

Replies to comments for article “Viscosity controls humidity dependence of N₂O₅ uptake to citric acid aerosol” by G. Gržinić et al.

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

Anonymous Referee #1

–General comments

The measured $\gamma_{\text{N}_2\text{O}_5}$ 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 $\gamma_{\text{N}_2\text{O}_5}$.

I certainly find the argument reasonable, though the spread in the estimates of diffusivity and that the full behavior of the measured $\gamma_{\text{N}_2\text{O}_5}$ 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 $\gamma_{\text{N}_2\text{O}_5}$ 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 [H₂O] effect was treated in the model, via $k^I = k^{II}[\text{H}_2\text{O}]$ embedded in equation (4), k^{II} ($1.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$), which is the apparent second-order rate constant for the reaction of N₂O₅ with water, as explicitly explained in the text below equation (4). Bertram and Thornton (2009) have indeed reported a strong dependence of $\gamma_{\text{N}_2\text{O}_5}$ 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 have revised 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 have emphasized 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 have added 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 has been emphasized more in the revised experimental section.

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 has been 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 N₂O₅ on deliquesced ammonium sulfate aerosol at 52 % RH and obtained an average value of $(1.4 \pm 0.4) \times 10^{-2}$ (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. Sentence has been slightly amended for clarity.

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 N₂O₅. The figure has been 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 have emphasised 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 al 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 $6\% \pm 3\%$, which is close to the lowest RH values at which Peng et al 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 has been amended accordingly (see also response to comment #4) and the point repeated wherever appropriate in the text.

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 has been 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_{H_2O}), which we have then used to calculate the diffusivity of N₂O₅ 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 has been 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 has been 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 has been made clearer and repeated at several places 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. This has been 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 supersaturated 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 has been amended to reflect that data for liquid particles only 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 N₂O₅ from measured diffusivity of H₂O 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 has been stated more clearly along with the stronger emphasis on the contribution of a surface reaction at low RH.

General response:

We have updated the reference list, which was lacking several references in the originally submitted manuscript

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1 Viscosity controls Humidity Dependence of N₂O₅ Uptake to 2 Citric Acid Aerosol

3
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13 Abstract

14 The heterogeneous loss of dinitrogen pentoxide (N₂O₅) to aerosol particles has a significant
15 impact on the night time nitrogen oxide cycle and therefore the oxidative capacity in the
16 troposphere. Using a ¹³N short lived radioactive tracer method we studied the uptake kinetics
17 of N₂O₅ on citric acid aerosol particles as a function of relative humidity (RH). The results
18 show that citric acid exhibits lower reactivity than similar di- and polycarboxylic acids, with
19 uptake coefficients between $\sim 3 \times 10^{-4}$ - $\sim 3 \times 10^{-3}$ depending on humidity (17-70% RH). At RH
20 above 50%, the magnitude and ~~This-the~~ humidity dependence can be best explained by ~~the a~~
21 ~~changing~~ viscosity of citric acid as compared to aqueous solutions of simpler organic and
22 ~~inorganic solutes and the variation of viscosity with RH~~ and, hence, diffusivity in the organic
23 matrix. ~~Since the diffusion rates of N₂O₅ in highly concentrated citric acid solutions isare not~~
24 ~~well established~~Since the viscosity of highly concentrated citric acid solutions is not well
25 established, we present four different parameterizations of N₂O₅ diffusivity based on the
26 available literature data or estimates for viscosity and diffusivity of H₂O. Above 50% RH,
27 uptake is consistent with the reacto-diffusive kinetic regime whereas below 50% RH, the
28 uptake coefficient is higher than expected from hydrolysis of N₂O₅ within the bulk of the
29 particles, and the uptake kinetics may-is most likely be-limited by loss on the surface only.

1 This study demonstrates the impact of viscosity in highly oxidized and highly functionalized
2 secondary organic aerosol material on the heterogeneous chemistry of N_2O_5 and may explain
3 some of the unexpectedly low loss rates to aerosol derived from field studies.

4

5 1 Introduction

6 Dinitrogen pentoxide (N_2O_5) is an important species of night-time atmospheric chemistry
7 (Abbatt et al., 2012; Chang et al., 2011; Dentener and Crutzen, 1993). Nitrogen dioxide (NO_2)
8 reacts with ozone (O_3) to give the nitrate radical (NO_3). N_2O_5 is formed via Reaction (R1).



Field Code Changed

10 The concentrations of N_2O_5 , NO_3 and NO_2 are controlled by the temperature dependent
11 equilibrium (R1). N_2O_5 hydrolyzes on any humid surface or in aqueous solution, to give
12 HNO_3 (R2).



Field Code Changed

14 In Reaction (R2), which is considered unimportant in the gas phase, H_2O represents either
15 adsorbed water, ice or liquid water, present on ground or on airborne particles. The detailed
16 mechanism behind R2 that drives heterogeneous uptake of N_2O_5 on aerosol particles is
17 complex (Hallquist et al., 2003; Mozurkewich and Calvert, 1988; Wahner et al., 1998). The
18 suggested elementary steps of the mechanism are:



Field Code Changed



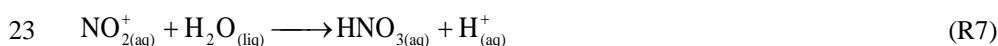
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Field Code Changed

24 A reversible disproportionation (R5, R6) precedes the actual reaction of the nitronium ion
25 NO_2^+ with water (R7). In case of nitrate already present in the particle phase, uptake is

1 considerably reduced through Reaction (R6), referred to as the nitrate effect (Mentel et al.,
2 1999). The aqueous HNO_3 formed in Reaction (R7) can either deprotonate to yield nitrate or
3 evaporate from the particle according to its volatility and acid-base chemistry with other
4 solutes in the system (Laskin et al., 2012). Water plays an important role in the mechanism,
5 not only for solvation of N_2O_5 (R3, R4) and hydration of the nitronium ion, but is also the
6 main reaction partner of the nitronium ion in absence of other nucleophiles (such as chloride,
7 which are not considered in this work).

8 Heterogeneous hydrolysis of N_2O_5 on aerosols acts as a sink for atmospheric NO_x species,
9 and has therefore a significant impact on ozone production and the oxidative capacity of the
10 atmosphere (Dentener and Crutzen, 1993). N_2O_5 uptake kinetics on aerosols has thus received
11 substantial interest over the past decades (Abbatt et al., 2012). The loss rate of N_2O_5 from the
12 gas phase to aerosol particles is expressed in terms of the uptake coefficient, γ , which
13 represents the probability that a gas kinetic collision of a N_2O_5 molecule leads to its uptake at
14 the interface. Extensive studies on inorganic aerosols or corresponding proxy systems have
15 shown that the primary factors influencing the uptake coefficient in the range of 0.0001 to
16 0.05 are relative humidity (RH), physical state, particle size and composition (Abbatt et al.,
17 2012; Davis et al., 2008; George et al., 1994; Hallquist et al., 2003; Hanson and
18 Ravishankara, 1991; Hu and Abbatt, 1997; Karagulian et al., 2006; Mozurkewich and Calvert,
19 1988; Vandoren et al., 1991; Wahner et al., 1998). Supersaturated liquid particles have shown
20 uptake coefficients up to 1-2 orders of magnitude higher than corresponding solid particles at
21 the same RH, pointing towards the importance of the hydrolysis reaction (R3-R7) of N_2O_5
22 with liquid water present in the bulk of aerosol particles (Hallquist et al., 2003; Thornton and
23 Abbatt, 2005).

