

## **Reply to comments on “Influence of acidity on liquid-liquid phase transitions of mixed SOA proxy-inorganic aerosol droplets” by Yueling Chen et al.**

### **Reply to Anonymous Referee #2**

1) This work systematically studied the influence of acidity on aerosol liquid-liquid phase separation and mixing by aerosol optical tweezers coupled with Raman spectroscopy. The results showed that the higher acidity decreased the separation relative humidity (SRH), and phase separation of organic acids was more sensitive to acidity compared to alcohols. The mixing relative humidity (MRH) was found to be higher than SRH. Additionally, the results on the influence of oxygen-to-carbon ratios (O:C) showed that, while phase separation occurred in the system with O:C of 0.33, 0.50 and 0.33, no phase separation was observed in the system with high O:C (i.e., 1). These findings are interesting and important. However, I have concerns about this work as detailed in the following.

**Response: We truly appreciate the constructive comments and suggestions raised by the referee. Those comments are valuable and very helpful for improving our paper, with the important guiding significance to our studies. Below we provide a point-by-point response to individual comment. The responses are shown in brown and bold fonts, and the added/rewritten parts are presented in blue and bold fonts.**

## Major comments:

1) **Figure1:** What are the origins of the spontaneous Raman peaks at  $\sim 3050$  and  $3300 \text{ cm}^{-1}$ ? The y axis showed the normalized intensity – please clarify to which peak the peaks were normalized to.

**Response:** Thanks for the suggestion. The spontaneous Raman peaks at  $3300 \text{ cm}^{-1}$  should be spurious peaks or weakened WGM peaks, because there is no spontaneous Raman peak at the same position in Fig.1b. And the origin of the spontaneous Raman peaks at  $\sim 3050 \text{ cm}^{-1}$  should be the vibration of N-H bond. The normalization of the peak is achieved by dividing it by the maximum value of the spectrum's intensity, respectively. For instance, in Fig. 1a, we observe a maximum vertical coordinate value of 4662 a.u. To normalize the light intensity of that spectrum, we divide it by 4662 and shift the entire spectrum downwards by 0.2 units. In Fig. 1b, the maximum vertical coordinate value is 871 a.u., so we divide the corresponding light intensity by 871 and shift the spectrum downwards by 0.7 units. In Fig. 1c, the maximum vertical coordinate value is 759 a.u., leading us to divide the associated light intensity by 759 and shift the spectrum downwards by 0.6 units. We have clarified it in the revised manuscript:

“The normalization of the peak is achieved by dividing it by the maximum value of the spectrum's intensity, respectively.”

“The origin of the spontaneous Raman peaks at  $3300 \text{ cm}^{-1}$  and  $\sim 3050 \text{ cm}^{-1}$  are identified as the spurious or weakened WGM peaks and the vibration of N-H bond, respectively.”

2) **Lines 141 - 142**, please explain why the area below the spontaneous Raman signal was used to normalize the Raman spectra. Normally, peak intensity is used to normalize peak intensity and peak area is used to normalize peak area.

**Response: Thanks for the suggestion. During the experiment with reduced RH, we had to adjust the laser power to stably capture droplet, which will affect the peak intensity. Therefore, we chose to normalize the area to eliminate this effect, as demonstrated by Tong et al. (2022). We have explained the reason in the revised manuscript:**

**“During the experiment with reduced RH, we had to adjust the laser power to ensure the stable capture of droplets, which will affect the peak intensity. To eliminate this effect, as demonstrated by Tong et al. (2022), we normalized all Raman spectra used in this study by the area below the spontaneous Raman signals.”**

3) **Lines 186 - 189**, can the different speciation of 3-MGA under different pH conditions be the underlying reason for the different SRH. For example, under highly acidic conditions, 3-MGA mainly appears in the protonated form (conjugated acid), while under high pH conditions, the deprotonated form (conjugated base) is the major species. Different species can show different phase separation properties.

