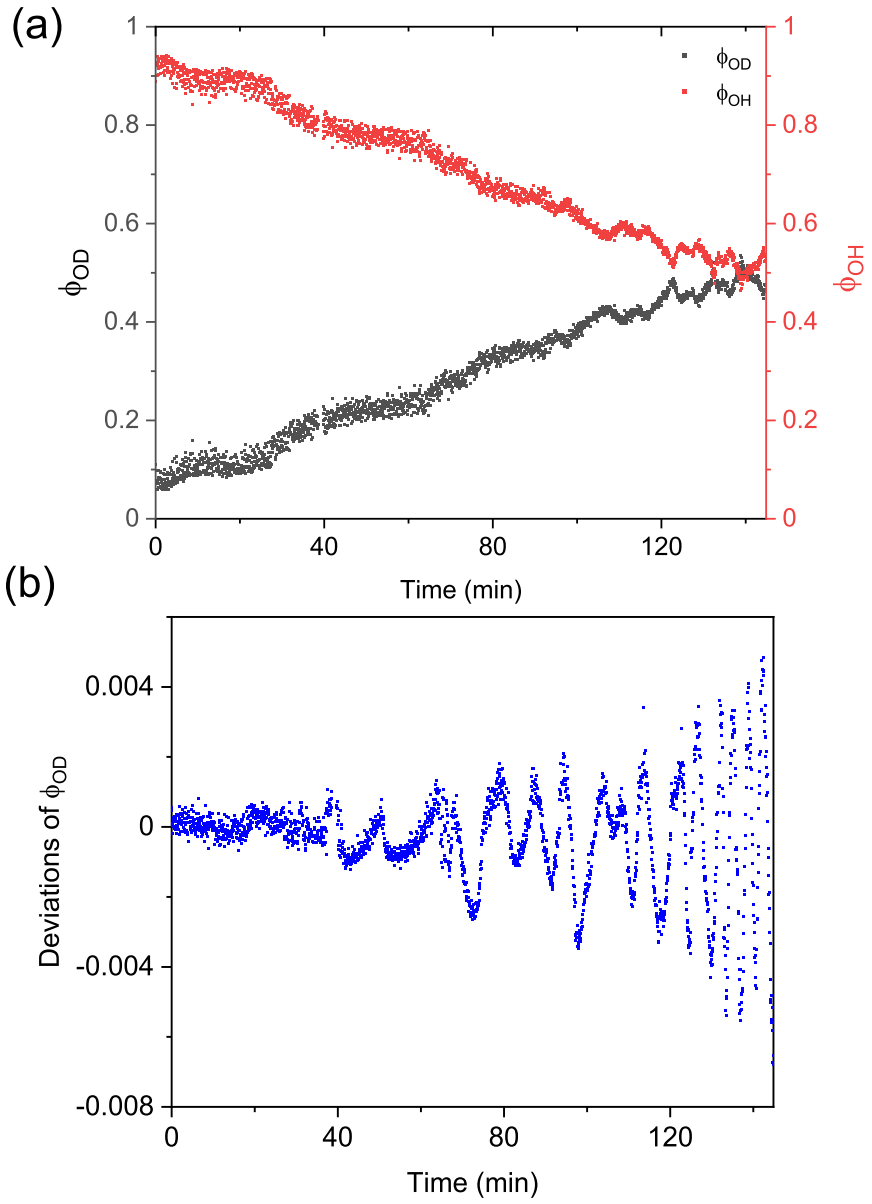
S3 Raman spectra of bulk mother solutions

Figure S3 Raman spectra of bulk solutions containing H_2O or D_2O - As O-D and O-H have different energy levels, the H_2O and D_2O solutions have strikingly different Raman peaks which respectively locates at 640∼660 nm and 605∼625 nm. Thus, the rise and fall of O-D/O-H peaks in Raman spectra can be used to trace water diffusion within aerosols.