24 Recently, the focus of N_2O_5 uptake studies has shifted towards organic and mixed inorganic
25 and organic aerosol particles (Anttila et al., 2006; Gaston et al., 2014; Griffiths et al., 2009;
26 Gross et al., 2009; Thornton et al., 2003). Hydrophobic organics may rather form organic
27 surface films or phase separated liquid coatings and thereby may suppress γ for N_2O_5
28 significantly compared to pure inorganic aerosols (Badger et al., 2006; Riemer et al., 2009;
29 Thornton and Abbatt, 2005). In turn, particles composed of hygroscopic organics, such as
30 polycarboxylic acids, show uptake coefficient values that in some cases approach those for
31 inorganic aerosols due to their high water content (Griffiths et al., 2009; Thornton et al.,

1 | 2003), and the humidity-dependent uptake can be understood in terms of the ~~concentration~~
2 | ~~activity~~ of water as reactant (Bertram and Thornton, 2009; Ammann et al., 2013).

3 | Organic aerosols account for a significant fraction of atmospheric particulate mass
4 | (Kanakidou et al., 2005). However there are still significant gaps in our knowledge regarding
5 | the chemistry and physical state of organic aerosols (De Gouw and Jimenez, 2009; Kanakidou
6 | et al., 2005; Zhang et al., 2007). Recent studies have shown that the previous assumptions of
7 | low-viscosity, well mixed liquid aerosol phases are not always correct, but must be
8 | considered depending on environmental conditions such as humidity and temperature.
9 | Especially under cold or dry conditions, aerosol particles dominated by organic compounds
10 | can exhibit a highly viscous or even glassy state (Koop et al., 2011; Murray, 2008; Renbaum-
11 | Wolff et al., 2013; Virtanen et al., 2010; Zobrist et al., 2008). Diffusion in these particles is
12 | significantly retarded (Price et al., 2014; Zobrist et al., 2011), leading to severe kinetic
13 | limitations in gas-particle partitioning (Shiraiwa et al., 2013; Vaden et al., 2011).

14 | Field measurements (Bertram et al., 2009; Brown et al., 2009) have shown that the observed
15 | reactivity of N_2O_5 on aerosol particles containing organics can be up to a factor of 10 lower
16 | than the values predicted by model parameterizations, which are based on laboratory
17 | measurements with organic compounds such as malonic acid. Also, a recent laboratory study
18 | has shown that uptake of N_2O_5 to laboratory SOA proxies does not only follow the expected
19 | trend with water content based on the correlation of the latter with O:C ratio (Gaston et al.,
20 | 2014).

21 | For this study we investigated the uptake of N_2O_5 on citric acid aerosol using the short-lived
22 | ^{13}N radioactive tracer technique developed at the Paul Scherrer Institute (Ammann, 2001;
23 | Gržinić et al., 2014). This technique has been used before to study the uptake kinetics of other
24 | nitrogen oxides on aerosol particles (Guimbaud et al., 2002; Sosedova et al., 2009; Vlasenko
25 | et al., 2009), and we have recently developed a method to produce ^{13}N labeled N_2O_5 for ~~use in~~
26 | ~~the kinetic experiments~~ this purpose (Gržinić et al., 2014). Citric acid was used as a proxy for
27 | highly oxidized organic species found in secondary organic aerosol (SOA). It has well-known
28 | thermodynamic properties and new studies on viscosity and water diffusivity in citric acid
29 | have recently become available (Lienhard et al., 2012; Lienhard et al., 2014). In our study,
30 | measurements were conducted over a wide RH range and several methods were used to
31 | estimate the diffusivity of N_2O_5 in citric acid as a basis for the kinetic analysis.

32

2 Experimental

The experimental method used in this study has been described in detail in our previous publication (Gržinić et al., 2014). N_2O_5 labeled with the ^{13}N short-lived radioactive isotope is mixed with citric acid aerosol in an aerosol flow tube. Gas and aerosol phase products are selectively separated and trapped in a parallel plate diffusion denuder system and a particle filter, respectively. The concentration of the various species can be measured simultaneously by monitoring the radioactive decay of the ^{13}N labeled species on each trap over time. A schematic representation of our experimental setup can be seen found in Gržinić et al. (2014).

2.1 Production of ^{13}N labeled N_2O_5

^{13}N ($\tau_{1/2} \approx 10$ min.) is produced online in a flow-through gas-target via the $^{16}\text{O}(\text{p},\alpha)^{13}\text{N}$ reaction in 10-15% O_2 in He, at a total flow rate of 1 standard liter per minute at ~ 2 bar (see (Ammann, 2001; Gržinić et al., 2014) for more details). The highly oxidized ^{13}N labeled nitrogen species, are reduced to ^{13}NO over a Mo converter (at ~ 380 °C) and transported from the production site to the laboratory through a 580 m long 4 mm inner diameter PVDF tube. A small amount of the ^{13}NO containing gas flow (50 ml/min) is mixed with nitrogen carrier gas and non-labeled NO (~ 2 ml/min) from a certified gas cylinder (10 ppm in N_2). O_3 at ~ 8 ppmv is produced by irradiating a flow (50 ml/min) of 10% O_2 in N_2 with 185 nm UV light in a cylindrical photolysis reactor. The ^{13}NO and O_3 flows are mixed in the N_2O_5 synthesis reactor (34 cm long and 4 cm inner diameter, with residence time ~ 4 min), where NO reacts with O_3 to produce first NO_2 and then NO_3 which then react via Reaction (R1) to form N_2O_5 . This reactor is covered inside with a thin PTFE foil to minimize heterogeneous N_2O_5 losses, and outside by a dark cloth shroud to prevent NO_3 photolysis. Design, performance and consistency of N_2O_5 production with simulations obtained via a gas kinetic model has been described previously (Gržinić et al., 2014).