**Response: Thanks for the suggestion. Indeed, the different speciation of 3-MGA under different pH conditions could be the underlying reason for the different SRH. Under low acidic conditions, 3-MGA mainly appears in the deprotonated form, which makes 3-MGA easier to precipitate. Once deprotonated, the organic component is charged and can interact with salt (i.e., ammonium sulfate) and water through ionic and dipole interactions, leading to an increase in solubility. These**

interactions prevent the salinization of organic components at high relative humidity (Losey et al., 2016). This trend is contrary to the phenomenon in this work that 3-MGA was more difficult to precipitate at highly acidity, so this explanation may not apply to our phenomenon. We believe that the different sorting out ability of inorganic salts under different pH is the reason for the different SRH. With a decrease in pH, ammonium sulfate transforms into ammonium bisulfate. Predicted by the Hofmeister series, ammonium bisulfate exhibits a weaker salting out effect compared to ammonium sulfate and thus hinders the ability of organic matter to precipitate out of the solution (Losey et al., 2018).

4) **Lines 234 - 236**, the statement may not be valid. Droplet pH may differ from the bulk solution pH, depending on the difference in the chemical composition between droplets and bulk solution.

**Response:** We agree that the droplet pH may differ from the bulk solution pH. But previous studies (Coddens et al., 2019; Li et al., 2023) have shown that at high RH (90%~100%), the difference in the pH values between droplets and bulk solution is relatively small. Coddens et al. (2019) reported that the calculated particle pH for trapped sulfate and carbonate aerosols was generally lower than the measured bulk pH, with an average difference of about 10%. Li et al. (2023) collected droplet Raman spectra over a relative humidity range of 100% to 90% and selected droplets with the same solute concentration as the corresponding bulk solution by using Raman proxy concentrations. The results showed that the pH of the phosphate buffered droplets and the parent bulk solution (i.e., the bulk solution with the same

**solute concentration as the droplets) were identical. Therefore, we used bulk solution pH as an indicator of pH at droplet phase transition. We have revised the manuscript:**

**“It is challenging to measure the droplet pH of the investigated system using AOT. However, previous study (Coddens et al., 2019; Li et al., 2023) have shown that at high RH (90%~100%), the difference in the pH values between droplets and bulk solution is relatively small. Therefore, we used bulk solution pH as an indicator of pH at droplet phase transition. ”**

5) **Lines 237 - 239**, the statement may not be valid, as evaporation of volatile species from microdroplets have been widely observed. The authors may want to confirm that the influence in your system is neglected from the droplet size change profile. For example, a constant droplet size under a constant RH can indicate that the evaporation is neglected in your system.

**Response: Thank you for the advice. We have discussed the volatility of each organics specifically in the manuscript:**

**“Nevertheless, the volatility of the organic compounds used in this study is low, for instance, the vapor pressure of 3-MGA is  $7.41 \times 10^{-7}$  to  $2.92 \times 10^{-4}$  mmHg (DTXSID50871000, United States Environmental Protection Agency), compare to normal volatile organics such as 2-Methyl-1-propanol with vapor pressure of 10.5 to 16.4 mmHg (DTXSID0021759, United States Environmental Protection Agency). Volatility information of other organics are provided in the Table S5. Also, the influence of droplet size change in our system can be neglected. For example, as shown in Fig. 2, the droplet size is basically same at the beginning and the end of the**

experiment at the same RH 93.0% (11.85  $\mu\text{m}$  at the beginning and 11.79  $\mu\text{m}$  at the end).”

