Replies to comments for article "Viscosity controls humidity dependence of N_2O_5 uptake to citric acid aerosol" by G. Gržinić et al.

G. Gržinić[1,2], T. Bartels-Rausch[1], T. Berkemeier[3], A. Türler[1,2] and M. Ammann[2]

[1]{Laboratory of Radiochemistry and Environmental Chemistry, Paul Scherrer Institute, 5232 Villigen, Switzerland}

[2]{Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland}

[3]{Multiphase Chemistry Department, Max Planck Institute for Chemistry, 55128 Mainz, Germany}

Correspondence to: M. Ammann (markus.ammann@psi.ch)

Reviewer comments are given in bold, our response in plain font.

Anonymous Referee #1

–General comments

The measured gamma_N2O5 is quite low, ranging from 3E-4 to 3E-3 at its maximum. The RH dependence, aside from a couple points, is more of a continuous function than a step-function that would be expected from efflorescence/deliquescence behavior. The authors use this behavior and some analogous behavior in the viscosity measured independently to conclude that it is viscosity (via diffusion limitations) that controls the observed humidity dependence and even the overall low absolute value for gamma_N2O5.

I certainly find the argument reasonable, though the spread in the estimates of diffusivity and that the full behavior of the measured gamma_N2O5 is not captured by any version does leave a little to be desired. This is the case not only for the citric acid aerosol but also for the application of the model to the previously published malonic acid data from Griffiths et al and Thornton et al. There is a strong fall off for the gamma_N2O5 on malonic acid aerosol with decreasing RH that the model doesn't capture. Why?

My recollection is that the uptake of N2O5 to malonic acid at low RH was explained by Bertram and Thornton 2009 as a [H2O] effect. Is that not treated in model? Or is it that the diffusivity parameterization for N2O5 in malonic acid needs to be steeper at low RH (or some combination) as it is with the Reid et al and Lienhard versions for citric acid? It seems like the authors are arguing that changes in [H2O] may affect diffusivity, not just reactivity, and so what is the [H2O] effect in Bertram and Thornton 2009 explaining (one or both)?

Response: Yes, the [H$_2$O] effect was treated in the model, via $k^I = k^{II}[H_2O]$ embedded in equation (4), k^{II} (1.0×10^5 M^{-1}s^{-1}), which is the apparent second-order rate constant for the reaction of N_2O_5 with water, as explicitly explained in the text below equation (4). Bertram and Thornton (2009) have indeed reported a strong dependence of gamma_N2O5 on water content at RH below 50%, as previously observed by Thornton et al. (2003) as well. Our

suggestion in the case of citric acid was that diffusivity, being related to the viscosity, is influenced by water content itself over the full RH. Thus the changing water content influences reactivity through both, its effect on viscosity and thus diffusivity, and its effect on the hydrolysis rate. Because of problems with estimating diffusivity of N_2O_5 at low water content (low RH), the traditional bulk reacto-diffusive uptake regime may not be granted anymore as discussed in the text. However, both, estimating the diffusivity from viscosity through the Stokes-Einstein relation and applying the resistor model would rather lead to an overestimation of gamma, so that the deviation of the measured gamma at low RH is likely to have other reasons. We prefer not speculating on the impact that would have in the case of the malonic acid as presented by Bertram and Thornton (2009), except that given the much lower viscosity of malonic acid compared to citric acid, diffusivity of N_2O_5 would be considerably higher. We will revise the text to also include the information that Thornton et al. (2003) also made some experiments with fully effloresced malonic acid for comparison that are not included in here.

I feel like the authors are on the cusp of being able to reconcile several disparate results and thus demonstrate a comprehensive understanding, but then stop short. For example, I think high viscosity (low diffusivity) can explain why citric acid mixed with ammonium sulfate was an outlier in the Gaston et al work, but again, this connection isn't made very strongly in this paper and is it necessary to also invoke a phase separation between ABS and citric acid as used in that paper to explain the other systems?

We have already raised the idea that the arguments presented here indeed suggest an explanation for the comparative observations by Gaston et al., and we are emphasizing this more strongly in the revised manuscript.

In addition, could the authors amend the uptake model to include a surface reaction term so that the different diffusivity parameterizations could be better evaluated against the data? It is certainly reasonable that there is a reaction with surface water as noted given the non-zero gamma_N2O5 measured on solid organics and reported by others previously. Then use the fact that model "works" for citric acid and invert it to put forth a viscosity vs RH curve for malonic acid that would be required to explain the gamma_N2O5 at low RH, if not just a [H2O] effect. If it is the latter, why is it not in the model?