2.2 Aerosol production

An ultrasonic nebulizer was used to generate an aerosol from a 0.07 % (by weight) solution of citric acid (HQ, Fluka, >99%) in MilliQ water. The resulting aerosol particles were dried over a Nafion membrane diffusion drier. [Citric acid particles remain in liquid \(supersaturated\) form over a very wide humidity range \(65-90% RH\) and neither crystallization \(efflorescence\) nor deliquescence has been reported over this range](#) (Peng et al., 2001; Zardini

1 | [et al., 2008](#)). To avoid [possible](#) efflorescence of the aerosol particles [in dry air](#), the sheath gas
2 used in the diffusion drier has been humidified to 15 - 17 % RH. The resulting aerosol gas
3 flow was passed through a homemade ^{85}Kr bipolar ion source to establish an equilibrium
4 charge distribution on the aerosol, followed by an electrostatic precipitator to remove all
5 charged particles. This was done to avoid uncontrollable wall losses of charged particles in
6 the insulating aerosol flow tube. A homemade Gore-TexTM membrane humidifier was placed
7 behind the precipitator for precise adjustment of RH, followed by an elution volume with ~2
8 min residence time to assure gas – particle equilibrium. Measurements were conducted from
9 17% to 70.3% RH.

10 A Scanning Mobility Particle Sizer (SMPS) was used to measure the suspended surface area
11 to gas volume ratio. The SMPS system consisted of an ^{85}Kr ion source (to re-establish the
12 equilibrium charge distribution), a Differential Mobility Analyzer (DMA, TSI 3071) and a
13 Condensation Particle Counter (CPC, TSI 3022). Filtered carrier gas was used as sheath gas
14 for the DMA to assure identical RH in the two flows and thus maintain the water content of
15 the particles during size separation. The SMPS was connected immediately after the aerosol
16 flow tube. A capacitance humidity sensor was placed in front of the SMPS to monitor RH.

17 **2.3 Aerosol flow tube**

18 The gas flows containing aerosol and N_2O_5 , respectively, were mixed in a cylindrical flow
19 tube reactor consisting of a PFA tube with an inner diameter of 7 cm. The inlet and outlet are
20 cylindrical PTFE stops with inverse cones milled into. The stops are equipped with a
21 pneumatic ring to seal the reactor. The inlet and outlet can be moved inside the reactor to vary
22 reaction time. The N_2O_5 gas flow (102 ml/min) is introduced into the aerosol flow tube along
23 the axis of the reactor. The distance between the N_2O_5 reactor and the aerosol flow tube was
24 kept short, and the N_2O_5 reactor was moved along with the inlet into the aerosol flow tube
25 when changing the reaction time. The aerosol flow (720 ml/min) is introduced via a stainless-
26 steel tubular injector (6 mm in diameter) which protrudes from the inlet and is bent in such a
27 way that the injector nozzle is equidistant from the walls of the flow tube. The aerosol flow is
28 injected perpendicularly to the N_2O_5 gas flow within the flow tube. Reaction times from 10 to
29 60 seconds were adjusted. For the flow rate used, a laminar flow profile is assumed to have
30 been established within the flow tube a few cm downstream of the aerosol injector. As with
31 the N_2O_5 synthesis reactor, a black shroud was used to shield the aerosol flow tube from
32 daylight to prevent NO_3 photolysis and thus loss of N_2O_5 . The overall system exhaust was

1 pressure controlled at slightly below ambient pressure (960-970 mbar). The aerosol flow tube
2 was kept at ambient temperature, which was controlled by the room ventilation system at
3 295 ± 1 K.

4 **2.4 Separation and detection of ^{13}N labeled species**

5 The gas flow from the aerosol flow tube was split with one fraction going to the SMPS
6 system or alternatively a NO_x (Teledyne T200) or O_3 analyzer (ML 9810) and the other being
7 directed into the parallel plate diffusion denuder system. This system consists of a series of
8 parallel plate sets placed 1 mm apart in an aluminium housing. The plates are prepared with
9 specific coatings and trap the ^{13}N containing gaseous species (N_2O_5 , NO_3 and NO_2) by lateral
10 diffusion and chemical reaction. Aerosol particles pass through the denuder without being
11 trapped and are deposited on a glass fiber filter located at the exit of the denuder system.
12 Citric acid has been used as a denuder coating for N_2O_5 . Citric acid mixes well with water,
13 has a well-known hygroscopic cycle (Peng et al., 2001; Zardini et al., 2008), and interferes
14 only weakly with NO_2 , i.e. only marginal amounts are trapped on the denuder plates. Citric
15 acid was used as a coating on the first two denuder plates, the first one capturing N_2O_5 while
16 the second one is used to quantify the small NO_2 interference. NO_3 , which is present in small
17 quantities in the gas phase, cannot be separated from N_2O_5 by this technique and is likewise
18 absorbed on the first denuder plate together with N_2O_5 . The citric acid coating was prepared
19 by applying a citric acid solution 2 % by weight in 50/50 % methanol/water to the plates and
20 allowed to dry at room temperature. The following two denuders were coated with a 1% N-(1-
21 naphthyl) ethylene diamine dihydrochloride (NDA) solution in 1% KOH and 10% water in
22 methanol. NDA reacts efficiently with NO_2 and the basic nature of the solution prevents the
23 re-evaporation of the so formed nitrite. Since NDA is sensitive to O_3 , which is present at
24 around ~ 550 ppbv in our system, two sets of denuder plates were installed in series to extend
25 the operating life. Fresh coatings were prepared and applied every day. An additional gamma
26 detector was attached to the non-coated, 10 cm long, and trapezoidally shaped aluminium
27 inlet to determine the amount of N_2O_5 trapped there.

28 The ^{13}N containing species that were trapped on the denuder plates, inlet and particle filter
29 were measured by monitoring the radioactive decay of ^{13}N . A CsI scintillator crystal with
30 integrated PIN diode detector (Carroll and Ramsey, USA) was placed on each of the traps.
31 ^{13}N , a well-known β^+ emitter, decays with emission of a positron which, upon annihilation
32 with an electron, emits two coincident γ -rays in opposite directions. These γ -rays are detected

1 by the scintillators and the signal is converted to the flux of the ^{13}N containing gaseous
2 species into the respective traps using the inversion procedure reported elsewhere (Kalberer et
3 al., 1996). The flux into a trap can be calculated using Eq. (1).

$$4 \quad I_j = \frac{A_{j(i)} - A_{j(i-1)} \exp(-\lambda(t_{(i)} - t_{(i-1)}))}{1 - \exp(-\lambda(t_{(i)} - t_{(i-1)}))} \quad (\text{Eq. 1})$$

5 Where I_j is the flux into trap j , $A_{j(i-1)}$ and $A_{j(i)}$ are two consecutive activity measurements
6 performed at times $t_{(i-1)}$ and $t_{(i)}$ and λ is the decay constant for ^{13}N ($\lambda=0.00116 \text{ s}^{-1}$). The
7 measured flux is proportional to the gas phase concentration of the respective species. By
8 comparing the value of the gas phase NO_2 concentration measured with the NO_x analyzer to
9 the $^{13}\text{NO}_2$ and $^{13}\text{N}_2\text{O}_5$ signals measured at the denuder traps and the particle filter it is possible
10 to calculate the concentration of N_2O_5 in the gas phase and its degradation products in the
11 particle phase. The overall signal of N_2O_5 in the gas phase was obtained by adding the inlet
12 and first citric acid coated denuder plate signals and subtracting the second citric acid denuder
13 signal (NO_2 interference). To correct for the small amounts of NO_3 present in the gas phase
14 the signal was multiplied with the $\text{N}_2\text{O}_5/(\text{NO}_3+\text{N}_2\text{O}_5)$ ratio obtained via the gas kinetic model
15 described in our previous study (Gržinić et al., 2014).

