

## Dear Editor:

Thanks for your letter and the reviewers' comments concerning our manuscript entitled "Measurement Report: Water diffusion in single suspended phase-separated aerosols" (Manuscript ID: egosphere-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 editor's comments:

**#1.** The revision does not yet convincingly address and incorporate the reviewers' questions and suggestions into the main text. Please adjust your responses to the following reviewer comments to be reflected in the revised manuscript: Reviewer 1's comments #2 and #3, Reviewer 2's comments #2, #4, #6, #8, and #9. In your point-by-point response, indicate clearly how you addressed the reviewer comments.

### Answer:

We added new sentences and figures in the revised manuscript to response more directly to the reviewers' comments.

For Reviewer 1's comment #2,

"The O-H band and O-D band were quite broad while the WGM peaks were pretty narrow (Fig. 2); the fractional concentration of D<sub>2</sub>O was retrieved from Raman band area rather than peak intensity, thus the interference of WGMs to  $\phi_{OD}$  was trivial." (Section 3.1, Line 146-148)

For Reviewer 1's comment #3, we have added the fitted droplet size in the update Fig. 3.

For Reviewer 2's comment #2,

"The spectrograph grating used herein was 1200 groove mm<sup>-1</sup> and the spectrometer resolution was ~4 cm<sup>-1</sup>." (Section 2.1, Line 82) and Section 3.1 Line 146-148.

For Reviewer 2's comment #4,

"The water diffusion of CA droplet at lower RH (20%) was shown in Supplementary Fig. S6. The retrieved  $\tau_{OD}$  was 13.67 min which was larger than that at RH = 60%, indicating that water diffusion was retarded under very low RH conditions. This result agreed well with previous works (Supplementary Tab. S1), validating the performance of our system." (Section 3.2, Line 171-174)

For Reviewer 2's comment #6,

"In this work, the H<sub>2</sub>O+AS+OA droplet was generated by nebulizing a mixed solution containing of AS, OA and water. Volume ratio of the OA+AS mother solution was 4/1 (aqueous AS/OA). The mixture was fully shaken to form an aqueous OA emulsion before nebulization. Thus, a number of OA-inclusions would be contained in the nascent droplet. The OA content in the droplet herein was random. If the droplet spectra cannot support a partly engulfed morphology, the droplet will be released until one spectra-confirmed partly engulfed droplet is captured." (Section 3.3, Line 178-

182)

For Reviewer 2's comment #8,

"The volume ratio of aqueous phase and hydrophobic phase in the trapped droplet cannot be preset because of the stochastic mixing of OA emulsions and water during nebulizing." (Section 3.3, Line 190-191)

For Reviewer 2's comment #9,

"Aerosol pH was reported to have significant impacts on liquid-liquid phase separation. However, the impacts were different and related to the organic component. Previous work found that the separation relative humidity (SRH, the RH level at which LLPS occurs) of some organic acids (e.g., 3-methylglutaric acid) increased as the aerosol pH decreased, while the SRH of other organics (e.g., polyols) decreased as the pH decreased [Losey et al., J. Phys. Chem. Lett. 2016, 7, 3861; Losey et al., J. Phys. Chem. A 2018, 122, 3819]. From a fundamental physical chemistry perspective, the fluctuations of local solute concentration will lead to thermodynamic instability in droplet structure and induce phase separation subsequently. In this work, the added sulfuric acid increased droplet viscosity and reduced its liquidity, which may limit concentration fluctuations and promote homogeneity." (Section 3.4, Line 268-275)

"Moreover, the existence of bound water may limit water molecule evaporation and reduce the equilibrium water vapor pressure at the surface of acidified homogenous droplet (solute effect). While the surrounding moisture was switched from H<sub>2</sub>O to D<sub>2</sub>O, H<sub>2</sub>O molecules within the droplet began to evaporate into the gas to maintain its vapor pressure equal the equilibrium pressure. Lower equilibrium vapor pressure means weaker driven force of diffusion, thus water molecule substitution in the droplet with low pH was not as fast as in neutral homogenous droplet." (Section 4, Line 316-321)

**#2.** Both reviewers commented on the shifting of whispering-gallery modes (WGMs). The response is rather brief and not sufficiently substantiated by experimental evidence. Please expand your response to this important point brought up by the reviewers.

**Answer:**

We supplemented more interpretations for this problem in the response letter to reviewers and in the revised manuscript in Line 155-163, as follow.

CA is a semi-volatile organic. Thus, after an CA aerosol was trapped, CA would volatilize from the droplet, inducing a decreasing solute concentration. However, in our experiments, the ambient RH maintained constant. To re-achieve an equilibrium with the surrounding moisture, the droplet would also evaporate water to maintain the solute concentration. Therefore, the co-volatilization of CA and water may slightly change droplet size. Such change of droplet radius was validated in the update Fig. 3 where the radius reduced by ~100 nm during 16 min. The WGMs were pretty sensitive to droplet size, thus the co-volatilization of CA and water and the induced changing size may result in the shifting WGMs. Furthermore, some 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]). Surface fluctuations disturbed the standing wave at the interface between droplet and air, which may also contribute to the unstable spectral WGMs.

**#3.** Please thoroughly discuss the reasons and implications of  $\phi_{OD}$  not going to 0 or 1 (Reviewer 1, comment #2).