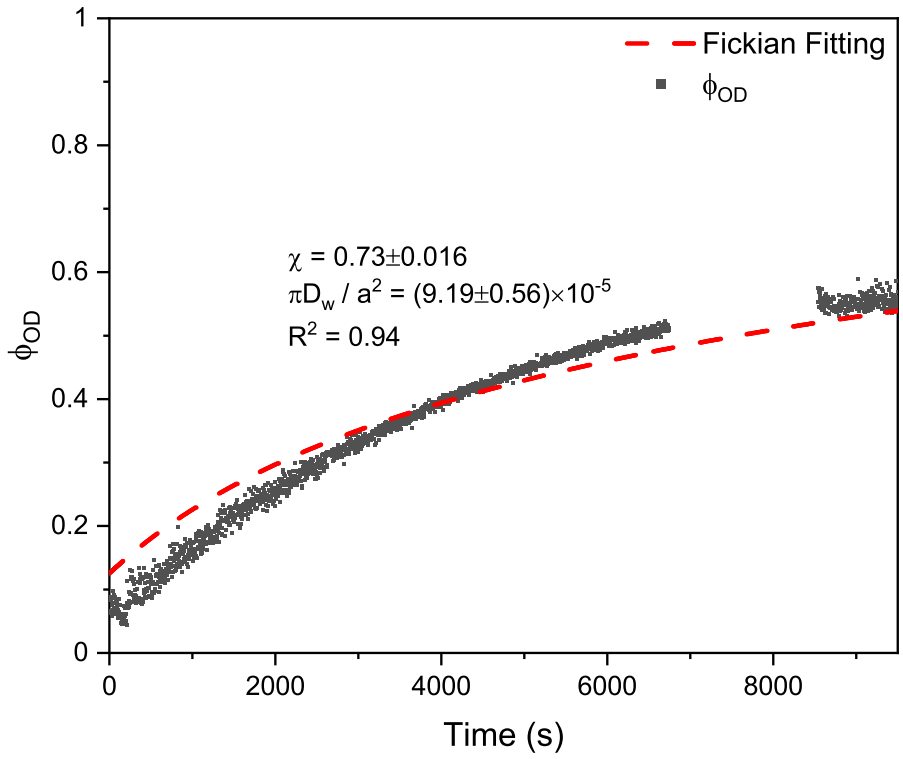
S4 Influence of WGMs on peak aera

Figure S4 Influence of WGMs of the calculated ϕ_{OD} - (a) The temporal variations of fractional concentration of water molecules within the droplet. The peak areas of O-D band and O-H band are calculated with excluding the WGMs in the Raman spectra. The results have no appreciable discrepancy with that in Fig. 7B in the main text. (b) The deviations of ϕ_{OD} when considering or ignoring the contribution of WGMs. It shows that the deviations are incredibly trivial of which the maximum is merely 7×10^{-3}.