16 Additional information on coating preparation, traps and measurement efficiencies can be
17 found in our previous publications (Ammann, 2001; Gržinić et al., 2014; Guimbaud et al.,
18 2002).

19

20 **3 Results and discussion**

21 **3.1 Uptake coefficient of N_2O_5 as a function of relative humidity**

22 A typical experiment was performed as follows: after a period of stabilization, during which
23 all flows were switched on, but the nebulizer switched off, the NO and NO_2 concentrations
24 were measured via the NO_x analyzer connected to the system (in place of the SMPS), before
25 turning on the O_3 generator. Concentrations around 9-10 ppbv of NO were obtained in the
26 aerosol flow tube reactor. From the measured gamma-ray detector signals of N_2O_5 and NO_2 ,
27 after switching on the O_3 generator, typically, a maximum initial concentration of ~ 5 ppbv of
28 N_2O_5 was calculated. Next, a wall loss measurement was performed by changing the length of
29 the aerosol flow tube and thus the reaction time, which is shown in the first part of the

1 exemplary record of an experiment in Fig. 1. Typical pseudo-first order wall loss rate
 2 constants, k_w , were $\sim 9 \times 10^{-3}$ and $\sim 3 \times 10^{-2} \text{ s}^{-1}$ for low and high humidity, respectively,
 3 indicating strong wall loss of the labeled N_2O_5 molecules. k_w was remaining constant over
 4 time after an initial passivation period. After the wall loss measurement was completed, the
 5 SMPS was connected to the system and the reactor length was adjusted to enable a 60 sec
 6 reaction time within the aerosol flow tube. The wall loss measurement was routinely
 7 performed for each set of aerosol experiment.

8 At this point the nebulizer was switched on to generate citric acid aerosol for 25-30 minutes
 9 and then switched off again for an interval of the same duration. The aerosol surface area was
 10 varied by changing the vibration frequency of the piezoelectric membrane in the ultrasonic
 11 nebulizer, leading to data as shown in Fig. 2.

12 The gas-aerosol interaction kinetics can be described by Eq. (2):

$$13 \quad \frac{C_p^{(t)}}{C_g^{(t=0)}} = \frac{1 - e^{-(k_w + k_p)t}}{1 + \frac{k_w}{k_p}} \quad (\text{Eq. 2})$$

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14 where $C_g^{(t=0)}$ is the gas-phase N_2O_5 concentration at time zero, $C_p^{(t)}$ is the N_2O_5 concentration
 15 in the particle phase at the end of the reactor, $t = 60 \text{ s}$, k_w is the wall loss rate constant,
 16 measured as described above, and k_p denotes the apparent first order rate coefficient for loss
 17 of N_2O_5 from the gas phase due to its heterogeneous reaction with the aerosol phase. Equation
 18 (3) relates k_p to the uptake coefficient, γ :

$$19 \quad \gamma = \frac{4k_p}{S_p \omega} \quad \omega = \sqrt{\frac{8RT}{\pi M}} \quad (\text{Eq. 3})$$

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20
 21 where S_p is the total aerosol surface area to gas volume ratio obtained with the SMPS, ω is the
 22 mean thermal velocity of N_2O_5 , R is the gas constant, T is the absolute temperature and M is
 23 the molar weight of N_2O_5 . Equation (2) was then used to fit the experimental data as shown in
 24 Fig. 2 with γ being the only variable. Note that this procedure of varying the aerosol surface
 25 area to volume ratio gave better reproducibility and lower scatter than varying the interaction

1 time. The resulting γ values ranged from 3×10^{-4} to $\sim 3 \times 10^{-3}$ over the RH range of 17% to 70%
2 as shown in Fig. 3.

3 The uncertainty in γ arises primarily from the fact that aerosol uptake rates (k_p) were smaller
4 than wall loss rates (k_w) as well as from the systematic error associated with the measurements
5 of surface to volume ratio of the aerosol by the SMPS (S_p), which amounts to $\sim 30\%$. The 95%
6 confidence interval from replication (as can be seen in Fig. 2) does not strongly influence the
7 overall uncertainty for γ . There are a few factors that may have influenced the scatter among
8 the measurements at different RH. We have noticed that a small but variable number of very
9 large particles fell outside the measurement range of the DMA, which for our settings was
10 limited to particle diameters up to 806 nm. Additionally, two separate batches of citric acid
11 (from the same manufacturer) have been used to prepare the solutions, and possible
12 contaminations, ~~which might induce phase separation or crystallization affecting the~~
13 ~~reactivity~~, may have affected the physical properties ~~and reactivity~~ of the resulting aerosol.

14 Compared to other aqueous polycarboxylic acids (Griffiths et al., 2009; Thornton et al., 2003)
15 the uptake coefficient on citric acid is more than an order of magnitude lower. As mentioned
16 in the experimental section, care was taken to avoid crystallization by ~~using a non-~~
17 ~~dry humidified gas flow and to equilibrating-equilibrate~~ the solution droplets resulting from the
18 nebulizer to the lowest RH used in the experiments. Therefore, the low uptake coefficients are
19 unlikely to represent uptake to crystalline citric acid. With respect to the humidity range, the
20 primary limitations were wall loss (at high RH) and potential efflorescence of the aqueous
21 aerosol (at ~~low~~ RH at or below 6 %, Peng et al. (2001)).

22 As a consistency test we measured the uptake coefficient of N_2O_5 on deliquesced ammonium
23 sulfate aerosol at 52 % RH as described by (Gržinić et al., 2014) and obtained an average
24 value of $(1.4 \pm 0.4) \times 10^{-2}$, similar to other studies compiled ~~in by~~ (Ammann et al., (2013)).

25 3.2 Physical state, reaction mechanism and parameterization

26 The data in Fig. 3 show a gradual increase of the uptake coefficient with increasing RH,
27 consistent with the expected increase in water content. Literature data suggests that citric acid
28 particles form supersaturated solutions down to low RH (Peng et al., 2001; Zardini et al.,
29 2008). Recent experiments have demonstrated high viscosity of highly supersaturated citric
30 acid solutions, obtained either from the kinetics of shape change of coalescing droplets (J.
31 Reid and C. Cai, personal communication, 2015, and using the method described by Power et

1 al. (2013)) or via the hygroscopic growth kinetics in single levitated droplets (Lienhard et al.,
 2 2014). It is thus not surprising that the observed uptake coefficient of N₂O₅ of around 10⁻⁴ at
 3 low humidity is comparable to succinic acid or oxalic acid in their effloresced (and thus solid)
 4 form (Griffiths et al., 2009). The difference between low and high humidity is also similar to
 5 that of solid (effloresced) vs. liquid (deliquesced) inorganic aerosol (Hallquist et al., 2003),
 6 but as mentioned above, the gradual increase observed here is consistent with the absence of a
 7 sharp deliquescence step and thus probably the result of continuously changing water content
 8 and hence diffusivity of N₂O₅ within the particles. This is in line with previous observations
 9 of the gradually ~~deliquescence-changing water content of in~~ amorphous organics (Mikhailov
 10 et al., 2009).