SI:

Table S5. Vapor pressure of organic compounds used in this study

Compounds	Vapor pressure (mmHg)	Reference
GL	$1.66 \times 10^{-4}$ to $6.68 \times 10^{-3}$	DTXSID9020663, EPA
	$7.41 \times 10^{-7}$ to $2.92 \times 10^{-4}$	DTXSID50211649, EPA
3-MGA	$(6.9 \pm 5.2) \times 10^{-6}$	Booth et al. (2010)
	$(5.5 \pm 2.0) \times 10^{-6}$	Mønster et al. (2004)
HEXT	$2.12 \times 10^{-4}$ to $1.82 \times 10^{-4}$	DTXSID0041224, EPA
	$(1.5 \pm 0.15) \times 10^{-6}$	Cotterell et al. (2010)
	$(8.7 \pm 0.19) \times 10^{-7}$	Cai et al. (2015)
HEXD	$1.51 \times 10^{-2}$ to $5.27 \times 10^{-2}$	DTXSID50871000, EPA

EPA means United States Environmental Protection, <https://comptox.epa.gov/> (last access: 20 April 2023).

### Minor comments:

1) Please spell out the abbreviation of OIR.

**Response: Added.**

“The pure organic and inorganic components were dissolved in ultrapure water (Millipore, resistivity of 18.2 M $\Omega$ ) to create solutions with organic-to-inorganic mass ratio (OIR) of 1:1. ”

2) Please provide the Raman spectra of droplets with different chemical composition and assign the spontaneous Raman peak in each spectrum.

**Response: Thanks, we have added the Raman spectra of droplets with different chemical composition in the supplement.**

SI:

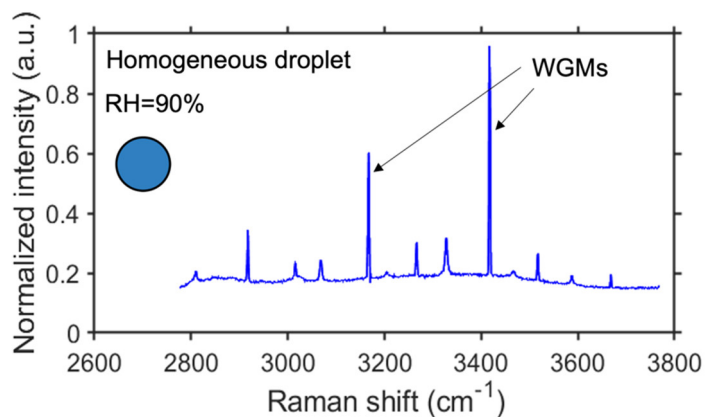


Figure S5. Raman spectra of GL microdroplets. The WGMs are marked by black arrows. The normalization of the peak is achieved by dividing it by the maximum value of the spectrum's intensity.