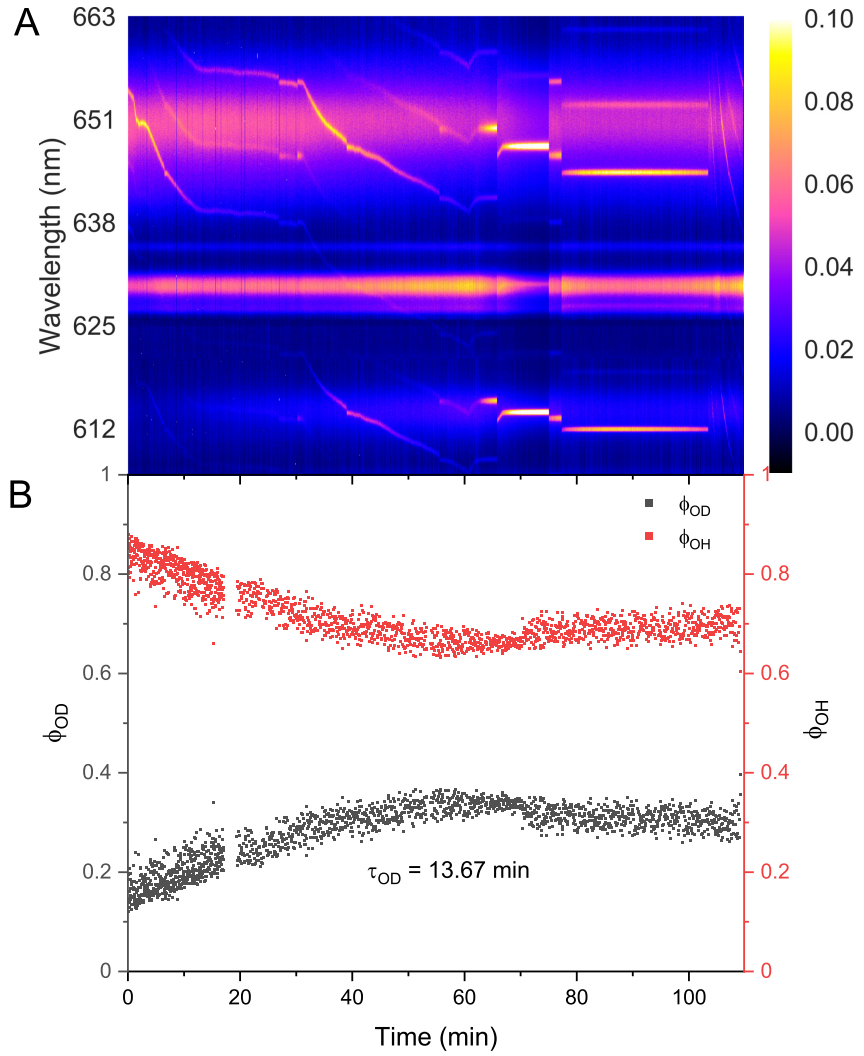
S5 Fickian fitting

Figure S5 Fitting the observed ϕ_{OD} with the modified Fickian diffusion model - An example of fitting the observed ϕ_{OD} data with the modified Fickian diffusion model. The data points are from H_2O+AS+DLT (Stage I). It shows the model works well with the data. The fitted parameter χ indicates the diffusion extent and $a^2/(\pi^2 D_{\mathrm{w}})$ means the time of diffusing to an isotropically stable state.



S6 Comparison of the water diffusion coefficients

Figure S6 Water diffusion in single homogenous H_2O+CA aerosol at RH = 20%



It showed that τ_{OD} at RH = 20% was larger than that at RH = 60% (1.45 min in Fig. 3 in the main text), indicating that water diffusion was retarded under low RH conditions. The D_w of H_2O+CA droplet (RH = 20%, radius = 7.3 μm) measured in this work was 7.44×10^{-15} $m^2 s^{-1}$ which was close to the result of Nadler et al[2] (Table S1). It validated the performance of the LTRS system used in this work.

Tab. S1 showed that the measured D_w of phase-separated droplets studied herein was considerably lower than the values of homogenous droplets studied in literature works, indi-

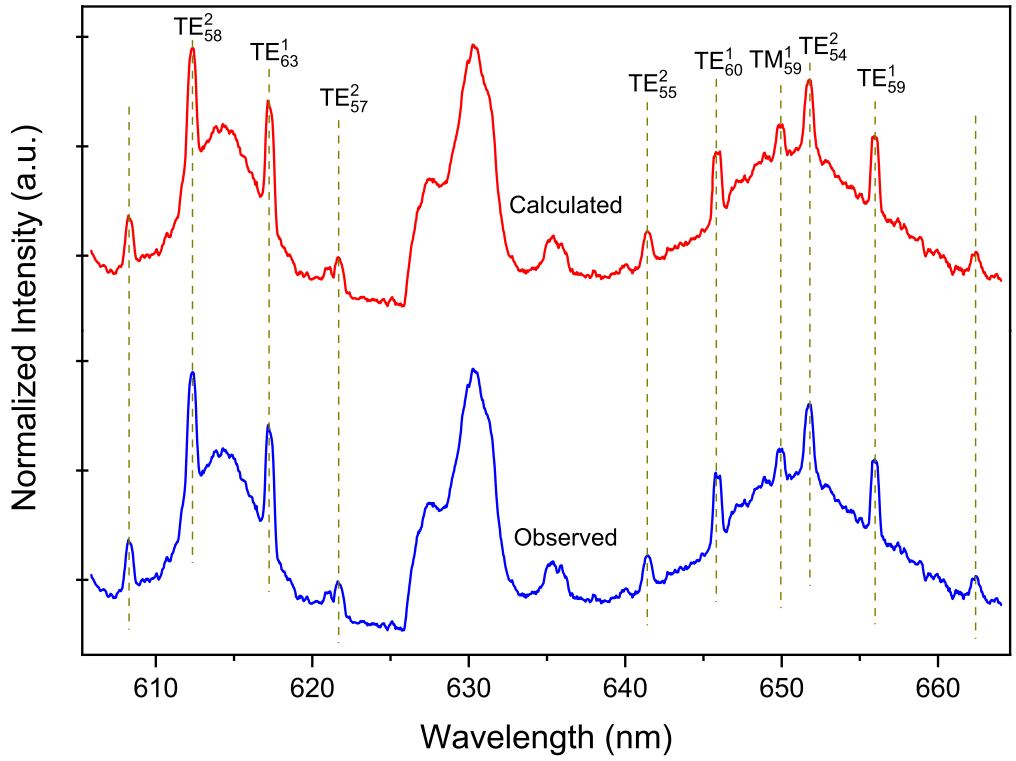
cating the occurrence of water diffusion limitations.