For the revised version, we will add a surface reaction resistor term into the model for gamma for the Berkemeier diffusivity parameterization (for the sake of clarity). However, we refrain from deriving viscosity for malonic acid data for essentially one data point at low RH available from the Thornton et al. (2003) data. At low RH the uncertainty in representing the relationship between diffusivity of N_2O_5 and viscosity is considerable as discussed in the manuscript. The parameterization used to represent the malonic acid case is based on the same method to estimate H_2O diffusivity as for citric acid for consistency.

–Detailed Comments

Line 6 21993, it seems wall loss was evaluated before and after aerosols were delivered to the flow tube, but please specify.

Wall loss was evaluated at the beginning of each measurement run (day), before aerosol measurements were performed as mentioned in lines 19-25, page 21992. This will be emphasized more in the revised text.

Line 4 21995, I think the appropriate reference is Griffiths et al, not Thornton et al (at least for the aerosol systems mentioned).

Correct, the text will be amended with the correct citation.

Line 5 21995, gamma_N2O5 for citric acid, even at its highest (3e-3), is almost an order of magnitude lower than an aqueous sea salt particle.

The relatively low values observed here for citric acid are indeed lower than on other aqueous salt particles and this is the basis for the whole discussion in the present manuscript. As mentioned at the end of this part of the results section, we measured the uptake coefficient of N_2O_5 on deliquesced ammonium sulfate aerosol at 52 % RH and obtained an average value of $(1.4\pm0.4)\times10^{-2}$ (as already reported by Gržinić et al. (2014)), similar to other studies compiled in Ammann et al. (2013) to validate our setup and make this difference clear.

Figure 1 legend, "N2O5 particle phase" - that isn't really the case right? I assume it is "N2O5 reacted" or "particulate nitrate"

Yes, it refers to reacted N_2O_5. The figure will be updated.

Figure 3, are the lower gammas at 35 and 53% RH evidence of possible efflorescence? Putting a drier inline at 17% RH before the flow tube seems to me to run the risk of causing efflorescence at times.

 Peng et al. (2001) and Zardini et al. (2008) have studied the water cycle of citric acid using an electrodynamic balance (EDB) and EDB/hygroscopicity tandem differential mobility analyzer (HTDMA) methods respectively. These studies have shown that citric acid particles remain in liquid form over the observed humidity range (5-90% RH) and neither crystallization nor deliquescence was observed. High supersaturation is maintained even at very low RH values. In the discussion we have left the caveat and will emphasise more that impurities may potentially induce an uncertainty here.

Anonymous Referee #2

1. If known, please state the deliquescence and efflorescence relative humidities for citric acid and malonic acid particles.

According to Peng et al, 2001 and Zardini et al, 2008, which have studied the water cycle of citric acid using an electrodynamic balance (EDB) and EDB/hygroscopicity tandem differential mobility analyzer (HTDMA) methods respectively, neither crystallization nor deliquescence was observed and high supersaturation is maintained even at very low RH values. Citric acid retains some water even at very low RH values of 5% or less. Pang et all have likewise studied the water cycle of malonic acid particles and have concluded that like with citric acid they do not present crystallization nor deliquescence and therefore do not exhibit hysteresis, which would be indicative of phase change; however Braban et al. (2003) have reported efflorescence of malonic acid at room temperature at RH values of 6% ± 3%, which is close to the lowest RH values at which Peng et all have performed their EDB measurements, while deliquescence is reported as starting at 69%. Thornton et al. 2003 report malonic acid efflorescence at <7% RH and deliquescence at 69%. In any case, for all intents and purposes the above mentioned studies indicate that both citric acid and malonic acid particles (the latter as long as humidity is not lowered below 5-9% first) being in liquid (supersaturated) form in the humidity range used in this study and the Thornton and Griffiths study respectively. The manuscript will be amended accordingly (see also response to comment #4).

2. Abstract: Consider changing "since the viscosity of highly concentrated citric acid solutions is not well established..." to "since the diffusion rates of N2O5 in highly concentrated citric acid solutions is not well established,..."

The manuscript will be updated accordingly.

3. Page 21987, line 22-24: Did Lienhard et al. measure viscosities of citric acid and water solutions? If not, consider adding a reference here to the recent measurements of viscosity of citric acid and water solutions by Reid and colleagues for clarify.

Lienhard et al. have not measured viscosities of citric acid solutions but diffusivity of water in citric acid (D_{H2O}), which we have then used to calculate the diffusivity of N_2O_5 in citric acid using the Stokes-Einstein equation. Reid and colleagues have measured viscosity of citric acid particles using the Optical Tweezers method, however they have not yet published the relevant data in a peer reviewed research article. We have therefore indicated in our manuscript that we have obtained the data via personal communication. Obviously, should the Reid et al. data be published before the publication of our manuscript, we will insert the relevant reference in our text.