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11 For moderate uptake rates and submicron particles, where gas-phase diffusion constraints can
 12 be neglected, the N₂O₅ uptake coefficient can be described according to the resistor model
 13 (Davidovits et al., 1995) with Eq. (4):

$$14 \quad \frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_b} = \frac{1}{\alpha_b} + \frac{\omega}{4HRT\sqrt{D_1k^1}} \left(\coth q - \frac{1}{q} \right)^{-1} \quad (\text{Eq. 4})$$

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15 where α_b is the bulk accommodation coefficient, H is the Henry's law constant, R is the gas
 16 constant, T is the absolute temperature, D_1 is the liquid-phase diffusion coefficient, k^1 is the
 17 apparent first-order loss rate constant for N₂O₅ in the liquid phase, ω is the mean thermal
 18 velocity of N₂O₅ molecules in the gas phase and q is the reacto-diffusive parameter which
 19 accounts for the competition between reaction and diffusion within the particle. The reacto-
 20 diffusive parameter is defined by Eq. (5):

$$21 \quad q = \frac{l}{r} \quad (\text{Eq. 5})$$

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22 where r is the radius of the particle and l is the reacto-diffusive length, defined by Eq. (6):

$$23 \quad l = \sqrt{\frac{D_1}{k^1}} \quad (\text{Eq. 6})$$

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24 The reacto-diffusive length is the characteristic distance that a molecule diffuses within a
 25 particle before reacting, which brings about a size dependence of γ when l is comparable to or
 26 larger than the radius of the particle ($q > 1$). Eq. (5), in which the complex mechanism (R3-R7)
 27 is lumped into the net Reaction (R2) by treating only one dissolved N₂O₅ species undergoing

1 a bimolecular reaction with liquid phase water, provides a reasonable parameterization to
2 describe uptake of N_2O_5 to laboratory generated aerosol particles (Ammann et al., 2013). An
3 analytical expression has been suggested to also take into account the nitrate effect (Griffiths
4 et al., 2009; Bertram and Thornton, 2009). Since we have worked at low N_2O_5 concentrations
5 (5 ppbv), where the maximum HNO_3 concentration expected in the particle phase was $\sim 10^{-3}$
6 M, we could safely neglect this.

7 The Henry's law constant for N_2O_5 , an important variable in Eq. (4), is unknown for organic
8 polycarboxylic aerosol particles. However, in several studies (Badger et al., 2006; Robinson
9 et al., 1997; Thornton et al., 2003), a generic value of $H = 2 \text{ M atm}^{-1}$ has been suggested for
10 liquid aerosol particle solutions. Recommended values (Ammann et al., 2013) for aqueous
11 organic aerosols have been used for α_b (0.035) and k^{II} ($1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), which is the apparent
12 second-order rate constant for the reaction of N_2O_5 with water, and $k^{\text{I}} = k^{\text{II}}[\text{H}_2\text{O}]$. The
13 recommended values are based on several studies with dicarboxylic and polycarboxylic acids
14 (Badger et al., 2006; Griffiths et al., 2009; Thornton et al., 2003). Note that as evident from
15 Eq. (4), experiments allow to safely constrain only the product $H \times \text{sqrt}(k^{\text{I}})$, so that the rate
16 constant values are linked to the choice of H .

17 Since water is the main reactant for the hydrolysis of N_2O_5 , the parameterization relies
18 heavily on the water concentration as a function of RH. Mass growth factor values (and
19 consequently mass fractions) for citric acid and water were obtained from Zardini et al.
20 (2008), while the citric acid solution densities have been obtained from several sources, each
21 relating to the particular parameterization used for viscosity further below (Laguerie et al.,
22 1976; Lienhard et al., 2012; Peng et al., 2001).

23 For the diffusion coefficient D_1 of N_2O_5 in an aqueous solution, previous studies were based
24 on an estimate of $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Badger et al., 2006; Griffiths et al., 2009; Hallquist et al.,
25 2003; Thornton et al., 2003), independent of water activity. Together with the other
26 parameters, this leads to a reasonable agreement of the parameterisation based on Eq. (4) with
27 the measured data for malonic acid. However, as it turns out, the parameterisation would
28 largely overpredict the reactivity for citric acid. Citric acid solutions exhibit a substantially
29 higher viscosity, i.e. for a solution of 1.04 M, the reported viscosity (Laguerie et al., 1976) of
30 CA is $1.49 \times 10^{-3} \text{ Pa s}$, while for malonic acid it is $1.09 \times 10^{-3} \text{ Pa s}$ (Chmielewska and Bald,
31 2008), close to that of water ($0.91 \times 10^{-3} \text{ Pa s}$). It is therefore likely that the lower uptake
32 coefficients of N_2O_5 in citric acid compared to those for malonic acid are caused by lower

1 diffusivity in the more viscous solution. Since the diffusivity of N₂O₅ is not known in either
2 medium, we used four methods for its estimation, based either on measured viscosities or on
3 measured or estimated diffusivity of H₂O. If the viscosity is known, D₁ for N₂O₅ can be
4 calculated by applying the Stokes-Einstein relation (Eq. (7)).

$$5 \quad D_1 = \frac{k_B T}{6\pi\eta r} \quad (\text{Eq. 7})$$

6 Where k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity and r is
7 the radius of the N₂O₅ molecule assumed spherical (2.5 Å). Uncertainty remains with respect
8 to the effective molecular radius to be used, since ~~we don't know~~ the identity of the solute for
9 the rate limiting step is not clear (dissolved N₂O₅ or NO₂⁺). Additionally, for high viscosity (at
10 low RH), the use of the Stokes-Einstein relation may be questioned: Power et al. (2013)
11 suggested that the diffusivity of water in sucrose droplets decouples from the viscosity at
12 viscosities around 1 Pa s, and at 10 Pa s the diffusivity calculated by Eq. (7) departs from
13 measured values already by an order of magnitude. For the cases, where the diffusivity of
14 H₂O is known or estimated, we also used Eq. (7) to estimate the diffusivity of N₂O₅ by
15 accounting for the change in molecular size.

