Dear Editors and Reviewers:

Thanks for your letter and the reviewers' comments concerning our manuscript entitled "Measurement Report: Water diffusion in single suspended phase-separated aerosols" (Manuscript ID: egusphere-2023-1346). Those comments are all valuable and helpful for revising and improving our paper, as well as the important guiding significance to our researches. We have studied comments carefully, and revised the article by supplementing corresponding interpretations, conducting theoretical analysis, and adding more illustrations according to the reviewers' suggestions. Accordingly, the framework of this manuscript has been adjusted to systematically show the results that fits the theme. The point-by-point responses are as follows, and the corrections excerpted from the main article are highlighted by yellow. We hope the corrections can meet with your approval.

Responds to the reviewers' comments:

Reviewer 1:

#1. Can you show H2O/D2O exchange for just aqueous AS (or LiCl if efflorescence is an issue)? This would give some idea of the response time in your cell when switching between H2O and D2O. For instance, the characteristic time reported in Fig. 3 is probably just the time required for the cell to switch between H2O and D2O.

Answer:

The experiment for just aqueous AS may be not necessary. As shown in supplementary Fig. S1, the cell we used herein had a height of 3.5 cm, an inner diameter of 3 cm, and an outer diameter of 5 cm. Hence, the volume of the cell was less than 24.74 cm^3. The gas-washing bottle used as a bubbler in this work had a volume of 100 ml and contained 30 ml D_2O. The total sccm (standard cubic centimeter per minute) of dry and wet N_2 used herein was 100. Considering that RH = 60%, the maximum of the time required for the cell to switch between H_2O and D_2O was $(24.74 + 70)/(100 \times 60\%) = 1.58$ min. The observed characteristic time for aerosol spectra shown in Fig. 3 was 1.45 min. Thus, D_2O had started to diffuse into droplet before gas exchange from D_2O to H_2O completed.

We have supplemented corresponding interpretations in the revised manuscript, as follow

"Volume of the aerosol chamber was < 24.7 cm^3 (Fig. S1). The gas-washing bottle used as a bubbler herein had a volume of 100 ml and contained 30 ml D_2O. The total flux of dry and wet N_2 used herein was 100 sccm. Thus, at RH = 60%, the maximum time required for the chamber vapor to switch between H_2O and D_2O was 1.58 min, which can be identified as the response time of the chamber (formally τ_{cell})." (Section 2.1)

"However, $\tau_{OD} < \tau_{cell}$ implies that H_2O had started to diffuse into the droplet before gas exchange from D_2O to H_2O completed. Hence, water diffusion in homogenous CA droplet may be even faster than Fig. 3 showed." (Section 3.2)

#2. Throughout the paper you have this issue with \phi_{OD} not going to 0 or 1 as the experiment time becomes very long. This leads to some fairly implausible proposals (in my opinion) towards the end of the discussion. Isn't it simply the well-known issue that strong WGMs heavily distort vibrational bands, making their use in quantitative work difficult? The classic example is Anal. Chem. 2005, 77, 7148-7155 where the authors, who had previously been using an EDB, switched to glass slides because of this very issue (they state this in the introduction to that paper).

Although I suppose the argument given on lines 205-207 that there is condensation of the species being replaced somewhere on the walls is also possible.

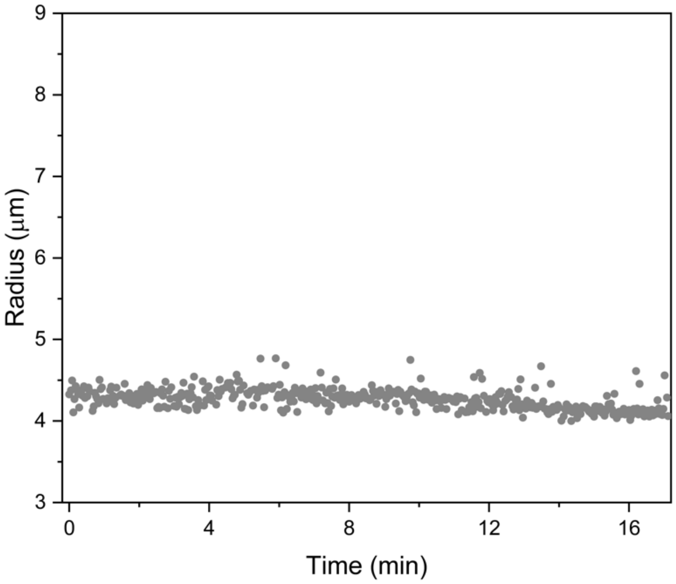
Answer:

As you mentioned, Wang et al. [Anal. Chem. 2005, 77, 7148] used Raman spectra to investigated the evolution of ion pairs during hygroscopic process of $MgSO_4$ droplets. Their focus was the intensity of certain sharp Raman peaks. However, in this work, we used Raman band area rather than peak intensity to trace the H_2O or D_2O concentration during water diffusion. As shown in Fig.2, the O-H band and O-D band were quite broad and the WGM peaks were pretty narrow. Thus, although WGMs distorted band silhouette, the area contribution of WGMs was trivial.

#3. Can you list the fitted droplet size where applicable, e.g. in Fig. 3.

Answer:

The particle radius of some studied droplets (e.g., H_2O+AS+DLT) has been presented in the manuscript (Fig. 6). The fitted radius of droplet shown in Fig.3 (D_2O+CA) is presented below.



#4. Why are the WGMs shifting in Fig. 3. Isn't the droplet in equilibrium with the surroundings? Is some other parameter changing?

Answer:

The experiments were conducted at room temperature (295±0.5 K). After capturing one aerosol droplet, the aerosol inlet was sealed immediately to maintain a constant RH in the chamber. No experimental parameters changed during the observation.

Nonetheless, because CA is a semi-volatile organic, the co-volatilization of CA and water may slightly change droplet size, resulting in the shifting WGMs. Furthermore, spontaneous surface fluctuations, e.g. thermally induced capillary waves, existed in the optically trapped droplet (see [Endo et al., J. Phys. Chem. C 2018, 122, 20684; Pigot et al., Anal. Chem. 2012, 84, 2557; Chung et al., Anal. Chem. 2017, 89, 8092]), which may also contribute to the unstable WGMs. We have supplemented corresponding interpretations in the revised manuscript, as follow

"Since CA is a semi-volatile organic, the co-volatilization of CA and water may slightly change droplet size, resulting in the shifting WGMs. Furthermore, spontaneous surface fluctuations (e.g. thermally induced capillary waves) existing in the optically trapped droplet may also contribute to the unstable WGMs." (Section 3.2)

#5. What are the uncertainties associated with the measured \tau reported in Table 1? Were any of these measurements repeated more than once?

Answer:

The uncertainties of χ and D_w were the parameter errors which were obtained by fitting temporal variation of ϕ_{OD} (see supplementary Fig. S5) using the modified Fickian diffusion model (Eq. 3). D_w is a process parameter that characterizes water diffusion process, the determination of which is highly time-consuming. Thus, we did not conduct multiple measurements and average to retrieve the uncertainties. The static parameters, e.g., RH and droplet size, were retrieved from multiple measurements.

#6. Awkward writing:

"surplus protons are considered to have appreciable impacts..." This is a weird way of saying low pH.

"panoramically presents a panorama"

"equilibrated in D2O in ambiance"

Answer:

Thanks for these comments. We have changed these expressions in the revised manuscript.

If you have any query, please do not hesitate to contact me at the address below.
Thank you and best regards.

Yours sincerely,
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