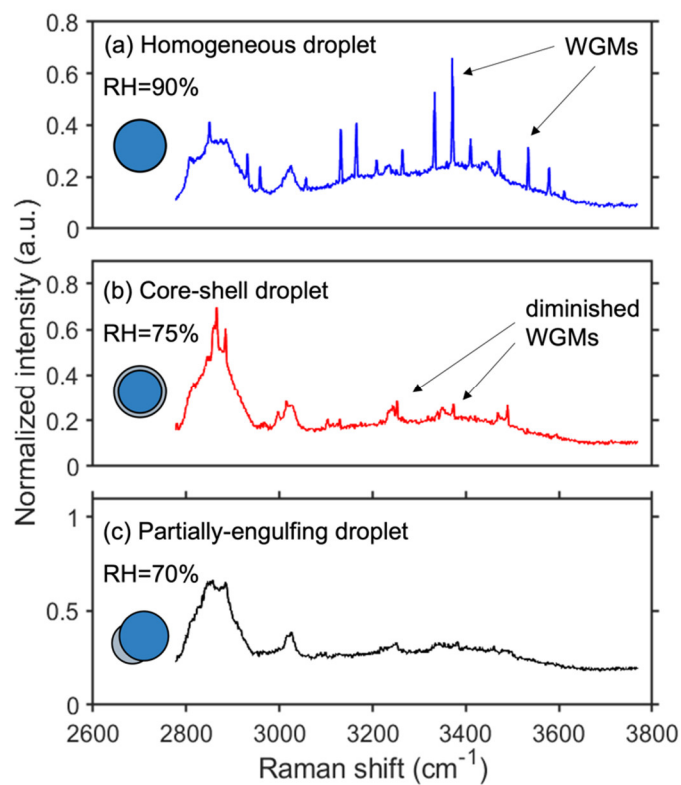


Figure S6. Raman spectra of HEXT-II microdroplets. The WGMs are marked by black arrows. The normalization of the peak is achieved by dividing it by the maximum value of the spectrum's intensity. The origins of the spontaneous Raman peaks at 2850 and  $\sim 3050 \text{ cm}^{-1}$  are vibration of C-H and N-H bonds, respectively.

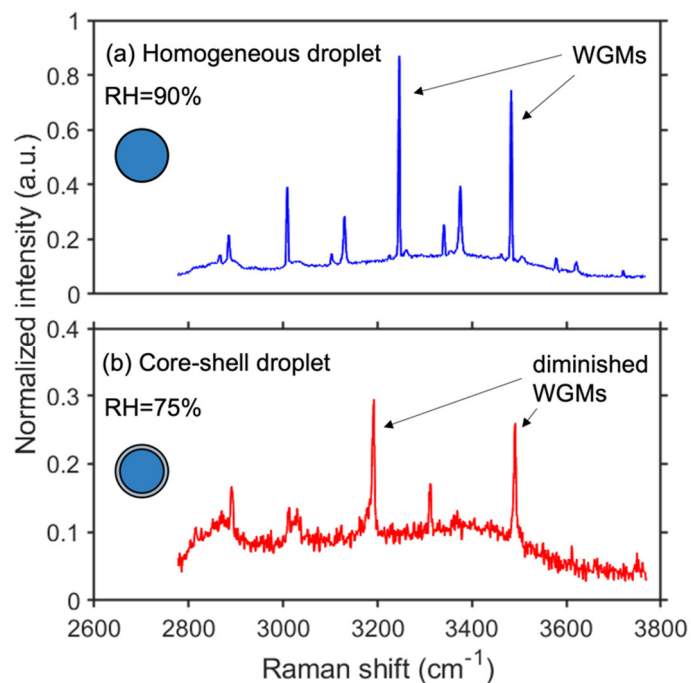


Figure S7. Raman spectra of HEXD-V microdroplets. The WGMs are marked by black arrows. The normalization of the peak is achieved by dividing it by the maximum value of the spectrum's intensity. The origins of the spontaneous Raman peaks at 2850 and  $\sim 3050$   $\text{cm}^{-1}$  are vibration of C-H and N-H bonds, respectively.

## Reference

- Coddens, E. M., Angle, K. J., and Grassian, V. H.: Titration of aerosol pH through droplet coalescence, *J. Phys. Chem. Lett.*, 10, 4476-4483, <https://doi.org/10.1021/acs.jpcclett.9b00757>, 2019. Corral Arroyo, P., David, G., Alpert, P. A., Parmentier, E. A., Ammann, M., and Signorell, R.: Amplification of light within aerosol particles accelerates in-particle photochemistry, *Science*, 376, 293-296, <https://doi.org/10.1126/science.abm7915>, 2022.
- Li, M., Kan, Y., Su, H., Pöschl, U., Parekh, S. H., Bonn, M., and Cheng, Y. F.: Spatial homogeneity of pH in aerosol microdroplets, *Chem*, in press, <https://doi.org/10.1016/j.chempr.2023.02.019>, 2023.
- Losey, D. J., Ott, E. J. E., and Freedman, M. A.: Effects of high acidity on phase transitions of an organic aerosol, *J. Phys. Chem. A*, 122, 3819-3828, <https://doi.org/10.1021/acs.jpca.8b00399>, 2018.