Table S1 Water diffusion coefficients of aerosols measured with various methods

Aerosol	RH (%)	D_w ($m^2 s^{-1}$)	Method	Reference
	60	2.51×10^{-11}	isotope exchange	Davies et al.[1]
H_2O+CA	20	15.8×10^{-15}	isotope exchange	Davies et al.[1]
	20	8.91×10^{-15}	isotope exchange	Nadler et al.[2]
	50	1.01×10^{-13}	RH oscillation	Preston et al.[3]
H_2O+Sucrose	60	3.98×10^{-12}	isotope exchange	Davies et al.[1]
	60	1.17×10^{-13}	diffusion model	Zobrist et al.[4]
H_2O+Sucrose+CA	40	1.01×10^{-13}	isotope exchange	Davies et al.[1]
H_2O+CA	20	7.44×10^{-15}		
H_2O+AS+OA	60	1.32×10^{-15}		
H_2O+AS+DLT	60	5.36×10^{-16}	isotope exchange	This work
H_2O+AS+HEX	60	2.25×10^{-16}		
H_2O+AS+DLT+H^+	60	3.99×10^{-15}		

S7 Core-shell model fitting

Figure S7 Fitting the observed Raman spectrum with a core-shell model - An example of fitting a spectrum extracted from Fig. 5 in the main text (time = ~93.5 min).



The inputs of the model were spectral WGM locations/assignments, initial guess for core/shell refractive index (RI), and range of radius ratios that were searched. The major outputs of the model were WGM locations, core radius, and particle radius. The parameters used herein were 1.33 for core RI initial guess, 1.6 for shell initial guess, and 0.5~0.99 for core/particle radius ratio. It showed that the core-shell model fitted the recorded spectrum very well.

S8 RH correction

The equilibrium vapor pressures of D_2O and H_2O are slightly different at the same temperature conditions. Thus, after switching from H_2O to D_2O, the RH probe measurement needs to be corrected. The relationship of the two equilibrium vapor pressures can be specified as

$$\ln \frac{p^0_{H_2O}}{p^0_{D_2O}} = A + \frac{B}{C+T} = \Lambda, \tag{1}$$

where $A = -0.30661$, $B = 9.14056$, $C = 75.753$, T is in Celsius, $p^0_{H_2O}$ is the equilibrium vapor pressure of H_2O, and $p^0_{D_2O}$ is the equilibrium vapor pressure of D_2O.

If not correcting the RH (i.e. not changing the setting value of RH after switching the moisture), the actual RH value will be e^{Λ} times the readout of the RH probe. Therefore, to keep a constant RH condition, the RH setting value should be corrected as $RH_{post} = RH_{pre} \cdot e^{\Lambda}$, where RH_{post} is the setting value after moisture switching and RH_{pre} is the setting value before switching.

S9 Reagents and sample preparation

The mother solutions used to generate the aerosol droplets were prepared by double-distilled water (18.2 MΩ cm; Milli-Q; MilliporeSigma, Burlington, MA, United States). Solute citric acid was purchased from Beijing Modern Oriental Fine Chemical Co., Ltd. (Beijing, China); Oleic acid was purchased from Xilong Scientific Co., Ltd. (Guangdong, China); Diethyl-L-tartrate was purchased from Shanghai D&B Biotechnology Co., Ltd. (Shanghai, China); 1,2,6-hexanetriol was purchased from Shanghai Macklin Biochemical Co.,Ltd. (Shanghai, China); Ammonium sulfate was purchased from Tong Guang Fine Chemical Co. (Beijing, China). The D_2O was purchased from Cambridge Isotope Laboratories, Inc. (Andover, USA).

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