16 The results are summarized in Fig. 4. The different parameterizations are represented by solid
17 lines, and by dashed lines where the use of the Stokes-Einstein relation may not be granted.
18 The first one (labeled 'Laguerie') is based on viscosity measurements by Laguerie et al.
19 (1976). The viscosity parameterization in this case covers a range of citric acid concentrations
20 up to ~4.3 M, which in our case corresponds to RH values >70%. More recent measurements
21 of viscosity of citric acid were provided by C. Cai and J. Reid (personal communication,
22 2015) from a combination of optical tweezers and electrodynamic balance (EDB) experiments
23 covering a range of 3 to 73% RH (labeled 'Reid' in Fig. 4). The third method is based on an
24 estimate of the diffusivity of H₂O in the organic matrix, which is in turn based on the
25 principal parameterization for the one of H₂O in sucrose from Zobrist et al. (2011). This
26 method uses the measured glass transition and hygroscopicity data to infer diffusion
27 properties of a target substance (e.g. citric acid) by extrapolation from a known reference
28 substance (e.g. sucrose) (Berkemeier et al., 2014) (labeled 'Berkemeier' in Fig. 4). The same
29 method has been used to estimate the diffusivity of N₂O₅ in malonic acid. Finally, Lienhard et
30 al. (2014) determined the diffusivity of H₂O in citric acid solution droplets by measuring the
31 kinetics of the size change in response to step changes in RH in an EDB. The data are

1 parameterized via an empirical Vignes-type equation (Lienhard et al., 2012; Lienhard et al.,
2 2014).

3 The result of calculating the uptake coefficient according to Eq. (4) and using diffusion
4 coefficients estimated according to these four methods is presented in Fig. 5. The solid and
5 dashed shape of the lines again indicate the validity or not, respectively, of the Stokes-
6 Einstein relation as a basis for diffusivity estimation. Figure 5 also shows data ~~of~~ for liquid
7 (supersaturated) malonic acid particles (Griffiths et al., 2009; Thornton et al., 2003) and ~~its~~
8 the calculated uptake coefficient based on Eq. (4), using the corresponding estimate of N_2O_5
9 diffusivity. Thornton et al. (2003) have reported malonic acid efflorescence to occur at <7%
10 RH and deliquescence at 69% RH, and have performed experiments on solid malonic acid
11 particles as well for comparison, which -However these have are not been included here.

12 The parameterization based on the Lienhard et al. H_2O diffusivity data starts to deviate
13 strongly from the rest as well as from the measured citric acid uptake coefficients above 30 %
14 RH, overestimating the uptake by about a factor 3-4. We note that the Vignes type
15 parameterization used by Lienhard et al. (2014) was constrained by measurements of the
16 diffusivity of water below 40% RH at max 281 K only. Since H_2O is much smaller than N_2O_5 ,
17 the diffusivity of N_2O_5 may exhibit a different slope as a function of humidity. The
18 parameterization based on the Laguerie viscosity data is limited by the small range of solution
19 compositions covered by measurements (RH >70%). The other parameterizations
20 (Berkemeier, Reid) follow the measured ~~uptake~~ values for the uptake coefficient fairly well
21 down to ~~values of~~ about 50% RH, indicating that the changing viscosity and associated
22 changes in diffusivity as a function of RH control the uptake coefficient of N_2O_5 . At lower
23 RH the measured data seem to level off, which may be related to the decoupling between
24 viscosity and diffusivity below 10 Pa s, ~~which would lead to underestimating the uptake~~
25 ~~coefficient~~ (Debenedetti and Stillingner, 2001; Power et al., 2013)-. However, this decoupling
26 would rather lead to lower diffusivity of N_2O_5 than expected based on the Stokes-Einstein
27 equation and thus fails to explain the higher than expected reactivity at low RH.

28 In spite of the uncertainties related to the diffusivity estimates, the uptake coefficient
29 parameterized by Eq. (4), while well describing the measurements at higher RH, thus clearly
30 underestimates the measurements at low RH. To assess the validity of the reacto-diffusive
31 regime, we consider the reacto-diffusive length (Table 1), which remains much smaller than
32 the particle dimensions, especially towards low humidity, due to the strong reduction in

diffusivity. Thus no size effects are expected. In turn, Eq. (4) assumes that water, the reactant for N_2O_5 , remains well mixed. Even for 15 % RH, using the diffusivity parameterization closest to our measured results (Berkemeier), the diffusivity of H_2O is about $1.34 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, and the characteristic time for diffusion across a particle, $t = d_p^2 / D_{H_2O}$, becomes about 0.75 s, which is significantly shorter than the ~~time scale of our uptake experiment~~ residence time in the flow tube. Other effects, such as salting in of N_2O_5 (thus effectively increasing H) or an increase in the apparent rate constant k^{II} are also not likely. Therefore, we suggest that at low RH, uptake of N_2O_5 becomes limited by its hydrolysis on the surface, which is not included in Eq. (4). Including a surface reaction term to the uptake model would lead to

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s + \left(\frac{1}{\Gamma_{sb}} + \frac{1}{\Gamma_b} \right)^{-1}} \quad (8)$$

Where α_s is the surface accommodation coefficient and $1/\Gamma_{sb}$ represents the resistance for surface to bulk transfer (Ammann et al., 2013), which together constitute the bulk accommodation coefficient $1/\alpha_b = 1/\alpha_s + 1/\Gamma_{sb}$. Γ_{sb} has been estimated by assuming that surface accommodation is not rate limiting and setting α_s to 1 and keeping α_b at 0.035 as above. Γ_s is the limiting uptake coefficient for the surface reaction. $1/\Gamma_b$ represents the bulk reaction-diffusion resistance given in equation (4).

The red line in Figure 5 represents the result of applying equation (8), keeping the bulk reactivity parameters as before for the Berkemeier diffusivity estimates for citric acid and setting the value of Γ_s to 2.5×10^{-4} , which leads to good agreement with the observed data. The value of Γ_s falls into the range of ~~The uptake coefficient in the 10^{-4} range is comparable to that uptake coefficients~~ observed on effloresced malonic, succinic or oxalic acids (Griffiths et al., 2009; Thornton et al., 2003). Even at low RH, adsorbed water is abundant on a polar surface like citric acid, so that surface hydrolysis of N_2O_5 on high viscosity citric acid may indeed become the rate limiting step at low RH.