4. page 21989, line 4-6: The authors indicate that they used a relative humidity above 15-17% to avoid efflorescence. However, this will only avoid efflorescence if efflorescence occurs below 15% RH. Has anyone measured the efflorescence point of citric acid-water particles? If so, this information should be added. If not, the authors should add the caveat that this RH may not prevent efflorescence.

As mentioned previously, Peng et al. (2001) and Zardini et al. (2008) have studied the water cycle of citric acid and their studies have shown that citric acid particles remain in liquid form over a very wide humidity range (5-90% RH) and neither crystallization nor deliquescence were observed. High supersaturation is maintained even at very low RH values and we are confident that the particles dried to 17% RH in our study are not in an effloresced state. The manuscript will be amended accordingly.

5. Page 21994, line 7-9: What physical properties may be affected by contamination? Please expand for clarity.

In case of contamination the possibility arises that such impurities might induce phase separation or crystallization, thus impacting the viscosity and reactivity of the particles. Text will be amended to state this again at this point.

6. Page 21994, line 12-14: Again, I don't think equilibrating the solution droplets from the nebulizer to the lowest RH used in the experiments will necessarily avoid crystallization. Please restate for clarity. Also add the efflorescence point if known.

According to Peng et al. (2001) and Zardini et al. (2008), who have studied the water cycle of citric acid, citric acid particles remain in liquid (supersaturated) form over a very wide humidity range (5-90% RH) and no efflorescence was observed even at the lowest RH values. Again, this point will be made clearer in the revised manuscript (see also response to comment #4 page 21989, line 4-6)

7. Page 21994, line 25-26: Please indicate the RH range over which citric acid-water particles remain supersaturated based on the previous studies.

Peng et al. (2001) and Zardini et al. (2008) report that citric acid particles remain in liquid (supersaturated) form over a 5-90% RH range and no efflorescence was observed even at the lowest RH values. The resulting humidity range will be included in the manuscript as part of the response to comment #4.

8. Page 21998, line 26-27: In Figure 5, are all the malonic acid data determined with supersatured solutions or were some data determined with solid malonic acid particles? This information should be added to the document.

The malonic acid data mentioned in Figure 5 were reported by Thornton et al., 2003 and Griffiths et al. (2009), as mentioned in the figure caption. Thornton et al. have also performed tests on solid malonic acid particles (by drying them first at <5% RH), however these values have not been reported in Fig. 5. According to their report, when liquid particles are subjected to a drying flow, the aerosol remains as super-saturated solutions down to RH<10% due to a free energy barrier to crystal formation. The manuscript will be amended to reflect that data for liquid particles has been presented.

9. Page 21999, lines 12-14: Perhaps I am wrong, but to me it seems unlikely that decoupling can explain the leveling off, since the parameterization based on water diffusion (Lienhard) does not level off. Here I am assuming that water diffusion represents an upper limit to the possible decoupling for N2O5.

Indeed. As we have postulated in our conclusions, decoupling makes estimating the diffusivity of N_2O_5 from measured diffusivity of H_2O or measured viscosity problematic and cannot explain the behavior at low RH values in a satisfactory way. Indeed, we have rather overestimated the contribution of bulk reactivity to uptake. This will be stated more clearly along with the stronger emphasis on the contribution of a surface reaction at low RH.

References

Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI - heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045-8228, doi:10.5194/acp-13-8045-2013, 2013.

Bertram, T. H. and Thornton, J. A.: Toward a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351-8363, 2009.

Braban, C. F., Carroll, M. F., Styler, S. A., and Abbatt, J. P. D.: Phase Transitions of Malonic and Oxalic Acid Aerosols, The Journal of Physical Chemistry A, 107, 6594-6602, 2003.

Gržinić, G., Bartels-Rausch, T., Birrer, M., Türler, A., and Ammann, M.: Production and use of ^{13}N labeled N_2O_5 to determine gas–aerosol interaction kinetics, Radiochim. Acta, 102, 1025–1034, 2014.

Peng, C., Chan, M. N., and Chan, C. K.: The hygroscopic properties of dicarboxylic and multifunctional acids: Measurements and UNIFAC predictions, Environ. Sci. Technol., 35, 4495-4501, 2001.

Thornton, J. A., Braban, C. F., and Abbatt, J. P. D.: N2O5 hydrolysis on sub-micron organic aerosols: the effect of relative humidity, particle phase, and particle size, Phys. Chem. Chem. Phys., 5, 4593-4603, 2003.

Zardini, A. A., Sjogren, S., Marcolli, C., Krieger, U. K., Gysel, M., Weingartner, E., Baltensperger, U., and Peter, T.: A combined particle trap/HTDMA hygroscopicity study of mixed inorganic/organic aerosol particles, Atmos. Chem. Phys., 8, 5589-5601, doi:10.5194/acp-8-5589-2008, 2008.