

Interactive comment on “Hygroscopic behavior and chemical composition evolution of internally mixed aerosols composed of oxalic acid and ammonium sulfate” by Xiaowei Wang et al.

Anonymous Referee #2

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In this paper the authors study the hygroscopic properties and phase transformations of mixed oxalic acid (OA) and ammonium sulfate (AS) particles using confocal Raman spectroscopy. In particular the authors study three different OA/AS ratios: 1:3, 1:1 and 3:1 at room temperature. Pure OA crystallizes into the dihydrate at 77% RH and converts into the dehydrated form at 5% RH. Pure AS particles deliquesce at ~80% RH and effloresce at ~44% RH (validating the Raman technique). The observed ERH for the mixed particles ranged from ~34 to 64% RH. The ERH increases as the amount of OA in the mixtures increase. The DRH for the mixed particles ranged from ~77 to 81% RH. The authors claim the formation of different compounds in OA/AS particles during a slow drying process affects the DRH during a subsequent hydration process.

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I have many of the same comments as Reviewer #1. In particular revising the discussion section to include atmospheric relevance is crucial before final publication. After revision, I believe the manuscript represents a contribution to scientific progress within the scope of ACP. The scientific approach and methods are valid. I recommend publication in ACP after the authors address the concerns of the reviewers.

Comments:

1) I was wondering if the authors considered referencing and discussing Amundson et al. (2007) which provides a sulfate/ammonium/oxalic acid phase diagram.

Amundson, N.R., Caboussat, A., He, J.W., Martynenko, A.V., and Seinfeld, J.H., A phase equilibrium model for atmospheric aerosols containing inorganic electrolytes and organic compounds (UHAERO), with application to dicarboxylic acids, *J. Geophys. Res.*, 112, D24S13, 2007.

2) Page 4, line 19: How did the authors create 30-40 micron particles with a syringe? This procedure needs to be explained better. Also, how was the environment of the particles maintained at 95% RH after injection? Aren't the particles subjected to the environment in the room which is surely less than 95% RH? Are 30-40 micron particles relevant in the atmosphere?

3) Page 5, line 11: The authors state that the particles were equilibrated with water vapor for 40 minutes at a given RH value and they state that the slow dehydration process occurred in the time scale of hours. Why was the time scale of 40 minutes chosen? Why not 30 minutes or 60 minutes? Is 40 minutes the amount of time for the Raman spectrum to remain constant?

4) Page 5, equation 1: I understand the equation for the growth factor but when the authors create the hygroscopic growth curve is the growth factor an average of many particles or only 1 particle?

5) Figure 1a: This is actually a problem I have with all the figures showing Raman

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spectra. There are just too many peak assignments and it clutters the figures up. Can the authors remove any peak assignments that don't illustrate the point of the figure? For example, in the OA dehydration process the peak at 1689 cm⁻¹ is obviously important because that's the peak associated with the dihydrate. That peak should clearly be highlighted. Also can the authors remove any of the Raman spectra that don't highlight something interesting happening? All that's happening is the water peaks are getting smaller. Also, the oxalic acid dihydrate spectrum at the bottom of Figure 1a looks like it is part of the dehydration process. It took me a little bit of time to figure out that the spectrum wasn't part of the dehydration process in the figure. I understand the importance of this spectrum but can it be boxed in or something so the reader doesn't think it is part of the dehydration process?

6) Page 6, line 5: This comment is associated with the comment above. Again, there are too many peak assignments in the text. It clutters the paragraph up. Focus on the most important peaks.

7) General comment: I think it would be interesting to see pictures of the particles during the hydration and the dehydration process. Do the authors have pictures of the particles they could associate with the Raman spectra? The reason I bring this up is Wise et al. (2012) found that when aqueous sodium chloride particles effloresced at low temperatures the dihydrate formed. The morphology of those particles was different than the morphology of the dehydrated form. I am also wondering if the authors could physically see evidence of NH₄HSO₄ or NH₄HC₂O₄ they claim to see spectral evidence of on page 7, line 4. Additionally can the authors see any coatings they argue are present on page 11, line 11?

Wise, M.E., K.J. Baustian, T. Koop, M.A. Freedman, E. J. Jensen and M.A. Tolbert, Depositional ice nucleation onto hydrated NaCl particles: A new mechanism for ice formation in the troposphere, *Atmos. Chem. and Phys.*, 12, 1121-1134, 2012

8) Page 7, line 10: There needs to be an arrow in the equation not an equal sign.

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9) Page 10, line 5: Again, I think pictures of the particles might help strengthen the case for water uptake prior to deliquescence. The authors should be able to see the particles gain water prior to full deliquescence. I am now wondering if the authors could create hygroscopic growth curves utilizing the physical size of the particles and if that correlates with the Raman growth factors.

10) General comment: Can the authors comment on the applicability of the data at temperatures lower than room temperature. Obviously, in the atmosphere the particles are going to experience temperatures much lower than room temperature.

11) Page 5, line 25: Why did the authors decide to put the mixed hydration Raman spectra in the supplemental section? Surely, this data is important to the findings described in the paper.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-454>, 2017.

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