4 Conclusions and atmospheric impact

We have conducted measurements of N_2O_5 uptake to citric acid aerosol over an atmospherically relevant RH range at room temperature. Our results have shown that uptake coefficients change by roughly one order of magnitude ($\sim 3 \times 10^{-4}$ - 3×10^{-3}) between low (17%)

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1 and high (70%) RH. The results can be described under the assumption that citric acid
2 remains a supersaturated liquid, even at low RH, and exhibits an increased viscosity at low
3 water content. Reactive uptake is found to be governed by reacto-diffusive limitation with the
4 reacto-diffusive length decreasing under the influence of increased viscosity (and thus
5 decreased diffusivity) from a few nm to the sub-nanometer range. Thus, the decreasing uptake
6 coefficients with decreasing RH are well explained by ~~the~~ the parameterization of N₂O₅
7 uptake by the bulk reacto-diffusive uptake regime at RH above 50%, essentially driven by the
8 decreasing diffusivity of N₂O₅. However, because eAt low RH, estimating the diffusivity of
9 N₂O₅ from the measured diffusivity of H₂O or the measured viscosity is problematic due to
10 the decoupling between viscosity and diffusivity at high viscosity. However, even when
11 taking these uncertainties into account, the reactivity observed at low RH cannot be explained
12 by reaction in the bulk of the particles. , the parameterization of N₂O₅ uptake by the
13 traditional bulk reacto-diffusive uptake regime alone becomes uncertain at low RH. It We
14 conclude cannot be ruled out that a surface reaction hydrolysis contributes dominates
15 significantly to uptake at low relative humidity.

16 Secondary organic aerosol (SOA) is likely to exhibit a similar, or even higher viscosity
17 compared to citric acid used here as model compound (Renbaum-Wolff et al., 2013). Thus
18 high viscosity at low RH could explain the discrepancy between N₂O₅ reactivity in field
19 measurements and model predictions based on laboratory measurements. A recent study
20 (Gaston et al., 2014) suggested that the organic O:C ratio in mixed inorganic-organic aerosols
21 may be used as an indicator of N₂O₅ reactivity, based on a trend of increasing uptake
22 coefficient with increasing O:C ratio. However, citric acid and some high O:C mixtures
23 containing citric acid and other highly functionalized oxidized organic compounds were an
24 exception to this trend. Hence, while O:C ratio can serve as an indicator for reactivity towards
25 N₂O₅ at low O:C, this trend might be reversed for highly oxidized organic compounds
26 forming high viscosity aqueous solutions. Parameterization of N₂O₅ reactivity in atmospheric
27 models should thus not only rely on particle O:C, but should also have means to take into
28 account high particle viscosity.

29

30 **Acknowledgements**

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32 production facility IP-2 for their invaluable help. Additionally, the authors would like to thank

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4 Mainz (MPGC) and thanks T. Koop for stimulating discussions.
5

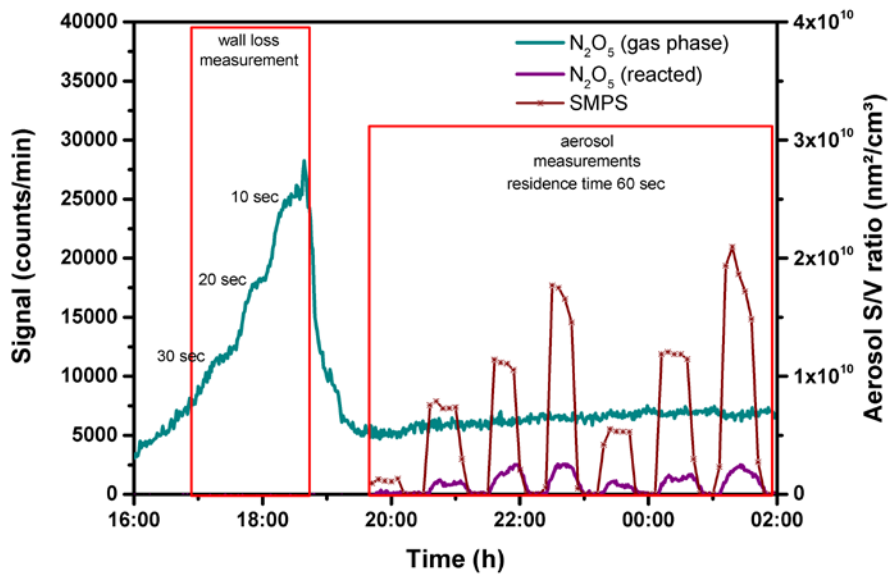
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1 Table 1. Reacto-diffusive lengths calculated using diffusivity values obtained via the four
2 above mentioned parameterizations.

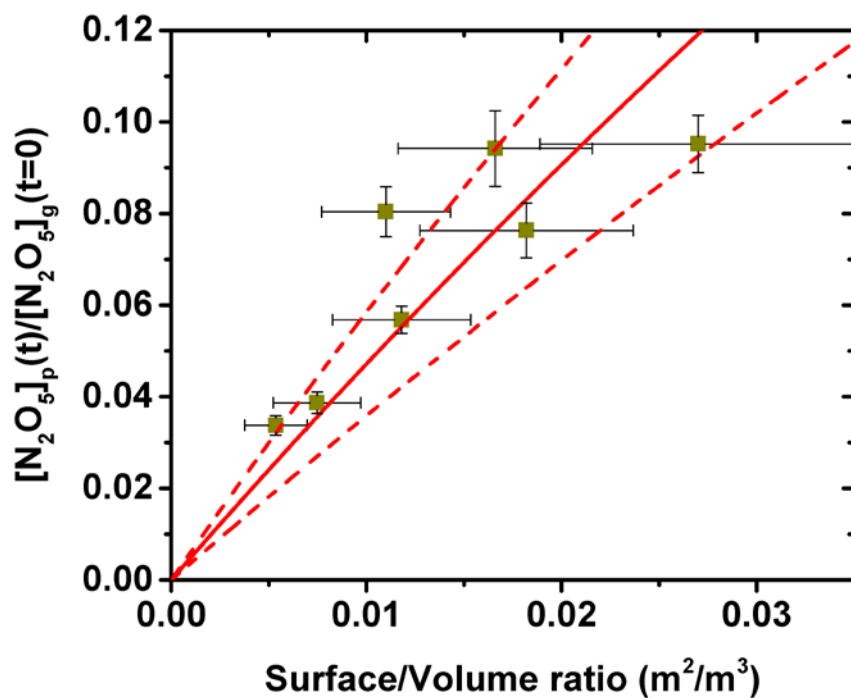
RH [%]	Reacto-diffusive length [nm]			
	Laguerie	Reid	Berkemeier	Lienhard
30	-	0.09	0.21	0.16
50	-	0.49	0.74	2.88
70	3.03	1.83	2.96	7.21
90	6.33	5.26	9.63	10.29