**Answer:**

We supplemented more interpretations for this issue in the response letter to reviewers, as follow.  $\phi_{OD}$  did not go to 0 or 1 meant that D<sub>2</sub>O in the trapped droplet cannot be completely substituted by H<sub>2</sub>O. It can be explained by two possible reasons. (i) The aerosol optical tweezer system has an inevitable experiment limitation. In the beginning of one experiment, an aerosol train was consecutively introduced into the chamber until one droplet was captured from the train. The other aerosols may condense on the walls of the chamber and tubes. Therefore, although the vapor was switched from H<sub>2</sub>O to D<sub>2</sub>O, the H<sub>2</sub>O molecules from the condensate aerosols may interfere water displacement extent, making  $\phi_{OD}$  unable to go to 0 or 1. (ii) Some water molecules within the droplet exist in the form of bound water, e.g. combined water in supersaturated AS inclusions and hydrated protons in acidified aerosols. Water displacement needed to overcome the bound water force which was much stronger than the diffusion force, making complete molecules substitution impossible.

**#4.** The discussions in the manuscript could use better referencing. It is sometimes not clearly indicated what is a known fact (provide reference to literature), an observation (provide reference to data), or speculation (indicate in your wording).

**Answer:**

Thanks for this problem. We have used more rigorous descriptions to distinguish these three circumstances (see Line 98, 126, 156, 160, 188, etc.).

**#5.** Consider adding the H<sub>2</sub>O + CA data (new in supplement) to main manuscript.

**Answer:**

This manuscript focused on water diffusion in phase-separated aerosol droplets. Since H<sub>2</sub>O+CA is not a phase-separated droplet, we think it is appropriate to put this discussion in the supplementary information. We have added enough corresponding interpretations on H<sub>2</sub>O+CA data in the manuscript (Line 171-174).

**#6.** Response to reviewer 2, comment #3: Please discuss in more detail how this may affect the conclusions of the manuscript.

**Answer:**

This comment provided an inspiring interpretation for the weak WGMs in spectrum of core-shell droplet (see Fig. S2 B). It supported the identification of core-shell droplet that spectra containing weak but noticeable WGMs indicated a core-shell morphology. It also provided a possible reason for the unstable WGMs in spectra of core-shell droplet. Thus, this comment supported the conclusion of this manuscript and made the discussions more comprehensive. We added this comment in Section 2.2 (Line 105-108) to make the statement more rigorous.

**#7.** I. 249 of revised manuscript: "the added sulfuric acid increased droplet viscosity, the plasticizing effect of which may limit local concentration fluctuations and promote homogeneity" - Please provide proper reference or indicate speculation. Also clarify which molecule's plasticizing effect is referred to here.

**Answer:**

This statement is flawed. We misunderstood the plasticizing effect of water. We revised this statement as follow,

"The added sulfuric acid increased droplet viscosity and reduced its liquidity, which may limit concentration fluctuations and promote homogeneity." (Section 3.4)

**#8.** I. 250 of revised manuscript: "Notably, what the characteristic diffusion time directly mirrors is diffusion rate of molecules in the size of water molecule into such droplet." - The meaning of the sentence is unclear, please revise.

**Answer:**

This statement is inappropriate and redundant. We deleted it in the update revised manuscript.

**#9.** I. 252 of revised manuscript: "However, the equilibrium water vapor pressure at the surface of acidified homogenous droplet may be different from that of neutral homogenous droplet at the same RH level." - This is unclear. Please provide reference or more detailed explanation for this statement. Are you suggesting that the relationship of water activity and vapor pressure may differ?

**Answer:**

We did not suggest that the relationship of water activity and vapor pressure may differ. According to Raoult's law, the equilibrium water vapor pressure at the surface of a droplet (denoted by  $p^0$ ) is influenced by the solute. Compared with a neutral droplet, a portion of water molecules in an acidified droplet were combined with protons in the form of hydrogen bond, preventing them from evaporating to the gas phase. Thus, the water vapor pressure at surface of an acidified droplet (denoted by  $p_a^0$ ) was lower than that of a neutral droplet (denoted by  $p_n^0$ ).

At an equilibrium state, H<sub>2</sub>O vapor pressure at the surface of a droplet (denoted by  $p_a$ ) equals  $p^0$ . While the surrounding moisture was switched from H<sub>2</sub>O to D<sub>2</sub>O,  $p_a$  decreased to zero. H<sub>2</sub>O molecules within the droplet began to diffuse into the gas phase to maintain  $p_a = p^0$ . However, since  $p_a^0 < p_n^0$ , the diffusion driven force in an acidified droplet was weaker than that in a neutral droplet, yielding a lower water molecules substitution rate.

We added these details in the update revised manuscript in Line 316-321.

**#10.** It is crucial that you consult the reviewer comments in detail and make more comprehensive adjustments to your manuscript. Please understand that failing to make these major revisions will likely result in the rejection of your manuscript. The revised manuscript will undergo another round of peer review to assess whether the issues have been adequately resolved.

**Answer:**

Thanks for this comment. The reviewers' opinions were pretty instructive for our work. We considered these comments carefully and revised the manuscript in detail. We hope the corrections can meet with your approval.

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

Thank you and best regards.

Yours sincerely,

Tong Yu-Kai

E-mail: tong.y.k@pku.edu.cn

Corresponding author:

Ye Anpei

E-mail: yap@pku.edu.cn