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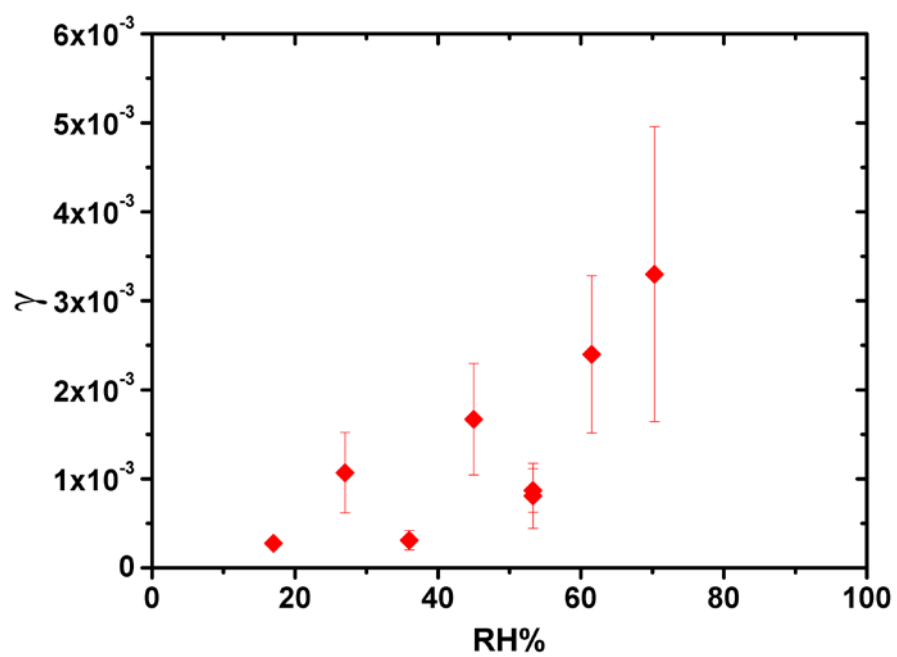


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Figure 1. Exemplary traces of inverted detector signals for an experiment: teal: gas-phase $^{13}\text{N}_2\text{O}_5$ signal; purple: particle-phase ^{13}N signal; red: SMPS signal (aerosol surface/volume ratio)

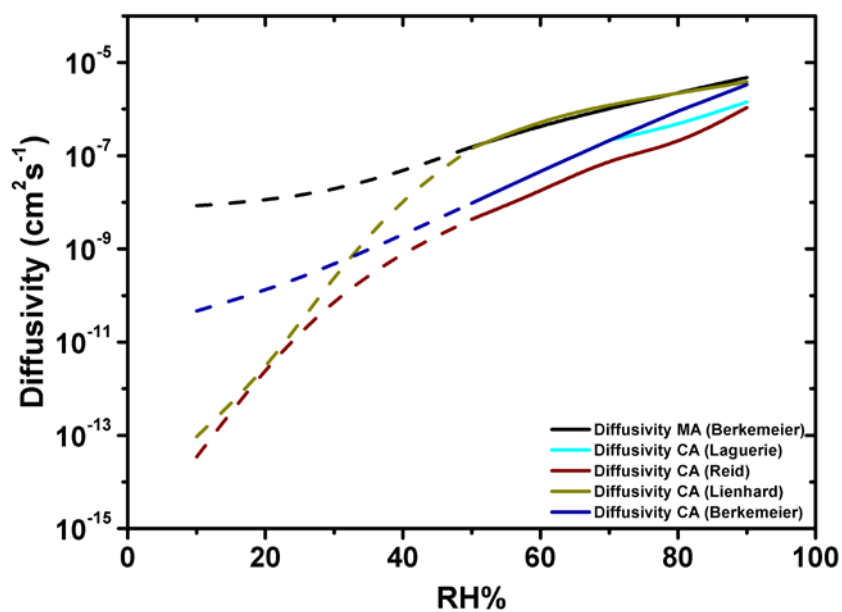


1
2
3 Figure 2. Normalized particle-phase N₂O₅ concentration vs. aerosol surface area to gas
4 volume ratio for the experiment from Fig. 1. The data points represent experimental data;
5 vertical error bars represent a 95% confidence interval, horizontal error bars represent the S/V
6 measurement error (30%), the full red line is the fitted series determined by least-squares
7 fitting of Eq. (2) to experimental data, the dashed red lines are 95% confidence intervals.
8



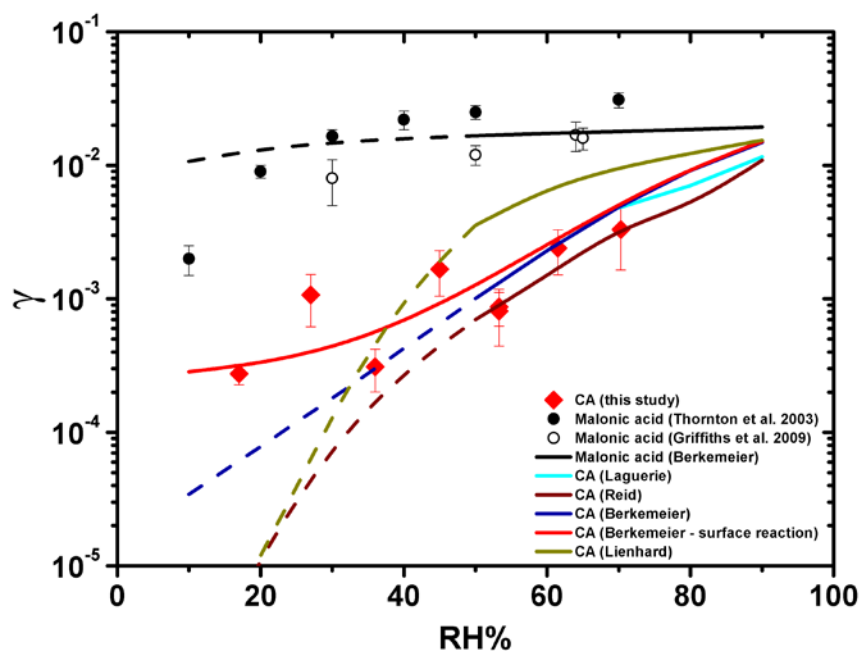
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Figure 3. Uptake coefficient of N_2O_5 on citric acid as a function of RH. Error bars represent 95% confidence bounds. The measured values can be found in Table S1 of the Supplement.



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Figure 4. Diffusivity of N_2O_5 in malonic and citric acid solutions as calculated according to four parameterization methods: black: Berkemeier (for malonic acid); teal: Laguerie; red: Reid; green: Lienhard; blue: Berkemeier; see text for details. Calculated values for a RH range between 10% and 90% can be found in Table S2 of the Supplement.



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Figure 5. Parameterization of N_2O_5 uptake on citric acid aerosol [according to equation \(4\) \(lines\)](#) based on diffusivities estimated by the four parameterization methods: teal: Laguerie; dark red: Reid; green: Lienhard; blue: Berkemeier. [Dashed lines indicate the RH range where the Stokes-Einstein relation \(equation \(7\)\) is not strictly applicable.](#) [The red line represents the extended parameterisation including a surface reaction term \(equation \(8\)\), based on the Berkemeier \$H_2O\$ diffusivity estimates, with included surface reaction term.](#) [The black line represents the parameterization for malonic acid using the same kinetic parameters and diffusivity data estimated using the same method as the Berkemeier method for malonic acid;](#) red diamonds: uptake coefficients measured in this study; solid circles: uptake coefficients for malonic acid according to Thornton et al. (2003); open circles: uptake coefficients for malonic acid according to Griffiths et al. (2009).

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